International
conference

«Chemistry of Organoelement Compounds and Polymers 2019»

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A.N. Nesmeyanov Institute
of Organoelement Compounds

Russian Academy of Sciences

Dedicated to the 65th anniversary of INEOS RAS
and
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academician A.N. Nesmeyanov

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PROGRAM OF THE INTERNATIONAL CONFERENCE «CHEMISTRY OF ORGANOELEMENT COMPOUNDS AND POLYMERS 2019»

18/11/19, MONDAY

09:20-10:00	***Registration (Moscow, 28 Vavilova str.)***	
10:00-10:25		**Opening Ceremony**
10:30-10:55	**PL-1**	**Recent advances in catalysis of organic reactions** *Irina P. Beletskaya* Chemistry Department, M.V. Lomonosov Moscow State University, Moscow
11:00-11:25	**PL-2**	**Polymers in supercritical media: synthesis, modification, and processing** *Alexei R. Khokhlov ,Marat O. Gallyamov* Faculty of Physics, Lomonosov Moscow State University,
11:30-11:50	***Coffe break***	
12:00-12:25	**PL-3**	**Beyond single-site catalysts. Through surface organometallic chemistry** *Christophe Copéret* ETH Zürich, Department of Chemistry and Applied Biosciences, Siwtzerland
12:30-12:55	**PL-4**	**Visible light photocatalysis for organic synthesis** *Burkhard König* Faculty of Chemistry and Pharmacy, University of Regensburg, Germany
13:00-14:20	***Lunch***	
14:30-14:55	**PL-5**	**Homolytically weak metal-carbon bonds and the persistent radical effect in metal-mediated radical polymerization** *Rinaldo POLI* Laboratoire de Chimie de Coordination – CNRS, France
15:00-15:25	**PL-6**	**Alkaline earth metal organometallics: from polymerization to catalysis** *Sjoerd HARDER* Universität Erlangen-Nürnberg,Germany
15:30-15:55	**PL-7**	**Alkane functionalization, the avenir of a new era in organic synthesis?** *Armando J. L. Pombeiro* Instituto Superior Técnico, Universidade de Lisboa, Portugal
16:00-16:20	***Coffee break***	
16:30-16:55	**PL-8**	**Metal-organic frameworks: chemical design and multifunctional properties** *Vladimir P. Fedin* Nikolaev Institute of Inorganic Chemistry SB RAS, Russia
17:00-17:15	**O-1**	**The influence of ortho-substituents on the properties of phenylboronic acids** *Andrzej Sporzyński, Agnieszka Adamczyk-Woźniak* Warsaw University of Technology, Poland
17:20-17:35	**O-2**	**The role of hydrogen-bonding in the structure and properties of compounds** *M. Fátima C. Guedes da Silva, Kamran Mahmudov* Universidade de Lisboa, Portugal
17:40	***Welcome Party***	

19/11/19, TUESDAY

10:00-10:25	**PL-9**	**Billion times more active atrp catalysts and benign initiation systems** *Krzysztof Matyjaszewski* Carnegie Mellon University, Center for Macromolecular Engineering, Pittsburgh
10:30-10:55	**PL-10**	**Active and passive mesoscale structures by comb copolymers** *Martin MOELLER , Cesar Rodriguez Emmenegger* INEOS RAS,Russia, DWI – Leibniz-Institut for Interactive, Germany
11:00-11:25	**PL-11**	**Bottlebrush bridge between soft gels and firm tissues** *Sergei S. SHEIKO, Andrew N. Keith, Mohammad Vatankhah-Varnosfaderani, Dimitri A. Ivanov, Andrey V. Dobrynin* University of North Carolina at Chapel Hill, USA
11:30-11:50	***Coffee break and Poster session (Polymers)***	
12:00-12:25	**PL-12**	**Functional and responsive polymer modified inorganic nanoparticles** *Maria Vamvakaki* Institute of ElectronicStructure& Laser, FORTH, Greece
12:30-12:55	**PL-13**	**50 years of hypercrosslinked polystyrene: from a non-trivial idea to industrial applications** *Vadim Davankov* Nesmeyanov-Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow
13:00-14:20	***Lunch***	
14:30-14:45 Room-1	**O-3**	**Self-healing polymers based on revesible diels-alder reaction** *Alexander Polezhaev, Elena Platonova, Daria Zakharova, Natalia Karelina, Alexey Kireynov, Evgeniy Vlasov,Tuyara Petrova, Vitaly Solodilov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia and Bauman Moscow State Technical University
14:30-14:45 Room-2	**O-4**	**New molecular clusters based on lanthanide carboxylates** *Dimitry Grebenyuk, Dmitry Tsymbarenko* Lomonosov Moscow State University, Russia
14:50-15:05 Room-1	**O-5**	**Organoelement compounds meet organic polymers - polyalkoxysiloxane-assisted heterophase polymerization** *Xiaomin Zhu, Yongliang Zhao, Zhi Chen, Martin Möller* DWI – Leibniz-Institute for Interactive Materials e.V., Germany
14:50-15:05 Room-2	**O-6**	**Rare-earth metal complexes supported by bis(amidinate) ligands and their role in cyclic ethers polymerization** *Anastasia Sachkova, Aleksei Tolpygin, Alexander Trifonov* National Research Lobachevsky State University of Nizhny Novgorod / Institute of Organometallic Chemistry of Russian Academy of Sciences, Russia
15:10-15:25 Room-1	**O-7**	**Oligochitosan: prospect for applications** *Vladimir Tikhonov , Evgeniya A. Bezrodnykh, Oxana V. Vyshivannaya, Boris B. Berezin, Inesa V. Blagodatskikh* Nesmeyanov-Institute of Organoelement Compounds, Russian Academy of Sciences, Moscow
15:10-15:25 Room-2	**O-8**	**Synthesis of symmetric and non-symmetric nickel(ii) pecep (e = s, o) pincer complexes** *Patrick Hasche, Anke Spanenberg, Torsten Beweries* Leibniz-Institute for Catalysis at the University of Rostock, Germany

19/11/19, TUESDAY

15:30-15:45 Room-1	**O-9**	**Graphite oxide as a polymer-like substance with a unique 3d structure** *Yulia V. Novakovskaya* Moscow State University, Russia
15:30-15:45 Room-2	**O-10**	**Rare-earth bis(alkyl)complexes containing tridentate amidopyridinate ligand** *Galina Gurina, Alexander Kissel, Dmitry Lyubov Alexander Trifonov, Lapo Luconi, Giuliano Giambastiani* G. A. Razuvaev Institute of Organometallic Chemistry, Russia
15:50-16:05 Room-1	**O-11**	**Amazing gel materials – poly(vinyl alcohol) cryogels** *V.I. Lozinsky, L.G. Damshkaln, O.Yu. Kolosova, D.A. Michurov, E.A. Podorozhko* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
15:50-16:05 Room-2	**O-12**	**Fluorene effect on metal complex-catalyzed reductive amination of carbonyl compounds** *Vladimir Kharitonov; Denis Chusov, Dmitry Loginov* A. N. Nesmeyanov Institute of Organoelement Compounds, Dmitry Mendeleev University of Chemical Technology of Russia, Russia
16:10-16:30	***Coffee break and Poster session (Polymers)***	
16:40-16:55 Room-1	**O-13**	**Hyper-crosslinked polystyrene as a support for mono- and bimetallic palladium-containing particles active in suzuki cross-coupling** *Linda Nikoshvili, Alexey Bykov, Elena Bakhvalova, Nadezhda Nemygina, Mikhail Sulman* Tver State Technical University, Russia
16:40-16:55 Room-2	**O-14**	**Parametrization of phosphine ligands to reveal an explanation of selectivity in hydrosilylation reaction of platinum complexes** *Ruslan Yu. Lukin, Aleksander D. Kachmarzhik, Dmitry G. Yakhvarov* Kazan Federal University, Kazan
17:00-17:15 Room-1	**O-15**	**Electrospun pyropolymer carbon nanofiber composite electrodes for ht-pem fuel cells** *Kirill Skupov, Igor Ponomarev, Olga Zhigalina, Alexander Modestov,YuryVolfkovich, Ivan Ponomarev, Victoria Basu, Alena Sufiyanova, Yulia Volkova, Dmitry Razorenov, Valentin Sosenkin, Alexander Naumkin* A. N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia
17:00-17:15 Room-2	**O-16**	**Ligand-to-metal charge transfer excited states in organometallic compounds** *Galina V. Loukova* Institute of Problems of Chemical Physics, Russia
17:20-17:35 Room-1	**O-17**	**Polymerization of 1-trimethylsilyl-1-propyne catalyzed by Niobium and Tantalum pentahalogenides: the effect of catalytic system on configuration, supermolecular organization and properties of polymer** *Samira Matson, Anton Kossov, Vladimir Makrushin, Elena Litvinova, Valeriy Khotimskiy* A.V.Topchiev Institute of Petrochemical Synthesis, Russia
17:20-17:35 Room-2	**O-18**	**Synthesis and catalytic activity study of cyanophenoxy-phthalocyanine sulfonated derivatives** *DmitryErzunov,Svetlana Tonkova,Anastasia Belikova,Arthur Vashurin* Ivanovo State University of Chemistry and Technology, Russia

19/11/19, TUESDAY

17:40-17:55 Room-1	**O-19**	**Functionalization of polyacrylamide derivatives for nanotrapping biomolecules** *Nadejda Davydova, Vladimir Sergeev, Andrés Gómez, Judith Guasch, Xavier R. Rodriguez,Imma Ratera Jaume Veciana and Elena Laukhina* A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia
17:40-17:55 Room-2	**O-20**	**Ruthenium (ii) complexes of 2-substituted imidazo-1,10-phenanthrolines as photosensitizers of inorganic semiconductors** *Sergey Tokarev, Olga Fedorova, Yuri Fedorov, Gediminas Jonusauskas, Marina Rumyantseva* A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia
18:00-18:15 Room-1	**O-21**	**Low Density Aerogel Preparation from Dianoformaldehyde Polymer** *E. E. Sheveleva, V.G. Pimenov, I.V. Blagodatskikh, O.V. Vishinannaja, A. M. Sakharov* N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia
18:00-18:15 Room-2	**O-22**	**Towards an explanation of discrepancies involving podipy: Why 31P NMR spectra don't match up?** *Artyom Shagurin, Sergey Usoltsev, Yuriy Marfin* Ivanovo State University of Chemistry and Technology, Russia

20/11/19, WEDNESDAY

10:00-10:25	**PL-14**	**Iron catalyzed carbon-carbon bond forming reactions** *Paul J. Chirik, C. Rose Kennedy, Megan Mohadjer Beromi, Jordan M. Hoyt* Department of Chemistry, Princeton University, USA
10:30-10:55	**PL-15**	**Dynamic catalytic systems for advanced synthetic applications** *Valentine P. Ananikov* Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia
11:00-11:25	**PL-16**	**Easy access to metal-N-heterocyclic carbene catalysts** *Steven P. Nolan* Department of Chemistry, Ghent University, Belgium
11:30-11:50	***Coffee break and Poster session (Organoelemeny Compounds)***	
12:00-12:25	**PL-17**	**Shuttle Catalysis – a Conceptual Blueprint for Reversible Functional Group Transfer** *Prof. Dr. Bill Morandi* ETH Zürich, Germany
12:30-12:55	**PL-18**	**Intramolecular catalyst transfer on functional groups** *T. Yokozawa , N. Harada, T. Kamigawara, H. Sugita, Y. Ohta* Department of Materials and Life Chemistry, Kanagawa University, Japan
13:00-14:40	***Lunch***	
14:50-15:05 Room-1	**O-23**	**Mechanistic insights into iron pnp complex catalysed amine borane dehydropolymerisation** *Torsten Beweries, Felix Anke, Delong Han, Susanne Boye, Albena Lederer* Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Germany

20/11/19, WEDNESDAY

14:50-15:05 Room-2	**O-24**	**Bacterial cellulose/chitosan composites with metal nanoparticles obtained by methods of green chemistry** *Marina Pigaleva, Margarita Rubina, Ilya Novikov, Butenko I.E., Alexander Budnikov, Alexander Naumkin, Alexander Vasil'kov, Tatiana Gromovykh, Lutsenko S.V., Marat Gallyamov* Lomonosov Moscow State University, Russia
15:10-15:25 Room-1	**O-25**	**Late transition metal catalyzed reactions under solvent-free conditions** *M.S. Nechaev, A.F. Asachenko, M.A. Topchiy, S.A. Rzhevskiy, A.A. Ageshina* Moscow State University, Russia
15:10-15:25 Room-2	**O-26**	**Oligo- and polydimethylsiloxane derivatives based on renewable natural resources** *Drozdov Fedor, Ryzhkov Alexey, Milenin Sergey, Ardabevskaia Sofia, Demchenko Nina, Buzin Igor, Muzafarov Aziz* Institute of Synthetic Polymeric Materials, a foundation of the Russian Academy of Sciences (ISPM RAS), Russia
15:30-15:45 Room-1	**O-27**	**Visualizing polymer dynamics with fluxional organometallic sensors** *Georgy A. Filonenko* Inorganic Systems Engineering group, The Netherlands
15:30-15:45 Room-2	**O-28**	**Dendron-functionalized hybrid organic-inorganic catalysts** *Svetlana A. Sorokina, Nina V. Kuchkina, Irina Yu. Krasnova, Linda Zh. Nikoshvili, Lyudmila M. Bronstein, Zinaida B. Shifrina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
15:50-16:05 Room-1	**O-29**	**Intramolecular ligand-ligand interaction as a driving force of isomerism of triptycene iridium pincer complexes** *Vladislava A. Kirkina ,Dmitri Gelman, Gleb A. Silantyev, Alexander A. Pavlov ,Oleg A. Filippov, Natalia V. Belkova, Elena S. Shubina* A.N. Nesmeyanov Institute of Organoelement Compounds, RussianAcademy of Sciences, Russia
15:50-16:05 Room-2	**O-30**	**New organosilicon compounds on the base of functional stereoregular organocyclosilsesquioxanes** *Anton Anisimov, Yulia Vysochinskaya , Yuriy Kononevich, AndreyZaytsev ,Valentina Ol'shevskaya , Olga Shchegolikhina, Aziz Muzafarov* A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
16:10-16:30	***Coffee break and Poster session (Organoelement Compounds)***	
16:40-16:55 Room-1	**O-31**	**Reductive Addition without an external hydrogen source** *Oleg Afanasyev, Alexey Tsygankov, Sofiya Runikhina, Evgeniya Podyacheva, Maria Makarova, Denis Chusov* A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia
16:40-16:55 Room-2	**O-32**	**Poly(ionic liquid)s as solid electrolytes** *Denis Ponkratov, Alexandr Shaplov, Elena Lozinskaya, Yakov Vygodskii* A.N. Nesmeyanov Institute of Organoelement Compounds Russian Academy of Sciences, Russia

20/11/19, WEDNESDAY

17:00-17:15 Room-1	**O-33**	**NCsp3N pincer type complexes of rare and alkaline earth metals – from synthesis to catalytic application** *Dmitry Lyubov, Dmitry Khristolyubov, Ahmad Fayoumi, Alexander Trifonov* Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
17:00-17:15 Room-2	**O-34**	**Increase of fire resistance of polyfoams based on epoxy-novolac resin** *Julia Rudnitskaya , Dmitry Panfilov* St. Petersburg State Institute of Technology, Russia
17:20-17:35 Room-1	**O-35**	**Non-covalent interactions in stoichiometric and catalytic reactions of iridium pincer complexes** *Elena Osipova, Ekaterina Gulyaeva, Oleg Filippov, Elena Shubina, Natalia Belkova* A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russia
17:20-17:35 Room-2	**O-36**	**Thermostable trifunctional phthalonitrile resin** *Maxim Yakovlev, Oleg Morozov, Boris Bulgakov, Alexey Kepman, Alexander Babkin* Faculty of Materials Science, Moscow State University, Russia
17:40-17:55 Room-1	**O-37**	**New approaches to generation of aminoheterocycles** *Dmitrii S. Bolotin* Institute of Chemistry, Saint Petersburg State University, Russia
17:40-17:55 Room-2	**O-38**	**Qualitative differences of thz absorption spectra of linear and branched polymers** *Anna Semenova, Vladimir Vaks, Yulia Guseva, Daria Babarina, Svetlana Morunova, Andrey Vilkov* Institute for Physics of Microstructures RAS, Nizhny Novgorod, Russia
18:00-18:15 Room-1	**O-39**	**“Chiral-at-metal” octahedral Cobalt(III) complexes as “organocatalysts in disguise” for asymmetric reactions** *Vladimir A. Larionov, Victor I. Maleev, Yuri N. Belokon* Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russian
18:00-18:15 Room-2	**O-40**	**The Conformation of Amphiphilic Polymer Spherical Brushes attached to a nanoparticle** *Alexandra Ushakova, Elena Govorun, Wan-Fen Pu, Valentina Vasilevskaya* Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Sciences, Russian

21/11/19, THURSDAY

10:00-10:25	**PL-19**	**Non-covalent interactions IN stoichiometric and catalytic reactions of metal hydrides** *Natalia V. Belkova, Oleg A. Filippov, Lina M. Epstein, Elena S. Shubina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
10:30-10:55	**PL-20**	**Design and Synthesis of Chiral Covalent Organic Frameworks** *Yong Cui* School of Chemistry and Chemical Engineering, China
11:00-11:25	**PL-21**	**Organometallic Macrocycles, Cages and Their Application** *Guo-Xin Jin* Fudan University
11:30-11:50	***Coffee break***	
12:00-12:25	**PL-22**	**Current state of chemistry of pentacoordinated phosphorus compounds**
		Vladimir F. Mironov , Mudaris N. Dimukhametov, Nadezhda R. Khasiyatullina, Yana S. Blinova A.E. Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of the Russian Academy of Sciences, Russia
12:30-12:55	**PL-23**	**Synthesis of Ene-diamido Rare earth complexes and their catalytic applications** *Jinxi Liu, Wufeng Chen, Jianfeng Li, Chunming Cui* Nankai University, China
13:00-14:20	***Lunch***	
14:30-14:45 Room-1	**O-41**	**Some aspects of hypercoordinated 14 group elements chemistry: reactivity, structure and properties** *Vadim Negrebetsky, Alexander Korlyukov, Eugene Kramarova, Yuri Baukov* Chemical Department, NI Pirogov Russian National Research Medical University, Russia
14:30-14:45 Room-2	**O-42**	**On the way to molecular switches: intramolecular stabilization of rotamers in transition metal bis(dicarbollide) complexes** *Igor B. Sivaev, Sergey A. Anufriev, Sergey V. Timofeev, Irina D. Kosenko* A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
14:50-15:05 Room-1	**O-43**	**Metal complexes based on polydentate O-, N-, S-ligands: synthesis, structure, properties** *Kirill V. Zaitsev* Chemistry Department, Moscow State University, Russia
14:50-15:05 Room-2	**O-44**	**Ruthenacarboranes with di- and triphosphine ligands: synthesis and interplay between exo-nido-, closo- and pseudocloso-isomers** *Ivan Grishin* Lobachevsky State University of Nizhny Novgorod, Russia
15:10-15:25 Room-1	**O-45**	**Transmetallation as a syntetic route to group 13 carbene complexes** *Igor V. Kazakov, Vladymir N. Mikhaylov, Alexey Y. Timoshkin* St. Petersburg State University, Russia
15:10-15:25 Room-2	**O-46**	**Novel synthetic approach to charge-compensated nido-carborane ligands** *Marina Stogniy, Svetlana Erokhina, Igor Sivaev, Vladimir Bregadze* A.N. Nesmeyanov Institute of Organoelement Compounds of Russian Academy of Science, Russia

21/11/19, THURSDAY

15:30-15:45 Room-1	**O-47**	**Stability and reactivity of the binuclear germylenes bearing N,N- and N,O-donor ligands** *Grigory Zhigulin, Anton Lukoyanov, Sergey Ketkov* G.A. Razuvaev Institute of Organometallic Chemistr, Russia
15:30-15:45 Room-2	**O-48**	**Brain as a target for bioactive ferrocene-based compounds** *Lubov V. Snegur, Alexey N. Rodionov, Yulia V. Dobryakova, V.A. Markevich, M.M. Ilyin, and Alexander A. Simenel* A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
15:50-16:05 Room-1	**O-49**	**Triphenylsilyl and triphenylgermyl hydroperoxides as the first examples of structurally characterised Si and Ge hydroperoxides** *Dmitry A. Grishanov, Alexander G. Medvedev, Alexey A. Mikhaylov, Andrei V. Churakov, Ovadia Lev, Petr V. Prikhodchenko* Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, Russia
15:50-16:05 Room-2	**O-50**	**N2O as a Reagent in Synthetic Chemistry** *Alexander G. Tskhovrebov* N.N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences, Russia
16:10-16:30	***Coffee break***	
16:40-16:55 Room-1	**O-51**	**The first all-C-deprotiotitanacyclobutadiene?** *Fabian Reiß, Melanie Reiß, Jonas Bresien, Anke Spannenberg, Haijun Jiao, Wolfgang Baumann, Perdita Arndt, Torsten Beweries* Leibniz Institute for Catalysis at the University of Rostock, Germsny
16:40-16:55 Room-2	**O-52**	**Investigation of physicochemical and catalytic properties of zeolitic imidazolate frameworks** *Maria N. Timofeeva, Ivan A. Lukoyanov, Valentina N. Panchenko, Sung Hwa Jhung* Institute of catalysis SB RAS, Russia
17:00-17:15 Room-1	**O-53**	**Interaction of the Buchwald seven-membered zirconacyclocumulene complex with carbonyl compounds**
17:00-17:15 Room-2	**O-54**	**P*,S-bidentate diamidophosphites for asymmetric palladium catalysis** *Konstantin Gavrilov, Sergey Zheglov, Vladislav K. Gavrilov, Marina Maksimova, Nataliya Goulioukina* Department of Chemistry, Ryazan State University named for S. Esenin, Russia
17:20-17:35 Room-1	**O-55**	**Pyrazolate anions as bridging bidentate ligands in the chemistry of copper(I) and silver(I) adducts: structures and properties** *Aleksei Titov, Oleg Filippov, Elena Shubina* A. N. Nesmeyanov Institute of Organoelement Compounds of RAS, Russia
17:20-17:35 Room-2	**O-56**	**The cytochrome b6f complex: DFT modeling of plastosemiquinone oxidation by the low-potential heme of cytochrome b6** *Alexander N. Tikhonov, Leila Y Ustynyuk* M.V. Lomonosov Moscow State University, Faculty of Chemistry, Russia
17:40-17:55 Room-1	**O-57**	**Metal-mediated intermolecular insertion of carbonyl compounds and nitriles into a p–p bond of the cyclic phosphine Cyclo-(p5ph5)** *Elena Gorbachuk, Toni Grell, Evamarie Hey-Hawkins, Dmitry Yakhvarov* A.E. Arbuzov Institute of Organic and Physical Chemistry, Russia

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17:40-17:55 Room-2	**O-58**	**Metal-organic frameworks based on novel zn12 carboxylate wheels: synthesis, structure and applications** *Anna Lysova, Danil Dybtsev, Kostantin Kovalenko, Denis Samsonenko, Vladimir Fedin* Nikolaev Institute of Inorganic Chemistry SB RAS, Russia
18:00-18:15 Room-1	**O-59**	**Synthesis, chemical propeties and applications of phosphorus heterocycles** *A. A. Zagidullin, E. S. Oshchepkova, T. I. Burganov, S. A. Katsyuba, Sh. K. Latypov, V. A. Miluykov, E. Hey-Hawkins* Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Russia
18:00-18:15 Room-2	**O-60**	**3d-material on the base of carbon nanotubes and phthalocyanine** *Ivanova V.N., Polyakov M.S., Basova T.V* Nikolaev Institute of Inorganic Chemistry SB RAS, Russia

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10:00-10:25	**PL-24**	**Electronic energy storage: molecular dyads, nanoparticles, molecular machines** *G. Jonusauskas, N. D. McClenaghan* CNRS / University of Bordeaux, Laboratoire Ondes et Matière d'Aquitaine, Talence, France
10:30-10:55	**PL-25**	**Heteroannulated acceptors for use in organic photovoltaic devices** *Oleg A. Rakitin* N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Russia
11:00-11:15	**O-61**	**II-VI quantum dots integrated with polyelectrolyte for photocatalysis in aqueous medium** *Victor Nadtochenko, Olga Antonova, Sergei Kochev, Yurii Kabachii, Petr Valetsky, Alexander Gulin, Aleksander Shakhov, Artyom Astafiev, Fedor Gostev* N. N. Semenov Federal Research Center for Chemical Physics, Russian Academy of Sciences
11:20-11:35	**O-62**	**Bacteriochlorin–Naphthalimide Conjugates for Simultaneous Photodynamic Therapy and Fluorescence Imaging** *Pavel Panchenko, Marina Zakharko, Mikhail Grin, Andrey Mironov, Dmitriy Pritmov, Gediminas Jonusauskas, Alexey Feofanov, Olga Fedorova* A.N. Nesmeyanov Institute of Organoelement Compounds of RAS, Moscow, Russia
11:40-11:55	***Coffe break***	
12:00-12:15	**O-63**	**Solution nmr techniques for molecular magnets** *Valentin Novikov* Nesmeyanov Institute of Organoelement Compounds RAS, Russia
12:20-12:35	**O-64**	**Computational and theoretical chemistry for metal-organic framework research** **Olga A. Syzgantseva** Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland
12:40-12:55	**O-65**	**Dipyrromethene metal complexes: Study of spectroscopic characteristics and practical application** *Iuliia Aksenova, Alexander Prokopenko, Rimma Kuznetsova,* *Mikhail Berezin, Elena Antina* National Research Tomsk State University, Russia
13:00-14:00	**Lunch**	

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14:00-14:15	**O-66**	**Photophysical characteristics of bodipy luminophores in aggregated state** *Elizaveta Banakova, Dmitriy Merkushev, Yuriy Marfin* Ivanovo State University of Chemistry and Technology, Russia
14:20-14:35	**O-67**	**Near infrared lanthanide luminescence in complexes with perfluorinated mercaptobenzothiazolate ligands** *Vasily Ilichev, Andrey Kukinov, Liubov Silantyeva, Anton Rogozhin, Mikhail Bochkarev* Laboratory of Chemistry of Rare Earth Elements, G.A. Razuvaev Institute of Organometallic Chemistry of RAS, Russia
14:40-14:55	**O-68**	**Playing with Photochemical reactions of Iron complexes** *Dmitry S. Perekalin, Petr A. Zhmurov, Andrei M. Shved, Dmitry S. Shved* Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Russia
15:00		**Closing Remarks**

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-1	**The use of microwave radiation for synthesis of water-soluble porphyrin polymers** *Ageeva Tatiana, Ivan Shilov, Nadezhda Pechnikova, Oskar Koifman* Institute of Macroheterocyclic Compounds, Ivanovo State University Chemistry and Technology
P-2	**Thermal dependence of luminescent characteristics of laser-induced luminescent structures formed in polybenzimidazole films** *Akovantseva Anastasiya, Aleksei Rybaltoivskii, Bato Kholhoev, Viktoriya Presnyakova, Yurii Isaakyan, Petr Timashev* Institute of Photonic Technology of Federal Research Centre «Crystallography and photonics of RAS», Russia
P-3	**Determination of the structure of the substance synthesized based on polycarbonate and aliphatic polyamine** *Alekseeva Kseniya* Department of Chemical Technology of Polymers, St. Petersburg State Technological Institute (Technical University), Russia
P-4	**The use of natural polymers to separate carbon dioxide from physical absorbents** *Anokhina Tatiana, Evgeniya Dmitrieva, Margarita Kostyanaya, Danila Bakhtin, Viktoria Ignatenko, Stepan Bazhenov* A.V. Topchiev Institute of Petrochemical Synthesis, Russia
P-5	**Carbosilane dendrimers with functional shell to create new supramolecular structures** *Ardabevskaia Sofia, Vadim Gorodov, Sergey Milenin, Aziz M. Muzafarov* Enicolopov Institute of Synthetic Polymeric Materials, Russia
P-6	**New Hydrophobic coatings on natural materials** *Baranov Oleg, Lyudmila Komarova, Sergey Golubkov* A.N Nesmeyanov Institute of Organoelement Compounds, Russia
P-7	**Main characteristics of apple, beet and needle pectin** *Belaya Tatiana, Alexander Mitin, Nadezhda Kuleshova, Lyudmila Semenycheva* Faculty of Chemistry, Lobachevsky State University of Nizhni Novgorod, Russia
P-8	**The synthesis of new organosilicon monomers and polymers with several types of functional groups in the molecule** *Bezlepkina Kseniya A., Valeriy Yu. Maiorov, Sergey A. Milenin , Aziz M. Muzafarov* Enicolopov Institute of Synthetic Polymeric Materials, Russia
P-9	**Biocompartable soluble polyelectrolyte complexes and Metal-containing nanocomposites** Blagodatskikh Inesa V., Oxana V. Vyshivannaya, Vladimir E. Tikhonov, Nadezda A. Samoilova, Alexey R. Khokhlov A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-10	**Functional materials based on nanoparticle modified polypropylene fibers** *Bocharnikova Elena, Olga Tchaikovskaya, Ilya Lysak, Tatiana Malinovskaya, Galina Lysak* Faculty of Physics, Tomsk State University, Russia

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-11	**Structure, phase composition, surface analysis and some functional properties of chitosan-based composite materials containing silver or gold nanoparticles** *Budnikov Alexander V., Margarita S. Rubina, Egor S. Afanasyev, Alexander V. Naumkin, Alexandra V. Shulenina, Roman D. Svetogorov, Alexander Yu. Vasil'kov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-12	**Macromolecule with amphiphilic monomer units in a binary solvent: Dissipative particle dynamics simulation** *Buglakov Aleksandr I., Daniil E. Larin, Valentina V. Vasilevskaya* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-13	**Preparation and study of structural features of sulfonated polyphenylquinoxalines with sulfactants** *Bulycheva Elena, Nataliya Belomoina, Mikhail Buzin, Lubov Wasserman* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-14	**New hybrid materials based on metal-containing bacterial cellulose obtained by metal vapor synthesis** *Butenko Ivan, Tatiana Gromovykh, Sergey Lutsenko, Alexander Naumkin,Vera Sadykova, Alexander Vasil'kov* A.N. Nesmeyanov Institute of Organoelement Compounds , Russia
P-15	**A study of chloro-p-xylylenes polymerization kinetics using high-vacuum in-situ differential scanning calorimetry** *Buzin Alexander I., Dmitry R. Streltsov, Petr V. Dmitryakov, Sergei N. Chvalun* Enikolopov Institute of Synthetic Polymer Materials, Russia
P-16	**Features of hydrolysis of marine collagen and fibrinogen proteins by thrombin** *Chasova Victoria, Lyudmila Semenycheva, Marfa Egorikhina, Natalya Valetova, Alexander Mitin* Faculty of Chemistry, Lobachevsky State University of Nizhny Novgorod, Russia
P-17	**A copolymer of butyl acrylate with vinyl butyl ether, synthesized by the triethylboron-oxygen system in a compensatory way as a macroinitiator** *Chasova Yuliia, Lyudmila Semenycheva, Natalya Valetova, Yuliia Matkivskaya, Tatyana Liogon'kaya, Alexandr Mitin, Yurii Kurskii* Faculty of Chemistry, Lobachevsky State University of Nizhni Novgorod, Russia
P-18	**Influence of plasticizers on processibility of polyacrylamide compositions** *Chistiakov Nikita , Andrey Muravsky, Hermann Litosov, Igor Dvorko* Department of Chemical Technology of Polymers, St. Petersburg State Technological Institute (Technical University), Russia
P-19	**Synthesis, properties and applications of copolyimides with dimethylsiloxane fragments of various lengths** *Chuchalov Aleksandr, Bato Bayminov, Dmitriy Sapozhnikov, Yakov Vygodskii, Aleksey Kosolapov, Sergey Semyonov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-20	**Effect of the synthetic strategy on the properties of liquid crystalline ollgoesters** *Deberdeev Timur, Liana Karimova, Alsu Akhmetshina, Sergey Grishin, Nail Galikhmanov, Rustam Deberdeev* Kazan National Research Technological University, Russia
P-21	**Morphology evolution during submonolayer growth of poly(chloro-p-xylylene) films formed by vapor deposition polymerization** *Dmitryakov Petr, Anastasiya Mitko, Alexander Nesmelov, Alexander Buzin, Dmitry Streltsov* National Research Center "Kurchatov Institute", Russia
P-22	**Rhodium and iridium catalysts allow to obtain silicone rubbers with enhanced properties** *Mikhail Dobrynin, Regina Islamova* Institute of Chemistry, St. Petersburg State University, Russia
P-23	**New magnetic nanomaterials based on soluble ferrocene-containing polymers** *Dvorikova Raisa, Aleksander Peregudov, Aleksander Korlukov, Mikhail Buzin, Irina Nagornova, Valeriy Vasnev* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-24	**Study of the physicochemical properties of new ferrocene-containing fluorinated monomers** *Dyachenko Victor, Ivan Chaschin, Olga Melnik, Sergej Igumnov and Alexej Khokhlov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-25	**Metal-containing chitosan-based films: morphology study** *Elmanovich Igor V., Margarita S. Rubina, Alexander Yu. Vasilkov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-26	**Metal polymeric nanocomposites ag based on hydrophilic nitrogen and sulfur containing polymer** *Emelyanov A.I., Kuznetsova N.P., Korzhova S.A., Prozorova G.F., Pozdnyakov A.S.* A.E. Favorsky Irkutsk Institute of Chemistry, Russia

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P-27	**Water insoluble organosilicon surfactants as stabilizers of polymer suspensions** *Ezhova Anna A., Nina E. Artamonova, Inessa A. Grytskova, Anatoly E. Chalykh, Sergey N. Chvalun* MIREA — Russian Technological University, Russia
P-28	**Comb-like polyelectrolytes for alkaline hydrolysis of esters** *Fetin Petr, Matvey Kadnikov, Veronica Fetina, Ivan Zorin and Alexander Bilibin* Institute of Chemistry, St Petersburg University, Russia
P-29	**The diffusion role in the kinetics of the interface polyaddition reaction** *Filatov D.A., Govorun E.N.* A.N. Nesmeyanov Institute of Organoelement compounds, Russia
P-30	**Coarse-grained simulation of molecular ordering in polylactic blends under uniaxial strain** *Glagolev Mikhail, Alexei Lazutin, Daria Guseva, and Valentina Vasilevskaya* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-31	**Hollow morphologies formed by interpolyelectrolyte complexes: computer simulation** *Glagoleva Anna, Valentina Vasilevskaya* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-32	**Aggregation of associating polyelectrolytes** *Glukhova Svetlana, Vyacheslav Molchanov, Olga Philippova* Faculty of Physics, Lomonosov Moscow State University, Russia
P-33	**Kinetic and structural features of 2,2,3,3-tetrafluoropropyl methacrylate raft-polymerization** *Grigoreva Alexandra, Sergey Zaitsev* Lobachevsky State University of Nizhni Novgorod, Russia
P-34	**Saturation of bacterial cellulose with lipid nanoparticles with silymarin flavolignans and study of its hemolytic and antimicrobial activity** *Gromovykh Tatyana I., Marjan Bahman, Nataliya B. Feldman, Sergey V. Lutsenko* Federal State Autonomous Educational Institution of Higher Education I.M. Sechenov First Moscow State Medical University of the Ministry of Health of the Russian Federation (Sechenov University), Russia
P-35	**The structure of rosinterpenomaleic adducts** *Hapankova Alena, Iryna Latyshevitch* Institute of physical organic chemistry of the national academy of sciences of Belarus, Belarus
P-36	**Distribution of pah between solid and liquid phases during deasphthalting of pyrolysis oil of tires** *Henarava Tatiana, Sergey Leschev, Valentina Levkina* A. V. Luikov Heat and Mass Transfer Institute of NAS of Belarus, Belarus
P-37	**Radical-induced curing of the Vinyl-containing polydimethylsiloxanes using Cyclic organosilicon triperoxides** *Ignatova Nina, Konstantin Deriabin, Regina Islamova, Terent'ev A.O.* Institute of Chemistry, Saint Petersburg State University, Saint Petersburg, Russia
P-38	**Synthesis of polyporphine films containing transition metal ion by electrochemical method** *Istakova Olga I., Dmitry V. Konev, Charles H. Devillers, Mikhail A. Vorotyntsev* Institute for Problems of Chemical Physics, Chernogolovka, Russia
P-39	**Silatran-containing branched polymers and their effect on crop growth** *Istratov Vladislav, Olga Yamskova, Valery Vasnev, Oleg Baranov, Boris Izmailov, Gali Markova* A.N. Nesmeyanov Institute of organoelement compounds,Russia
P-40	**Silatrane-containing biodegradable polymeric networks** *Istratov Vladislav, Valery Vasnev, Oleg Baranov, Boris Izmailov, Elena Rodlovskaya* A.N. Nesmeyanov Institute of organoelement compounds, Russia
P-41	**Spectral and structural properties modification of poly(p-xylylene)–cadmium sulphide nanocomposites on dependence of filler content and film thickness** *Ivanova O.P., E.P. Krinichnaya, A.A. Piryazev , S.A. Zavyalov , T.S. Zhuravleva* Emanuel Institute of Biochemical Physics, Russia
P-42	**New oligo(dimethyl)silanes with 1,7-bis(methyl)-m-carborane units** *Izmaylov Boris, Valerii Vasnev, Galy Markova* A.N. Nesmeyanov Institute of Organoelement compounds, Russia
P-43	**Conformation and flexibility of poly(4-vinylpyridine) aT the hydrophobic core – hydrophilic corona interface** *Kalinin Pavel V., Alexander L. Kwiatkowski, Vyacheslav S. Molchanov, and Olga E. Philippova* Physics Department, Lomonosov Moscow State University, Russia

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-44	**Investigation of impact of nanosized sio2 on abrasion resistance of transparent silicone coatings** *Katnov Vladimir, Sergey Stepin* Kazan' National Research Technological University, Russia
P-45	**Luminescence of impregnated laser-induced structures in polybenzimidazole films** *Kholkhoev Bato Ch., Alexey O. Rybaltovskii, Anastasia A. Akovantseva, Yurii A. Isaakyan, Viktoria S. Presnyakova, Peter S. Timashev, Vladimir I. Yusupov, Vitaliy F. Burdukovskii* Baikal Institute of Nature Management SB RAS, Russia
P-46	**Polyphenylene and Polyazomethyne based on 1,2-bis-(4'-acetylbenzyl)-o-carborane** *Khotina Irina, Alexey Kovalev, Natalia Kushakova, Irina Syntsova, Daria Kupriyanova, Victoria Kharitonova* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-47	**Synthesis of poly(vinylidene fluoride-co-chlorotrifluoroethylene)-grafted-poly(acrylonitrile) polymers for ferroelectric organic field-effect transistors** *Khudyshkina A.D., Yu. N. Luponosov, S.A. Ponomarenko* Enikolopov Institute of Synthetic Polymeric Materials, Russia
P-48	**Copolymers based on undecenoic acid diamides and polydimethylsiloxane** *Klokova Kseniia S., Sergey A. Milenin, Fedor V. Drozdov, Sofia N. Ardabevskaia, Michael I. Buzin, Aziz M. Muzafarov* Russian Technological University (Fine Chemical Technologies Institute), Russia
P-49	**Metal-free photocontrolled polymerization of vinyl monomers using phenoxazine derivative systems** *Knyazeva Nadezhda, Pavel Grushin, Ivan Grishin* Lobachevsky State University of Nizhny Novgorod, Nizhny Novgorod, Russia
P-50	**Influence ofamino acids of the h2n(ch2)ncooh series on the formation and properties of poly(vinyl alcohol) cryogels** *Kolosova O.Yu., Karelina P.A., Lozinsky V.I.* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-51	**Atom transfer coupling reactions performed with radical traps of various structure** *Kolyakina Elena, Fatima Shoipova, Alisa Alyeva, Dmitriy Grishin* Lobachevsky State University of Nizhny Novgorod, Russia
P-52	**Thermogravimetric analysis of thermal stability of polymers synthesized in the presence of non-transition and transition metals complexes with redox-active ligands** *Kolyakina Elena, Alexey Markin, Dmitriy Grishin* Lobachevsky State University of Nizhny Novgorod, Russia
P-53	**Novel conjugated polymers based on dithienophtalimide derivatives for application in non-fullerene solar cells** *Konstantinov Igor, Mukhamed Keshtov, Sergey Kuklina, Alexander Nikolaev, Zhi-Yuan Xie, Chuandong Dou, Ganesh Sharma* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-54	**Formation of 3d-structures based on aromatic heterochain polymers by laser stereolithography** *Korkunova Olgs S., Daria S. Dudova, Nikita V. Minaev, Peter S. Timashev, Vitaliy F. Burdukovskii* Baikal Institute of Nature Management SB RAS, Russia
P-55	**State diagram of densely grafted amphiphilic homopolymer brushes: grafting density vs solvent quality** *Kosmachev Alexei, Alexei Lazutin, Valentina Vasilevskaya* Faculty of Physics, M. V. Lomonosov Moscow State University, Russia
P-56	**New hybrid materials based on fish collagen with the inclusion of poly butyl acrylate** *Kozina Marina, Yulia Kuznezhova, Alexandr Mitin, Ludmila Semenycheva* National Research Lobachevsky State University of Nizhny Novgorod, Russia
P-57	**Wetting properties of fluorinated polysiloxanes coatings based on dimer of hexafluoropropylene** *Krapivko Alena, Fedor Drozdov, Natalya Sheremet'eva, Georgij Cherkaev, Viktor Myakushev, Lev Gervic, Aziz M. Muzafarov* Russian Technological University, Institute of Fine Chemical Technologies, Russia
P-58	**VDP synthesis and study of surface structure of poly(p-xylylene) films containing PbSe and PbTe nanoparticles** *Krinichnaya E.P., O.P. Ivanova, S.A. Zavyalov, T.S. Zhuravleva* N.M. Emanuel Institute of Biochemical Physics, Russia
P-59	**Novel antibacterial chitosan derivatives** *Kritchenkov Andreii, Niyaz Yagafarov, Victor Khrustalev* Faculty of Science, Department of Inorganic chemistry and Research Institute of Chemistry, RUDN University, Russia

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-60	**Synthesis of copolymers of buthylmethacrylate and vinylbenzotriazole and its films conductivity** *Kropacheva Olga, Kseniya Butorina, Fedor Yaroshenko* Faculty of Chemistry, Chelyabinsk State University, Russia
P-61	**Polymer supported Pd placed on magnetic silica as effective catalyst in suzuki reaction** *Kuchkina Nina, Svetlana Sorokina, Alexandra Torozova, Linda Nikoshvili, Lyudmila Bronstein, Zinaida Shifrina* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-62	**Hybrid magnetic nanocomposites based on nipam-paa and iron(III)-containing nanoparticles for doxorubicin loading and anticancer therapy** *Kusaia Victoriia, Vasily Spiridonov, Mikhail Afanasov, Lyudmila Makarova, Maria Romodina, Natalia Pozdnyakova, Anna Shibaeva, Sergey Zezin, Alexander Yaroslavov* Department of Chemistry, Lomonosov Moscow State University, Russia
P-63	**Ultrasonic synthesis of Water-soluble Polymer-metal(oxide) magnetic nanocomposite based on cross-linked calcium/sodium alginate and maghemite nanoparticles** *Kuznetsov Valeriy, Vasily Spiridonov, Andrey Sybachin, Mikhail Afanasov, Lyudmila Makarova, Yulia Alyokhina, Eleonora Shtykova, Sergey Zezin, Alexander Yaroslavov* Department of Chemistry, Lomonosov Moscow State University, Russia
P-64	**Stabilization of mesoglobules by a solute via specific interactions** *Larin Daniil, Elena Govorun* A.N. Nesmeyanov Institute of Organoelement Compound, Russia
P-65	**Catalytic cross-linking of Si–H-containing silicone copolymers** *Lobanovskaia Ekaterina, Konstantin Deriabin, Regina Islamova* Institute of Chemistry, Saint Petersburg State University, Russia
P-66	**Reaction of propiolic acid with 1,3-bis(3-azidopropyl)-1,1,3,3-tetramethyldisiloxane** *Majorov Valeriy Yu., Kseniya A. Bezlepkina,, Sergey A. Milenin, Aziz M. Muzafarov* Enicolopov Institute of Synthetic Polymeric Materials, Russia
P-67	**Polymer nanoparticals from self-organized monomers** *Makarov I.A., P.A. Fetin, A.S. Senchukova, I.M. Zorin, A.Yu. Bilibin* St.-Petersburg State University, Department of Chemistry, Russia
P-68	**Catalytic oxidation of benzene on the metal polymer catalyst** *Mammadova U.A., A.F. Isazade, S.M. Mammadova,N.A. Zeynalov* Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of ANAS, Azerbaijan
P-69	**Synthesis and luminescent properties of composites of poly(αlpha-fluoroacrylates) doped with tb(iii) complex** *Melnik Olga, Andrey Tyutyunov, Ilya Taydakov, Vladislav Korshunov, Andrey Lobanov, Sergey Igumnov, Yakov Vygodskii* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-70	**Thiazole-based (mix)mofs: synthesis, characterization and applications in gas adsorption and catalysis** *Mercuri Giorgio, Lapo Luconi,Giulia Tuci, Giuliano Giambastiani, Andrea Rossin* Consiglio Nazionale delle Ricerche - Istituto di Chimica dei Composti Organometallici (CNR-ICCOM), Italy
P-71	**New monosodiumoxyorganoalkoxysilanes for production of functional polyalkyl(aryl)triazolealkoxysiloxanes with controlled molecular architecture** *Migulin D., S. Milenin, G. Cherkaev, A. Muzafarov* N.S. Enikolopov Institute of Synthetic Polymer Material, Russia
P-72	**Carborancarbosilane Dendrimers: Synthesis and Properties** *Minyaylo E.O., A.A. Anisimov, A.V. Zaytsev, V.A. Ol'shevskaya, S.A. Milenin, A.M. Muzafarov* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-73	**New multiblock copolymers containing norbornenes and carbosilane/carbosiloxane blocks** *Morontsev Aleksandr, Maria Gringolts, Yulia Denisova, Georgiy Shandryuk, Aleksander Peregudov, Yaroslav Kudryavtsev, Eugene Finkelshtein* A.V. Topchiev Institute of Petrochemical Synthesis, Russia
P-74	**Tuning the wetting angle of the fluorinated polymer by means of modified nanodiamonds** *Naumova Alina, Pavel Melnikov, Anastasia Alexandrovskaya, Nikolay K. Zaitsev* MIREA - Russian Technological University, Russia
P-75	**Patterns of forming composite chitosan gels with metal nanoparticles in carbonic acid solutions under high pressure** *Novikov Ilya, Marina Pigaleva, Marat Gallyamov* Faculty of Physics, Lomonosov Moscow State University, Russia

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-76	**Heterophase raft-polymerization in the presence zinc oxide nanoparticles** *Ogay Valeria, Natalia Serkhacheva, Daniil Tselousov, Elena Chernikova, Ksenia Mineeva* MIREA – Russian Technological University, Russia
P-77	**A study of the sorbtion capacity, physico-chemical characteristics and structure of ureaformaldehyde oligomers for decoration of the ceramic surfaces** *Papulova Galina*
P-78	**Reversible inhibition in the formation of (co)polymers based on alkyl(meth)acrylates with vinylalkyl ethers under compensation of the active monomer depending on their nature when initiated by the triethylborane-oxygen system** *Pegeev Nikita, Lyudmila Semenycheva, Natalya Valetova, Yuliia Matkivskaya, Tatyana Liogon’kaya, Alexandr Mitin, Yurii Kurskii* Faculty of Chemistry, Lobachevsky State University of Nizhni Novgorod, Russia
P-79	**Hydrophobic coatings based on fluorinated and non-fluorated copolymers obtained via supercritical carbon dioxide depostion** *Pestrikova Anastasiya, Alexander Nikolaev, Viktor Dyachenko, Olga Serenko* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-80	**Proton conduction of sulphonated polyphenylquinoxalines** *Pisareva Anna V., R. V. Pisarev, N. M. Belomoina, E. G. Bulycheva, Yu. A. Dobrovolsky* Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia
P-81	**Properties and microstructure of poly(vinyl alcohol) cryogels containing different forms of chitosan** *Podorozhko E.A., G.R. Ul’yabaeva N.R., Kil’deeva , V.I. Lozinsky* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-82	**The influence of the duration of the synthesis on the properties of the obtained oligomer** *Polyakova Julia* St. Petersburg State Technological Institute (Technical University), Russia
P-83	**Ferrocene- and thiophene-containing polymers as precursors of magnetic materials** *Rodlovskaya Elena, Raisa Dvorikova, Valerii Vasnev* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-84	**Liquid-crystalline polymers as surface agents for semiconductors quantum dots according to quantum-chemical calculations** *Romanova Ksenia, Yuriy Galyametdinov* Kazan National Research Technological University, Russia
P-85	**Research of influence of recycled polyethylene terephthalate products on properties of foam materials** *Rudnitskaya Julia, Michael Alikin* St. Petersburg State Institute of Technology(Technical University), Russia
P-86	**Synthesis of bioside chitosan derivatives as a drug carrier** *Safaraliyeva S.F., Sh.Z. Tapdigov, U.A. Mammadova, N.A. Zeynalov, D.B. Taghiyev* Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of ANAS, Azerbaijan
P-87	**Polycondensation in supercritical carbon dioxide: ineos contribution** *Said-Galiev Ernest, Alexei Khokhlov, Mukhamed Keshtov, Yakov Vygodskii, Valerii Vasnev, Raisa Dvorikova, Nataliya Belomoina, Elena Bulycheva* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-88	**Polysaccharide based magnetic composite for removal of pollutants** *Samoilova Nadezhda, Maria Krayukhina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-89	**Preparation and evaluation of gels based on poly(trimethylene carbonate) for regenerative medicine applications** *Samokhin,Alexander, Anastasia Korel, Vasiliy Kuznetsov, Ekaterina Zemlyakova, Vladimir Tkachenko, Denis Nesterov, Alexander Pestov* Novosibirsk research institute of traumatology and orthopaedicsn.a. L.A. Tsivyan Ministry of Health, Russia
P-90	**Heterophase raft-polymerization in the presence copolymers of acrylic acid and n-isopropylacrylamide with trithiocarbonate group** **Serkhacheva Natalia, Mikhail Balashov, Valeria Ogay, Elena Chernikova** MIREA – Russian Technological University, Russia
P-91	**The influence of the plasticizers on elasticity of the polymer composition** *Polyakova Julia, Kseniya Alekseeva, Olga Shabotina* St. Petersburg State Technological Institute (Technical University), Russia
P-92	**Viscoelastic properties pH sensitive suspensions of wormlike micelles and halloysite nanotubes** *Shatalina Ekaterina I., Vyacheslav S. Molchanov, Olga E. Philippova* Physics department, Lomonosov Moscow State University, Russia

POSTER SESSION 1 (NOVEMBER 19): P1-P104

P-93	**Wormlike micelles and oppositely charged halloysite nanotubes networks** *Shishkhanova Kamilla, Vyacheslav Molchanov, Olga Philippova* Faculty of Physics, Lomonosov Moscow State University, Russia
P-94	**Small angle x-ray scattering examination of chitosan-based powders, films, and aerogels with silver or gold nanoparticles prepared using metal vapor synthesis** *Shulenina Alexandra V., Margarita S. Rubina,Georgy S. Peters, Alexander Yu. Vasil'kov* Faculty of Physics, M.V. Lomonosov Moscow State University, Russia
P-95	**Hybrid metal(oxide)–polymer nanocomposites based on carboxymethylcellulose cross-linked by in-situ formed copper (i) oxide nanoparticles for photocatalytic applications** *Spiridonov Vasily, Liu Xiang Yao, Andrey Sybachin, Irina Panova, Sergey Zezin, Alexander Yaroslavov* Department of Chemistry, Lomonosov Moscow State University, Russia
P-96	**Controlled synthesis of polymers based on acrylonitrile catalyzed by copper complexes with nitrogen-containing ligands** *Stakhi Sergey, Ivan Grishin* Lobachevsky State University of Nizhny Novgorod, Russia
P-97	**Chemical structuring of polyorganosiloxane coatings** *Stepin Sergey, Vladislav Suchkov* Kazan' National Research Technological University, Russia
P-98	**Synthesis of graft-copolymers of acrylamide and gelatin in the presence of tributylboron** *Sustaeva Karina, Vavilova Anna, Kuznetsova Yulia, Markin Alexey, Mitin Alexander, Podguzkova Marina, Semenicheva Lyudmila* Faculty of Chemistry, Lobachevsky State University, Russia
P-99	**Synthesis and properties of 128-arm polydimethylsiloxanes with different length of arms** *Tikhonov P.A., N.G. Vasilenko, G.V. Cherkaev, N.V. Demchenko, V.G. Vasil'ev, A.M. Muzafarov* Enikolopov Institute of Synthetic Polymeric Materials, Russia
P-100	**Catalytic systems based on New macromolecular compounds for betulin oxidation** *Torozova Alexandra, Angelina Korolkova, Zinaida B. Shifrina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-101	**Controlled radical polymerization of styrene in the presence of blatter radical** *Vavilova A.S., T.O. Burdyukova, Yu.L. Kuznetsova* Faculty of Chemistry, N.I. Lobachevsky Nizhny Novgorod State University,Russia
P-102	**Synthesis of vinyl derivatives from sustainable source and developing new approaches for controlled materials design** *Vikenteva Yulia, Konstantin Rodygin, Valentine Ananikov* Saint Petersburg State Universit, Russia
P-103	**2,3-dihydro-1,2,4-oxodiazole chitosan derivatives and their antibacterial activity** *Yagafarov Niyaz, Andreii Kritchenkov, Victor Khrustalev* RUDN University, Russia
P-104	**Synthesis of disentangled uhmwpe using binuclear and hexanuclear ti(IV) complexes supported by [OOOO]4–- type ligand** *Zubkevich Sergey V., Dmitry A. Kurmaev, Vladislav A. Tuskaev, Svetlana Ch. Gagieva* Department of Chemistry, M. V. Lomonosov Moscow State University, Russia

POSTER SESSION 2 (NOVEMBER 20): P1-P138

P-1	**Chemistry of Hydrophosphoryl and Hydrothiophosphoryl Compounds** *Aimakov Orazkhan, Nurgul Nurmukhanbetova* S.Seifullin Kazakh Agro Technical University, Republic of Kazakhstan
P-2	**The synthesis of 1,3-oxazolidines and 1,4-dihydro-2h-3,1-benzoxazines containing (η6-arene)tricarbonylchromium group** *Aksenova N.A., Sazonova E.V., Artemov A.N.* Lobachevsky State University of Nizhny Novgorod, Russia
P-3	**Novel base-initiated cascade reactions of hemiindigos to produce dipolar γ-carbolines and indole-fused pentacycles** *Alekseeva Ekaterina, Valeriya Velezheva, Olesya Babii, Aleksander Khodak, Konstantin Majorov and Boris Nikonenko* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-4	**Carborane conjugates of β- andmeso-maleimide-substituted porphyrins and chlorins: synthesis and biological properties** *Alpatova Viktoriya, Andrei Zaitsev, Alexandra Radchenko, Alexey Kostyukov, Albina Petrova, Vladimir Kuzmin, Alexander Shtil, Valentina Ol'shevskaya* A.N.Nesmeyanov Institute of Organoelement Compounds, Russia
P-5	**X-ray diffraction analysis of hybrid materials based on carbon nanotubes and nanosized WO3, CuO** *Andreev Pavel, Ksenia Smetanina, Ilya Vilkov, Kirill Kremlev, Galina Zabrodina* Faculty of Physics, Lobachevsky State University of Nizhniy Novgorod, Russia
P-6	**The effect of the metalloalkoxysiloxane filler structure on the resistance of the polyimide composites to atomic oxygen** *Andropova Ulyana, Nadezhda Tebeneva, Alexander Tarasenkov, Dmitry Sapozhnikov, Vladimir Chernik, Lev Novikov, Ekaterina Voronina, Olga Serenko* A.N.Nesmeyanov Institute of Organoelement Compounds, Russia
P-7	**Preparation of fused heterocyclic compounds via iodine exchange** *Antonkin Nikita S., Yulia A. Vlasenko, Mehman S. Yusubov, Alexandr Shafir, Pavel S. Postnikov* National Research Tomsk Polytechnic University, Russia
P-8	**A way to new ortho-carborane arylazo derivatives** *Anufriev Sergey, Akim Shmalko, Marina Stogniy, Igor Sivaev* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-9	**Synthesis of polycyclic aromatic hydrocarbons via c–h activation for organic light-emitting devices** *Arsenov Mikhail, Alexander Molotkov, and Dmitry Loginov* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-10	**Structural-energies properties of isostructural acetylene alcohols c15, c20 and their solutions** *Baev A.K., A.A. Baev* G.A. Krestov Institute of Solution Chemistry of the RAS, Russia
P-11	**Generalization of the founderic new idies and creation of theory specific interactions of organic compounds** *Baev Alexei K.* G.A. Krestov Institute of Solution Chemistry of the RAS, Russia
P-12	**Development of new chelators for radiopharmaceuticals** *Bakhareva Anna, Anastasia Zubenko* The A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-13	**Synthesis and structure of gadolinium complexes in aqueous solution of carboxylate phosphabetaines** *Bakhtiyarov Dmitry, Semyon Romanov, Khasan Khayarov, Aleksander Gerasimov, Vladimir Galkin and Irina Galkina* Faculty of Chemistry, Kazan Federal University, Russia
P-14	**Synthesis and structure phosphonium salts, based on 3-diphenylphosphino)propionic and ω-haloalkylcarboxylic acids** *Bakhtiyarova Yulia, Maxim Morozov, Vladimir Galkin* Kazan Federal University, Russia
P-15	**Novel donor-acceptor luminophores based on triphenylamine** *Balakirev Dmitry O., Yuriy N. Luponosov, Evgeniya A. Svidchenko, Sergey A. Ponomarenko* Enikolopov Institute of Synthetic Polymer Materials Russia
P-16	**Model of selectivity on methyl nonanoate of 1-octene hydrocarbomethoxylation catalyzed by Pd(PPh3)2Cl2 / PPh3 / p-toluenesulfonic acid system** *Batashev Sergey, Nadezhda Sevostyanova* Research and Production Center "Himreaktivdiagnostika", Tula State Lev Tolstoy Pedagogical University, Russia
P-17	**Magnesium and zinc cyanophenoxy- phthalocyanine complexes. Synthesis and spectroscopic-luminescent properties** *Belikova Anastasia, Svetlana Tonkova, Kristina Kazaryan, Dmitry Erzunov, Arthur Vashurin* Ivanovo State University of Chemistry and Technology, Russia

POSTER SESSION 2 (NOVEMBER 20): P1-P138

P-18	**Anion effect on the cumene hydroperoxide decomposition in the presence of CU(II) 1,10-phenanthrolinates** *Berestneva Yuliya, Nikolaj Turovskij, Elena Raksha, Alexander Eresko* Federal State Budget Scientific Institution "Federal Scientific Centre of Agroecology, Complex Melioration and Protective Afforestation of the Russian Academy of Sciences", Russia
P-19	**Research of the reaction of oxidation of thiols in the presence of metal complexes** *Berestova Tatyana, Liana Nizametdinova, Olga Lusina, Ruslan Gizatov, Alexey Pishkin, Ludmila Kuzina, Akhat Mustafin* Faculty of Chemistry, Bashkir State University, Russia
P-20	**Dinuclear zirconocene catalysts for amine borane dehydropolymerisation** *Beweries Torsten, Kevin Lindenau, Michael Trose, Felix Anke, Susanne Boye, Albena Lederer, Fabian Reiß* Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Germany
P-21	**Synthesis of hybrid polymeric materials with bodipy and their use as sensors** *Bobrov Alexander, Mariya Kishalova, Yuriy Marfin* Department of Inorganic Chemistry, Ivanovo State Universityof Chemistry and Technology, Russia
P-22	**Towards automatic processing of esi-ms data: the case study of the palladium chloride pre-catalyst** *Bondarenko Anton A., Daniil A. Boiko, Konstantin S. Rodygin, Mikhail V. Polynsky, Valentine P. Ananikov* Saint Petersburg State University, Russia
P-23	**“Click” synthesis and electrochemical behaviour of redox-active pyridylphenylene dendrimers** *Chamkin Aleksandr A., Elena S. Serkova, Zinaida B. Shifrina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-24	**Two synthetic pathways for the preparation of the 4-pyridyl-terminated iron(II) cage complexes with non-equivalent capping groups: transmetallation vs direct template condensation** *Chuprin Alexander S., Semyon V. Dudkin, Svetlana A. Belova(Savkina), Genrikh E. Zelinskii, Anna V. Vologzhanina, Yan Z. Voloshin* A.N. Nesmeyanov Institute of Organoelenent Compounds, Russia
P-25	**Synthesis of new lipophilic aminophosphine oxides by the pudovik reaction** *Davletshin Rustam R., Aidar M. Gayneev, KamilaI. Karimova, Irina V. Galkina, Kamil A. Ivshin, Ol’ga N. Kataeva* A.M. Butlerov Chemical Institute, Kazan (Volga region) Federal University, Russia
P-26	**Membrane extraction of rare-earth metal ions by new bisphosphoryldiamines and bisphosphoryldiazapodands** *Davletshina Natal’ya V., Albina R. Khabibullina, Il’yas R. Nasyrov, Aynaz Z. Gaynullin, Rustam R. Davletshin, Rafael A. Cherkasov* A.M. Butlerov Chemical Institute, Kazan (Volga region) Federal University, Russia
P-27	**Copper (I) bromide complexes bearing phospholanylpyridines** *Dayanova Irina, Aliya Shamsieva, Robert Fayzullin, Elvira Musina, Andrey Karasik* Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Russia
P-28	**Intramolecular electron transfer in copper (II) complexes with aril-imidazo-1,10-phenanthrolines** *Dyachenko Natalia, SergeyTokarev, Yulia Sotnikova Olga Fedorova, Yuri Fedorov* Chemistry Department, Moscow State University, Russia
P-29	**Synthesis and characterization of novel transition metal oxo- clusters** *Fedulin Andrey, Uttam Chakraborty, Axel Jacobi von Wangelin* Department of Chemistry, University of Hamburg, Germany
P-30	**Binuclear complexes (BATH)2GD2(PIV)6•XSOLV: the effect of the structure on termal behavior and magnetic and luminescent properties** *Fomina I.G., A.B. Ilyukhin, Yu.S. Zavorotny, A.S. Bogomyakov, M.V. Fedin, I.L.Eremenko* Kurnakov Institute of General and Inorganic Chemistry, Russia
P-31	**Pd-catalyzed enantioselective allylic substitution with diastereomeric diamidophosphite-thioether ligands from glutamic and tartaric acids** *Gavrilov Vladislav K., Ilya V. Chuchelkin, Vladislav S. Zimarev, Ilya D. Firsin, Nataliya Goulioukina* Department of Chemistry, Ryazan State University named for S. Esenin, Russia
P-32	**Oxidation of hydride and p-tolylsiloxanes: development of catalytic approaches** *Goncharova Irina K., Ashot V. Arzumanyan, Aziz M. Muzafarov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia

POSTER SESSION 2 (NOVEMBER 20): P1-P138

P-33	**Metal organic frameworks based on 1,2,3-triazole-4,5-dicarboxylates of ree: kinetic aspects of energy transfer between lanthanides** *Gontcharenko V.E., Belousov Yu.A., Lunyov A.M., Sidoruk A.V.* M.V. Lomonosov Moscow State University, Faculty of Chemistry, Russia
P-34	**Molecular dynamics of the palladium-mediated carbon-heteroatom bonds formation** *Gordeev Evgeniy, Valentine Ananikov* N.D. Zelinsky Institute of Organic Chemistry, Russia
P-35	**On the mercury poisoning test selectivity: from amalgamation of palladium(0) to redox-transmetallation of p,c-palladacycle** *Gorunova Olga N., Ivan M. Novitskiy, Yuri K. Grishin, Igor P. Gloriozov, Victor N. Khrustalev, Konstantin A. Kochetkov, and Valery V. Dunina* A.N.Nesmeyanov Institute of Organoelement Compounds, Russia
P-36	**The features of the Interaction between pentaphenylantimony with pyrimidine-4(3H)-one derivatives** *Gubanova Yulia O., Vladimir V. Sharutin, Olga K. Sharutina, Dmitriy G. Kim, Kseniya Yu. Petrova* South Ural State University (National Research University), Russia
P-37	**Synthesis of new bis(styrilasageterocycles)** *Guskova Elena* D. Mendeleev University of Chemical Technology of Russia, Russia
P-38	**Sinthesis of hydrophobic glutathione-capped gold nanoclusters and it's aplication in chemiluminescense** *Iakimov Nikolai, Nikolay Melik-Nubarov* Department of Chemistry, Lomonosov Moscow State University, Russia
P-39	**Tertiary phosphines are effective catalysts for the α- / bis-addition of dialkylphosphites and diarylphosphine oxides to alkynes** *Il'in A.V., Antonova A.A., Frizen A.D., Galkin V.I.* A.M. Butlerov Institute of Chemistry, Kazan (Volga region) Federal University
P-40	**Modification of epoxy coatings with functional siloxanes** *Il'ina Maria A., Elena V. Khomko, Leonid N. Mashlyakovskii, Ekaterina A. Lebedeva* Saint-Petersburg State Institute of Technology, Russia
P-41	**Electrochemical synthesis, properties and reactivity of organonickel sigma-complexes of type [NiBr(aryl)(L)]** *Kagilev Aleksey, Zufar Gafurov, Ilyas Sahapov, Dmitry Yakhvarov* Kazan (Volga region) Federal University, Kazan, Russia
P-42	**Synthesis of the carborane complexes of ruthenium (II) with η3-phosphorus-containing and η3-nitrogen-containing ligands** *Kaltenberg Alexandr, Ivan Grishin* Lobachevsky State University of Niznhy Novgorod, Russian Federation
P-43	**Novel imidazole-based ligands for transition metal complexes** *Karnaukh Ksenia M., Igor A. Nikovskiy, Alexander V. Polezhaev Physics* Department, Lomonosov Moscow State University, Russia
P-44	**Cobaltocenium acetylsalicylate: synthesis and study of interactions with dna using circular dichroism** *Kaverin Mihail V. , Kirill K. Babievsky, and Lubov V. Snegur* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-45	**Dft analysis of the unprecedented reactivity of some organoarsenic and organoantimony compounds towards carbon-carbon multiple bonds** *Ketkov Sergey, Elena Rychagova, Libor Dostal* G.A Razuvaev Institute of Organometallic Chemistry RAS, Russia
P-46	**Synthesis of novel diphosphonium salts bearing 1,4-dihydroxynaphthalene fragment** *Khasiyatullina Nadezhda, Anastasiya Shinkareva, Vladimir Mironov* Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russia
P-47	**Cross-coupling of secondary phosphine selenides with mercaptoalcohols in the CCL4/Et3N system** *Khrapova Kseniya O., Anton A. Telezhkin, Pavel A. Volkov* A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Russia
P-48	**The first NCsp3N pincer ligand in the coordination chemistry of lanthanides and synthesis homoleptic stable complexes** *Khristolyubov D.O., D.M. Lyubov, A.V. Cherkasov, A.S. Shavyrin, A.A. Trifonov* G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-49	**Methanolysis of aryl(alkyl)hydrosilanes and ahpc of their dehydrocondensation products** *Klimova N.V., Ivanov A.G., Kuznetsova M.G., Shulyat'eva T.I., Lebedev A.V.* SSCRFJSC "GNIIChTEOS", Russia

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P-50	**Silver ion stabilization of cytosines in the structure of nucleic acids: a theoretical study using the combined QM/MM method** *Kliuev Pavel, Ruslan Ramazanov, Sokolov Petr* Department of Molecular Biophysics and Polymer Physics, Faculty of Physics, Saint-Petersburg, Russia
P-51	**Functional aryloxycyclotriphosphazenes for dentistry** *Kolpinskaya Natalya, Evgeniy Chistyakov, Vladimir Chuev, Vyacheslav Kireev* D. I. Mendeleyev University of Chemical Technology of Russia, Moscow, Russia
P-52	**Diels-alder reaction between 2,5-dimethylthiophene and n-phenylmaleimide at high pressure** *Kornilov Dmitry A., Oleg V. Anikin, Alexey A. Shulyatiev* Faculty of Chemistry, Kazan Federal University, Russian Federation
P-53	**Catalytic activity of novel lanthanide cymantrenecarboxylates with ferrocene phosphine oxido ligand in polymerization processes** *Koroteev Pavel S., Andrey B. Ilyukhin, Nikolay N. Efimov, Marina V. Pavlovskaya, Dmitry F. Grishin* N.S. Kurnakov Institute of General and Inorganic Chemistry, Russia
P-54	**Reactions of zirconacyclopentadiene complexes of zirconozene with acenaphthenequinone** *Kozulin Konstantin V., Vladimir V. Burlakov, Maxim V. Andreev, Vyacheslav S. Bogdanov, Vladimir B. Shur* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-55	**Varios methods of activation of titanium complex with saligenin ligand to obtain UHMWPE** *Kurmaev Dmitrii, Svetlana Gagieva, Vladislav Tuskaev* Faculty of Chemistry, Moscow State University, Russia
P-56	**Cobalt-catalyzed alkylation of indoles with methyl 3,3,3-trifluoro-2-diazopropionate** *Kuvshinova Sofya S., Daria V. Vorobyeva, Sergey N. Osipov, Dmitry A. Loginov* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-57	**New type of Hoveyda-Grubbs catalysts for ROCM reactions of oxabicycloheptenes with alkenes** *Kvyatkovskaya Elizaveta, Fedor Zubkov, Pavel Kumadin, Pavel Paspertov, Kirill Polyanskii* Peoples' Friendship University of Russia (RUDN University), Russia
P-58	**Divalent ytterbium, samarium and calcium complexes coordinated by NHC ligands – versatile catalysts for highly regio- and chemoselective hydrophosphinations** *Lapshin Ivan, Alexander Trifonov* G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-59	**Ruthenium (II) mixed-ligand complexes with 2-arylbenzimidazoles and 4,4`-dicarboxy-2,2`-bipyridine: synthesis, optical and electrochemical properties** *Lavrova Maria, Sergei Mishurinskiy, Sergei Tatarin, Stanislav Bezzubov, Vladimir Dolzhenko* Department of Chemistry, Lomonosov Moscow State University, Russia
P-60	**Derivatives of closo-decaborate anion with pendante polyamine groups** *Limarev I.P., Matveev E.Yu., Zhizhin K.Yu.* Kurnakov Institute of General and Inorganic Chemistry, Russia
P-61	**Amido rare earth complexes coordinated by tridentate amidinate ligand. The synthesis, structure and catalytic activity** *Linnikova O.A., A.A. Trifonov* G. A. Razuvaev institute of organometallic chemistry of russian academy of sciences, Nizhny novgorod, Russia
P-62	**Development of molecular materials based on porphyrin derivatives of metals with high-performance optoelectronic and magnetocaloric properties** *Lomova Tatyana* Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Russia
P-63	**Facile access to aldehydes from calcium carbides as sustainable carbon source** *Lotsman Kristina, Konstantin Rodygin, Valentine Ananikov* Saint Petersburg State University, Russia
P-64	**Unraveling structural, orbital, and spectral properties of D^0 organometallics: effective computational route** *Loukova Galina V., Alexey A. Milov, Vladimir I. Minkin* Institute of Problems of Chemical Physics, Russian Academy of Sciences, Russia
P-65	**Tris(pyrazolyl)methane and tris(pyrazolylmethyl)amine –versatile ligands for design of In(III) complexes featuring magnetic and luminescent properties** *Lyubov Dmitry, Tatyana Mahrova, Jérôme Long, Julia Larionova, Alexander Trifonov* Institute of Organometallic Chemistry of Russian Academy of Sciences, Russia

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P-66	**Carboranyl tetrazoles as high energy compounds: synthesis and a computational study** *Makarenkov Anton, Elena Kononova, Andrey Ponomaryov, Sergey Kiselev, Yurii Borisov, Valentina Ol'shevskaya* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-67	**Molecular structure of zirconium carbosilanes** *Mapolis A.P., G.I. Shcherbakova, P.A. Storozhenko* MIREA - Russian Technological Universityof Fine Chemical Technologies named after M.V. Lomonosov, Russia
P-68	**Bis(arene)chromium 1-(1-(N-phenylpropionamido)ethyl)-1-hydrofullerides** *Markin Gennady, Sergey Ketkov, Mikhail Lopatin, Andrei Shavyrin, Vyacheslav Kuropatov, Alexey Belikov* G.A. Razuvaev Institute of Organometallic Chemistry, Nizhny Novgorod, Russia
P-69	**Perfluorocarbon emulsion with porphyrinoids in photodynamic therapy** *Markova Alina, Elizaveta Belyaeva, Aida Ataeva, Sergey Kurkov, Nikolay Chkanikov, Alexander Shtil'* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-70	**Synthesis of derivatives of anion [B10H10]2- with biologically active pendante groups** *Matveev E.Yu., Akimov S.S., Zhizhin K.Yu.* MIREA – Russian Technological University, Russia
P-71	**New tripodal ligands on the triphenylphosphine oxide platform as ancestors of atrane-type lanthanide complexes** *Matveeva Anna, Igor Kudryavtsev, Margarita Pasechnik, Sergey Matveev, Tat'yana Baulina, Olga Bykhovskaya, Valery Brel* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-72	**Synthesis of new bulky phosphite and phosphoramidite ligands and their application in asymmetric hydrogenation** *Mikhel Igor S., Sergey E. Lyubimov, Marina V. Sokolovskaya, Kirill P. Birin, Vadim A. Davankov* A.N. Frumkin Institute of Physical Chemistry and Electrochemistry, Russia
P-73	**Synthesis and cytotoxicity of novel daunorubicin derivatives** *Moiseeva Aleksandra, Oleg Artyushin,Valery Brel* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-74	**Charge-compensated rhodacarboranes as catalysts for annulation of arylcarboxylic acids with acetylenes** *Molotkov Alexander P., Dmitry A. Loginov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-75	**Monosubstituted pillar[5]arenes containing phosphoryl fragment as hosts for some metal cations** *Nazarova Anastasia A., Alsu I. Gilyazeva, Pavel L. Padnya, Ivan I. Stoikov* A. M. Butlerov Chemical Institute, Kazan Federal University, Russia
P-76	**Electrochemical properties of n-substituted α-diphenylphosphinoglycines** *Nesterova Alina, Olga Soficheva, Dmitry Yakhvarov* Kazan (Volga region) Federal University, Kazan, Russia
P-77	**Terpenylammonium salts in catalytic and stoichiometric reactions with dibenzylideneacetone-palladium (0) complexes** *Nikolaev Semen E., Dmitry V. Khomishin, Zoya A. Starikova, Fedor M. Dolgushin, Elena A. Petrushkina* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-78	**Synthesis of O-trimethylsilyl-N-(phenylsulfonyl)acetimidate** *Nikonov Alexey, Valeriy Serykh, Nikita Kolyvanov, Irina Sterkhova* A. E. Favorskii Irkutsk Institute of Chemistry, Siberian Division of Russian Academy of Sciences, Russia
P-79	**The Study of METHYL(R)CYCLOSILOXANES (R=H, ViNYL, Phenyl) with 1D- ^{1}H, ^{13}C, ^{29}Si and 2D-HSQC, DOSY NMR** *Nosova Valentina, Alexander Kisin, Dmitry Cheshkov, Vera Ivanova, Michail* State Research Institute of Chemistry and Technology of Organoelement Compounds, Russia
P-80	**Adenine and guanine perrhenates** *Novikov A.P., Grigoriev M.S. Safonov A.V., German K.E., Khrustalev V.N.* Peoples' Friendship University of Russia, Moscow, Russia
P-81	**Activation of C–H bonds of aromatic hydrocarbons under the action of DL-N-butylhafnocene** *Nurzhanova Elizaveta R., Vladimir V. Burlakov, Maxim V. Andreev, Vyacheslav S. Bogdanov, Vladimir B. Shur* A.N. Nesmeyanov Institute of Organoelement Compounds, Russian
P-82	**Peroxo complexes as models of metalloenzymes** *Oleksiienko Anna-Mariia, Alexandrova Lyubov Sergeevna, Smakotina Valeria Valeryevna, Scherbakova Elena Alekseevna, Danilova Marina Victorovna, Sharipov Mikhail Yuryevich* Institute of General and Inorganic Chemistry RAS N.S. Kurnakova, Russia

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P-83	**Epoxy-poss as a modyfier for epoxy compositions** *Olikhova Yulia V., Alexander G. Ivanov* D. Mendeleev University of Chemical Technologyof Russia, Russia
P-84	**The use of (α-ferrocenylalkyl) carbonates in the synthesis of ferrocene containing amino acids** *Opredelennova Ksenia, Ekaterina Shevaldina, Sergey Moiseev* MIREA – Russian Technological University, Russia
P-85	**Organometallic Chemistry of new carbon materials: DFT investigation** *Oprunenko Yu. F., Nechaev M. S., Gloriozov I. P., Kovalenko A. A., Zhulyaev N. S.* Department of Chemistry, Moscow State University, Russia
P-86	**The lacking ruthenium cluster $Cp_4Ru_4(CO)_4$** *Osintseva Svetlana, Nikollay Shtel'tser, Arkadii Kreindlin, Fedor Dolgushin, Oleg Semeikin* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-87	**The biological decomposition of aromatic hydrocarbons as a way to improve of ecology** *Osipov Yaroslav* Vilnius Gediminas Technical University, Lietuva
P-88	**Advanced analysis of thermochemical properties of metallic alkanes of i-iv groups of mendeleev's table** *Ovchinnikov Vitaly, Alexey Kulakov* Department of General Chemistry and Ecology, Kazan national research technical university, named after A.N. Tupolev-KAI, Russia
P-89	**Synthesis of bis-NHC-silver(I) ionic complexes with 13 group metal halides** *Parfenyuk Tatyana, Igor Kazakov, Alexey Timoshkin* St. Petersburg State University, Russia
P-90	**Development of new receptors for heavy metal cations** *Pashanova Anna, Anastasia Zubenko* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-91	**Carborane complexes of ruthenium (II) with diphosphine ligands: synthesis and use in catalysis** *Penkal Anastasia M., Nikolay V. Somov, Ivan D. Grishin* Lobachevsky State University of Nizhny Novgorod, Russia
P-92	**Regularities of direct synthesis of methylchlorogermanes** *Pererva Oleg V., Sofiya A. Medvedeva, Yurii P. Endovin* SSC RF JSC GNIIChTEOS , Russia
P-93	**1-(2,7-dimethyl-2,7-octadien-1-yl) – benzimidazole and 1-(2,7-dimethyl-1,7- octadien-3-yl) benzimidazole as fungicides** *Petrushkina Elena A.* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-94	**Synthesis and investigation of structure of m-cresolesulfonis acid salts with NH4+, K+, RB+ and CS+ cations by X-RAY structural and vibrational spectroscopy methods** *Pisarev Rostislav V., Pisareva Anna V., G. V. Shilov, A. I. Karelin, Yu. A. Dobrovolsky* Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia
P-95	**Two new polymorphs of cis-perinone: crystal structures, physical and electric properties** *Polozov M. A., , V.V. Polozova, D. A. Zherebtsov, C. P. Sakthidharan,* *R. Kanthapazham, S. A. Nayfert, V. V. Avdin.* Faculty of chemistry, South Ural State University, Russia
P-96	**Study of the cation-dependent resonance energy transfer in the crown-containing bischromophoric system based on 4-alcoxy- and 3,4-dimetoxystyril-1,8-naphthalimide** *Polyakova Anna, Pavel Panchenko* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-97	**Cyclohexadienyl rhodium complexes. synthesis and reactivity** *Pototskiy Roman A., Dmitry S. Perekalin* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-98	**Rotaxane strucrures based on monophosphorylated pillar[5]arenes** *Potrekeeva Olga S., Anastasia A. Nazarova, Ivan I. Stoikov* A. M. Butlerov Chemical Institute, Kazan Federal University, Russia
P-99	**Synthesis of new functionalized aryl and hetaryl aminomethylenebisphosphonic acids via silicon-assisted methodology** *Prishchenko Andrey A., Roman S. Alekseyev, Mikhail V. Livantsov, Olga P. Novikova, Ludmila I. Livantsova, Valery S. Petrosyan* Department of Chemistry, M.V. Lomonosov Moscow State University, Russia
P-100	**Quantum chemical investigation of dipyrromethene complexes with D-elements** *Prokopenko Aleksandr, Rimma Kuznetsova , Vladimir Pomogaev, Ruslan Ramazanov, Mikhail Berezin* National Research Tomsk State University, Tomsk, Russia

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P-101	**Fluorine-containig enaminones as europium (III) complexonates** *Pugachov Dmitry, George Zatonskii, Natal'ya Sverdlova, Nikolai Vasil'ev* Moscow Region State University, Russia
P-102	**Bis(alkyl) rare-earth (III) complexes supported by amidinate-type ligands** *Rad'kova Natalia, Grigorii Skvortsov, Anton Cherkasov, Alexander Trifonov* G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Russia
P-103	**First example of intermolecular homo-coupling of alkynyl phosphins with the formation of metallacyclopentadienes** *Ramazanov Ilfir R., Rita N. Kadikova, Aliya K. Amirova, Usein M. Dzhemilev* Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences, Russia
P-104	**A general benzylic C-H activation and C-C coupling reaction at zirconocenes mediated by C-N bond cleavage in tert-butylisocyanide – unusual formation of iminoacyl complexes** *Reiß Fabian, Melanie Reiß, Perdita Arndt, Anke Spannenberg, Claas Schünemann, and Torsten Beweries* Leibniz Institute for Catalysis at the University of Rostock, Germany
P-105	**Tertiary phosphines in reactions with substituted cinnamic acids** *Romanov Semyon, Alfiya Aksunova, Yulia Bakhtiyarova, Vladimir Galkin* Kazan Federal University, Russia
P-106	**Theoretical and experimental-theoretical approach to the study of the topology of electron density in $\{Yb^{2+}{}_2(\mu_2\text{-}OCH(CF_3)_2)_3(\mu_3\text{-}OCH(CF_3)_2)_2\,Yb^{3+}(OCH(CF_3)_2)_2(DME)_2\}$** *Rumyantcev Roman, Georgy Fukin* G.A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-107	**Synthesis of functionalized azo dyes and their siloxane derivatives to obtain colored polymer microspheres** *Ryzhkov A.I., Drozdov F.V., Cherkaev G.V., Gritskova I.A., Muzafarov A.M.* ISPM RAS, Moscow, Russia
P-108	**New ruthenocene-based palladium and ruthenium pincer complexes bearing the C5(CH3)4(CF3) ligand** *Safronov Sergey V., Alexander A. Pavlov, Alla A. Kamyshova, Viacheslav I. Sokolov, Elena S. Shubina, Avthandil A. Koridze* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-109	**Controlling the functions of biomolecules in solution using [2+2] photocycloaddition** *Saifutiarova Alina, Elena Guskova, Elena Gulakova, Olga Fedorova, Yuri Fedorov* A. N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-110	**Stable alkyl- and cationic alkyl complexes of LN (II, III) as effective catalysts for functionalization of six-membered N-containing heterocycles** *Selikhov A.N. and A.A. Trifonov* G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-111	**Synthesis of N-(silylmethyl)benzenesulfonamides** *Serykh Valeriy, Alexey Nikonov, Nikita Kolyvanov* A. E. Favorskii Irkutsk Institute of Chemistry, Siberian Division of Russian Academy of Sciences, Russia
P-112	**One-pot cyclohexyl cyclohexanecarboxylate synthesis from cyclohexanol and co at catalysis by Pd(PPh3)2Cl2 / PPh3 / p-toluenesulfonic acid system** *Sevostyanova Nadezhda, Sergey Batashev* Research and Production Center "Himreaktivdiagnostika", Tula, Russia
P-113	**Synthesis of biologically active metal complexes based on 3-formilchromone derivatives** *Shatokhin Stanislav S., Vladislav A. Tuskaev, Svetlana Ch. Gagieva, Eduard T. Oganesyan* Pyatigorsk Medical and Pharmaceutical Institute – branch of Volgograd State Medical University, Russia
P-114	**Condensation of organoyttriumoxanalumoxanes with chromium acetylacetonate** *Shcherbakova Galina, Natalia Kutinova, Maxim Shaukhin, Oleg Abramova* State Research Institute for Chemistry and Technology of Organoelement Compounds, Russia
P-115	**The synthesis of new compounds with potencial biologic activity based on fullerene C_{60} and a derivative of vitamin B_{12}** *Shepeta Nadezhda, Valentina Romanova, Konstantin Kochetkov* A.N.Nesmeyanov Institute of Organoelement Compounds, Russia
P-116	**Sydnone imines – plant growth regulators** *Shevaldina Ekaterina, Ilya Cherepanov, Yury Spiridonov, Sergey Moiseev* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia

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P-117	**1-aminophosphonic acid derivatives of p-tert-butylthiacalix[4]arene for construction of biocompatible hybrid nanomaterial for bone implantants: synthesis and supramolecular properties** *Shibaeva Ksenia, Dmitriy Shurpik, Ivan Stoikov* Alexander Butlerov Institute of Chemistry, Kazan Federal University, Russia
P-118	**2,2'-Dihydroxyazobenzene as (ONO')TRIDENTATE ligand: Synthesis and Structure of pentacoordinate silicon complexes** *Soldatenko Anastasiya S., Irina V. Sterkhova and Nataliya F. Lazareva* A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Russia
P-119	**Features of the electronic structure of neutral complexes of Fe (III) with salicylaldehyde thiosemicarbazone ligand** *Spitsyna Nataliya, Maxim Blagov, Vladimir Krapivina* Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia
P-120	**Oxaphospholenes and phosphacoumarins in synthesis of functionaly substituted phosphonium salts and phosphine oxides with antimicrobial activity and antitumor activity** *Tatarinov D. A., N. V. Terekhova A.D., Voloshina A.S., Sapunova A.P., Lyubina V. F. Mironova* Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Russia
P-121	**Chemoselective oxidative phosphorylation of aminothiophenols with the secondary phosphine selenide/CCL_4/ET_3N system** *Telezhkin Anton A., Kseniya O. Khrapova, Pavel A. Volkov* A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Russia
P-122	**Oxaphosphole 2-oxides on a basis of 2-Hydroxy-α,α-dimethylarylmethanol in reactions with organomagnesium compounds** *Terekhova Natalia V., Dmitry A. Tatarinov, Valery K. Brel, Vladimir F. Mironov* Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center, Russian Academy of Sciences, Russia
P-123	**Tetra-4-(4-butyl/butoxyphenoxy)phthalocyanines of cobalt and copper** *Tikhomirova Tatiana, Dmitry Erzunov, Vladimir Maizlish, Arthur Vashurin* Department of Inorganic Chemistry. Ivanovo State University of Chemistry and Technology, Russia
P-124	**Single molecule magnets based on DY3+ complexes supported by diazabutadiene and alkoxide ligands** *Tolpygin A.O., Jérôme Long, A.A. Trifonov* Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-125	**Mesoionic derivatives of siloxanes** *Trankina Ekaterina, Ilya Cherepanov, Natalia Frolova, Ivan Godovikov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-126	**Reductive amidation without external hydrogen source** *Tsygankov Alexey A., Maria Makarova, Karim M. Muratov, Oleg I. Afanasyev and Denis Chusov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-127	**Complexation of the perfluorinated three-mercury anticrown (o-C6F4Hg)3 with monohalobenzenes** *Tugashov K.I., S.M. Yunusov, E.S. Kalyuzhnaya, F.M. Dolgushin, A.S. Peregudov, Z.S. Klemenkova, M.Kh. Minacheva, I.A. Tikhonova, V.B. Shur* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-128	**Synthesis of new cage systems based on 1,3,5-trihydroxy-1,3,5-triazacyclohexanes** *Ushakov Pavel, Ivan Golovanov, Alexey Sukhorukov* M.V. Lomonosov Moscow State University, Moscow, Russia
P-129	**Synthesis and study of crown-containing bisstyryl dye complexes with various metal cations by using fret process** *Ustimova Mariya A., Olga A. Fedorova, Yuriy V. Fedorov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-130	**Electron-microscopic analysis of hybrid materials based on multi-wall carbon nanotubes and WO3 and CUO nano-coatings** *Vilkov Ilya, Kirill Kremlev, Pavel Andreev, Galina Zabrodina, Anatoly Obyedkov, Boris Kaverin, Nicolay Semenov, Sergey Ketkov, Sergey Gusev, Dmitry Tatarsky* Institute of Metalorganics Chemistry G.A. Rasuvaeva RAS, Nizhny Novgorod, Russia
P-131	**Catalyst-free phosphorylation of pyridines with secondary phosphine chalcogenides triggered by acylacetylenes: novel type of S_n^har reaction** *Volkov Pavel A., Anton A. Telezhkin, Kseniya O. Khrapova* A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, Russia

POSTER SESSION 2 (NOVEMBER 20): P1-P138

P-132	**Synthesis of α-cf3-α-ornithine derivatives via copper (I)-catalyzed hydroamination of alennes** *Vorobyeva Daria, Anna Philippova, Sergey Osipov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-133	**Synthesis of hydrophobic, hydrophilic and amphiphilic stereoregular organocyclosilsesquioxanes** *Vysochinskaya Yulia, Anton Anisimov, Olga Shchegolikhina, Aziz Muzafarov* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-134	**Synthesis and photophysical properties of ruthenium (II) complexes containing 1H-imidazo[4,5-f] [1,10]phenanthroline and bipyridine derivatives** *Yaltseva Polina, Sergey Tokarev, Olga Fedorova, Yuri Fedorov* Chemistry Department, Lomonosov Moscow State University, Russia
P-135	**Novel hybrid materials based on multi-walled carbon nanotubes and nanoscale coatings of copper oxide or tungsten oxide** *Zabrodina Galina, Kirill Kremlev, Ilya Vilkov, Anatoly Obiedkov* G. A. Razuvaev Institute of Organometallic Chemistry of Russian Academy of Sciences, Nizhny Novgorod, Russia
P-136	**Efficient access to the carborane triazole porphyrins via copper-catalyzed 1,3-dipolar cycloaddition reaction and their photophysical and biological properties** *Zaitsev Andrei, Anton Makarenkov, Alexandra Radchenko, Alexey Kostyukov, Alina Markova, Vladimir Kuzmin, Alexander Shtil, Valentina Ol'shevskaya*. A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-137	**Conjugates of naphthalimide dyes and bacteriochlorin derivative as theranostic agents for photodynamic therapy** *Zakharko M.A., Panchenko P.A., Fedorova O.A., Pritmov D.A., Grin M.A., Mironov A.F.* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-138	**Comparison of complexing properties of amide-type benzo- and pyridine-azacrown compounds** *Zubenko Anastasia, Bayirta Egorova, Olga Fedorova* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia
P-139	**Protolysis os seven-membered zirconacyclocumulenes** *Andreev Maxim V., Vladimir V. Burlakov, Vyacheslav S. Bogdanov, Perdita Arndt, Wolfgang Baumann, Anke Spannenberg, Uwe Rosenthal, Torsten Beweries, Vladimir B. Shur* A.N. Nesmeyanov Institute of Organoelement Compounds, Russia

1. PLENARY SPEAKERS

RECENT ADVANCES IN CATALYSIS OF ORGANIC REACTIONS

Irina P. Beletskaya

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New trends in Pd- and Cu-catalyzed reactions of substitution and addition will be considered.

References

1. C. Najera, I. P. Beletskaya, M. Yus, *Chem. Soc. Rev*. **2019**, *48*, 4515.
2. A. Y. Mitrofanov, I. P. Beletskaya, *Mendeleev Comm*. **2019**, *29*, 378.
3. I. P. Beletskaya, F. Alonso, V. Tyurin, *Coord. Chem. Rev.* **2019**, *385*, 137.
4. A. D. Averin, I. P. Beletskaya, *Pure and Appl. Chem*. **2019**, *91*, 633.

POLYMERS IN SUPERCRITICAL MEDIA: SYNTHESIS, MODIFICATION, AND PROCESSING

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The presentation will address various aspects of the usage of supercritical media for the synthesis, modification, and processing of polymers. The advantageous features of this type of solvent are related to the ability to fine-tune its parameters (dissolving power, density, dielectric constant, etc.) by varying temperature and pressure. The absence of capillary effects caused by surface tension for ordinary liquid solvents provides new possibilities concerning the problems of forming highly homogeneous coatings on various surfaces. The fundamentally non-perturbing nature of the solvent removal procedure, in this case, allows the formation of nanoscale and well-defined structures from polymeric materials on substrates. It becomes possible to pattern regularly the substrates and this is important for practical tasks of (electro)catalysis. The advantages of a supercritical solvent are especially pronounced when solving the problem of modifying substrates with developed relief geometry of the surface. The unhindered penetration of the polymer solution in the supercritical fluid into any open pores and the non-perturbing nature of the solvent removal allows the deposition of both ultrathin and homogeneous defect-free coatings. Minimal amounts of polymeric material are already sufficient due to these features for modifying the surface properties of substrates: such as hydrophobicity, oleophobicity, biocompatibility, etc. Improved textile materials with the minimum amount of modifying polymer agent (due to its negligibly small presence it does not manifest itself in other properties of the fabric: color, mechanics, the comfort of wearing, etc.), are in high demand for real applications in light industry. Special prospects also are related to the uniform impregnation of matrices with solutions in supercritical fluids and the subsequent formation of polymer-polymer or polymer-inorganic composites.

Acknowledgements

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BEYOND SINGLE-SITE CATALYSTS THROUGH SURFACE ORGANOMETALLIC CHEMISTRY

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The rational design and development of catalysts require structure – reactivity relationship approach, hence the need for strategies to obtain well-defined surface sites and their detailed characterization.

Here, we discuss the method to control and understand the chemistry at the surface of materials towards the development of well-defined – so-called single-site – heterogeneous catalysts and show how this approach can bring about information about industrial catalysts and very complex systems such as supported metal nanoparticles.[1]

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References

1. C. Copéret, *Acc. Chem. Res.* **2019**, *in press*, DOI: 10.1021/acs.accounts.9b00138.

VISIBLE LIGHT PHOTOCATALYSIS FOR ORGANIC SYNTHESIS

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The use of visible light in organic synthesis has received a lot of attention over the last decade, although the concept is more than 100 years old.[1] Visible light is easily generated, safe, leaves no trace as a reagent in the reaction mixture and can provide energy to initiate kinetically hindered or even endothermic reactions. This improves the efficiency and selectivity of known organic reactions, but also enables hitherto unknown transformations.[2]

However, the energy of visible light photons is small compared to chemical bond energies. To overcome this limitation more than one visible light photon is required. By consecutive photoinduced electron transfer (conPET)[3] a colored and persistent radical anion of the photocatalysts is generated, which is subsequently again excited gaining additional redox energy. Transfer of the electron to a substrate closes the catalytic cycle. Our first generation of conPET catalysts, perylenediimides (PDI), suffered from low solubility and strong aggregation. Rhodamine 6G, a second-generation conPET catalyst, is commercially available, highly soluble and provides upon visible light excitation a reduction power of up to -2.4 V vs SCE.[4,5]

We discuss synthetic applications of photocatalysis including the utilization of carbon dioxide as a C1 building block in synthesis,[6] the selective C-F bond activation[7] and dual photo-metal catalytic cross-coupling and isomerization strategies.[8,9]

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References

1. G. Ciamician, *Science***1912** September 27.
2. L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed*. **2018**, *57*, 10034.
3. I. Ghosh, T. Ghosh, J. I. Bardagi, B. König, *Science***2014**, *346*, 725.
4. I. Ghosh, B. König, *Angew. Chem. Int. Ed.***2016***55*, 7676.
5. I. Ghosh, R. S. Shaikh, B. König, *Angew. Chem. Int. Ed*. **2017**, *56*, 8544.
6. (a) Q.-Y. Meng, S. Wang, G. S. Huff, B. König, *J. Am. Chem. Soc*. **2018**, *140*, 3198. (b) Q.-Y. Meng, S. Wang, B. König, *Angew. Chem. Int. Ed*. **2017**, *56*, 13426. (c) Q.-Y. Meng, T. E. Schirmer, A. L. Berger, K. Donabauer, B. König, *J. Am. Chem. Soc.***2019**, *141*, 11393.
7. K. Chen, N. Berg, R. Gschwind, B. König, *J. Am. Chem. Soc*. **2017**, *139*, 18444.
8. I. Ghosh, J. Khamrai, A. Savateev, N. Shlapakov, M. Antonietti, B. König, *Science***2019**, *365*, 360.
9. Q.-Y. Meng, T. E. Schirmer, K. Katou, B. König, *Angew. Chem. Int. Ed.***2019**, *58*, 5723.

HOMOLYTICALLY WEAK METAL-CARBON BONDS AND THE PERSISTENT RADICAL EFFECT IN METAL-MEDIATED RADICAL POLYMERIZATION

RinaldoPoli

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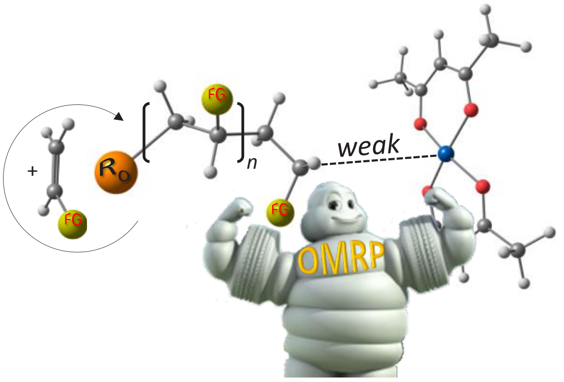

Transition metal alkyl complexes are the quintessence of organometallic chemistry. Their high reactivity often requires strictly controlled conditions for their synthesis and study, but this reactivity (e.g. reductive elimination, insertion, etc.) can be harvested to accomplish many useful catalysed processes. Homolytic cleavage of the metal-carbon bond is another possible decomposition pathway of organometallic compounds, thus most investigated systems feature sufficiently strong bonds. However, homolytic bond cleavage to produce carbon-based radicals can also be harvested, via the principle of the "persistent radical effect" (PRE),[1] to accomplish useful chemical processes such as selective transformations in metal-mediated organic synthesis[2]and controlled radical polymerization.[3] Specifically, there has been an explosion of research activity in the polymer area after the discovery of various methods to insure pseudo-living chain growth and to engineer elaborate, high-added-value polymeric architectures. Transition metal complexes may serve as moderating species, as in Atom Transfer Radical Polymerization (ATRP) and Organometallic Mediated Radical Polymerization (OMRP). This lecture will illustrate how the accurate calculation,[4] backed up by experimental benchmarking,[5] of homolytic metal-carbon bond dissociation energies has permitted to achieve unprecedented control for the radical polymerization of challenging monomers such as vinyl acetate[6] and vinylidene fluoride.[7]

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References

1. H. Fischer, *Chem. Rev.* **2001,** *101*, 3581-3610.
2. S.W.M. Crossley, C. Obradors, R.M. Martinez, R.A. Shenvi, *Chem. Rev.* **2016,** *116*, 8912-9000.
3. (a) R. Poli, *Angew. Chem. Int. Ed.* **2006,***45*, 5058–5070. (b) R. Poli, *Chem. Eur. J.* **2015,** *21*, 6988-7001. (c) C. Fliedel, R. Poli, *J. Organomet. Chem.* **2019,***880*, 241-252.
4. R. Poli, S. M. W. Rahaman, V. Ladmiral, B. Améduri, *J. Organomet. Chem.* **2018**, *864*, 12-18.
5. R. Morales-Cerrada, C. Fliedel, J.-C. Daran, F. Gayet, V. Ladmiral, B. Améduri, R.; Poli, *Chem. Eur. J.* **2019**, *25*, 296-308.
6. A. N. Morin, C. Detrembleur, C. Jérôme, P. D. Tullio, R. Poli, A. Debuigne, *Macromolecules* **2013,** *46*, 4303–4312.
7. (a) S. Banerjee, V. Ladmiral, A. Debuigne, C. Detrembleur, R. Poli, B. Améduri, *Angew. Chem. Int. Ed.* **2018**, *57*, 2934–2937. (b) P. G. Falireas, V. Ladmiral, A. Debuigne, C. Detrembleur, R. Poli, B. Ameduri, *Macromolecules* **2019**, *52*, 1266-1276.

ALKALINE EARTH METAL ORGANOMETALLICS: FROM POLYMERIZATION TO CATALYSIS

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Grignard reagents have been known for over a century and its early recognition by the 1912 Nobel prize has certainly been a forebode to its important role in the progress of organic chemistry. In contrast, the organometallic chemistry of the heavier group 2 metals Ca, Sr and Ba only started to develop since the beginning of this century. This is mainly due to their very high reactivity and air-sensitivity but also to the weak metal-ligand bonding that makes syntheses of well-defined complexes a challenge.

Our endeavors in heavier alkaline earth metal chemistry started in the late 90's in the form of a cooperation with BASF on the development of initiators for the living and stereoselective polymerization of styrene. The last decades have seen rapid developments in the general use of these highly reactive entities in catalysis.[1] Highlights include alkene functionalization by hydrosilylation, hydroamination or phosphination, hydroboration or even hydrogenation. Key to their catalytic activity is the formation of metal hydride complexes.

Latest advancements include the isolation of highly reactive strontium hydride and alkyl complexes which show facile nucleophilic aromatic substitution with benzene.[2] We present a short overview of these developments.

Powerful Sr hydride and alkyl nucleophiles

References

1. (a) S. Harder, *Chem. Rev.* **2010**, *110*, 3852-3876; (b) M. S. Hill, D. J. Liptrot, C. Weetman, *Chem. Soc. Rev.* **2016**, *45*, 972-988.
2. B. Rösch, T. X. Gentner, H. Elsen, C. A. Fischer, J. Langer, M. Wiesinger, S. Harder, *Angew. Chem. Int. Ed.* **2019**, *58*, 5396-5401.

ALKANE FUNCTIONALIZATION, THE AVENIR OF A NEW ERA IN ORGANIC SYNTHESIS?

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The extensive use as non-renewable fossil fuels of alkanes, which are abundant and carbon-rich species, is a subject of concern not only associated to their irreversible loss, but also to the transfer of carbon to the atmosphere leading to the accumulation therein of carbon dioxide with environmental sequels.

This lecture addresses the following issues: can the current general application and loss of alkanes be replaced by their use as alternative raw materials for organic synthesis, and can that be achieved under sustainable conditions?

The approaches followed by the author´s research Group towards the development of selective catalytic processes for alkane functionalization under mild conditions to afford organic compounds with an added value concern the following types of reactions:

- Oxidation of alkanes to alcohols and ketones;
- Oxidation of cyclohexane to adipic acid;
- Carboxylations (including hydrocarboxylation) of alkanes to carboxylic acids.

The use of different types of media (namely water, ionic liquid or organic solvent) and of catalysts (based on either transition or non-transition metals, with various types of ligands; homogeneous or supported ones) and of different types of promoters and energy inputs are discussed.

Some catalytic systems exhibit the highest reported activities in this field. Mechanistic proposals and prospects are also addressed.

Acknowledgements

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References

A.J.L. Pombeiro, M.F.C. Guedes da Silva (eds.), “Alkane Functionalization”, J. Wiley& Sons, Hoboken, NJ, USA, 2019 (ISBN: 9781119378808).

Selected Chapters: Preface (A.J.L. Pombeiro, M.F.C. Guedes da Silva); Ch.1 (A.J.L. Pombeiro): Overview; Ch.7 (D.S. Nesterov, O.V. Nesterova, A.J.L. Pombeiro): Oxidation with multinuclear heterometallic catalysts; Ch.16 (M. Sutradhar, L.M.D.R.S. Martins, M.F.C. Guedes da Silva, A.J.L. Pombeiro): Oxidation with V and Cu catalysts; Ch.19 (A.M.F. Phillips, A.J.L. Pombeiro): Carbonylation and hydroxycarboxylation; Ch.24 (A.P.C. Ribeiro, E.C.B.A. Alegria, A. Palavra, A.J.L. Pombeiro): Functionalization under unconventional conditions; Ch.25 (K.T. Mahmudov, M.F.C. Guedes da Silva, F.I. Zubkov, A.J.L. Pombeiro): Non-covalent interactions in alkane chemistry.

METAL-ORGANIC FRAMEWORKS: CHEMICAL DESIGN AND MULTIFUNCTIONAL PROPERTIES

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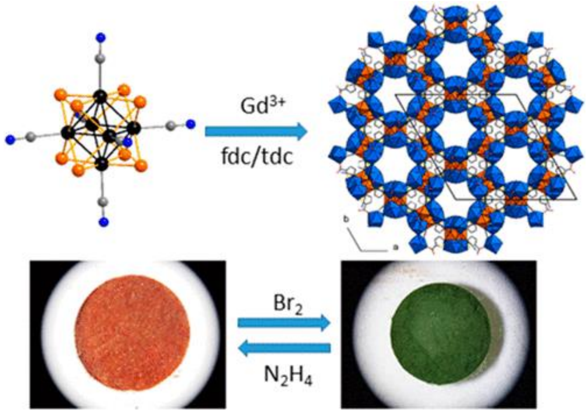
Metal-organic frameworks (MOFs) are among the most fascinating families of solid-state materials, because of their highly tunable compositions, structures, and functional properties. Lying on the crossing of fundamental inorganic/organic/supramolecular chemistry and development of novel materials, MOFs have become one of the most attractive research fields during the past two decades. Here we describe some of the work on chemical design, synthesis, structural characterization and investigation of multifunctional materials based on MOFs carried out at NIIC SB RAS during last years.

For the first time we report synthesis of MOFs based on Re_6 octahedral chalcogenide clusters. The frameworks demonstrate excellent CO_2/N_2 and CO_2/CH_4 selectivity, red luminescence, paramagnetic behavior and an ability to react with oxidizing agents due to the presence of redox-active cluster fragment. The oxidation of cluster nodes changed dramatically properties of the framework, and this process if fully reversible.



We report isostructural series of microporous and mesoporous zinc(II) – thiophene-2,5-dicarboxylate MOFs based on novel polynuclear building blocks such as Zn_{12} carboxylate wheels and polyatomic alcohols. The obtained MOFs demonstrated excellent adsorption selectivity for CO_2/N_2 gas mixture, and in separation of benzene/cyclohexane mixtures both in gas and liquid phases. Most interestingly, the affinity of the porous MOF towards either benzene or cyclohexane could be rationally switched by the nature of the polyatomic alcohol.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (Grant No. 18-29-04001) and Russian Science Foundation (Grant No. 19-73-20087).

BILLION TIMES MORE ACTIVE ATRP CATALYSTS AND BENIGN INITIATION SYSTEMS

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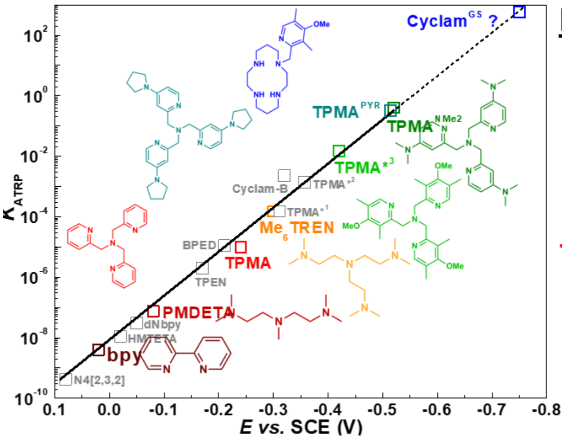
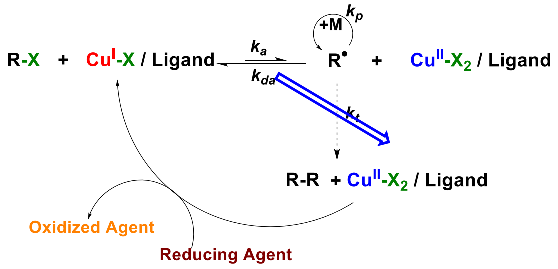
We have developed a family of powerful copper-based ATRP (atom transfer radical polymerization) which are billion times more active than original 2,2’-bipyridine based systems They can be used at very low concentrations (ppm). To combat unavoidable radical termination, several techniques for the regeneration of the catalytic systems have been developed. They include various benign chemical reagents such as ascorbic acid or sugars but also external stimuli: electrical current, light, mechanical forces and ultrasound. ATRP can be carried out without organic solvents, in bulk and in aqueous media under homogeneous conditions or in dispersed media. Reducing agent permit the reaction without deoxygenation in the flasks open to air. This is additionally aided by enzymatic degassing systems.





References

(1) Wang, Z.; Lorandi, F.; Fantin, M.; Wang, Z.; Yan, J.; Wang, Z.; Xia, H.; Matyjaszewski, K., Atom Transfer Radical Polymerization Enabled by Sonochemically Labile Cu-carbonate Species, *ACS Macro Lett.* **2019**, *8*, 161-165.
(2) Dadashi-Silab, S.; Lorandi, F.; Fantin, M.; Matyjaszewski, K., Redox-switchable atom transfer radical polymerization, *Chem. Commun.* **2019**, *55*, 612-615.
(3) Ribelli, T. G.; Lorandi, F.; Fantin, M.; Matyjaszewski, K., Atom Transfer Radical Polymerization: Billion Times More Active Catalysts and New Initiation Systems, *Macromolecular Rapid Communications* **2019**, *40*, 1800616.
(4) Pan, X.; Fantin, M.; Yuan, F.; Matyjaszewski, K., Externally controlled atom transfer radical polymerization, *Chem. Soc. Rev.* **2018**, *47*, 5457-5490.
(5) Matyjaszewski, K., Advanced Materials by Atom Transfer Radical Polymerization, *Adv. Mater.* **2018**, *30*, 1706441.
(6) Enciso, A. E.; Fu, L.; Russell, A. J.; Matyjaszewski, K., A Breathing Atom-Transfer Radical Polymerization: Fully Oxygen-Tolerant Polymerization Inspired by Aerobic Respiration of Cells, *Angewandte Chemie International Edition* **2018**, *57*, 933-936.
(7) Ribelli, T. G.; Fantin, M.; Daran, J.-C.; Augustine, K. F.; Poli, R.; Matyjaszewski, K., Synthesis and characterization of the most active copper ATRP catalyst based on tris[(4-dimethylaminopyridyl)methyl]amine, *J. Am. Chem. Soc.* **2018**, *140*, 1525-1534.

ACTIVE AND PASSIVE MESOSCALE STRUCTURES BY COMB COPOLYMERS

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Block-copolymers have been investigated intensively regarding their self-assembly in bulk and solution. Self-assembly in solution was shown to yield well-defined vesicle structures, denoted "polymersomes". Such polymersomes can serve as microscopic containers of drugs and other active components as well as for the building of protocells. In contrast to small vesicle forming molecules, such as lipids, block-copolymers form rather thick double layers, which are less flexible and less permeable. For cell mimicking constructions where vesicles are equipped with functional biomolecules, polymersomes have the advantage of a significantly higher stability compared to liposomes but do not fit in thickness and the molecular ordering within the hydrophobic layer. Furthermore, membrane flexibility and also the lateral mobility within the vesicle wall are significantly reduced compared to liposomes. These are, however, important factors, that determine the functionality and biological interaction of such vesicles. Here we report on polymersomes where short aliphatic side chains have been linked to a hydrophilic backbone. Such polymers can form double layer structures, such as single and multilayer vesicles. Because the aliphatic side chains match the chain length of the fatty acids in lipids, the double layers fit to biological membrane molecules. We will demonstrate that such comb-polymer vesicles exhibit a significantly improved stability against decomposition, break up and fusion, but exhibit at the same time superior flexibilities. Introduction of photoisomerizable side chains allowed light controlled opening of the vesicles. Furthermore, we demonstrate that such vesicles can spontaneously engulf nanoparticles and bacteria even by weak interaction with such objects.

Acknowledgments

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References

1. Rodriguez-Emmenegger, C.; Xiao, Q.; Kostina, N. Y.; Sherman, S. E.; Rahimi, K.; Partridge, B. E.; Li, S.; Sahoo, D.; Reveron Perez, A. M.; Buzzacchera, I.; Han, H.; Kerzner, M.; Malhotra, I.; Moller, M.; Wilson, C. J.; Good, M. C.; Goulian, M.; Baumgart, T.; Klein, M. L.; Percec, V. (2019) *Encoding biological recognition in a bicomponent cell-membrane mimic*. **Proceedings of the National Academy of Sciences**, 116 (8), 5376-5382
2. Kostina, N. Yu.; Rahimi, K.; Xiao, Q.; Haraszti, T.; Dedisch, S.; Spatz, J.; Schwaneberg, U.; Klein, M. L.; Percec, V.; Möller, M.; Rodriguez-Emmenegger, C. (2019): *Membrane-Mimetic Dendrimersomes Engulf Living Bacteria via Endocytosis.* ***Nano Letters,*** (DOI: 10.1021/acs.nanolett.9b02349)
3. Ludwig, A.-K.; Michalak, M.; Xiao, Q.; Gilles, U.; Medrano, F. J.; Ma, H.; FitzGerald, F. G.; Hasley, W. D.; Melendez-Davila, A.; Liu, M.; Rahimi, K.; Kostina, N. Y.; Rodriguez-Emmenegger, C.; Möller, M.; Lindner, I.; Kaltner, H.; Cudic, M.; Reusch, D.; Kopitz, J.; Romero, A.; Oscarson, S.; Klein, M. L.; Gabius, H.-J.; Percec, V. (2019) *Design–functionality relationships for adhesion/growth-regulatory galectins*. **Proceedings of the National Academy of Sciences**, 116 (8), 3837-2842.
4. L. Li, M. Rosenthal, H. Zhang, J.J. Hernandez, M. Drechsler, K.H. Phan, S. Rütten, X.-M. Zhu, D.A. Ivanov, M. Möller, *Light-switchable vesicles from liquid-crystalline homopolymer-surfactant complexes,* **Angewandte Chemie, International Edition** 51, 11616-11619 (2012)

BOTTLEBRUSH BRIDGE BETWEEN SOFT GELS AND FIRM TISSUES

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Softness and firmness are seemingly incompatible traits that synergize to create the unique soft-yet-firm tactility of living tissues pursued in soft robotics, wearable electronics, and plastic surgery.[1] This dichotomy is particularly pronounced in tissues like fat and brain that are known to be both ultrasoft and ultrafirm. However, replicating the mechanical response found in such tissues remains elusive since ubiquitously employed soft gels are unable to concurrently reproduce tissue firmness. We have addressed this challenge through the self-assembly of linear-brush-linear (LBL) block copolymers into thermoplastic elastomers.[2] This hybrid molecular architecture delivers hierarchical network organization with a cascade of deformation mechanisms responsible for initially low moduli followed by intense strain-stiffening. By bridging the firmness gap between gels and tissues, we have replicated the mechanics of fat, fetal membrane, spinal cord, and brain. These solvent-free elastomers also do not leach into the body, which is vital for the safety and longevity of biomedical devices.

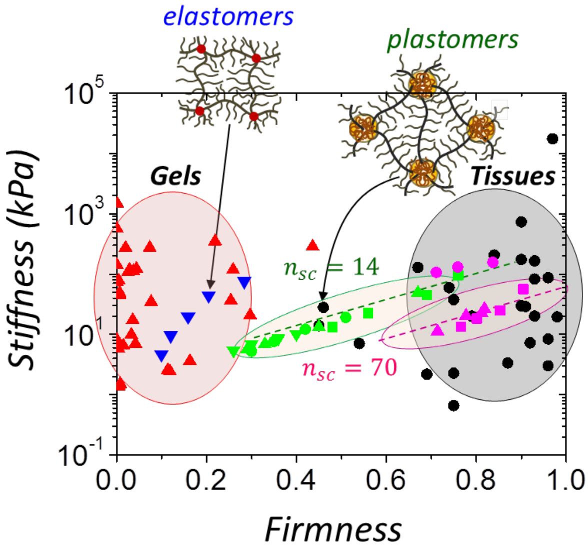

Figure 1. The Young's modulus vs. firmness parameter plot where plastomers successfully bridge the gap between polymeric gels and soft biological tissues.

Acknowledgments

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References

1. S.S. Sheiko, A.V. Dobrynin, "Architectural Code for Rubber Elasticity: From Supersoft to Superfirm Materials" *Macromolecules* (2019) ASAP. DOI: 10.1021/acs.macromol.9b01127.
2. M. Vatankhah-Varnosfaderani, et al, *Science* **2018**, *359*, 1509.

FUNCTIONAL AND RESPONSIVE POLYMER MODIFIED INORGANIC NANOPARTICLES

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Polymer modification of inorganic nanomaterials is a facile route to enhance the stability, activity and functionality of the inorganic colloids.[2] Herein, we present novel approaches in polymer chemistry used to embed or coat inorganic nanomaterials, in the form of metal or metal oxide particles, with functional and/or responsive polymers: i) emulsion copolymerization has been employed to prepare responsive microgel particles into which different metal nanocatalysts (i.e. Ag, Pt, Ru, Pd and Au) were grown [2]. Such pH-responsive microgels impregnated with the nanoparticulate catalysts have attracted great attention for use as microreactors in the field of catalysis both in batch and flow processes; ii) the facile functionalization of anatase TiO_2 nanoparticles by an in-situ surface modification approach, using preformed polymer chains synthesized by RAFT polymerization, was employed to enhance the photocatalytic performance of the inorganic colloids (Fig. 1a, 1b);[3] iii) multi-responsive polymers have been anchored onto the surface of SiO_2 nanospheres and rod particles using the “grafting from” approach (Figure 1c). This has enabled the synthesis of functional core-shell particles,[4] hollow polymer capsules,[5] hybrid Janus nanoparticles[6] and responsive and hollow microrod particles.[7] The unique multi-responsive properties and the novel phase behavior of these nanoobjects were investigated in aqueous media.

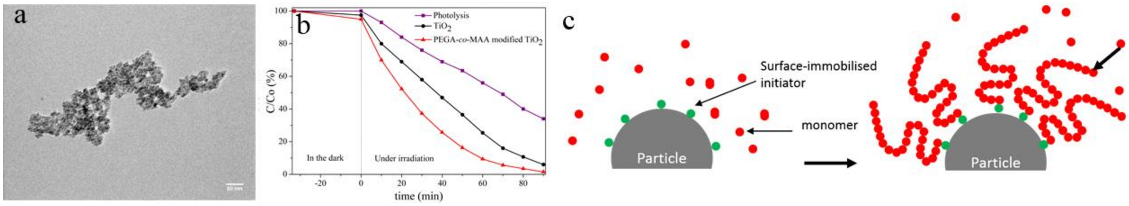

Figure 1.TEM image (a) and photocatalytic activity (b) of polymer modified TiO_2 nanoparticles. “Grafting from” approach to grow responsive polymers onto inorganic surfaces (c).

Acknowledgements

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References

1. R. B.Grubbs,*Polymer Reviews* **2007,** *47,* 197-215.
2. D. Palioura, et al., *Langmuir* **2007,** *23,* 5761-5768. K. E. Christodoulakis, et al.*Topics in Catalysis: Special Issue* **2009,** *52,*394-411. E. Pavlopoulou, et al.,*Macromolecules* **2010,** *43,* 9828-9836. M. Kaliva, et al., *Macromol. Symp.* **2013,** *331-332,* 17-25.
3. E. Vasilaki, et al, *Appl. Surf. Sci.* **2017,***399,* 106-113.
4. D. S. Achilleos, et al., *Langmuir* **2016,** *32,* 5981-5989.
5. D. S. Achilleos, et al., *J. Am. Chem. Soc.* **2012**, *134,* 5726-5729.
6. P. G. Falireas and M. Vamvakaki, *Polymer* **2017,** *130,* 50-60.
7. L. Chambon and M. Vamvakaki, *Soft Matter* **2019,** submitted, and manuscript in preparation.

50 YEARS OF HYPERCROSSLINKED POLYSTYRENE: FROM A NON-TRIVIAL IDEA TO INDUSTRIAL APPLICATIONS

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As early as 1969, Davankov, Rogozhin and Tsyurupa applied and obtained patents for making “Macronet isoporous” polystyrene which proved to become the first representative of a whole new class of materials, hypercrosslinked polymeric networks. The general principle of their preparation reads: Formation of a **highly expanded 3D rigid open-type network** in the presence of large amounts of a **thermodynamically good solvent**. Basic distinguishing features of these polymers are: highly developed microporous structure with apparent S_{sp} up to 1000-2000 m^2/g, increasing in volume (swelling) with any type of liquid media irrespective of their affinity to the polymer, extremely high adsorption ability toward both polar and non-polar compounds.

These rather unusual properties were soon recognized as essential for producing on an industrial scale a series of novel largely universal adsorbing materials. They found wide application in many industrial adsorption technologies. Not less interesting and efficient is their use in the capacity of a stable matrix for the preparation of various composites by incorporation of nanodispersed particles with, e.g., catalytic or magnetic properties.

Moreover, the new materials opened ways to the development of some principally new processes and applications. Among them, to mention are: (I) manufacturing (also in Russia) of new hemosorbents with an unprecedented hemocompatibility and the ability of removing the whole complex of toxic blood contaminants, which already saved life to hundreds of patients with sepsis and acute poisonings; (ii) developing of principally new approach to separating mineral electrolytes (acids, bases and salts) according to the size of their hydrated ions, unique features of the method are that its productivity rises with the concentration of the initial mixture increasing and that the separated components experience significant self-concentration during their passage through the column with the nanoporous neutral polymer.

It was further shown that it is possible to involve each phenyl ring of the initial polystyrene chains into the formation of more than one, in fact - up to five, cross-bridges in the final hypercrosslinked network. Such products with the ultimate crosslinking density (200-500%) exhibit expressed ability to enter electronic interactions with polar and aromatic groups of numerous analytes, in addition to the usual hydrophobic interactions. Using the enhanced network density of such sorbents, it was possible to develop new “restricted access materials, RAMs” that efficiently adsorb small polar and non-polar molecules while rejecting proteins and other larger molecules. They selectively extract traces of target analytes directly from complex matrixes, as human plasma, thus facilitating analysis of drugs, their metabolites and sepses markers.

Hypercrosslinked Polymeric Networks and Adsorbing Materials, Synthesis, Structure, Properties and Application, V.A. Davankov, M.P. Tsyurupa, Elsevier, USA, **2010**; ISBN: 978-0-444-53700-3, ISSN: 0166-526X, 648 pages

IRON CATALYZED CARBON-CARBON BOND FORMING REACTIONS

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The development of vast global shale gas reserves has created a glut of ethylene and other linear α-olefins; chemists are tasked with discovering new catalytic methods for the unique enchainment of alkenes to new valuable products. The abundance of plastics in the oceans inspires processes other than olefin polymerization for these valuable hydrocarbon feedstocks. Our laboratory has developed a family of iron catalysts bearing redox-active pyridine(diimine), pyridine(imine) and diimine ligands that promote highly selective and unique carbon-carbon bond forming reactions with commodity olefins and dienes. One notable is the [2+2] cycloaddition between dienes and α-olefins to yield vinyl cyclobutanes.[1] Recent efforts in our laboratory have been devoted to understanding the origin of this unique reactivity and my lecture will focus on the application of kinetic measurements, isotopic labeling and both deuterium and carbon kinetic isotope effects and the role of orbital symmetry to understand C(sp^3)-C(sp^3) reductive elimination. These insights have also enabled rational design of next generation catalysts that have resulted in methods for the regio- and in some cases diastereoselective iron-catalyzed [4+4] cycloaddition of dienes to yield disubstituted cyclooctadienes[2] or selective hydrovinylation reactions.[3] These molecules have proven to be useful precursors following ROMP and hydrogenation to precision polyolefins that may have interesting properties. Control over block length and stereochemistry is enabled by the selective iron-catalyzed cycloaddition. Extension of these studies to the coupling of CO_2 and ethylene with also be presented.[4]

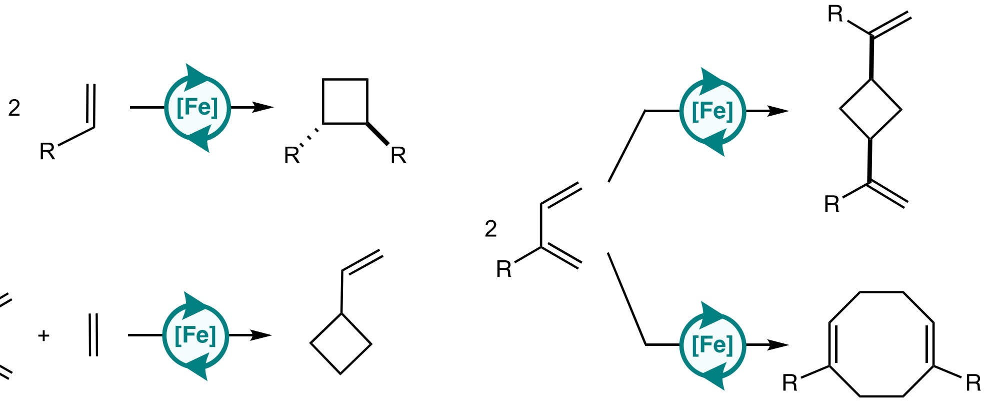

Figure 1. Iron-catalyzed cycloadditions for the selective upgrading of hydrocarbons.

Acknowledgements

We thank the Firmenich, the National Institutes of Health and United States Department of Energy for providing support for our iron-catalyzed carbon-carbon bond-forming program.

References

1. J. M. Hoyt, V. A. Schmidt, A. M. Tondreau, P. J. Chirik *Science* **2015**, *349*, 3200.
2. C. R. Kennedy, H. Zhong, R. MacCauley, P. J. Chirik *J. Am. Chem. Soc.* **2019**, *141*, 8557.
3. V. A. Schmidt, C. R. Kennedy, M. J. Bezdek, P. J. Chirik *J. Am. Chem. Soc.* **2018**, *140*, 3443.
4. S. M. Rummelt, H. Zhong, I. Korobkov, P. J. Chirik *J. Am. Chem. Soc.* **2018**, *140*, 11589.

DYNAMIC CATALYTIC SYSTEMS FOR ADVANCED SYNTHETIC APPLICATIONS

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Transition metal catalysis is a well-established tool for carrying out selective organic transformations in a diverse range of reactions developed in fine organic synthesis as well as in a number of key industrial applications. Revealing dynamic phenomena in catalysis facilitates sustainable technologies,[1] opens new possibilities to use nano-structured reagents,[2] helps addressing reproducibility issues[3] and improves mechanistic understanding.[4,5]

Several challenges and opportunities of dynamic catalysis will be presented and discussed in view of design of advanced synthetic applications.

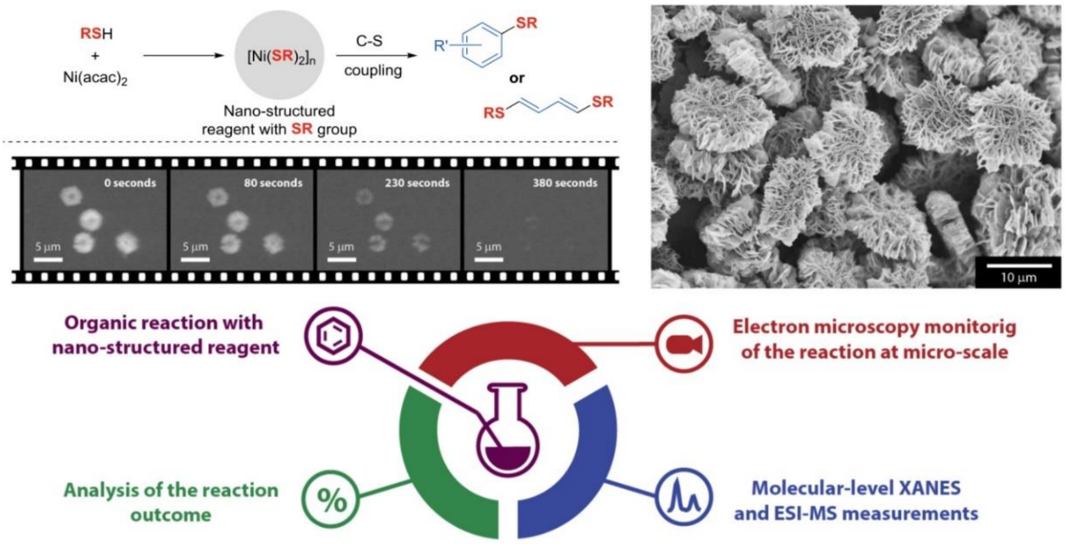

Figure 1. Dynamic catalytic system with nanostructured reagents.[2]

Acknowledgements

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References

1. Egorova K.S., Ananikov V. P., "Which Metals are Green for Catalysis? Comparison of the Toxicities of Ni, Cu, Fe, Pd, Pt, Rh, and Au Salts", Angew. Chem. Int. Ed., **2016**, 55, 12150.
2. Kashin A. S., Degtyareva E. S., Eremin D. B., Ananikov V. P., "Exploring the performance of nanostructured reagents with organic-group-defined morphology in cross-coupling reaction", Nature Commun., **2018**, 9, 2936.
3. Pentsak E.O., Eremin D.B., Gordeev E.G., Ananikov V.P., "Phantom Reactivity in Organic and Catalytic Reactions as a Consequence of Microscale Destruction and Contamination-Trapping Effects of Magnetic Stir Bars", ACS Catal., **2019**, 9, 3070
4. Eremin D.B., Ananikov V. P., "Understanding Active Species in Catalytic Transformations: from Molecular Catalysis to Nanoparticles, Leaching, “Cocktails” of Catalysts and Dynamic Systems", Coord. Chem. Rev., **2017**, 346, 2-19.
5. Kashin A.S., Ananikov V.P., "Monitoring chemical reactions in liquid media using electron microscopy", *Nat. Rev. Chem.*, **2019**, doi: 10.1038/s41570-019-0133-z.

EASY ACCESS TO METAL-N-HETEROCYCLIC CARBENE CATALYSTS

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We have reported on the use of an external weak base as an effective method to generate Au- and Cu-NHC complexes.[1,2] In the course of our studies, an unusual intermediate was isolated, an “ate” complex, that could be easily observed within minutes of mixing the metal precursor, copper or gold and now palladium and further examples of transition metals, and the imidazolium salt in air. Action of a weak base upon this intermediate led to the well-defined M-NHC complex (M= Au, Cu and Pd) (Figure 1). We suspected that such “ate” complexes might be more prevalent than imagined in the context of the organometallic chemistry of M-NHC complexes and might even offer a uniquely simple, greener and more sustainable approach to catalyst synthesis and catalysis.[3] To test this hypothesis, synthetic studies have shown the route to be so far quite general and these studies and the reactivity of the M-NHC family of catalysts will be presented.

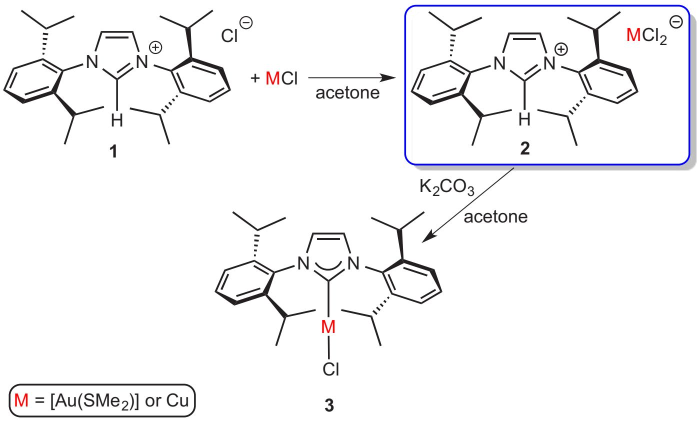

Figure 1. Synthetic route leading to well-defined Au, Cu and Pd-NHC catalysts.

Acknowledgements

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References

1. A. Collado, A. Gómez-Suárez, A. R. Martin, A. M. Z. Slawin and S. P. Nolan, *Chem. Commun.*, **2013**, *49*, 5541.
2. O. Santoro, A. Collado, A. M. Z. Slawin, S. P. Nolan and C. S. J. Cazin, *Chem. Commun.,* **2013**, *49*, 10483.
3. C. M. Zinser, F. Nahra,M. Brill, R. E. Meadows, D. B. Cordes,A. M. Z. Slawin,C. S. J. Cazin, S. P. Nolan, *Chem. Comm.* **2017**, *53*, 7990.

SHUTTLE CATALYSIS – A CONCEPTUAL BLUEPRINT FOR REVERSIBLE FUNCTIONAL GROUP TRANSFER

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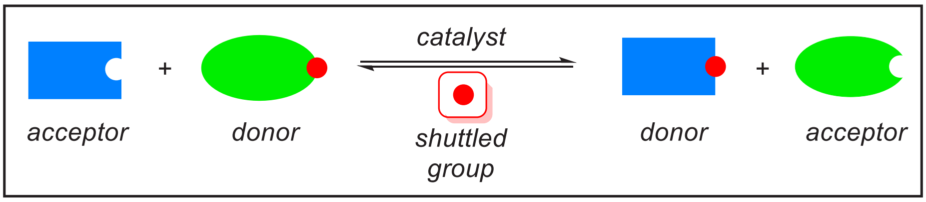
Catalytic reversible reactions, such as alkene metathesis and transfer hydrogenation, have had an auspicious impact on the molecular sciences. This presentation will describe our efforts to develop related "shuttle catalysis" reactions for the functionalization and defunctionalization of organic compounds.[1-5] These reactions avoid the use of toxic reagents (e.g. HCN, CO) through the reversible transfer of chemical moieties between organic molecules. Shuttle catalysis has further been employed in the development of novel C–X (X = S, P) bond metathesis reactions that can help to address significant synthetic challenges across the molecular sciences.



Selected References

1. Xianjie Fang, Peng Yu, Bill Morandi, *Science* **2016**, *351*, 832.
2. Xianjie Fang, Bastien Cacherat, Bill Morandi, *Nat. Chem*. **2017**, *9*, 1105.
3. Benjamin N. Bhawal, Bill Morandi, *ACS Catal.* **2016**, *6*, 7528.
4. Zhong Lian, Benjamin N. Bhawal, Peng Yu, Bill Morandi, *Science* **2017**, *356*, 1059.
5. Yong Ho Lee, Bill Morandi, *Nat. Chem*. **2018**, *10*, 1016.

INTRAMOLECULAR CATALYST TRANSFER ON FUNCTIONAL GROUPS

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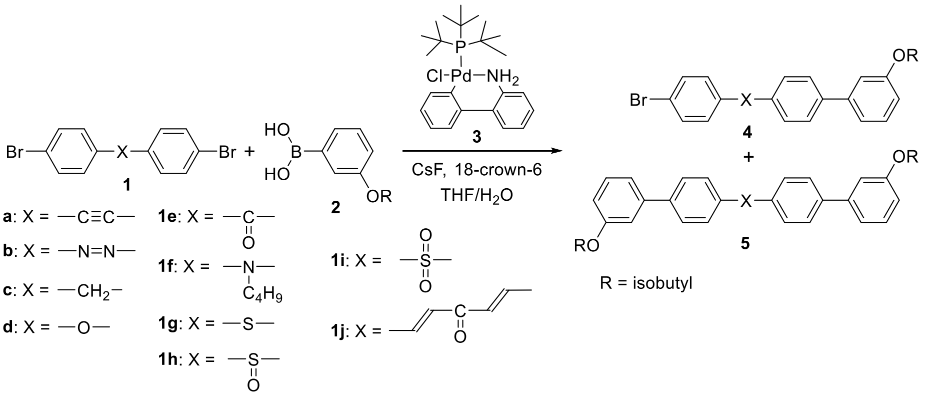
Suzuki-Miyaura coupling reaction is a powerful protocol for the synthesis of polyarylenes containing π-conjugated polymers. We have found that t-Bu$_3$PPd(Ar)Br initiates chain-growth Suzuki-Miyaura coupling polymerization of haloarylboronic acid (ester) as an AB type monomer to afford well-defined π-conjugated polymers.[1] When this t-Bu$_3$PPd(0) catalyst, which has a propensity for intramolecular catalyst transfer on a π-electron face, was used for Suzuki-Miyaura coupling polymerization of dibromoarene and arenyldiboronic acid ester (AA + BB polycondensation), high-molecular-weight π-conjugated polymer with a boronate moiety at both ends was obtained, even though excess dibromoarene was used.[2] However, Suzuki-Miyaura coupling reaction of 4,4'-dibromostilbene with phenylboronic acid in the presence of t-Bu$_3$PPd(0) catalyst did not selectively afford diphenyl-substituted stilbene, implying that the Pd catalyst did not walk from one benzene ring to the other through the carbon-carbon double bond (C=C) in the stilbene after the first substitution of 4,4'-dibromostilbene with phenylboronic acid.[3] Herein, we report investigation of propensity for intramolecular transfer of Pd catalyst on functional group other than C=C between benzene rings by means of Suzuki–Miyaura coupling reaction of **1** with 3-isobutoxyphenylboronic acid **2** (Scheme 1) and applied to unstoichiometric Suzuki–Miyaura polycondensation of **1** and phenylenediboronic acid.

The model reaction of 2 equiv of **1** and 1 equiv of **2** was conducted in the presence of 0.05 equiv of **3** and CsF/18-crown-6 in THF and a small amount of water. If the catalyst walks from one benzene ring to the other through X in **4** after the first substitution with **2**, disubstituted product **5** should be selectively obtained. When **1a**-**f**, and **1i** were reacted with **2**, disubstituted products **5a**-**f**, and **5i** were selectively obtained, respectively. These results indicated that the Pd catalyst walks on the bridge of C≡C, N=N,[4] methylene, oxygen, keto, amino, and sulfonyl group between benzene rings. In contrast to these cases, **1g-h**, and **1j** resulted in preferential formation of monosubstituted **4**.[5]



Scheme 1

References

1. T. Yokozawa, Y. Ohta, *Chem. Rev.*, **2016**, *116*, 1950.
2. M. Nojima, K. Kosaka, M. Kato, Y. Ohta, T. Yokozawa, *Macromol. Rapid Commun.* **2016**, *37*, 79.
3. M. Nojima, Y. Ohta, T. Yokozawa, *J. Am. Chem. Soc.* **2015**, *137*, 5682.
4. T. Kamigawara, H. Sugita, K. Mikami, Y. Ohta, T. Yokozawa, *Catalysts*, **2017**, *7*, 195.
5. T. Yokozawa, N. Harada, H. Sugita, Y. Ohta, *Chem. Eur. J.*, **2019**, *25*, 10059.

NON-COVALENT INTERACTIONS IN STOICHIOMETRIC AND CATALYTIC REACTIONS OF METAL HYDRIDES

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Today it is widely recognized that hydrogen bonds and other non-covalent interactions are very important for chemistry and biochemistry, in catalytic and stoichiometric reactions, in the design of supramolecular assemblies and materials. Studying the hydrogen bonds involving transition metal and main group hydrides we have established spectroscopic criteria, structural and electronic parameters that evidence formation of dihydrogen, $M\text{-}H^{\delta-}\cdots H^{\delta+}\text{-}X$ (M = transition metal or metalloid), bonds and define their properties.[1] Despite rather low energy, the hydrogen bonding or Lewis acid-base interactions activate the participating M-H (and X-H) bonds and prepare them for a subsequent heterolytic bond splitting.[2] These non-covalent interactions generally remain covert although they play an important role in various catalytic processes. Our recent studies on the reactions mechanisms involving hydrido complexes such as dehydrogenation of alcohols and amine boranes showed the importance of relatively weak interactions for keeping active conformation of catalyst[3] or for its activation[4] as well as the role of different hydrogen bonds in amine boranes dehydrogenation.[4,5]

Acknowledgments

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References

1. (a) N. V. Belkova, L. M.Epstein, E. S. Shubina, *Eur. J. Inorg. Chem.* **2010**, *2010*, 3555; (b) N. V. Belkova, L. M. Epstein, O. A. Filippov, E. S. Shubina, *Chem. Rev.* **2016**, *116*, 8545.
2. N. V. Belkova, O. A. Filippov, E. S. Shubina, *Chem. Eur. J.* **2018**, *24*, 1464
3. G. A.Silantyev, E. M.Titova, O. A.Filippov, E. I.Gutsul, D.Gelman, N. V. Belkova, *Russ. Chem. Bull.* **2015**, *64*, 2806.
4. (a) E. M.Titova, E. S.Osipova, A. A.Pavlov, O. A.Filippov, S. V.Safronov, E. S.Shubina, N. V. Belkova, *ACS Catal.* **2017**, *7*, 2325; (b) E. S. Osipova, E. S. Gulyaeva, O. A. Filippov, S. V. Safronov, A. A. Pavlov, A. V. Polukeev, V. A. Kirkina, E. M. Titova, E. S. Shubina, N. V. Belkova, *Eur. J. Inorg. Chem.* **2019**, *2019*, 1389-1397.
5. S.Todisco, L.Luconi, G.Giambastiani, A.Rossin, M.Peruzzini, I. E.Golub, O. A.Filippov, N. V. Belkova, E. S. Shubina, *Inorg. Chem.* **2017**, *56*, 4296.

DESIGN AND SYNTHESIS OF CHIRAL COVALENT ORGANIC FRAMEWORKS

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Among the recognized porous materials, covalent organic frameworks (COFs) are a fascinating class of crystalline porous polymers with significant prospects for addressing current energy and environmental challenges, including gas storage, separations, catalysis, smart sensors, optoelectronics, and energy storage. Chiral COFs have shown excellent performance in chiral separation, asymmetric heterogeneous catalysis and chiral recognition. However, it remains a challenge to design and synthesize chiral COFs efficiently and controllably by organizing building blocks that rely only on covalent bonds.

Here I will present design and synthesis of chiral organic frameworks for asymmetric catalysis and chiral separation, including: (1) multivariate modular strategy for the synthesis of chiral COFs with one or more chiral active sites for organic catalytic reactions and the separation of racemes; (2) synthesize chiral COFs by direct method or chiral induction method and clarified the mechanism of storage, transmission and expression of chiral information in porous solids

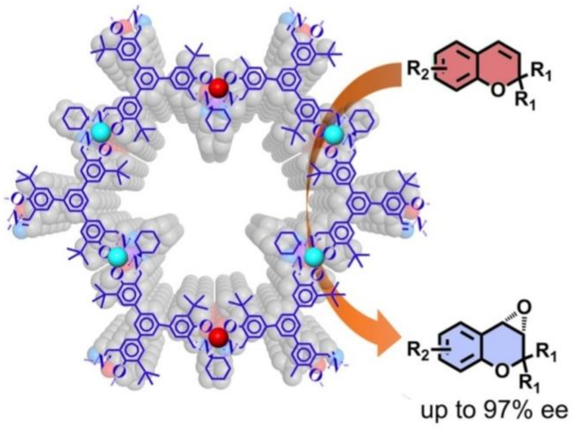

Figure 1. Chiral 3D COFs for heterogeneous asymmetric catalysis

References

1. X.Han, J.Huang, C.Yuan, Y.Liu, Y.Cui, *J. Am. Chem. Soc.* **2018**, *140*, 892.
2. X.Wang,; X.Han, J.Zhang, X.Wu, Y.Liu, Y.Cui,. *J. Am. Chem. Soc.* **2016**, *138*, 12332.
3. X. Han, Q. Xia, J. Huang, Y. Liu, C. Tan, Y. Cui, *J. Am. Chem. Soc.* **2017**, *139*, 8693.

ORGANOMETALLIC MACROCYCLES, CAGES AND THEIR APPLICATION

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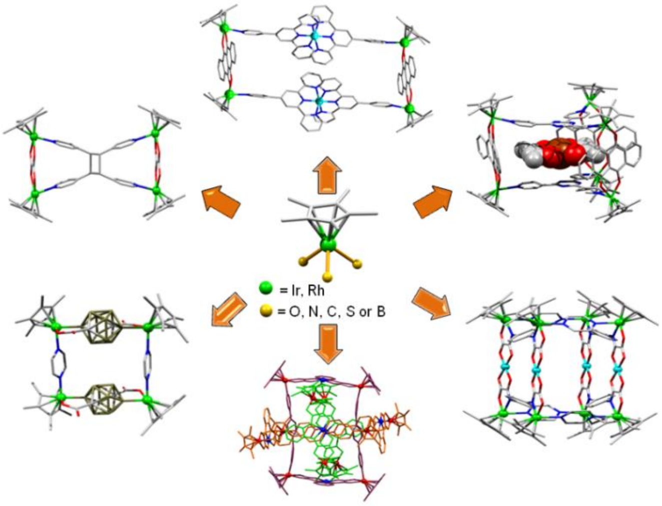
The construction of new inorganic and organometallic macrocycles and cages with interesting structural features and technologically useful functions have been topics of intense study with considerable potential.[1] One of the chief motivating factors to growth in this field is the development of new, functional and tunable donor building blocks that can bridge transition metals. Ideal building blocks should be easily accessible, exhibit high affinities toward transition metals, and possess facial coordination sites can undergo exchange reactions with various ligands. Half-sandwich transition metal complexes (Cp*M, Cp* = η^5-C_5Me_5) are useful model compounds in which one hemisphere of the coordination shell is blocked by the voluminous Cp* rings. In the protected space below the Cp* ligands, various bidentate or tridentate ligands can be accommodated.



Motivated by interest in supramolecular chemistry with organometallic half-sandwich complexes, we have initiated a new approach for preparing organometallic macrocycles via C-H and B-H activations with Terephthalate and dicarboxylate carborane.[2] We report herein an efficient method for synthesizing molecular macrocycles of half-sandwich iridium and rhodium complexes via C-H and B-H activation directed muticomponent self-assembly under mild condition.[3]

References:

1) a). Y.-F. Han, G.-X. Jin, **Chem. Soc. Rev**., **2014, *43*, 2799**; b). Y.-F. Han, G.-X. Jin, **Accounts of Chemical Research 2014**, *47*, 3571; c). S. L. Huang, T. S. A. Hor, G.-X. Jin, **Coord. Chem. Rev.**, **2017,** *333*, 1-23; a) Y. Lu, H.-N. Zhang and, G.-X. Jin, **Accounts of Chemical Research 2018**, *51*, 2148−2158.

2) a) Y. Lu, Y.-X. Deng, Y.-J. Lin, Y.-F. Han, L.-H. Weng, Z.-H. Li and, G.-X. Jin, **Chem**., **2017**, *3*, 110-121; b). S-L. Huang, Y-J. Lin, T. S. A. Hor; G-X. Jin, **J. Am. Chem. Soc.**, **2013**, *135*, 8125; c). S-L. Huang, Y-J. Lin, Z-H. Li, G-X. Jin, **Angew. Chem. Int. Ed**., **2014**, *53*, 11218; d). L. Zhang, Y.-J. Lin, Z. Li, G.-X. Jin, **J. Am. Chem. Soc.**, **2015**, *137*, 13670; e). W.-Y. Zhang, Y.-J. Lin, Y.-F. Han, G.-X. Jin, **J. Am. Chem. Soc**., **2016**, *138*, 10700; f). L-L. Dang, Z-B. Sun, W-L. Shan, Y-J. Lin, Z-H. Li[1], G-X. Jin, **Nature Commun.**, **2019**, *10*, 2057

3) a). H. Li, Y-F. Han, Y-J. Lin, G.-X. Jin, **J. Am. Chem. Soc.**, **2014**, *136*, 2982; b). Y-F. Han, L. Zhang, L-H. Weng, G-X. Jin, **J. Am. Chem. Soc**., **2014**, *136*, 14608; c). Y-Y. Zhang, X-Y. Shen, L-H. Weng, G-X. Jin, **J. Am. Chem. Soc.**, **2014**, *136*, 15521; d). L. Zhang, L. Lin, D. Liu, Y.-J. Lin, Z.-H. Li, G.-X. Jin, **J. Am. Chem. Soc.**, **2017**, *139*, 1653-1660; d). W-X. Gao, H-J. Feng, Y-J. Lin, G-X. Jin, **J. Am. Chem. Soc.**, **2019**, *141*, 9160.

CURRENT STATE OF CHEMISTRY OF PENTACOORDINATED PHOSPHORUS COMPOUNDS

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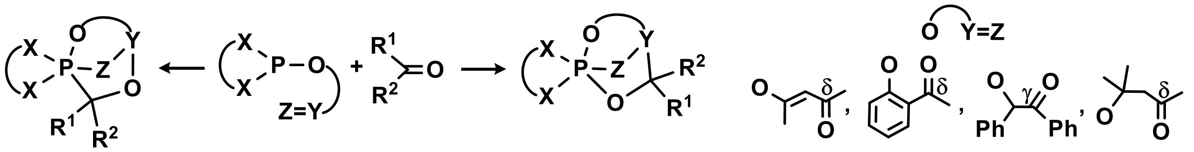
The penta- and hexacoordinated phosphorus derivatives (phosphoranes and phosphorates) are key intermediates in the phosphorylation and dephosphorylation reactions that occur in a living cell and play an important role in its energy, recording information in the form of DNA and RNA, and other processes[1]. Phosphoranes are as well key intermediates of many reactions important for organic synthesis, such as the Wittig, Mitsunobu, Evans reactions, oxaphosphorane condensation, etc.[2] To understand the mechanism of these reactions, knowledge is needed not only about the thermodynamics and kinetics of processes involving phosphoranes, but and the features of their structure and reactivity. The report analyzed current chemistry features of penta- and hexacoordinated phosphorus, such as the effect of stabilization of pentacoordinated phosphorus by electron-withdrawing and cyclic substituents, new types of optical activity of phosphoranes, synthesis of phosphoranes with anti-apicophilic arrangement of substituents in trigonal bipyramid, unusual reactivity of phosphoranes. Among the new methods for the synthesis of phosphoranes containing several chiral centers, the preparation of derivatives of 5-carbaphosphatranes containing a four-membered ring was considered; a method for the synthesis of cage phosphoranes based on reactions of derivatives of P (III) containing a carbonyl group at the γ- or δ-position to phosphorus, with compounds having activated multiple bonds (Scheme 1); a new spontaneous rearrangement of bis(2-benzylideneaminophenyl) phenylphosphonite to spirophosphorane; PCO/POC-rearrangement in a series of cage phosphoranes; cycloaddition reactions of vinyl esters of acids P(III) to carbonyl compounds[3-6]. The chemoselectivity of the hydrolysis of cage phosphoranes was analyzed.



Z = O, NR, Y = CR; Z = RCH, Y = N

Scheme 1.

Acknowledgements

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References

1. Chemical Biology of Nucleic Acids: Fundamentals and Clinical Applications. Ed. by V. A. Erdmann, W. T. Markiewicz, J. Barciszewski. Springer-Verlag. Berlin, Heidelberg. 2014. 599 p.
2. K. C. K. Swamy, N. S. Kumar. *Acc. Chem. Res*. **2006**, 39, 324.
3. V. F. Mironov, M. N. Dimukhametov, S. V. Efimov et al. *J. Org. Chem*. **2016**, 81, 5837.
4. N.R. Khasiyatullina, V.F. Mironov et al. *RSC Advances*. 2016, **6**, 85745.
5. N. R. Khasiyatullina, T. A. Baronova, E. V. Mironova, et al. *Org. Chem. Front*. 2018, **5**, 3113.
6. V. F. Mironov, T. A. Baronova, M. N. Dimukhametov, et al. *Mendeleev Commun*. **2019**, 29, 506.

SYNTHESIS OF ENE-DIAMIDO RARE EARTH COMPLEXES AND THEIR CATALYTIC APPLICATIONS

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Well-defined rare-earth complexes have emerged as powerful catalysts for a number of transformations given their unique selectivity and mechanistic distinctions.[1] Herein, we report the synthesis and characterization of rare-earth ene-diamido complexes and their applications in selective catalytic hydrosilylation, hydrophosphination and polymerization of styrenes. These complexes exhibit high regioselectivity and stereoselectvity for these important transformations. The samarium complexes **1** and **2** are highly active and regioselective catalysts for hydrosilylation of terminal and internal alkenes, whereas **3** is effective for selective hydrosilylation of alkynes (Figure 1). In addition, polymerization of styrene with **1** as catalyst led to the formation of silyl-capped, highly syndiotactic polystyrene. The experiments and density functional theory (DFT) calculations disclosed the highly selective formation of the samarium hydride intermediates, which, in combination with the electronic and steric factors of the ligand, is responsible for the high regio- and stereoselectivity. In addition, the corresponding samarium alkyl complex enabled highly regioselective hydrosilylation of internal alkenes.

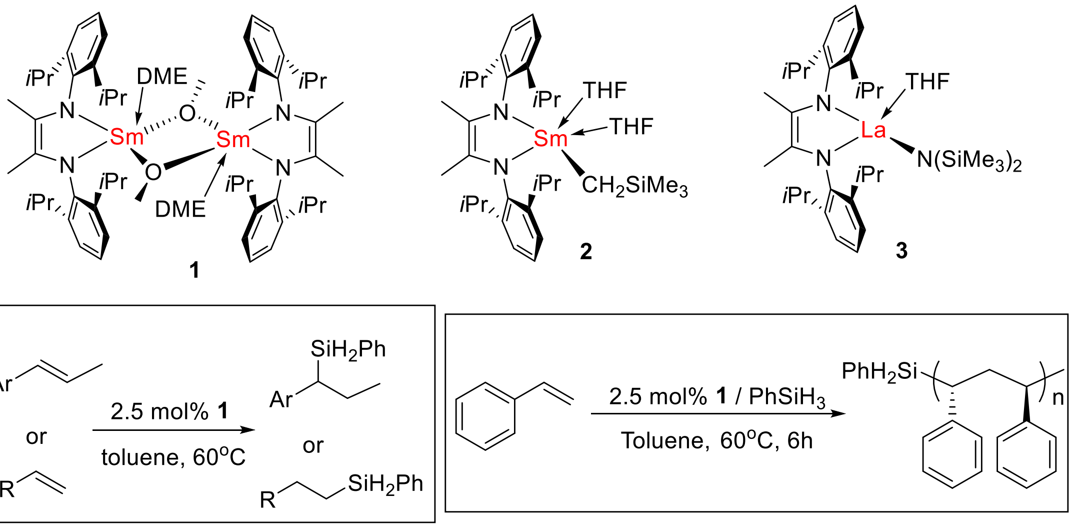

Figure 1. Synthesis and Reaction of Rare-Earth Complexes

Acknowledgements

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Reference

1. (a) Molander, G. A.; Romero, J. A. C. *Chem. Rev.* **2002**, *102*, 2161. (b) Gottfriedsen, J.; Edelmann, F. T. *Coord. Chem. Rev.* **2006**, *250*, 2347. (c) Edelmann, F. T. *Coord. Chem. Rev.* **2006**, *250*, 2511.
2. Li, J.; Zhao C.; Liu, J.; Huang, H.; Wang, F.; Xu, X.; Cui. C. *Inorg. Chem.* **2016**, *55*, 9105.
3. Liu, J.; Chen, W.; Li, J.; Cui, C. *ACS Catl.* **2018**, *8*, 2230.

ELECTRONIC ENERGY STORAGE: MOLECULAR DYADS, NANOPARTICLES, MOLECULAR MACHINES

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The efficient use of energy following light absorption is of extreme importance in natural photosynthetic assemblies as well as in artificial systems. Small supramolecular systems have been used successfully to absorb light energy and transfer it to a specific site, while reversible energy transfer processes in polypyridine complexes with transition metals have been reported to temporarily stock energy and prolong excited-state lifetimes.

Here we report the unique excited-state equilibration between three different excited states in a structurally simple bichromophoric Copper(I)-phenanthroline complex coupled through a short spacer with an auxiliary anthracene chromophore acting as an energy reservoir[1] (Figure 1). The unprecedented increasing of luminescence lifetimes in Ruthenium(II) complexes based on tridentate polypyridine ligands linked to anthracene chromophore[2] and emissive cyclometallated Iridium(III) centre connected to pyrene[3] already used as a sensor for molecular oxygen[4] will be also presented.

Not only the organic chromophores could be the emissive units in reversible energy transfer systems, but recently demonstrated spectacular modification of the CdSe quantum dot emission lifetime are also in the scope of our research[5].

Finally, our new research on the diffusion controlled excited-state equilibration of triplet energies between Ruthenium(II) tris-bipyridine complex and freely moving pyrene in molecular machines (rotaxanes) will be discussed in this report.

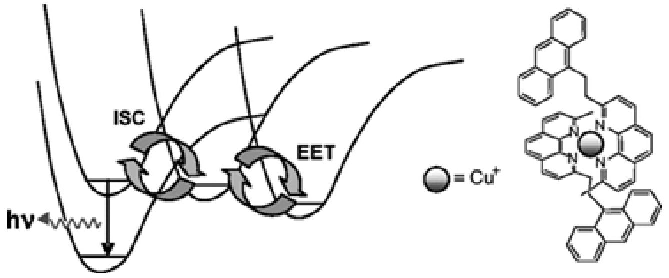

Figure 1. Equilibration between excited states in Cu(I)-phenanthroline – anthracene system.

Acknowledgments

We are grateful for financial support from the Agence Nationale de la Recherche, University of Bordeaux, CNRS.

References

1. Y. Leydet, D. M. Bassani, G. Jonusauskas, N. D McClenaghan, Journal of the American Chemical Society **2007**, 129, 8688.
2. G. Ragazzon, P. Verwilst, S. A. Denisov, A. Credi, G. Jonusauskas, N. D. McClenaghan, Chemical Communications **2013**, 49, 9110.
3. S. A. Denisov, Y. Cudré, P. Verwilst, G.Jonusauskas, M. Marín-Suárez, J. F Fernández-Sánchez, E. Baranoff, N. D McClenaghan, Inorganic Chemistry **2014**, 53, 2677.
4. S. Medina-Rodriguez, S. Denisov, Y. Cudré, L. Male, M. Marín-Suárez, A. Fernández-Gutiérrez, J. F. Fernandez-Sanchez, A. Tron, G. Jonusauskas, N. D. McClenaghan, E. D. Baranoff, Analyst **2016**, 141, 3090.
5. M. La Rosa, S. A Denisov, G. Jonusauskas, N. D. McClenaghan, A. Credi, Angewandte Chemie International Edition **2018**, 57, 3104.

HETEROANNULATED ACCEPTORS FOR USE IN ORGANIC PHOTOVOLTAIC DEVICES

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The ability to precisely tune properties such as light absorption, conductivity, charge-carrier mobility, and light emission in π-conjugated materials determines the performance of such devices as organic photovoltaics (OPVs), dye-sensitized solar cells (DSSCs), organic light-emitting diodes (OLEDs) and organic field-effect transistors (OFETs). The use of organic materials instead of traditional inorganic materials gives many advantages such as simple processing, low cost manufacturing, versatile molecular design and easy control of physical properties of materials. 2,1,3-Benzothiadiazoles were considered as one of the most perspective internal acceptors for the preparation of the organic dyes (as well polycyclic, as polymeric).[1-3] Other fused chalcogen-nitrogen heterocyclic systems are much less investigated.

Design, synthesis and photophysical characteristics of novel dyes based on fused chalcogen-nitrogen heterocycles including 2,1,3-benzochalcogenadiazolesbenzo[*d*][1,2,3]thiadiazole, [1,2,5]thia(selena)diazolo[3,4-*c*]pyridine, [1,2,5]thiadiazolo[3,4-*d*]pyridazine and others will be discussed. The properties of electronic devices constructed from these sensitizers will be reported.

Acknowledgements

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References

1. L. S. Konstantinova, E. A.Knyazeva, O. A. Rakitin, *Org. Prep. Proc. Int.*, **2014**, *46*, 475.
2. O. A.Rakitin, A. V. Zibarev, *Asian J. Org. Chem.*, **2018**, *7*, 2397.
3. O. A. Rakitin, *Synthesis*, **2019**, in press.DOI: 10.1055/s-0039-1690679.

2. ORAL PRESENTATIONS

THE INFLUENCE OF ORTHO-SUBSTITUENTS ON THE PROPERTIES OF PHENYLBORONIC ACIDS

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Phenylboronic acids are compounds of great importance due to their wide applications in organic synthesis, catalysis, supramolecular chemistry, biology, medicine and material engineering.[1]Their properties are strongly influenced by the type and location of the substituent in the phenyl ring. Compounds containing substituents at the ortho position with respect to the boronic group are different from their meta and para isomers. Compared to the latter, for ortho-substituted compounds, the interaction between the $B(OH)_2$group and the substituent may occur, e.g. by hydrogen bond formation or steric hindrance (Figure 1).This influences the physicochemical properties such as acidity, receptor binding capacity or biological activity.[2-5] In this presentation, examples of important boronic compounds with ortho substituents will be presented, and a discussion of the relationship between their structures and properties will be carried out.

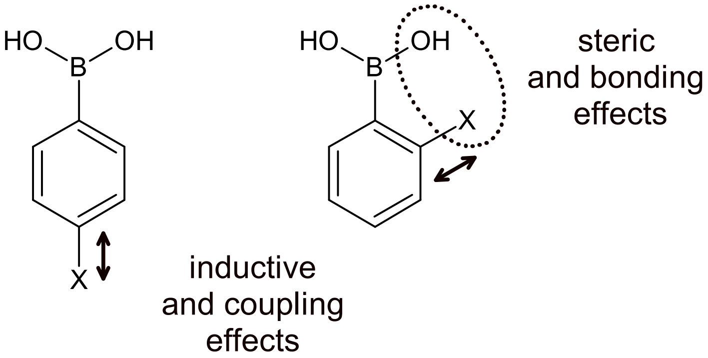

Figure 1. Possible interactions in substituted phenylboronic acids.

Acknowledgements

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References

1. Boronic Acids. Preparation and Applications in Organic Synthesis, Medicine and Materials, 2nd ed.; D. G. Hall, Ed.; WILEY-VCH:Weinheim, Germany, 2011.
2. M. K. Cyrański, P. Klimentowska, A. Rydzewska, J. Serwatowski, A. Sporzyński, D. K. Stępień, *CrystEngComm*, **2012**, *14*, 6282.
3. A. Adamczyk-Woźniak, K. Ejsmont, B. Gierczyk, E. Kaczorowska, A. Matuszewska, G. Schroeder, A. Sporzyński, B. Zarychta, *J. Organomet. Chem.,***2015**, *788*, 36.
4. I. D. Madura, A. Adamczyk-Woźniak, A. Sporzyński, *J. Mol. Struct.,***2015**, *1083*, 204
5. A. Adamczyk-Woźniak, E. Kaczorowska, J. Kredatusova, I. Madura, P. H. Marek,A. Matuszewska, A. Sporzyński, M. Uchman, *Eur. J. Inorg. Chem.,* **2018**, 1492.

THE ROLE OF HYDROGEN-BONDING IN THE STRUCTURE AND PROPERTIES OF COMPOUNDS

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Understanding the diverse non-covalent interactions is essential for the design of new compounds and their application as drugs, novel materials or in catalysis. Such contacts can be of the hydrogen, halogen, chalcogen, pnictogen, tetrel and triel types as well as cation-π, anion-π, π-π interactions, etc.. The bond lengths are considerably longer and the involved energies are lesser than those in the respective covalent bonds. A detailed understanding of the nature of those weak interactions in terms of directionality, tunability, hydrophobicity, donor atom size, multiplicity, among others, is essential to the design of novel compounds aiming for their rational application.

The results obtained in the authors laboratory towards the use of noncovalent interactions, specifically H-bonding, in the synthesis of organic and coordination compounds, as well as in catalysis, will be highlighted.

Acknowledgements

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References

1. K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Dalton Trans. 46 (2017) 10121.
2. K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, Coord. Chem. Rev. 345 (2017) 54.
3. Noncovalent Interactions in Catalysis, K.T. Mahmudov, M.N. Kopylovich, M.F.C. Guedes da Silva, A.J.L. Pombeiro, (Eds.) Royal Society of Chemistry, UK, 2019.
4. Noncovalent Interactions in the Synthesis and Design of New Compounds. A.M. Maharramov, K.T. Mahmudov, M.N. Kopylovich, A.J.L. Pombeiro, (Eds.) John Wiley & Sons, Inc., Hoboken, NJ, 2016.
5. K.T. Mahmudov, A.V. Gurbanov, F.I. Guseinov, M.F.C. Guedes da Silva, Coord. Chem. Rev. 387 (2019) 32.

SELF-HEALING POLYMERS BASED ON REVESIBLE DIELS-ALDER REACTION

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Traditional reactoplastic polymers such as epoxy resins and polyurethanes are widely used in many areas, but the majority of such polymers cannot be recycled or repaired after damage due to their cross-linked nature, that limits material lifetime and leads to waste production. Thermoreversible Diels-Alder reaction is one of the most powerful tools in the development of self-healing polymers and composites. The idea behind is to create thermally reversible covalent cross-links between polymer chains. Once the material is damaged, thermal treatment should be applied and heal a crack restoring bonds between two surfaces. We present here a series of soft (polyurethanes) and hard (epoxides) thermally remeandable polymers capable of restoration of their mechanical properties after damage. We prepared a recyclable polyurethanes based on difurfurylamine-terminated isocyanate-polypropylenglycol oligomer cross-linked with various amounts of bismaleimide. Flexible polyurethanes demonstrate up to 95% recover of mechanical properties after damage and healing cycle. Kinetic experiments and variation of bismaleimide content allow optimizing both mechanical properties and the healing process.

We are also working toward a new green synthetic approach to low viscous self-healing epoxy resins. We explored a known system based on furfurylamine and find out that the addition of triethyleneglycol to the composition allows us to significantly decrease the duration of a healing cycle required to restore properties. We developed a new fast and simple method to determine self-healing ability based on pull-out test. We designed and synthesized a series of polyfuranic monomers using the reductive amination of commercial aromatic diamines with furfural that can be used for the development of both epoxy and polyurethane self-healing compositions. An unusually high temperature required for the reverse Diels-Alder process (up to 300 ^{o}C) achieved for several model compounds that potentially allow significantly increase thermal window available for self-healing materials. We present DFT insight into this reaction thermodynamics.

NEW MOLECULAR CLUSTERS BASED ON LANTHANIDE CARBOXYLATES

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Polynuclear clusters of lanthanides and their coordination polymers continue to attract researchers' attention due to the vast variety of their crystal structures and unique physical properties. At the same time, high coordination numbers of lanthanides and structural flexibility of their compounds often make their reproducible and predictable synthesis a challenge. Therefore, it is important to find approaches for the synthesis of the new stable lanthanide clusters.

The objects of this study are polynuclear lanthanide hydroxo pivalates $[Ln_4(OH)_2(piv)_{10}(H_2O)_2]_\infty$ (Ln = La−Er; Hpiv — pivalic, 2,2-dimethylpropanoic acid) and their complexes with diethylenetriamine. The compounds were synthesized by the controlled hydrolysis of lanthanide nitrates in an aqueous solution containing $Hpiv/piv^-$ buffer mixture. According to single crystal XRD data, the compounds are 1D coordination polymers with tetranuclear 'butterfly' $\{Ln_4(\mu_3\text{-}OH)_2\}$ building blocks.The LnO_8 coordination environment is best described as a triangular dodecahedron.There are two distinct packing polymorphs of $[Ln_4(OH)_2(piv)_{10}(H_2O)_2]_\infty$with a similar structure of 1D ribbon. Triclinic polymorph exhibits parallel packing of the ribbons, the monoclinic one — 'herringbone' packing.

The former can be transformed into the latter by a dehydration-rehydration process. The intermediate $Ln_4(OH)_2(piv)_{10}$ compound is of poor crystallinity which obstructs its study by conventional diffraction techniques. PDF (Pair Distribution Function) analysis combined with DFT calculations were employed to reveal structure transformation upon rehydration and to gain some insight into the structure of $Ln_4(OH)_2(piv)_{10}$.

DFT optimization of isolated $\{Ln_4(OH)_2(piv)_{10}\}$ fragment demonstrates the change of two pivalate anions coordination mode to compensate for the elimination of two water molecules from the structure. The optimized model fits well the experimental PDF curve for the dehydrated compound, which confirms a similar structural transformation upon rehydration.

Upon addition of diethylenetriamine (deta) to the hydroxo pivalates, they undergo further hydrolysis and form octahedral clusters $Ce_6O_8(piv)_8(deta)_4$, $Pr_6(OH)_8(piv)_{10}(deta)_4$, $Ln_6(OH)_8O(piv)_8(deta)_4$ (Ln = Gd; Eu, Tb).[1]

Acknowledgments

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References

1. D. Grebenyuk, I. Martynova, D. Tsymbarenko, *Eur. J. Inorg. Chem.* **2019**, 3103.

ORGANOELEMENT COMPOUNDS MEET ORGANIC POLYMERS - POLYALKOXYSILOXANE-ASSISTED HETEROPHASE POLYMERIZATION

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Heterophase polymerization is a generic term describing polymerization reactions taking place in heterogeneous media, which are used for manufacturing polymer dispersions. Aqueous emulsion polymerization is by far the most relevant, but also a special case, as the polymer particles are formed via nucleation in the continuous aqueous phase. In contrast, polymerization occurs in monomer droplets during suspension and miniemulsion polymerization. Polymerization in microemulsions aims to obtain thermodynamically stable dispersions of ultrasmall polymer particles, however, it is often complicated by the fact that the initial microemulsion may not stay in the thermodynamic equilibrium through the whole polymerization process.

In this work, we report on a new series of heterophase polymerization techniques for synthesis of well-defined nanostructured hybrid particles. Instead of classical organic surfactants, hyperbranched polyethoxysiloxane (PEOS) and its PEGylated derivatives (PEG-PEOS) are used as both silica precursor and emulsion stabilizer. When styrene is employed as monomer, monodisperse core–shell polystyrene@SiO_2 nanoparticles are obtained via a miniemulsion polymerization mechanism.[1] In the case of methyl methacrylate / PEOS system, the formation of monodisperse core–shell nanoparticles is the result of emulsion polymerization.[2]In both cases, PEOS, which is per se a water-insoluble liquid, becomes amphiphilic upon hydrolysis at the oil/water interface.Nanoscale water-in-oil-in-water double emulsions can also be prepared, wherePEOS stabilizes both interfaces.[3] The resulting double miniemulsions are eventually solidified via subsequent conversion of PEOS to silica and polymerization of the oil phase to yield robust water@SiO_2@polymer@SiO_2nanocapsules. Other interesting nanostructures such as nanorattles and Janus-like nanomushroom scan be obtained just by changing preparation conditions.

Amphiphilic PEG-PEOS can reduce the interfacial tension between oil and water close to zero.[4] An oil phase containing such kind of surfactants can be emulsified in water spontaneously or just under low-energy stirring. Polymerization of the oil phase in the resulting emulsions leads to formation of monodisperse polymer@SiO_2core-shell particles, whose size can be precisely adjusted by PEGylation degree and reach as small as 30 nm. The PEGylation degree also dictates the reaction mechanism that varies from suspension polymerization with breakup of monomer droplets and miniemulsion polymerization to microemulsion polymerization leading to exact “copying” of initial emulsion droplets.

References

1. Y. Zhao, Z. Chen, X. Zhu, M. Möller, M. *Macromolecules* **2016,** *49*, 1552.
2. Y. Zhao, H. Wang, X. Zhu, M. Möller, *Polym. Chem.* **2017**, *8*, 6263.
3. Y. Zhao, J. Liu, Z. Chen, X. Zhu, M. Möller, *Nat. Commun.* **2018**, *9*, 1918.
4. Z. Chen, Y. Zhao, X. Zhu, M. Möller, *Macromolecules* ***2019***, *52*, 5670.

RARE-EARTH METAL COMPLEXES SUPPORTED BY BIS(AMIDINATE) LIGANDS AND THEIR ROLE IN CYCLIC ETHERS POLYMERIZATION

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Biocompatible and biodegradable polyethers find application in medical supplies and packaging materials production. Mechanical properties and rate of biodegradation of polyethers depend on their molecular-mass parameters. That brings us to the task of creating non-toxic catalysts which could be used to control polymerization process. Non-toxic rare earth metal species are one of the most perspective catalysts nowadays.

Our research is devoted to obtaining of catalysts in *rac*-lactide and ε-caprolactone polymerization, based on rare-earth complexes supported by an *ansa* bis(amidinate) ligands. For this purpose,we synthesized neodymium (**1**-**4**) and yttrium complexes (**5**-**6**), including bis(amidinate) *amides* - $[C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N(2,6\text{-}Me_2C_6H_3)\}_2]NdN((SiMe_3)_2)_2{*}(DME)$(**1**), $[\kappa^3\text{-}C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N(2,6\text{-}\textit{i}Pr_2C_6H_3)\}_2]NdN((SiMe_3)_2)_2(THF)$(**2**), *chloro-amide* $\{\kappa^3\text{-}N\text{-}[C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N\text{-}2,6\text{-}\textit{i}Pr_2C_6H_3\}_2]\}Nd(N(SiMe_3)_2)(Cl)[Li(DME)_3]$(**3**), *ionic pairs* $\{\kappa^n\text{-}N\text{-}[C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N\text{-}2,6\text{-}\textit{i}Pr_2C_6H_3\}_2]\}M\{\kappa^m\text{-}N\text{-}[C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N\text{-}2,6\text{-}\textit{i}Pr_2C_6H_3\}_2]\}[Na(DME)_3]$ (M = Nd, n = 3, m = 2 (**4**); M = Y, n = 3, m = 3 (**5**)), *mixed-ligand*complex $[C_6H_4\text{-}1,2\text{-}\{NC(\textit{t}Bu)N(2,6\text{-}Me_2C_6H_3)\}_2]Y((2,6\text{-}Me_2C_6H_3N)_2C(\textit{t}Bu)$.

Amide complex **1** showed high activity in cyclic ethers polymerization- full conversion of 500 equivalents of monomer was reached in 15 minutes. By molecular-mass distribution best results have polylactides, obtained in the presence of complexes **6**, **1** and **3** (PDI = 1.22, 1.34 and 1.35 respectively).

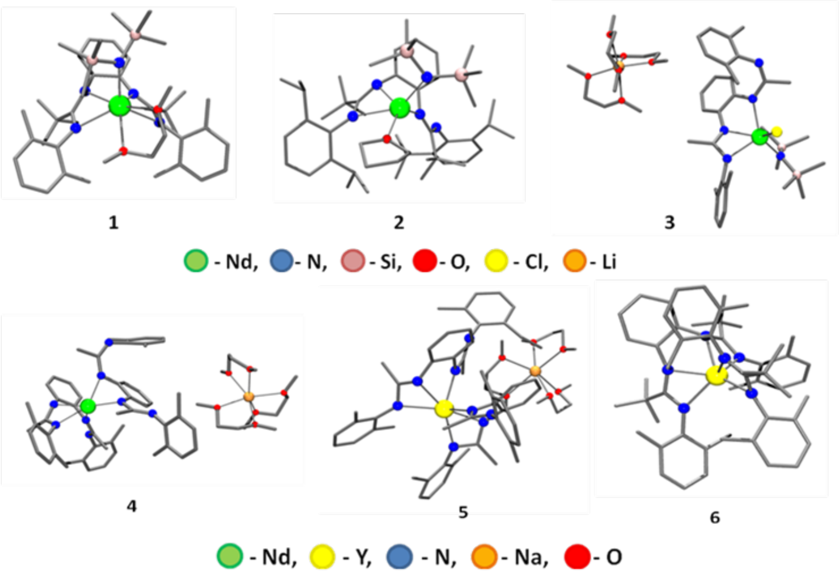
1 2 3 4 5 6

Figure 1. Structures of obtained complexes (**1**-**6**)

Acknowledgments

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THE INFLUENCE OF ORTHO-SUBSTITUENTS ON THE PROPERTIES OF PHENYLBORONIC ACIDS

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During the last decades, bacteria, molds and yeasts have become more resistant towards classic antibiotics and synthetic biocidal compounds. Therefore, there is a need for new non-toxic biocides possessing a broad spectrum of antimicrobial activity and could, at least, reduce both the level of administration of classic antibiotics and potentially harmful synthetic biocides in the area of their application, i.e. food, pharmaceutical and personal care compositions. These products are susceptible to microbial contamination both during manufacturing in nonsterile conditions and during normal use by consumers so that preservatives are required to maintain quality and shelf-life of the products preventing the products from growth of pathogenic microorganisms, degradation and malodor. Unfortunately, safety of many synthetic preservatives are the subject of debate among regulators specializing in food chemistry, cosmetics and toxicology.

In this respect, oligochitosan – an artificial polyaminosaccharide – is considered as a safe, biocompatible and biodegradable biopolymer possessing a broad range of antimicrobial activity against bacteria, molds and yeasts and potential candidate for practical applications in pharmaceutical, food and household products. Nevertheless, the application of oligochitosan is restricted in some formulations. The first restriction is that chitosan is insoluble in water but dissolves in acidic aqueous media, and its solubility and antimicrobial activity dramatically decreases as pH increases above critical pH (pH_c) threshold point at~6.2-6.6. The second restriction for chitosan application in a series of products as a preservative is the interaction of positively charged in aqueous acidic media chitosan macromolecules with anionic surfactants (SDS), stabilizers, emulsifiers and thickening agents, whose are widely used in food, household and industrial cleaners, and personal care products, that leads to precipitation of a surfactant-polyelectrolyte complex (SPEC) from acidic aqueous media. As a result, insolubility of chitosan in alkaline solution and insolubility of chitosan-anionic additive complex make impossible or highly restrict the application of chitosan in the products.

Recently, we have found that reacetylated chitosan (RA-CHI) having a random-type distribution of acetyl groups forms a transparent solution in the presence of SDS without SPEC formation and possesses a high antibacterial activity against Gram-positive and Gram-negative in both weakly acidic and weakly alkaline environments. Antibacterial activity and compatibility with SDS make RA-CHI promising for application of as an artificial antimicrobial agent in food, personal care and household products containing liquid or semiliquid anionic surfactants.

SYNTHESIS OF SYMMETRIC AND NON-SYMMETRIC NICKEL(II) PECEP (E = S, O) PINCER COMPLEXES

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Pincer ligands have become ubiquitous in organometallic chemistry.[1] Following our interest in the development of new pincer systems,[2] we present the synthesis and characterization of new Ni(II) complexes, which display phosphinito-thiopshosphinito ^{iPr}POCSP^{iPr} and bis(thiosphosphinito) ^{iPr}PSCSP^{iPr} pincer ligands.[3] The lack of studies for the ^{iPr}POCSP^{iPr} and especially the ^{iPr}PSCSP^{iPr} ligand motivated us to further investigate whether the introduction of sulfur to the side arms of the ligands does have a noticeable effect on the complex preparation or its properties.

Reaction of the Ni(II) chloride complexes with one equivalent of base and nitrile furnishes cyanomethyl complexes like Guan already reported for the well-known ^{iPr}POCOP^{iPr} pincer ligand.[4] Increase of the amount of base and nitrile results in the formation of 3-amidocrotononitrile complexes. In contrast, similar reactions using [(^{iPr}PSCSP^{iPr})NiCl] resulted in the formation of a tetranuclear Ni cluster and a dinuclear 1,3-dithiolate bridged PSCSP complex by unexpected cleavage of the P-S bonds.[5]

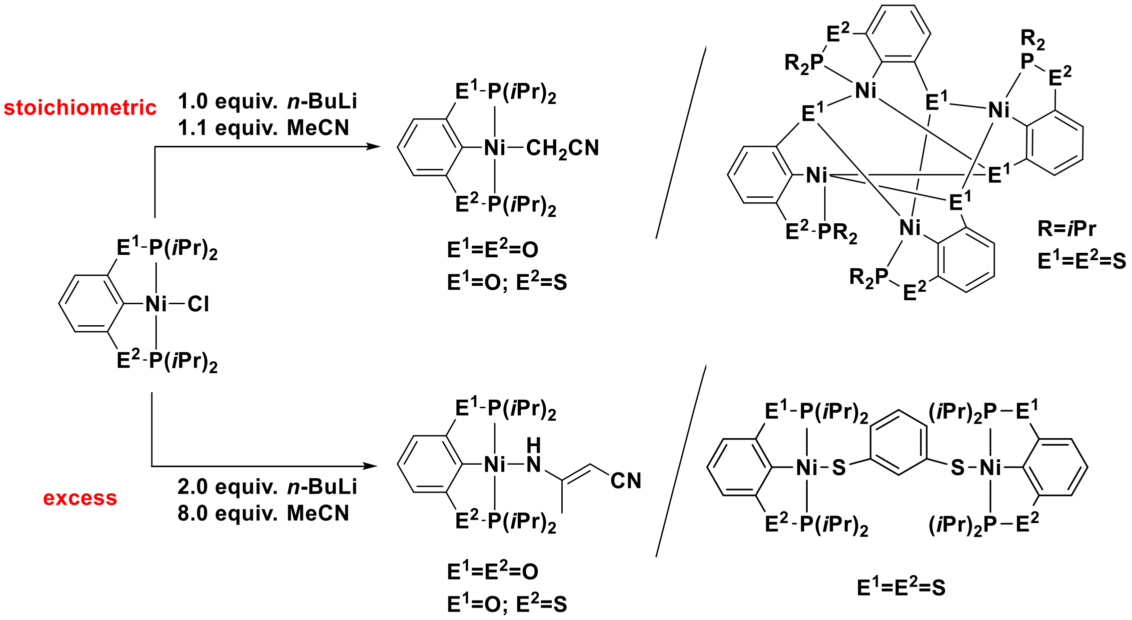

Figure 1. Overview of the formation of Ni(II) cyanomethyl and amidocrotonitrile complexes.

References

1. M. E. Van der Boom, D. Milstein, *Chem. Rev.* **2003**, *103*, 1759-1792.
2. G. Vlahopoulou, S. Möller, J. Haak, P. Hasche, H. J. Drexler, D. Heller, T. Beweries, *Chem. Commun.* **2018**, *57*, 6292-6295.
3. a) P. Hasche, M. Joksch, G. Vlachopoulou, H. Agarwala, S. Spannenberg, T. Beweries, *Eur. J. Inorg. Chem.* **2018**, *2018*, 676-680; b) S. Kaur-Ghumaan, P. Hasche, A. Spannenberg, T. Beweries, *submitted*.
4. S. Chakraborty, Y. J. Patel, J. A. Krause, H. Guan, *Angew. Chem., Int. Ed.* **2013**, *52*, 7523-7526.
5. P. Hasche, A. Spannenberg, T. Beweries, *submitted*.

GRAPHITE OXIDE AS A POLYMER-LIKE SUBSTANCE WITH A UNIQUE 3D STRUCTURE

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A century and a half-long story of graphite oxide has added much to its diversity and multivariance but did not make it absolutely bright as a substance. It can be referred to as a polymer with a unique structure, which can reversibly be 2D–3D transformed under the effect of such a widely used solvent as water. Each graphite oxide (GO) layer can be considered as an irregular polymer, which contains domains with different chemical properties. The layers are cross-linked and sewed by GO functional groups and water molecules, the role of latter depending on their relative content. When the amount of water is substantially increased, they are no longer sewing units, but dividing agents that provide the possibility of GO layers to exist independently. This peculiar feature of graphite oxide, which, being actually a complex organic substance, can change its properties when absorbing or releasing water, makes it very interesting subject of investigation. However, its experimental study can only provide information about its gross composition and some averaged characteristics. Even structural details of local GO sheet domains remain unclear.

We have carried out nonempirical simulations of model GO sheet fragments with the aim to clarify the nature and possible location of its functional groups and their interaction with each other and with water molecules, which, judging from the experimental data, can never be completely removed from specimens under any drying conditions. For this purpose, different combinations of functional groups were added to basic C_{54} graphene fragment so that systems of the following general composition were considered: $C_{54}H_q(OH)_k(O)_l(O')_m(COOH)_n(H_2O)_p$, where the numbers of OH hydroxide, O epoxide, O' keto, and COOH carboxyl groups varied in the ranges of $0≤k≤8$, $0≤l≤3$, $0≤m≤3$, and $0≤n≤5$, respectively. The number (n) of solvating water molecules was up to 12. Simulations were carried out at the density functional level with a B3LYP hybrid functional and 6-31G(d,p) extended Gaussian basis set. Simulated infrared absorption spectra were compared to the experimental spectra recorded for the specimens synthesized according to modified Hummer's method. For a number of experimental bands in characteristic and high-frequency ranges, a more reliable assignment was proposed that shed light on the prevailing structure motives, the role of water, and the nature of GO specimen's acidity.

Acknowledgments

Simulations were carried out with the use of shared facilities of the Lomonosov Supercomputing Center of the Moscow State University[1].

References

1. V. Sadovnichy, A. Tikhonravov, Vl. Voevodin, V. Opanasenko, "Lomonosov": Supercomputing at Moscow State University. In *Contemporary High Performance Computing: From Petascale toward Exascale* (Chapman & Hall/CRC Computational Science), **2013** ,Boca Raton, USA, CRC Press, 283-307.

RARE-EARTH BIS(ALKYL)COMPLEXES CONTAINING TRIDENTATE AMIDOPYRIDINATE LIGAND

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A new series of rare-earth bis(alkyl)compounds incorporating NNN-amidopyridinate ligand has been synthesized via alkane elimination reactions between the potentially tridentate aminopyridine and the corresponding tris(alkyl) precursor $Ln(CH_2SiMe_3)_3(THF)_2$ (Ln = Sc, Y).

It was found that depending on the reaction and workup solvents different coordination compounds of yttrium could be isolated. The reaction performed in toluene followed by slow re-crystallization from cold toluene afforded the pentacoordinateyttrium species **1Y**. Replacing toluene with n-hexane with the subsequent re-crystallization of the product from cold THF/hexane mixture (1/4) led to formation of hexacoordinate compound **1Y**$^{\mathbf{THF}}$. In case of scandium, the only non-solvated pentacoordinate compound **1Sc** was isolated regardless the solvent. All obtained compounds have been crystallographically characterized.

The novel complexes were evaluated as pre-catalysts for the polymerization of isoprene. Ternary catalytic systems **1Ln**/AlBui^3/borate allowed the formation of polyisoprene with predominant 1,4-cis-content (up to 98%) within the period of 6–18 h. Notably, unlike in the case of scandium species, the catalytic performance of the yttrium compounds was found to be totally dependent on the borate nature.

All the complexes **1Ln** were also tested as catalyst precursors for the intermolecular C-N, C-S and C-P bond formation reactions. For these hydroelementation trials, styrene was allowed to react with equimolar amounts of amines, phosphines and thiols in the presence of the compounds **1Ln**. The complexes showed 100% regioselectivity giving exclusively anti-Markovnikov addition products in all cases regardless the nature of E-H (E = N, S, P) reagent used.

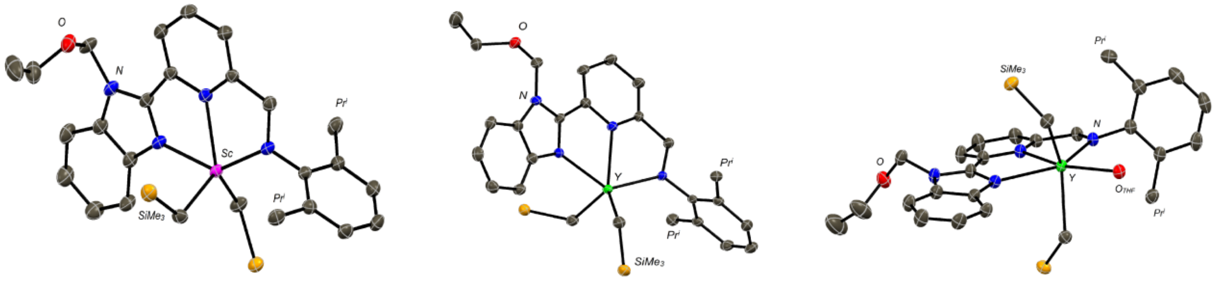

Figure 1.Molecular structures of bis(alkyl) compounds **1Ln**

Acknowledgments

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AMAZING GEL MATERIALS – POLY(VINYL ALCOHOL) CRYOGELS

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Poly(vinyl alcohol) cryogels (PVACGs) are formed as a result of consecutive freezing, incubating frozen and then thawing of concentrated solutions of the polymer [1,2]. The key characteristic feature of PVACGs is their macroporosity, i.e. the presence of interconnected pores (cross-section of 1-5 µm) in the gel bulk. Such pores are generated by the crystals of frozen solvent; therefore the size and architecture of macropores in such cryogels depend on many factors capable of influencing the solvent crystallization behaviour. These factors are as follows: (i) solvent used (water or dimethylsulfoxide); (ii) properties of the gel-forming polymer (molecular weight characteristics of the PVA itself, chains' tacticity, the amount of residual O-acyl groups) and polymer concentration in the initial solution; (iii) conditions of the cryogenic processing (freezing rate, temperature and duration of frozen storage, defrosting regime, the number of freeze-thaw cycles); (iv) the presence of low- or/and high-molecular additives that possess the pore-modifying abilities. The rigidity and heat endurance of PVACGs increase as the initial polymer concentration grows. The same is also true for the influence of PVA molecular weight, whereas the increased amount of residual O-acyl groups is the unfavourable factor. The freezing rate within rather wide diapason (~0.1..~20°C/min) affects weakly on the rheological properties and porous morphology of PVACGs, while frozen storage temperature biases a bell-like influence. The most principal significance has the regime of thawing: the slower the defrosting rate, the stronger the resultant cryogels and the more uniform and perfect their macroporous structure is. The increase in the number of freeze-thaw cycles results in the growth of gel's rigidity and heat endurance with simultaneous certain widening of macropores. The additives of various low- and high-molecular weight solutes in the initial PVA solutions exert more sophisticated influence on the properties of the PVACGs. The solutes with chaotropic abilities cause weakening of PVACGs and decrease in their fusion temperature, whereas kosmotropic agents strengthen PVA cryogels. The presence of surfactant additives causes "rounding" of the macropores due to a decrease in the surface tension at the solid-liquid interface upon the ice crystals growth. In turn, the presence of certain macromolecular additives in the initial PVA solution is able to induce the liquid-liquid phase segregation thus resulting in the formation of spongy cryogels possessing the system of interconnected gross (100-250 µm) pores in addition to smaller those usual for PVACGs.

Owing to the unique combinations of excellent physical properties, macroporosity, chemical stability and biocompatibility these amazing gel materials are of significant practical interest in various applied fields, e.g., biotechnology (carriers of immobilized molecules and cells, etc.), medicine (drug delivery systems, artificial cartilages, covers on wounds and burns, gel standards for the verification of MRI and ultrasound apparatus), chemistry (carriers of catalysts), environment protection (reinforcing of thawed ground and soil), construction (antifiltration screens and watertight elements for dams of thawed or frozen types), etc.

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[1] V.I. Lozinsky. *Russ. Chem. Revs*. **67** (7) 573-586 (1998).
[2] V.I. Lozinsky. *Adv. Polym. Sci*. **263**, 1-48 (2014).

FLUORENE EFFECT ON METAL COMPLEX-CATALYZED REDUCTIVE AMINATION OF CARBONYL COMPOUNDS

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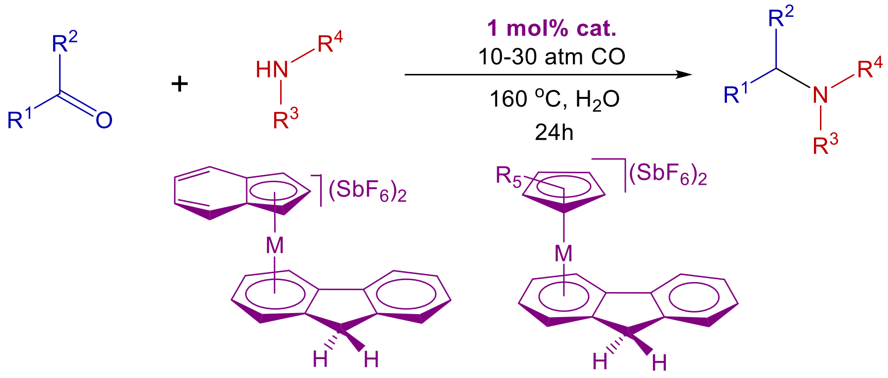
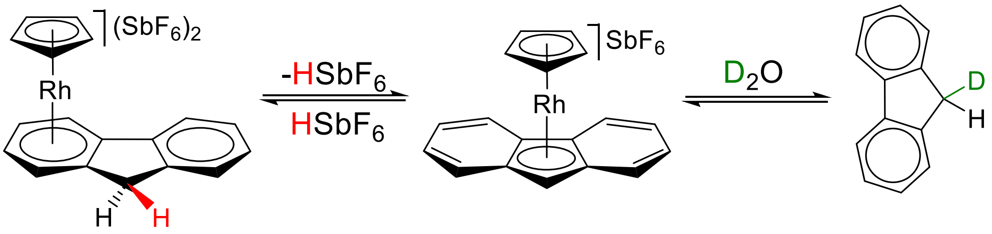
The catalytic applications of arene complexes of 9 group metals are well known [1,2,3]. Elimination of arene ligand results in three vacant coordination sites on the metal atom.For this reason, the catalytic activity strongly depends on the lability of arene ligand. In the present work, we developed general approaches to η^6-fluorene complexes of 9 group metals with supporting cyclopentadienyl and indenyl ligands from the respective halide complexes. We also demonstrated their efficiency as catalysts for reductive amination of aldehydes or ketones in the presence of carbon monoxide.



R=Me M=Co, Rh, Ir

We found that the η^6-fluorene complexes have higher catalytic activity than benzene analogues. It is in accordance with higher lability of fluorene as compared with benzene that can be explained by easy fluorene deprotonation and following η^6→η^5→η^1 haptotropic rearrangement. In particular, we showed that the rhodium complex undergoes rapidly decomposition by D_2O to give 9-D-fluorene..



Acknowledgements

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References

[1] D. A. Loginov, L. S. Shul'pina, D. V. Muratov G. B. Shul'pin, *Coord. Chem. Rev.*, **2019**, *387*, 1–31.
[2] V. B. Kharitonov, D. Chusov, D.A. Loginov, et al., *Organometallics*, **2018**, *37*, 2553–2562.
[3] V. B.Kharitonov, D. V.Muratov,D. A.Loginov*, Coord. Chem. Rev.*, **2019,** 399**,** 213027.
[4] V. B. Kharitonov, D. Chusov, D. A. Loginov, et al.,*Organometallics* **2019**, 38, 16, 3151-3158.

HYPER-CROSSLINKED POLYSTYRENE AS A SUPPORT FOR MONO- AND BIMETALLIC PALLADIUM-CONTAINING PARTICLES ACTIVE IN SUZUKI CROSS-COUPLING

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At present, ligandless cross-coupling catalysts are the subject of intensive study. Regarding to such catalysts, the term “cocktail” type catalysts was proposed, because ligandless catalytic systems contains different forms of palladium (bulk nanoparticles (NPs), soluble Pd(II) species, soluble Pd(0) species) [1]. It is assumed that these forms of palladium act simultaneously and are mutually transformed into each other during the reaction [2, 3]. In this context, the rates of palladium dissolution and precipitation, as well as reaction location (in the solution or inside the pores of catalytic support) are of crucial importance.

In this work, different combinations of hyper-crosslinked polystyrene (HPS) and palladium precursors (chlorine-containing precursors and palladium acetate) were studied in the Suzuki reaction.

For as-synthesized unreduced Pd/HPS catalysts containing mostly Pd (II) as an active phase, it was shown that Pd activation occurs under the action of arylboronic acid, which in turn leads to the formation of noticeable amounts of the homocoupling product and to the deposition of Pd(0) NPs. Moreover, it was found that, in some cases, fast Pd precipitation, which is in turn due to high migration ability of palladium salt inside the polymer, is responsible for fast catalyst deactivation during the reaction. In contrast, in the case of optimal combinations of Pd precursor for the samples with highest activity, the process of NPs formation occurs relatively slow and results to rather small NPs (about 2-4 nm). In the case of catalysts preliminarily reduced in hydrogen flow, Pd(0) NPs are “reservoirs” of active soluble catalytic species formed under the influence of aryl-halide. This assumption was confirmed by the study of LSPR (local surface plasmon resonance) effect for well-defined core-shell Pd-Au NPs stabilized in HPS: application of visible light irradiation was found to result in noticeable increase of catalytic activity.

As a result, Pd-containing HPS-based catalytic systems with relatively high activity (more than 98% of aryl-halide for the reaction time about 1 h) working at mild reaction conditions (60^{o}C, ethanol-water mixture as a solvent) and at the absence of phase-transfer agents were developed. It is noteworthy that the ratio of aryboronic acid and aryl-halide as well as the presence of the excess of base play crucial role in ensuring a high yield of cross-coupling product.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research, project 18-08-00429.

References

1. D.B. Eremin, V.P. Ananikov, *Coord. Chem. Rev.* **2017**, *346*, 2.
2. A.F. Schmidt, A.A. Kurokhtina, E.V. Larina, *Kinetics and Catalysis* **2012**, *53*, 84.
3. A.A. Kurokhtina, A.F. Schmidt, *ARKIVOC* **2009**, *11*, 185.

PARAMETRIZATION OF PHOSPHINE LIGANDS TO REVEAL AN EXPLANATION OF SELECTIVITY IN HYDROSILYLATION REACTION OF PLATINUM COMPLEXES

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A series of platinum(0) dialkylbiarylphosphine complexes with 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (DVTMS) were synthesized with 72-96% yield and structurally characterized using NMR, IR and XRD. Prepared complexes found to be efficient catalysts in hydrosilylation reaction between phenylacetylene and diphenylsilane in mild conditions and in cross-linking process of PDMS. The ligand set was based on commercially available XPhos, JohnPhos and SPhos and their tailored derivatives and in total contained 7 ligands. These catalysts sufficiently increased the selectivity of *β-(E)* isomer formation up to 98% with increasing of total yield up to 95%. The structural parameters were extracted from both XRD structures and optimized phosphine oxide derived template structures. Constructed library of complexes allow to include other types of ligands with the same structural scaffold for further optimization of hydrosilylation processes and study QSPR for selectivity and activity of homogeneous catalysts in Si-H activation processes.

For complex **1a** platinum(0)-*ortho* carbon atom from aryl group distance averages 3.204 Å platinum(0)-*ipso* carbon distance was 3.293 Å, these values are less than the sum of platinum and carbon Van der Waals radii (3.57 Å). Estimation of hapticity for Pt-arene interaction in **1a** using Kochi and co-workers proposed equation [1] equation gave hapticity value of x=1.68, this is comparable with gold(I) complexes with x in range 1.55-1.95.

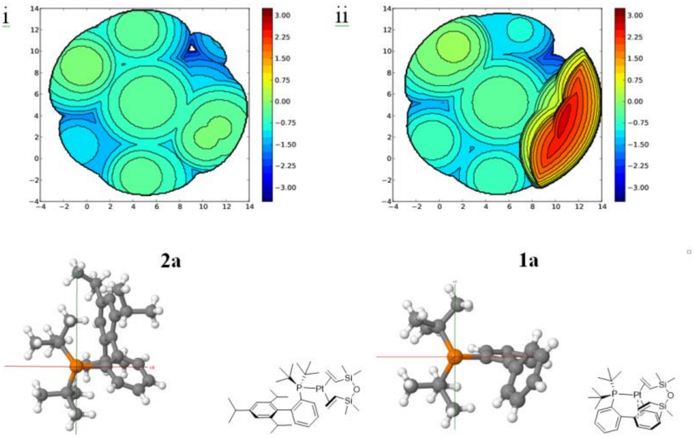

Figure 1. Chemical structure of part of the crystallographically determined complexes **1**, used in the calculation of buried volume, 34.9% $V_{bur}$and **2** with 45.0% V_{bur}.

References

1. Gómez-Suárez, Adrián, David J. Nelson, and Steven P. Nolan. *Chemical Communications* 53.18 (2017): 2650-2660.

ELECTROSPUN PYROPOLYMER CARBON NANOFIBER COMPOSITE ELECTRODES FOR HT-PEM FUEL CELLS

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Carbon nanofibers are known to be more stable electrocatalyst support under operation conditions of high temperature polymer electrolyte membrane fuel cell (HT-PEM) compared to carbon black.[1] Carbon nanofiber electrodes were obtained by the polyacrylonitrile (PAN) or polyheteroarylene solution electrospinning method with following oxidation, pyrolysis and platinization.[2-4]In order to find the impact of micropore specific surface area (SSA) in total SSA, the method of standard contact porosimetry (MSCP)[5] was used for pyrolyzed carbon nanofibers. The influence of heat treatment conditions was studied. An increase of stabilization (oxidation) temperature (from 330 to 350 °C) and/or an increase of pyrolysis temperature (from 900 to 1000 °C) lead to higher macro- and mesopore SSA with a simultaneous lowering of micropore SSA.

Composite electrodes were prepared by adding Ni and Zr salts to the electrospinning polymer solution. After pyrolysis Ni and Zrare uniformly distributed in a form of Ni^0 and ZrO_x. Pt deposition was conducted from aqueous solution of $H_2[PtCl]_6$ with HCOOH addition as reducing agent. As a result, different platinum nanoparticle morphology, such as needle-like Pt and small size spherical Pt was found by changing heat-treatment conditions for platinized material (100 – 500 °C) and conditions of HCOOH addition by using electron microscopy. The cyclic voltammetry data shows higher stability to heat treatment of needle-like Pt nanoparticles compared to small-size spherical ones.

Acknowledgments

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References

1. Q.Li, D.Aili, H.A. Hjuler, J.O. Jensen. High Temperature Polymer Electrolyte Membrane Fuel Cells, Approaches, Status and Perspectives. Cham, Heidelberg, New York, Dordrecht, London: Springer, **2016**. 545 p.
2. V.G. Zhigalina, O.M. Zhigalina, I.I. Ponomarev, K.M. Skupov, D.Y. Razorenov, I.I. Ponomarev, N.A. Kiselev, G. Leitinger, *CrystEngComm* **2017**,*19*, 3792.
3. I.I. Ponomarev, O.M. Zhigalina, K.M. Skupov, A.D. Modestov, V.G. Basu, A.E. Sufiyanova, I.I. Ponomarev, D.Y. Razorenov, *RSC Adv*. **2019**, *9*, 27406.
4. K.M. Skupov, I.I. Ponomarev, D.Y. Razorenov, V.G. Zhigalina, O.M. Zhigalina, I.I. Ponomarev, Y.A. Volkova, Y.M. Volfkovich, V.E. Sosenkin, *Macromol. Symp.* **2017**, *375*, 1600188.
5. Yu. M. Volfkovich, V. E.Sosenkin, V. S. Bagotsky, *J. Power Sources* **2010**, 195, 5429.

LIGAND-TO-METAL CHARGE TRANSFER EXCITED STATES IN ORGANOMETALLIC COMPOUNDS

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Most organometallic compounds dissipate excitation energy very rapidly in nonradiative fashion, and only a small fraction have electronic excited states with moderate lifetimes, from which luminescence typically can occur. Nevertheless, in photochemistry of coordination compounds, research has traditionally concentrated on the search for long-lived excited states and utilization of their reactions in light energy conversion, information processing, and photocatalysis.Unfortunately, many classes of organometallic complexes are regarded as rather unstable to air/water and, historically, this fact has drastically hampered development of organometallic photophysics and photochemistry. The present report will be devoted to the properties of ligand-to-metal charge transfer (LMCT) excited states as an extremely rare, much less studied type of electronically-excited states.

A great deal has been learned about ligand-to-metal charge transfer excited states, based on organometallic compounds. The comprehensive knowledge on LMCT excited states[1,2], based on organometallic complexes, will be surveyed and fundamental properties will be discussed and thus generalized. Principle emphasis will be given to the recent studies on solvatochromism[3,4], relation between LMCT transition energies and differences in oxidation and reduction potentials[5-7], relation between emission quantum efficiency and lifetime[8,9], electron-exchange (Dexter) resonant energy transfer[10-12], and photolysis of organometallic compounds in their LMCT excited states. Representative LMCT excited state cases, mainly referred to the group III – V organometallic complexes, will be discussed aiding rationalization of the observed unique photophysics and photochemistry.

There is great scope for novel chemical, photophysical, and photochemical studies of organometallic species, having long-lived emissive LMCT excited states, and their organized systems.

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References

1. G.V. Loukova,*Photophysics of group IV metallocenes*, in: H.F. Chin (Ed.), *Organometallic Compounds: Preparation, Structure and Properties*. Nova Sci. Pub., N.Y. **2010**, 159–196.
2.G. Loukova, *Ligand-to-metal charge transfer excited states in organometallic compounds*, *In*: Springer Handbook of Inorganic Photochemistry, **2019**, *in press*.
3. G.V. Loukova, A.A. Milov, V.P. Vasiliev, V.I. Minkin, *Phys. Chem. Chem. Phys*. **2016**, *18*, 17822.
4.G.V. Loukova, V.P. Vasiliev, A.A. Milov, V.A. Smirnov, V.I. Minkin, *J. Photochem. Photobiol. A: Chem.*, **2016**, *327*, 6.
5. G.V. Loukova, V.V. Strelets, *J. Organomet.Chem*. **2000**,*606*, 203.
6. G.V. Loukova, V.V. Strelets, *Collect. Czech. Chem. Commun*. **2001**, *66*, 185.
7. G.V. Loukova, *Chem Phys. Lett*. **2002**, *353*, 244.
8. G.V. Loukova, W. Huhn, V.P. Vasiliev, V.A. Smirnov, *J. Phys. Chem. A*, **2007**, *111*, 4117.
9. G.V. Loukova, V.P. Vasiliev, V. A. Smirnov, W. Huhn, *Dokl. Phys. Chem*. **2007**,*413*, 66.
10.G.V. Loukova, V.A. Smirnov, S.E. Starodubova, *J. Phys. Chem. A* **2007**, *111,* 10928.
11. G.V. Loukova, V.A. Smirnov, S.E. Starodubova, *Russ. Chem. Bull., Int. Ed.* **2007**, *56*, 35.
12. G.V. Loukova, A.A. Milov, V.A. Smirnov, *High Energy Chem*. **2010**, *44,* 146.

POLYMERIZATION OF 1-TRIMETHYLSILYL-1-PROPYNE CATALYZED BY NIOBIUM AND TANTALUM PENTAHALOGENIDES: THE EFFECT OF CATALYTIC SYSTEM ON CONFIGURATION, SUPERMOLECULAR ORGANIZATION AND PROPERTIES OF POLYMER

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Due to the high gas and vapor permeation properties glassy polymers of 1,2-disubstituted draw the great interest of researchers. Unique transport characteristics of these polymers are the result of their nanoporous organization in which micropores are interconnected. Rigid sterically hindered macrochains, containing alternating C=C double bonds and bulky substituents, prevent close packing of macrochains and that lead to extremely high fractional free volume (FFV ~ 30%) and high BET specific surface area values (1000 m^2/g).

In our presentation, we shall present the results of the investigation of stereospecific polymerization of Si-containing acetylene 1-trimethylsilyl-1-propyne catalyzed by Nb and Ta pentahalogenides-based systems – conventional pentachlorides-based systems as well as novel systems based on pentabromides and pentafluorides. We shall address the effect of polymerization conditions on macrochain stereoregularity, supermolecular organization and porous structure of poly(1-trimethylsilyl-1-propyne) [PTMSP]. Also the effect of macrochain configuration on the functional properties of PTMSP from the point of its application as membrane material for separation processes will be discussed.

Acknowledgments

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SYNTHESIS AND CATALYTIC ACTIVITY STUDY OF CYANOPHENOXY- PHTHALOCYANINE SULFONATED DERIVATIVES

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Phthalocyanine molecules are ubiquitous in most areas of human activity. Effective catalysts, sensitizers, dyes and pigments, PDT applications, drugs for getting rid of alcohol addiction - and this is not a complete list of known practical ways of using compounds of this class.[1-2] This work is devoted to obtaining water-soluble complexes of phthalocyanine type with promising catalytic properties. Heterogeneous complexes of this type showed high values of catalytic activity in the oxidation reactions of sulfur-containing substrates.[3] The introduction of sulfo- groups to the periphery will expand the field of application of the studied compounds and increase their effectiveness as catalysts.

The initial cyanophenoxyphthalocyanines were obtained by template condensation in the absence of a solvent, according to the procedure described earlier.[3] The introduction of sulfo- groups to the periphery of the molecule was carried out by sulfonation of complexes with chlorosulfonic acid in the presence of thionyl chloride as a water-withdrawing agent that suppresses premature hydrolysis (**Figure 1**). The structure of the obtained complexes was confirmed by IR and NMR spectroscopy, mass spectrometric analysis. Using the standard oxidation reaction of sodium diethyldithiocarbamate the catalytic activity of phthalocyanine sulfonic acids under conditions of homogeneous catalysis were studied.

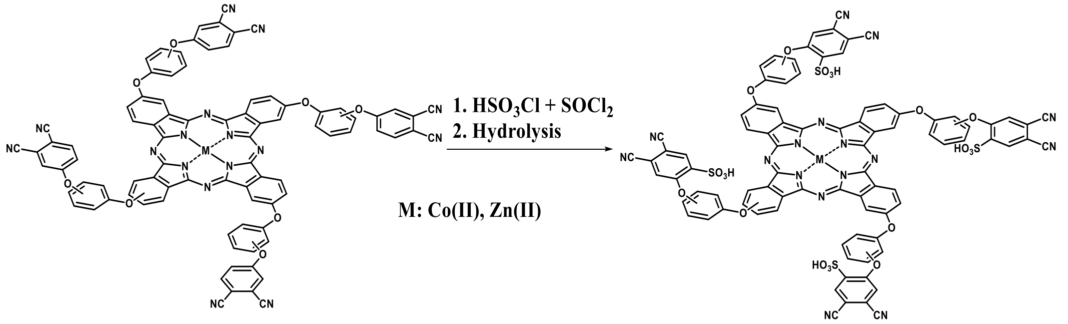

Figure 1. Introduction of sulfo- groups into cyanophenoxy- phthalocyanine complexes

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References

1. T. Birnbaum,T. Hahn,C. Martin, J. Kortus, M. Fronk, F. Lungwitz, D. R. T. Zahn, *J. Phys. Condens. Matter* **2014**, *26*, 104201.
2. R. Zhang, B. Xu, J. Wang, J. Zhao, *J. Mater. Res.,***2014**, *29*, 793–800.
3. D. A. Erzunov, A. S. Vashurin, O. I. Koifman, *Russ. Chem. Bull. Int. Ed.*, **2018**, *67*, 2250-2252.

FUNCTIONALIZATION OF POLYACRYLAMIDE DERIVATIVES FOR NANOTRAPPING BIOMOLECULES

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The development of bioactive synthetic polymers for stable nanotrapping is an important goal of polymer-based biomedical applications. The versatility of synthetic chemistry enables the tailoring of polymers for any given biological application. Various templates that may be quantified with presentation of bioactive polymeric molecules and control over their density and orientation are required Taking into account that the basis of many promising sensors and diagnostic systems are based on specific molecular interactions,[1-2] we developed new copolymers capable of establishing electrostatic and π-π interactions with either DNA[3-5] or proteins[6]. We demonstrated that controlled free radical copolymerization enables the preparation of water soluble cationic as well as anionic acrylamide-based copolymers with desired amounts of different monomeric units. From the fact that functional monomeric units determine the net charge of a copolymer molecule in its water solution, this synthetic approach permits one to make polymeric molecules with different electrostatic behavior. AFM study confirmed that developed copolymers self-assembled as thin films containing arrays of nanoscale cavities, whose sizes significantly dependent on the net charges of the copolymers. The ability of the nanocavities formed by cationic and anionic acrylamide-based copolymers to trap DNA and myoglobin, respectively, was demonstrated (Figure1). This result justifies our approach to engineering the novel functionalities that are able to expand the trapping possibilities of organic polymeric materials.

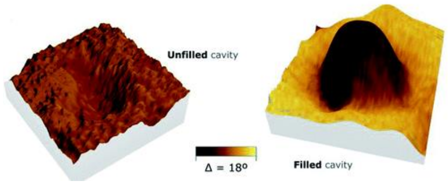

Figure 1. Bimodal AFM phase image of the myoglobin-filled self-assembled anionic acrylamide-based copolymer film, 3D representations of an unfilled and a filled cavity of the copolymer film

References

1. Z. Adamczyk and P. Warszyński, *Adv. Colloid Interface Sci.* **1996**, *63*, 41-149.
2. E. Katz and I. Willner, *Electroanalysis* **2003**, *15*, 913-947.
3. N. K. Davydova, O. V. Sinitsyna, I. V. Yaminsky, E. V. Kalinina and K. E. Zinoviev, *Macromolecular Symposia* **2012**, *321-322*, 84-89.
4. O. V. Sinitsyna, N. K. Davydova, V. N. Sergeev and E. E. Laukhina, *RSC Adv*. **2014**, *4*, 55565-55570.
5. N. K. Davydova, O. V. Sinitsyna, V. N. Sergeev, I. Perevyazko and E. E. Laukhina, *RSC Adv*. **2016**, *6*, 58212-58217.
6. N. K. Davydova, X. R. Rodriguez, C. Blázquez, A. Gómez, I. Perevyazko, J. Guasch, V. N. Sergeev, E. E. Laukhina, I. Ratera and J. Veciana, *RSC Adv*. **2019**, *9*, 15402-15409.

RUTHENIUM (II) COMPLEXES OF 2-SUBSTITUTED IMIDAZO-1,10-PHENANTHROLINES AS PHOTOSENSITIZERS OF INORGANIC SEMICONDUCTORS

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In this work, a series of imidazo[4,5-f][1,10]phenanthroline-containing ligands and their complexes with ruthenium (II) cation was synthesized (**Fig. 1**). Polypyridine imidazophenanthroline-containing Ru(II) complexes are capable of photo-induced electron transfer, including to the conduction band of some semiconductor materials.[1,2] Such photosensitization process will reduce the operating temperature of semiconductor gas sensors and thus reduce their energy consumption.

Energies of HOMO and LUMO of the synthesized complexes are suitable for electron transfer from excited state of photosensitizer to the conduction band of semiconductor oxides SnO_2 and In_2O_3 (**Fig. 2**). By means of time-resolved fluorescent spectroscopy, it was shown that the excited states of complexes are of a triplet nature with a high lifetime sufficient for electron transfer to the conduction band of semiconductor.

Hybrid organic-inorganic materials with synthesized complexes based on SnO_2 and In_2O_3 were obtained. Various optical methods have shown that electron transfer to the conduction band of the semiconductor does occur. Such electron injection is accompanied by the emerging of an additional short-lived emission component, bathochromically shifted relative to the phosphorescence of the organic complex. Obtained composites were also studied as sensitive elements of NO_2 and NO gas sensors.

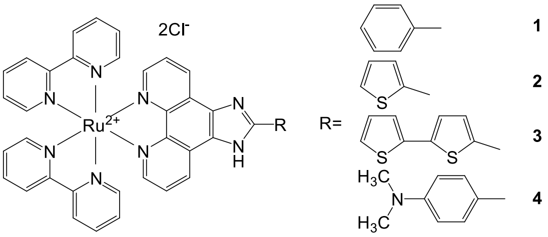

Figure 1. Structures of synthesized complexes

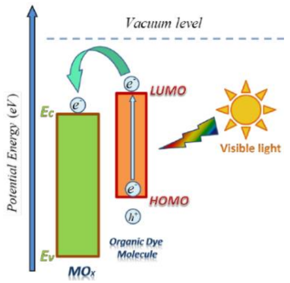

Figure 2. Photoinduced sensitization in a hybrid semiconductor-dye

Acknowledgements

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References

1. Manbeck G.F., Fujita E., Concepcion J.J, *J. Am. Chem. Soc.* **2016,** *138*, 11536.
2. Zeng L., Chen Y., Liu J., Huang H., Guan R., Ji L., Chao H. *Sci. Rep.* **2016**, *6*, 19449.

LOW DENSITY AEROGEL PREPARATION FROM DIANOFORMALDEHYDE POLYMER

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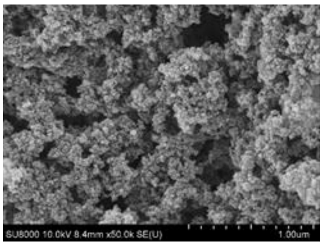
Polymeric organic low density aerogels (~ 10 mg/cm^3) are in demand as targets in controlled laser thermonuclear fusion research. Our approach to the preparation of low density dianoformaldehyde (DF) aerogel is based on a two-step DF gel synthesis which made it possible to dramatically reduce the concentration of starting substances necessary for generating strong aerogel with a high pore volume. In the first step, a synthesis of resin was performed with condensation of diane (2,2-bis-[4,4'-dihydroxydiphenyl]propane) and formaldehyde in an alkali aqueous solution at 27ºC. By GPC data, the resin was a mixture of oligomeric diane derivatives. In the second step, gel was prepared from the dilute resin after its heat treatment at T=220ºC and extra formaldehyde addition; the prepared gel was transformed to aerogel by supercritical drying. A minimum resin concentration necessary for attaining aerogel (6 mg/ml) was determined and optimal conditions for the preparation of aerogel with an at most lower density were identified. The prepared DF aerogel is among the best low density arylformaldehyde aerogels by its properties: porosity 0.988, pore size 0.6-1.5 μm, specific surface 600-700 m^2/g, and density 10.9 mg/cm^3 [1].

The sol and gel formation mechanism was studied using methods of dynamic and static light scattering, gelpermation chromatography and electron microscopy. It was for the first time shown for arylformaldehyde aerogels that the gelation process is diffusion-limited cluster-cluster fractal aggregation of sol nanoparticles generated in the course of condensation [2]. A role of formaldehyde additionally inserted prior to heat treatment, in comparsion with the stoichiometric formaldehyde amount, was revealed and the minimum formaldehyde amount necessary to ensure cross-linking of low density fractal aggregates accross the volume and to lead to the formation of the macro pore structure with the high pore volume and hierarchy structure with micro, meso and macro pores was determined (Fig. 1).

Figure 1. SEM image of the DF aerogel structure



Acknowledgments

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References

1. Sheveleva E. E.; Pimenov V. G.; Pikulin I.V.; A. M. Sakharov. Polymer Science Series B. **2016**, *58(2),* 173.
2. Sheveleva E.E.; Pimenov V.G.; Blagodatskikh I.V.; Vyshivannaya O. V.; Abramchuk S.S.; Sakharov A.M.Colloid and Polymer Science. **2018**, *296*, 1313.

TOWARDS AN EXPLANATION OF DISCREPANCIES INVOLVING PODIPY: WHY 31P NMR SPECTRA DON'T MATCH UP?

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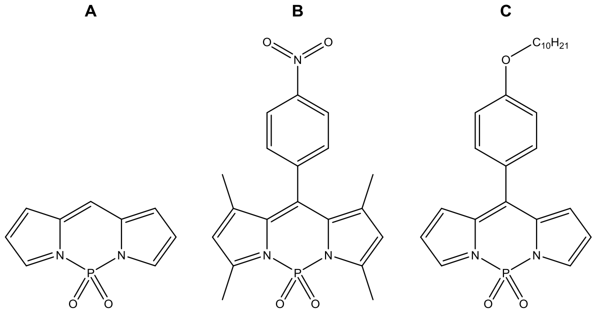
Oxophosporus dipyrromethenes, also known as PODIPY, are a relatively new family of dyes. They were first obtained in 2015 by Jiang et al.[1] and since then have been featured only in a handful of papers. PODIPY dyes have narrow absorption and fluorescence peaks, good quantum yields and better solubility in polar solvents than their boron counterparts. As such, PODIPY dyes are a promising scaffold for molecular probes. Another use lies in "naked eye" detection of ions in polar solvents – a followup paper by Jiang et al.[2] demonstrated this on the Hg^{2+} in acetonitrile/water mixture. Indeed, PODIPY have many appealing qualities, but the mismatch between data from different research groups makes it harder to draw any conclusions from experiments.

The most prominent example that we have encountered is the 31P NMR. Given the right conditions, 31P NMR is a moderately sensitive, but powerful tool. As was demonstrated in phthalocyanine chemistry, 31P NMR can help to characterize coordination environment and coordination number of phosphorus atom.

Jiang et al. obtained a value of -50.1 ppm[1] for 31P NMR of compound B (Figure 1) in D_2O. In our laboratory, the value of -19.9 ppm was obtained for compound C in $CDCl_3$. It can be shown, that the difference in dipyrrin substituents and solventshas negligeble impact on the 31P NMR signal. Many more discrepancies, most notably between theoretical and experimental spectra, can be found in the same way.In this study we employ quantum-chemical calculations to propose a number of solutions for mentioned discrepancies. We compare theoretical predictions for 31P NMR of compounds B and C with model compound A ("PDOIPY core") and experimental data. We additionally characterize the compounds via theoretical vibrationally-resolved absorption and emission spectra.



Phosporus Chemical Shift	A	B	C
Experimental	------	-50.1	-19.8
Theoretic	-13.5	-15.8	-13.3

Figure 1. Study objects and their 31P NMR chemical shifts

Acknowledgments

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References

1. Jiang, X.-D. et al., Chem. - A Eur. J. 2015, 6079–6082.
2. Jiang, X.-D. et al., Chinese Chem. Lett. 2015, 1241–1245.

MECHANISTIC INSIGHTS INTO IRON PNP COMPLEX CATALYSED AMINE BORANE DEHYDROPOLYMERISATION

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The catalytic dehydropolymerisation of amine boranes allows for the synthesis of polymeric B-N materials that are valence isoelectronic to ubiquitous polyolefins. Although this class of main group polymers is known for more than a decade now, only comparably few catalyst systems are known that allow for its selective formation.[1] Also, despite several important contributions that look into the mechanistic aspects of this reaction and ways to control polymer properties, the elementary steps of dehydropolymerisation[2], especially the nature of the B-N bond formation event require further studies.

In this contribution, we present catalytic and mechanistic studies of Fe PNP complex catalysed dehydropolymerisation of methylamine borane.[3] Additionally, we will show that incorporation of different functional groups into the amine borane starting materials allows for the synthesis of new heteroatom functionalised polyaminoboranes that could be of interest as precursors for alternative BN ceramics.

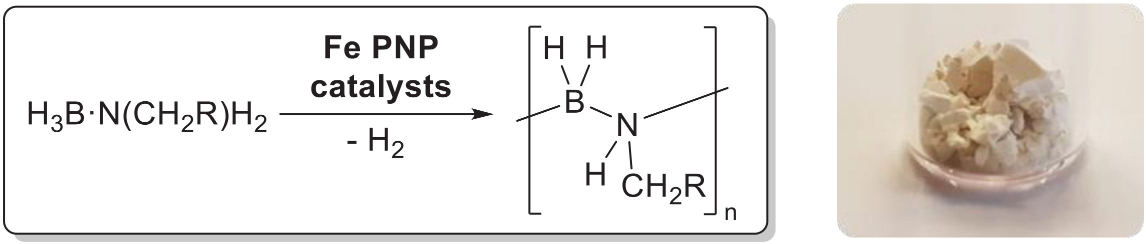

Figure 1. Dehydropolymerisation of amine boranes.

Acknowledgments

We thank our technical and analytical staff for assistance. Financial support by the DFG (BE 4370/2-1 and BE4370/9-1) is gratefully acknowledged.

References

1. a) H. Johnson, T. Hooper, A. Weller, *Top. Organomet.Chem.* **2015**, 153; b) D. Han, F. Anke, M. Trose, T. Beweries, *Coord.Chem. Rev.* **2019**, *380*, 260.
2. *Selected recent examples:* a) G. M. Adams, A. L. Colebatch, J. T. Skornia, A. I. McKay, H. C. Johnson, G. C. Lloyd−Jones, S. A. Macgregor, N. A. Beattie, A. S. Weller, *J. Am.Chem. Soc.* **2018**, *140*, 1481; b) T. Jurca, T. Dellermann, N. E. Stubbs, D. A. Resendiz-Lara, G. R. Whittell, I. Manners, *Chem. Sci.* **2018**, *9*, 3360. c) M. Trose, M. Reiß, F. Reiß, F. Anke, A. Spannenberg, S. Boye, A. Lederer, P. Arndt, T. Beweries, *Dalton Trans.* **2018**, *47*, 12858.
3. a) F. Anke, D. Han, M. Klahn, A. Spannenberg, T. Beweries, *Dalton Trans.* **2017**, *46*, 6843; b) R. Knitsch, D. Han, F. Anke, L. Ibing, H. Jiao, M. R. Hansen, T. Beweries, *Organometallics* **2019**, *38*, 2714; c) F. Anke, S. Boye, A. Spannenberg, A. Lederer, D. Heller, T. Beweries, submitted.

BACTERIAL CELLULOSE/CHITOSAN COMPOSITES WITH METAL NANOPARTICLES OBTAINED BY METHODS OF GREEN CHEMISTRY

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Nowadays films and other products from bacterial cellulose (BC) are actively utilized in the medical industry due to a set of their unique properties, such as high moisture absorption capacity, mechanical strength, high porosity, good biocompatibility - these properties are especially important when used as wound and burn healing dressing materials and artificial skin[1]. However, BC does not possess antibacterial activity[2], so there is a need to create composites based on it with antibacterial agents (such as biopolymer chitosan, or metal nanoparticles).

We proposed a “green” method for formation of BC/chitosan films with new functionality in water saturated with CO_2 under high pressure (several hundred atmospheres) taking into account that chitosan was proven to be soluble in such solutions before[3]. Such solvents are self-neutralizing at atmospheric pressure, and therefore much more biocompatible than traditional ones. IR spectroscopy and XPS showed the presence of chitosan on the surface of BC, as well as proved the hypothesized mechanism of composite formation due to hydrogen bonds between chitosan and BC. Scanning electron microscopy allowed to conclude that chitosan coats the BC fibers not only on the surface of the film, but also inside the matrix, increasing the effective diameter of the fibers. Moreover, by the method of labeled atoms, it was shown that the amount of chitosan in the BC film when applied from carbonic acid solutions under high CO_2 pressure is 3 times greater than when applied from acetic acid by traditional method.

For the first time we proposed to obtain composites from bacterial cellulose, chitosan and metal nanoparticles by the “green” metal-vapor synthesis method (without the use of reducing agents harmful to medical applications). The surface of the obtained composite materials was characterized using a number of methods, including XPS and IR spectroscopy, which is important for subsequent biological studies.

Acknowledgments

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References

1. N. Petersen, P.Gatenholm, *Applied microbiology and biotechnology* **2011**,91(5), 1277.
2. T. Maneerung, S. Tokura, R.Rujiravanit, Carbohydrate polymers 2008, 72(1), 43.
3. M.A. Pigaleva, I.V.Portnov, A.A.Rudov, I.V.Blagodatskikh, T.E.Grigoriev, M.O.Gallyamov, I.I. Potemkin, *Macromolecules* **2014**, 47(16), 5749.

LATE TRANSITION METAL CATALYZED REACTIONS UNDER SOLVENT-FREE CONDITIONS

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One of the most important requirements for organic materials in medicinal and electronic applications is their purity. Of special importance is the contents of transitions metals that should not exceed ppm or even ppb values. Admixtures of transition metals can influence semi-conductor properties of organic materials and/or catalyze unwanted chemical transformations under photo- or electro-activation leading to degradation of the organic layer, and, consequently, the whole device.Strict limitations of metal content in drugs are due to their toxicity.

Many organic materials of interest for medicinal and electronic applications are synthesized using transition metal catalyzed reactions. Of interest are:

- Palladium catalyzed Suzuki C-C, and Buchwald-Hartwig C-N cross-coupling.
- Copper catalyzed alkyne-azide cycloaddition.
- Gold catalyzed additions of nucleophiles to alkynes.

Strict industrial requirements prompted us to develop new approaches for the known catalytic reactions – transition metal mediated transformations under solvent-free conditions. Apart from applied importance new methods are of high fundamental interest. We succeeded to develop new synthetic procedures that yield high purity products. Reactions under study proceed in absence of solvent, in melt. After completion of the reaction the product can be sublimed-off directly from the reaction vessel under reduced pressure. Such isolation procedure secures us from impurities such as transition metals, bases, and etc. due to their low volatility. Moreover, new synthetic methodologies turned out to be high yielding, selective, scalable and robust. Finally, these methods are highly atom economical and “green”, since produce low amount or virtually now waste. Sheldon's E-factor values for most examples are in a range 1.0–3.0, and in some cases reach unprecedented values of 0.1-0.01.

Acknowledgements

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OLIGO- AND POLYDIMETHYLSILOXANE DERIVATIVES BASED ON RENEWABLE NATURAL RESOURCES

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Nowaday, a large number of polymers derived from various natural compounds have been synthesized and investigated: unsaturated fatty acids and their triglycerides, vegetable oils, and also from various aromatic derivatives. Nevertheless, interest in large-tonnage natural compounds is constantly growing for building a monomeric base. In this work, the commercially available natural terpene — limonene — was chosen as the starting material. This compound has a chemical potential due to the presence in its structure of two double bonds, which implies their further transformation into various derivatives. Recently, it has been found that limonene undergoes hydrosilylation reaction selectively on the terminal double bond [1]. The presence of the second double bond in difunctional siloxane derivatives of limonene allowed their further transformation by the hydrothiolation reaction. This approach allowed us to obtain a series of the copolymers with different alternation of siloxane and methylene units containing thiol and amide fragments in the polymer chain [2]. To compare their physical properties, analogs that do not contain limonene fragment were obtained (Figure 1).

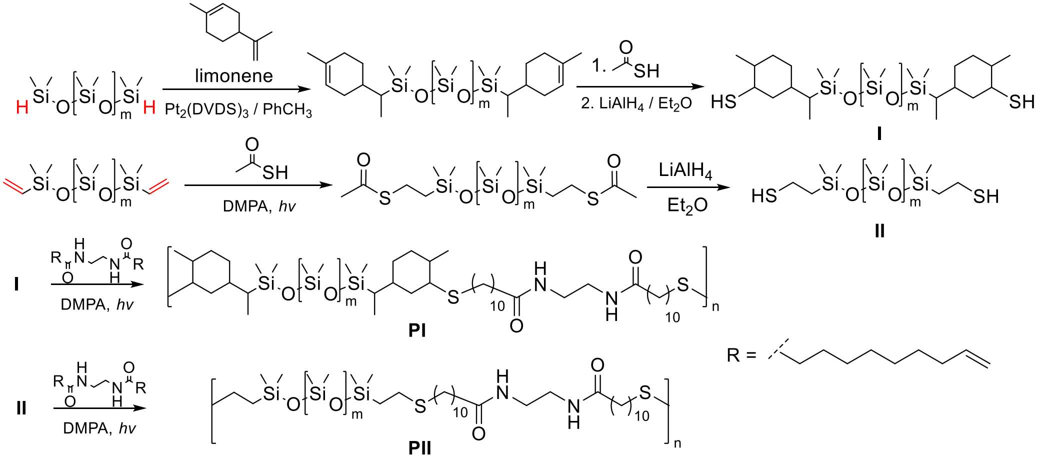

Figure 1. Synthesis of the copolymers, containing limonene fragments in their main chain, and analogues without limonene fragments

Obtained copolymers were characterized by NMR, IR spectroscopy, GPC. Their thermal characteristics were measured by TGA and DSC methods.

Acknowledgments

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References

1.F.V. Drozdov, G.V. Cherkaev, A.M. Muzafarov. J. Organomet. Chem., 2019, V.880, P. 293F.V.
2. F.V. Drozdov, A.N. Tarasenkov, G.V. Cherkaev, N.V. Demchenko, M.I. Buzin, L.A. Leites, A.M.Muzafarov. Polym. Int., 2019 (accepted). doi: 10.1002/pi.5913

VISUALIZING POLYMER DYNAMICS WITH FLUXIONAL ORGANOMETALLIC SENSORS

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Dynamics in photoluminescent compounds is typically a disadvantage rather than a virtue. Typically acting as a non-radiative relaxation pathway dynamics is often avoided to preserve quantum yield characteristics of emissive compounds. In this work, however, we use intrinsic dynamics of photoluminescent copper complexes to visualize thermal and mechanically induced phenomena in polymers.

A development of our work in this field,[1-3] the current contribution deals with structural dynamics of phosphorescent Cu(I) complexes in the excited state. We found that the latter can induce thermo and mechanochromic behaviour in Cu complexes enabling them to perform in a sensory setting. When embedded in segmented polyurethanes, Cu complexes can quantify mechanical stress and report phase transition phenomena. Moreover, new phosphors can be synthetically tuned to provide distinction between discrete polymer phases and characterize disorder in them. Finally we will discuss the use of new complexes as tools for polymer dynamics characterization relying on simple spectroscopic methods.

In broad context, particularly valid for organometallic community, our work implies that emission colour variations that we often view as thermally-governed might in factbe a structural phenomenon that is influenced by temperature indirectly. The same observation suggests that our mechano-/thermophores are likely not unique in their operation mechanism and more exciplex-driven mechanophores are yet to be discovered.

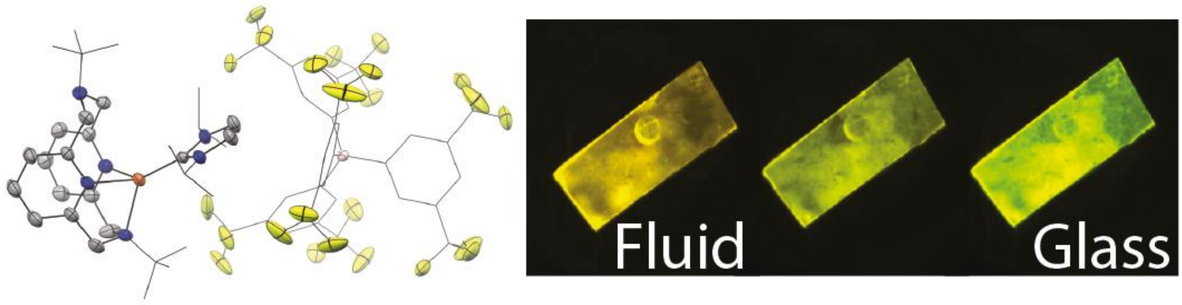

Figure 1.Solid state structure of Cu(I) sensors used in this work and eye-readable colour change upon glass transition reported by this sensor

References

1.G. A. Filonenko, J. R Khusnutdinova, *Adv. Mater.* **2017**, *29*, 1700563

2. G. A.Filonenko, J. A. M. Lugger, C. Liu, E. P. A. van Heeswijk, M. M. R. M. Hendrix, M. Weber, C. Müller, E. J. M. Hensen, R. P. Sijbesma, E. A. Pidko, *Angew. Chem. Int. Ed.* **2018,** *57*, 16385

3. G. A.Filonenko, D. Sun, M. Weber, C. Müller, E. A. Pidko, *J. Am. Chem. Soc.* **2019,***141*, 9687

DENDRON-FUNCTIONALIZED HYBRID ORGANIC-INORGANIC CATALYSTS

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Development of the new efficient catalysts for cross-coupling reactions is still of particular interest. The major efforts in this field are directed at combining high performance with easy catalyst recovery, which can be achieved due to magnetic separation.To combine the advantages of magnetic recovery with high activity and selectivity of homogeneous catalysis, dendrons can be attached to a magnetic support. The dendritic molecules can coordinate transition metal compounds due to multiple functional groups, creating pseudo-homogeneous catalysts.

In this work novel efficient magnetically recoverable catalysts for the Suzuki-Miyaura cross-coupling reaction have been developed[1]. The catalysts were synthesized by the attachment of rigid pyridylphenylene dendrons to magnetic silica followed by complexation with Pd acetate (Figure 1). Two approaches to the dendron attachment have been explored depending on the structure of flexible linkers on magnetic silica and dendron focal groups with a formation of ether or amide bonds. The complexation with Pd acetate was shown to result in a “cocktail” of Pd^{2+} and Pd^0 species (the latter forming Pd nanoparticles).The catalysts were tested in Suzuki reaction of 4-Br-anisole and phenylboronic acid and showed excellent catalytic activity, selectivity and conversion which were well maintained in three consecutive catalytic cycles.

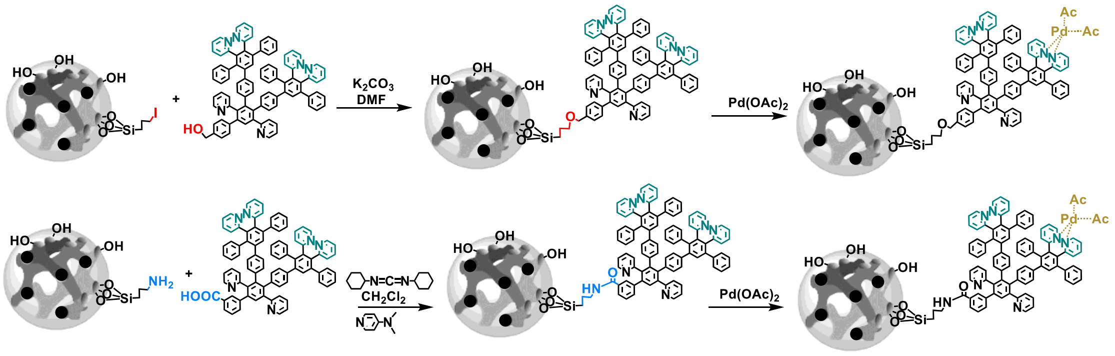

Figure 1. Formation of dendron supported Pd complexes attached to magnetic silica

Acknowledgments

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References

1. S. A. Sorokina, N. V. Kuchkina, B. P. Lawson, I. Yu. Krasnova, N. A. Nemygina, L. Zh. Nikoshvili, V. N. Talanova, B. D. Stein, M. Pink, D. G. Morgan, E. M. Sulman, L. M. Bronstein, Z. B. Shifrina, *Appl. Surf.Sci.* **2019**, *488*, 865.

INTRAMOLECULAR LIGAND-LIGAND INTERACTION AS A DRIVING FORCE OF ISOMERISM OF TRIPTYCENE IRIDIUM PINCER COMPLEXES

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The behaviour of transition metal hydrides in stoichiometric and catalytic processes is determined by nature of metal, its coordination sphere or reaction conditions.[1] Transition metal complexes with κ^3-PCP-pincer-ligands are of great interest because of their stability and potency to structural and electronic modifications.[2] Although PC(sp^3)P scaffold is far less common in pincer ligands design than the one containing C(sp^2), the iridium(III) complexes with triptycene PC(sp^3)P ligand have found application in such catalytic reactions as hydrogen transfer[3] or dehydrogenation of different substrates.[4-6]

In this contribution we present our recent results of spectroscopic (IR, UV, NMR) and theoretical (DFT) investigation of acetonitrile and pyridine coordination to the different isomers of iridium(III) complex (PCP)IrH(Cl) (PCP = 1,8-bis-(diisopropylphosphino)triptycene) (Figure 1)[4,7]. It was established that the *intra*-molecular hydrogen bonding between the ligands plays a key role in determining the geometry and stability of hexacoordinate Ir(III) complexes. This interactions should be important for the mechanisms of catalytic reactions mentioned above.

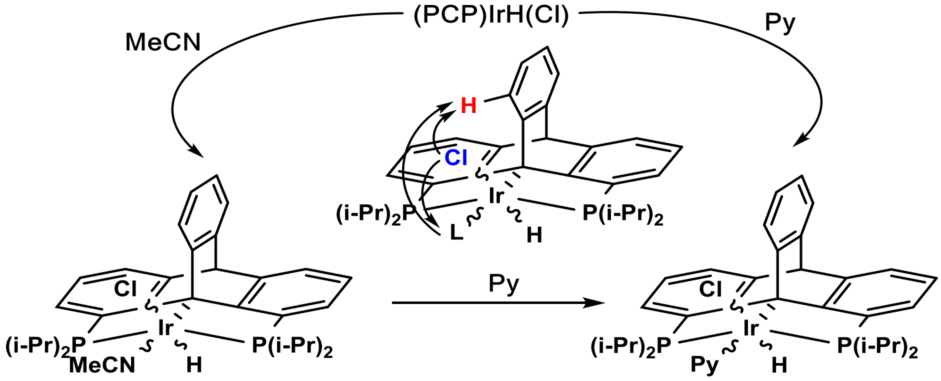

Figure 1

Acknowledgments

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References

1. N. V. Belkova, L. M. Epstein, O. A. Filippov, E. S. Shubina, *Chem. Rev.* **2016**, *116*, 8545.
2. van Koten, G.; Milstein, D. (Eds.) *Organometallic Pincer Chemistry,* in *Topics in Organometallic Chemistry, Vol. 40*, Springer Berlin Heidelberg, **2013**, 356 pp.
3. C. Azerraf, D. Gelman, *Chem. Eur. J.* **2008**, *14*, 10364.
4. D. Bézier, M. Brookhart, *ACS Catal.* **2014**, *4*, 3411.
5. S. Cohen, V. Borin, I. Schapiro, S. Musa, S. De-Botton, N. V. Belkova, D. Gelman, *ACS Catal.* **2017**, *7*, 8139.
6. S. De-Botton, S. Cohen, D. Gelman, *Organometallics* **2018**, *37*, 1324.
7. S. Musa, R. Romm, C. Azerraf, S. Kozuch, D. Gelman, *Dalton Trans.* **2011**, *40*, 8760.

NEW ORGANOSILICON COMPOUNDS ON THE BASE OF FUNCTIONAL STEREOREGULAR ORGANOCYCLOSILSESQUIOXANES

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The creation of new hybrid organo-inorganic materials is one of the relevant objectives of modern chemistry. To solve this problem, different approaches are used. One of the main approaches is the use of functional precursors having a well-defined molecular geometry. Such an approach should give a possibility to establish the structure – property relationship of the obtained compounds.

We will demonstrate a simple and effective method for creating new polymer and oligomeric systems based on a unique series of functional stereoregular organosilsesquioxanes using hydrosilylation and thiol-ene reactions.

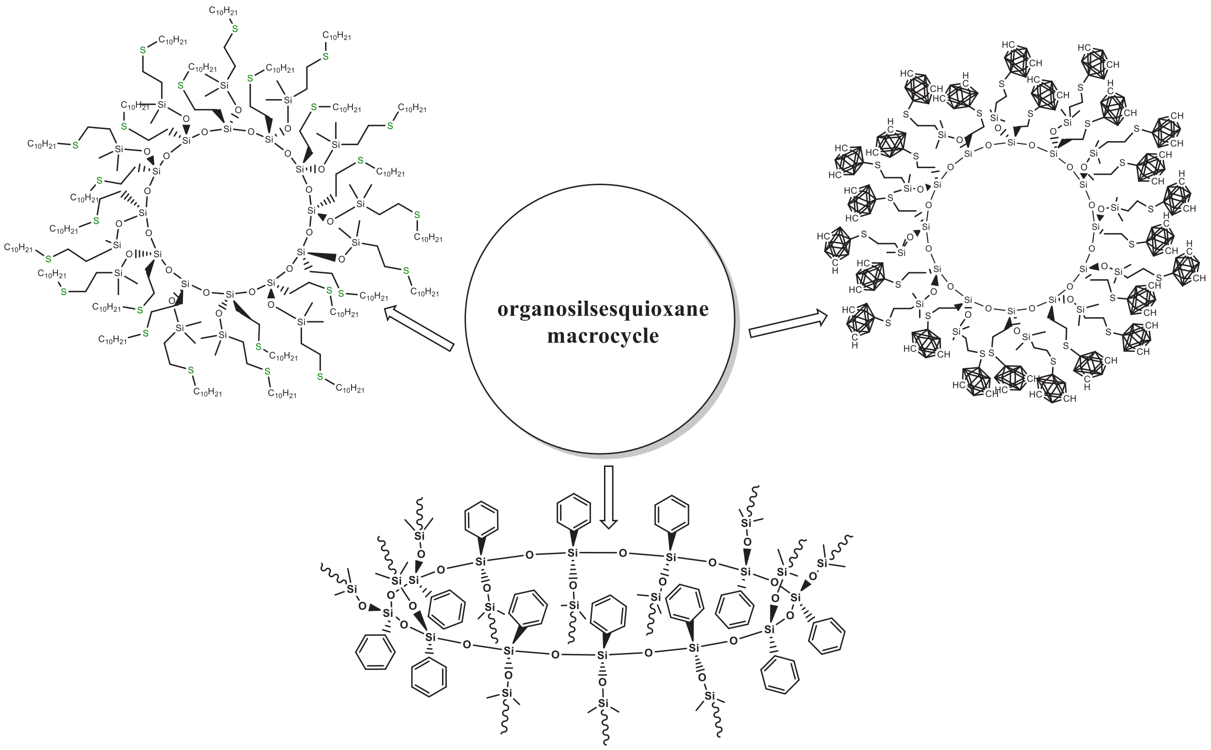

Figure 1.

Acknowledgments

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References

1. Y. S. Vysochinskaya, A. A. Anisimov, A. S. Peregudov, A. S. Dubovik, V. N. Orlov, Y. N. Malakhova, A. A. Stupnikov, M. I. Buzin, G. G. Nikiforova, V. G. Vasil'ev, O. I. Shchegolikhina, and A. M. Muzafarov. *Journal of Polymer Science, Part A: Polymer Chemistry*, **2019**, *57(11)*:1233.

REDUCTIVE ADDITION WITHOUT AN EXTERNAL HYDROGEN SOURCE

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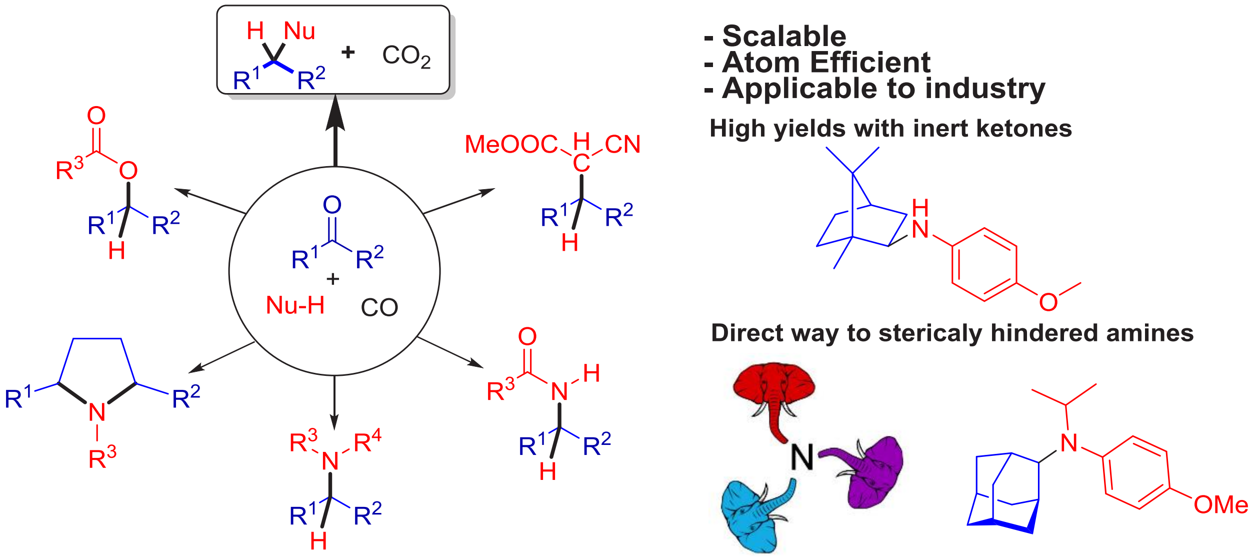
A concept for atom-efficient reductive addition was developed (figure 1). Carbon monoxide, a multi-tonnage byproduct in steel manufacture, is an efficient reducing agent in reactions between hydrogen-containing nucleophiles and carbonyl compounds. Great scope of this approach was demonstrated. We have shown that substances with low nucleophilicity (amides and carboxylic acids) can be utilized in such process as well as active nucleophiles like amines (reductive amination) and CH-acids (reductive Knoevenagel addition). Developed approach represents an easy, efficient and ecologically friendly way to secondary and tertiary amines (even sterically hindered amines), substituted amides, nitriles, heterocycles and esters.[1]



- Scalable
- Atom Efficient
- Applicable to industry

High yields with inert ketones

Direct way to stericaly hindered amines

Figure 1. Reductive addition without an external hydrogen source

Acknowledgments

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References

1. a) O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. S. Perekalin, N. V. Shvydkiy,V. I. Maleev,A. R. Kudinov,D. A. Chusov,*ACS Catal.* **2016**, *6*, 2043; b) E. S. Podyacheva, O. I. Afanasyev, A. A. Tsygankov, M. V. Makarova, D. A. Chusov,*Synthesis*, **2019**, *51*, 2667; c) D. A. Chusov, B. List, *Angew. Chem. Int. Ed.* **2014**, *53*, 5199; d) P. N. Kolesnikov, K. M. Muratov, D. L. Usanov, D. A. Chusov, *Org. Lett.*, **2017**, *19*, 5657; e) N. Z. Yagafarov, P. N. Kolesnikov, D. L. Usanov, V. V. Novikov, Yu. V. Nelyubina, D. A. Chusov, *Chem. Commun.*, **2016**, *52*, 1397; f) P. N. Kolesnikov, D. L. Usanov, E. Barablina,V. I. Maleev, D. A. Chusov, *Org. Lett.* **2014**, *16*, 5068; g) O. I. Afanasyev, D. L. Usanov, D. A. Chusov, *Org. Biomol. Chem.*, **2017**, *15*, 10164; h) O. I. Afanasyev, A. A. Tsygankov, D. L. Usanov, D. A. Chusov, *Org. Lett.*, **2016**, *18*, 5968; o) S. A. Runikhina, D. L. Usanov, A. O. Chizhov, D. A. Chusov, *Org. Lett.*, **2018**, *20*, 7856.

POLY(IONIC LIQUID)S AS SOLID ELECTROLYTES

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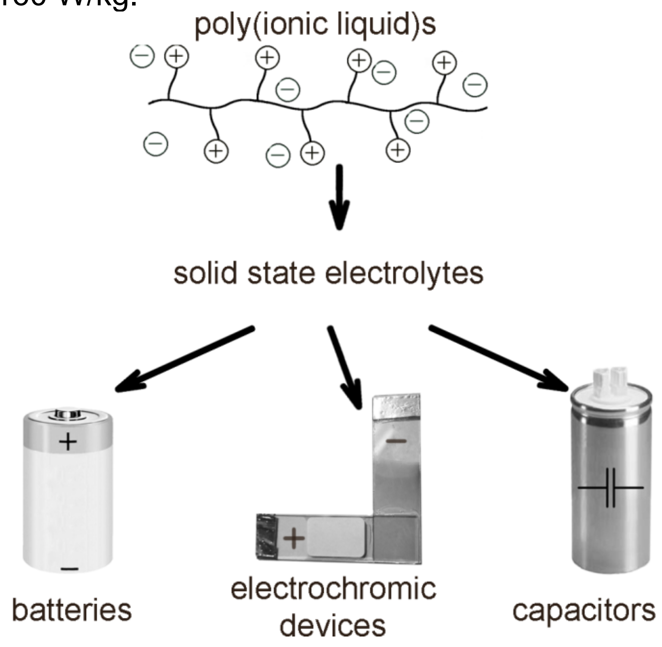
Replacing a liquid electrolyte with solid polymer electrolyte can greatly simplify and reduce the design price of electrochemical devices, as well as improve their performance. Due to the high ionic conductivity and electrochemical stability, as well as thermal and chemical resistance, polymer analogues of ionic liquids (PILs) were proposed as ion-conducting separators [1].

The properties of PILs vary widely depending on the chemical structure of both the cation and the anion. More than 40 new ionic methacrylate monomers with imidazolium and pyrrolidinium cations and various anions have been synthesized. By polymerizing such monomers, along with the chemical modification of poly (epichlorohydrin-ethylene oxide), PILs having high molecular weight and conductivity (up to 10^{-6} S / cm) were obtained.

Using PILs as electrolyte, all solid-state electrochemical devices were developed: electrochromic “smart windows”, lithium batteries and supercapacitors. “Smart windows” differ from their analogues in quick switching (3.0–4.5 s), high staining efficiency coefficient (390–430 cm^2/s) and the ability to work in a vacuum. Batteries with relatively high charge/discharge current C/15 and 70 °C exhibit a capacity of 115 mAh/g. The assembled ionistors had capacity up to 2.8 F/g and specific energy up to 160 W/kg.



Acknowledgments

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References

1. A.S. Shaplov, D.O. Ponkratov, Ya.S. Vygodskii, *Polym. Sci., Ser. B,* **2016**, *58*, 73.

THE INFLUENCE OF ORTHO-SUBSTITUENTS ON THE PROPERTIES OF PHENYLBORONIC ACIDS

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Rare earth metal σ-bonded alkyl complexes are widely investigated through last decades due to their unique reactivity in various stoicometric and catalytic reactions. Despite the large amount of known alkyl species of Ln^{III} their divalent analogues (Yb, Sm and Eu) remain scars. Alkyl complexes of heavy alkaline-earth metals (Ca and Sr), which in most cases are isostructural and demonstrate chemistry similar to Yb^{II} and Sm^{II} respectively, are also poorly investigated.

In present study for the first time a series of tridentate diphenylmethanido $NC_{sp3}N$ pincer type ligands were employed for the preparation of rare- and alkaline earth metal alkyl complexes. Various synthetic protocols were used for the preparation of the titled compound and it was demonstrated that structure and stability of $NC_{sp3}N$ pincer type complexes determined both by structure of the ligand and by the nature of central metal (Ln(III) vs Ln(II) and Ln(II) vs Ca).

The reactivity of diphenylmethanido $NC_{sp3}N$ pincer type complexes of Ln(III), Ln(II) and Ca are discussed including their catalytic application for intermolecular C-C and C-E (E = N, Si, P, S) bond formation.

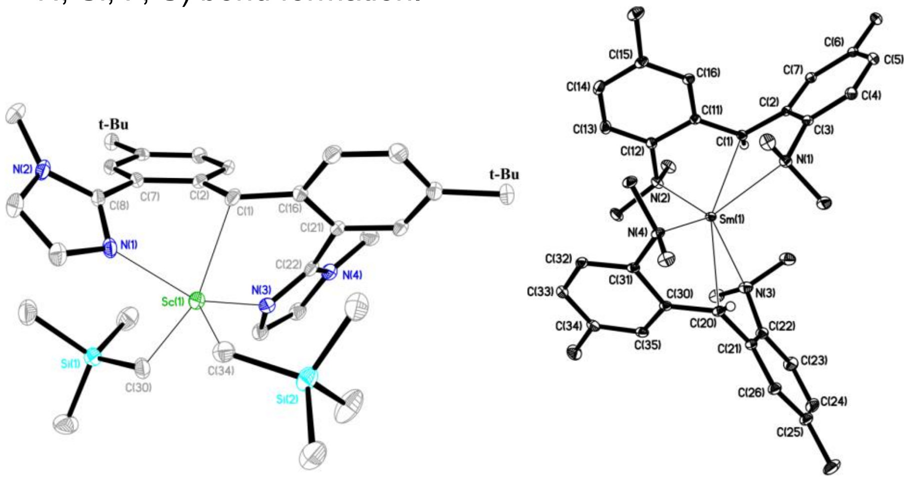

Figure 1. Molecular structures of $NC_{sp3}N$ pincer type alkyl complexes of Sc(III) and Sm(II)

Acknowledgments

This work was financially supported by the Russian Science Foundation (grant 17-73-20262)

References

1. D. O. Khristolyubov, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. S. Shavyrin, A. A. Trifonov. *Organometallics* **2018**, 37, 1627.
2. A. Fayoumi, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. A. Trifonov. *Mendeleev Commun.* **2019**, 29, 331–333.

INCREASE OF FIRE RESISTANCE OF POLYFOAMS BASED ON EPOXY-NOVOLAC RESIN

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PEN-I epoxy-novolac foams were developed by Chemical Technology of Polymers department of the Technological Institute. Such advantages as reagent resistance to various severe atmospheres and also high strength characteristics, provided great demand on the presented grade of foams within the domestic market. However, this material has a drawback that limits the scope of its application - flammability. The creation of new non-combustible polymeric materials is a problem of modern science.

The work investigated the effect on the properties and flammability of the foam brand PEN-I as additives classic for these purposes, as well as innovative ones. As a result of many studies, it was found that the use of a special carbon filler is most preferred. When exposed to high temperatures, the filler increases in volume several tens of times, blocking the further spread of the flame inside the product.

By changing the content of the blowing agent (2,2'-azo-bisisobutyronitrile) it is possible to obtain foams with an apparent density in the range of 100-300 kg / m^3. In this work, we studied such properties of the obtained materials as breaking stress under compression, bending, apparent density, water and gas absorption, impact strength and resistance to burning.

Formulations of new fire-resistant epoxy-novolac foams meeting the technical specifications shown to PEN-I polyfoams are developed (table 1).

Table 1. Formulations of fire-resistant foams of various densities

Recipe	C, mass.parts	Blowing agent, mass.parts	Density, kg/m^3	Compressive strength, MPa
1	10	2,3	205-210	2,9-3,0
2	10	3,5	145-150	1,5-1,6
3	10	5,8	100-105	0,9-1,0

NON-COVALENT INTERACTIONS IN STOICHIOMETRIC AND CATALYTIC REACTIONS OF IRIDIUM PINCER COMPLEXES

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The chemistry of pincer ligated metal complexes has experienced tremendous development and been applied to various reactions. Hydrogen bonds and other non-covalent interactions are well recognized as very important for both catalytic and stoichiometric transformations with the participation of these complexes.

Recently we analyzed the spectral, X-ray and theoretical data on benzene-based hydrido chloride complexes of Ir(III) (1-4) as well as the peculiarities of their electronic structure and Lewis acidity.[1] The complexation of these compounds with the nitrogen bases was studied in terms of the activation of Z-H and Ir-Cl bonds due to low-energy (non-covalent) interactions (hydrogen bonded or Lewis complexes).[2,3] The non-covalent interactions studied in model reactions with alcohols and bases gave the keys to understanding the mechanism of amine-boranes dehydrogenation catalyzed by pincer iridium hydrido chlorides.[4,5] We have shown how the steric and electron properties of the pincer ligand as well as the Lewis acidity of the iridium atom affect the catalytic activity of the complexes considered.

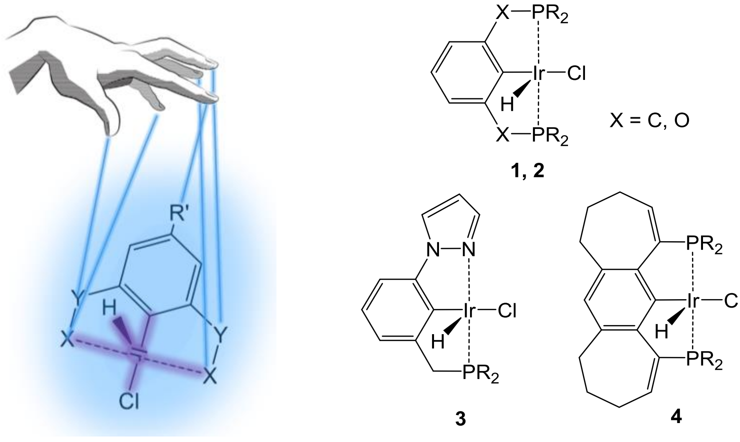

Figure 1.

Acknowledgments

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References

1. E.S. Osipova, O.A. Filippov, E.S. Shubina, N.V. Belkova, *Mendeleev Commun.*, **2019**, *29*, 121-127
2. E.S. Osipova, E.S. Gulyaeva, O.A. Filippov, S.V. Safronov, A.A. Pavlov, A.V. Polukeev, V.A. Kirkina, E.M. Titova, E.S. Shubina, N.V. Belkova, *Eur. J. Inorg. Chem.*, **2019**, *10*, 1389-1397.
3. E.M. Titova, E.S. Osipova, E.S.Gulyaeva, V.N. Torocheshnikov, A.A. Pavlov, G.A. Silantyev, O.A. Filippov, E.S. Shubina, N.V. Belkova, *J. Organomet. Chem.*, **2017**, *827*, 86-95.
4. L. Luconi, E.S. Osipova, G. Giambastiani, M. Peruzzini, A. Rossin, N.V. Belkova, O.A. Filippov, E.M. Titova, A.A. Pavlov, E.S. Shubina, *Organometallics*, **2018**, *37*, 3142–3153.
5. E.M. Titova, E.S. Osipova, A.A. Pavlov, O.A. Filippov, S.V. Safronov, E.S. Shubina, N.V. Belkova, *ACS Catalysis*, **2017**, *7*, 2325–2333.

THERMOSTABLE TRIFUNCTIONAL PHTHALONITRILE RESIN

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Heat-resistant fiber reinforced plastics are in a high demand of the aerospace industry. Phthalonitrile resins are known as matrices the most stable at elevated temperature[1]. Recently, phosphate-bridged phthalonitrile resin (fig. 1a) with high elasticity modulus and wide processing window were obtained in our research group[2]. A new tri-functional phthalonitrile monomer (fig.1b) tris(3-(3,4-dicyanophenoxy)phenyl) phosphate (TPP) was first synthesized and characterized with the intent of increasing the cross-linking rate of phthalonitrile resins.

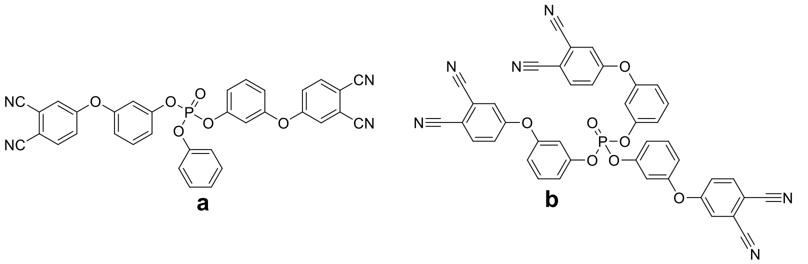

Figure 1. Di- and tri-functional phosphate-based phtalonitrile monomers

TTP was synthesized from the corresponding phenol and $POCl_3$. The structure and purity of the obtained phthalonitrile was confirmed by ^{1}H, ^{13}C, ^{31}P NMR. The tri-functional monomer is a light-yellow crystalline powder with a melting point of 172°C.

To study the effect of crosslinking degree on the mechanical and thermal properties of the matrix, mixtures of tri-functional monomer with di-functional phthalonitrile were cured. The resin was cured in the presence of 10 wt.% 1,3-bis (aminophenoxy) benzene (m-APB). The mechanical, thermal, and rheological properties of the obtained resins were studied by DMA, TGA and viscometry. The optimal composition was selected based on the complex of the characteristics.

As a result of the work, the new resin was obtained, superior in mechanical characteristics (table 1) to commercial polyimide PMR-15 and phthalonitrile PN-3M.T_g of the resin is practically no different from the previously described phthalonitriles (about 450°C). $T_{5\%}$ for the new matrix was about 504°C, and the char yield in nitrogen at 900°C exceeds 78%.

Table 1. Mechanical properties of high temperature resins.

Matrix	Flexural strenght, MPa	Flexural modulus, GPa	Tensile strenght, MPa	Tensile modulus, GPa	Elongation at break, %	Resin Tg, ℃
New composition	81 ± 9	7,2 ± 0,1	51 ± 6	6,9 ± 0,1	0,8 ± 0,1	>450
PMR-15	76	3,2	43-84	4,0	1,4-2,5	327
PN-3M	86	4,5	36	4,7	-	>450

Acknowledgments

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References

1. T.M. Keller, J.R. Griffith, *Am. Chem. Soc.* **1980**, *3*, 25.
2. B.A. Bulgakov, A.V. Babkin et al, *Eur. Polym. J.* **2016**, *84*, 205.

NEW APPROACHES TO GENERATION OF AMINOHETEROCYCLES

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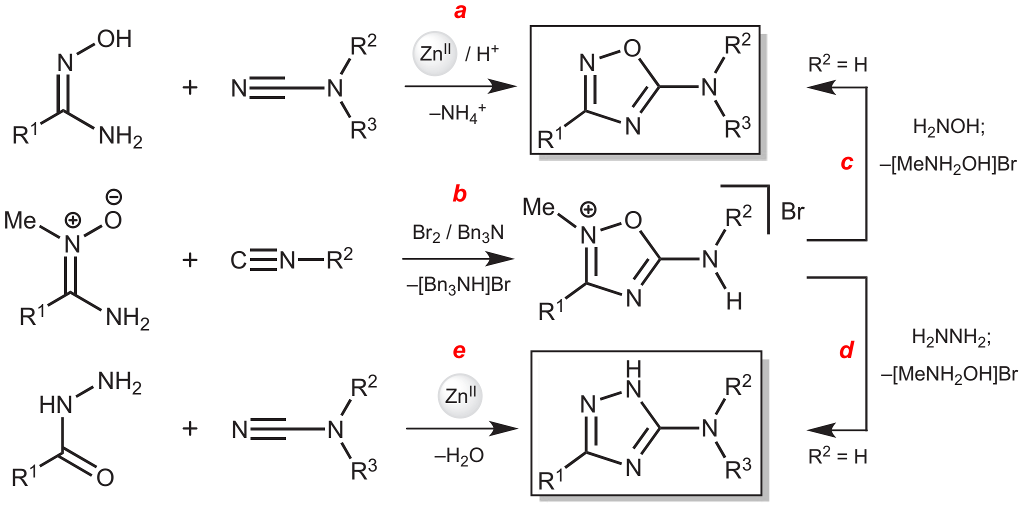
1,2,4-Oxadiazoles and 1,2,4-triazoles are important classes of five-membered heterocycles, which are widely used both in coordination chemistry and material chemistry, and in organic chemistry and pharmacology. In the framework of the studies, new effective routes were developed for generation of these heterocyclic compounds from bifunctional nucleophiles and cyanides (Scheme 1), which was also reflected in our reviews.[1,2]



Scheme 1. New approaches to 5-amino-1,2,4-oxadiazoles and 5-amino-1,2,4-triazoles.

One the one hand, it was shown that the reaction of amidoximes with mono- and disubstituted cyanamides in the presence of zinc(II) salts (1 equiv.) and strong acid in EtOAc at 80° C for 20–48 leads to 5-amino-1,2,4-oxadiazoles with high preparative yields (a).[3] On another hand, acyl hydrazides have been shown to react with disubstituted cyanamides in the presence of catalytic amounts of zinc(II) salts (10 mol%) to form 3-amino-1,2,4-triazoles (e).[4]

Third approach to aminooxadiazoles is the reaction of aminonitrones with isocyanides in the presence of bromine (1 equiv.) and a base, resulting in electrophilically activated 2-methyl-1,2,4-oxadiazolium bromides (b), which react with hydroxylamine to form neutrally charged 5- amino-1,2,4-oxadiazoles (c). In the event that the oxadiazolium salts are reacted with hydrazine, 3-amino-1,2,4-triazoles (d) are formed.[5]

Acknowledgments

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References

1. Bolotin, D.S., et al., *Chem. Rev.*, **2017**,*117*, 13039.
2. Bolotin, D.S., et al..*Coord. Chem. Rev.*, **2016**, *313*, 62.
3. Bolotin, D.S., et al., *Inorg. Chem.*, **2014**, *53*, 10312.
4. Yunusova S.N., Bolotin D.S., et al., *ACS Omega*, **2018**, *3*, 7224.
5. Il'in M.V., Bolotin D.S., et al., *New J. Chem.*, **2018**, *42*, 9373.

QUALITATIVE DIFFERENCES OF THZ ABSORPTION SPECTRA OF LINEAR AND BRANCHED POLYMERS

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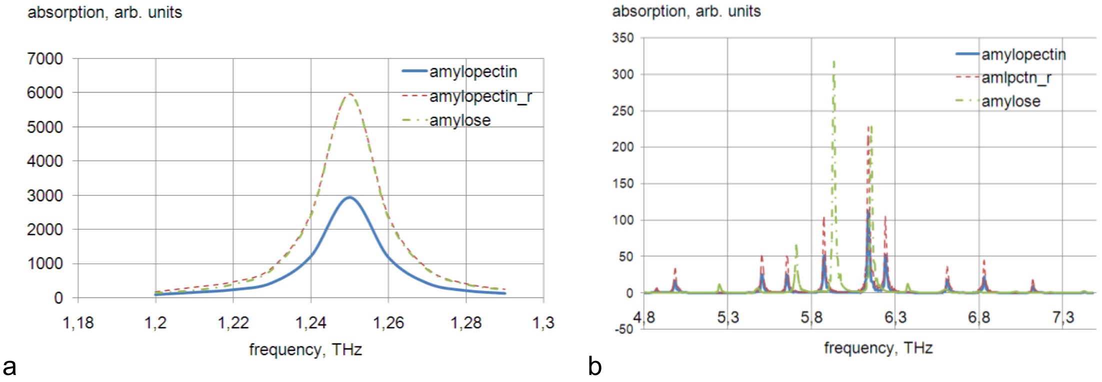
Terahertz (THz) spectroscopy has tremendous potential for investigations of molecular and supramolecular structure because the molecular spatial structure, mutual displacement of molecules and intra- and intermolecular hydrogen bonds are reflected on the THz spectra of the sample.[1]

THz absorption of polymer materials is particularly caused by the excitation of eigenmodes of the molecules with the electrical field of the THz irradiation. However the characteristic scale of almost any molecule is several orders of magnitude smaller than the THz radiation wavelength, the interaction between the polymer molecules and THz wave depends on the helix step of the molecule.[2]

In the presented work, THz absorption spectra were simulated for linear (amylose) and branched (amylopectin) polymeric molecules which consist of the same blocks (glucose). The mathematical model was simplified extremely; it can't predict quantitatively eigenfrequencies of the amylose and amylopectin molecules but it can illustrate the qualitative difference between the spectra.

The obtained spectra in the arbitrary units are shown in the figure 1; solid line corresponds to amylopectin, dotted-dashed line corresponds to amylose and dashed line corresponds to amylopectin spectra multiplied of some constant. The results of the calculation showed that the absorption of the branched molecule is arbitrary twice weaker than of the linear molecule. This difference in spectra is possible to be used to determine the degree of branching of the sample by THz spectroscopy.



a b

Figure 1. Qualitative THz absorption spectra, calculated for amylose and amylopectin at the range of acoustic (a) and optic (b) eigenfrequencies.

Acknowledgments

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References

1. X.-C. Zhang, *Phys. Med. Biol*. **2002**, 47, 3667–3677.
2. V.L. Vaks, A.V. Semenova, Yu.S. Guseva, A.N. Panin, *Opt. Quant. Electron*. **2017**, 49:193.

“CHIRAL-AT-METAL” OCTAHEDRAL COBALT(III) COMPLEXES AS “ORGANOCATALYSTS IN DISGUISE” FOR ASYMMETRIC REACTIONS

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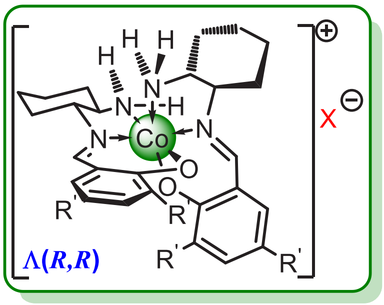
Now days, the most popular area of research is so-called chiral organocatalytic systems, where no metal ions are involved in catalysis.[1] However, for the last 10 years there appeared several papers reported use of octahedral kinetically-inert chiral, coordinatively saturated chiral-at-metal complexes for the asymmetric catalysis.[2] In those complexes the metal center serve, mainly, a structural role as a "scaffold" for the participating ligands, keeping them in space in an asymmetrically designed manner. An additional role of the metal is the activation of the acidic groups (OH or NH) of the ligands. As a result, the catalytic activity of the complexes originated not from metal/substrate relations but from the ligand/substrate multiple cooperative hydrogen-bonding interactions in a chiral environment.[2]

Herewith, we report the synthesis of a novel type of chiral octahedral inert Co(III) complexes, featuring chirality centered both at metal and ligands (Figure). Additionally, their application as “organocatalysts in disguise” is disclosed for many asymmetric transformations such as asymmetric alkylation, Michael addition, epoxidation, trimethylsilylation and etc.[3]



Acknowledgments

This work has been supported by the Russian Foundation for Basic Research (No. 19-03-00659).

References

1. J. Seayad, B. List, *Org. Biomol. Chem.* **2005**, *3*, 719.
2. a) L. Gong, L.-A. Chen, E. Meggers, *Angew. Chem. Int. Ed.* **2014**, *53*, 10868; b) T. Cruchter, V. A. Larionov, *Coord. Chem. Rev.* **2018**, *376*, 95.
3. a) Y. N. Belokon’, V. A. Larionov, A. F. Mkrtchyan, V. N. Khrustalev, A. Nijland, A. S. Saghiyan, I. A. Godovikov, A. S. Peregudov, K. K. Babievsky, N. S. Ikonnikov, V. I. Maleev, *Russ. Chem. Bull.* **2012**, *61*, 2252; b) Y. N. Belokon, V. I. Maleev, M. North, V. A. Larionov, T. F. Savel’yeva, A. Nijland, Y. V. Nelyubina, *ACS Catal* **2013**, *3*, 1951; c) V. I. Maleev, M. North, V. A. Larionov, I. V. Fedyanin, T. F. Savel’yeva, M. A. Moscalenko, A. F. Smolyakov, Y. N. Belokon, *Adv. Synth. Catal.* **2014**, *356*, 1803; d) V. A. Larionov, E. P. Markelova, A. F. Smolyakov, T. F. Savel’yeva, V. I. Maleev, Y. N. Belokon, *RSC Adv.* **2015**, *5*, 72764; e) V. A. Larionov, S. M. Peregudova, V. I. Maleev, Y. N. Belokon, *Russ. Chem. Bull.* **2016**, *65*, 685; f) Z. T. Gugkaeva, V. A. Larionov, M. A. Moskalenko, V. N. Khrustalev, Y. V. Nelyubina, A. S. Peregudov, A. T. Tsaloev, V. I. Maleev, Y. N. Belokon, *Synthesis* **2018**, 50, 607.

THE CONFORMATION OF AMPHIPHILIC POLYMER SPHERICAL BRUSHES ATTACHED TO A NANOPARTICLE

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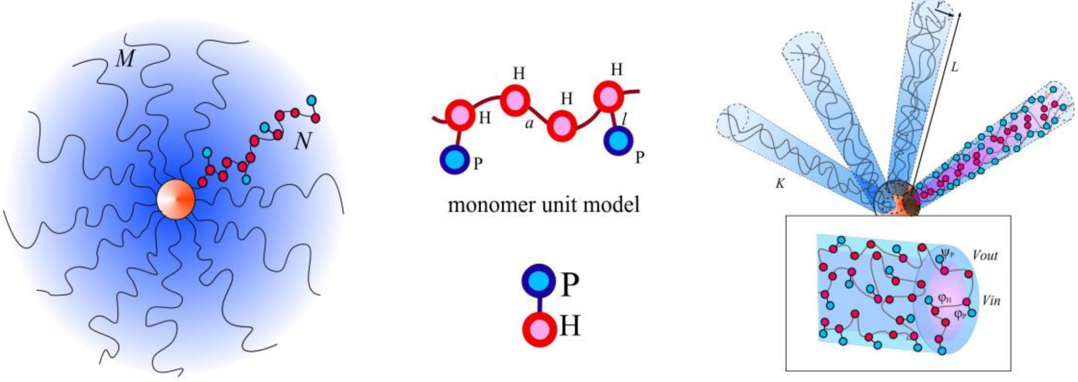
The structure of amphiphilic spherical brush consisting of ananoparticle as a core and long amphiphilic chains as a shell is considered using scaling approaches and the mean-field theory for the comprehensive study of aggregate structure in aqueous solution.

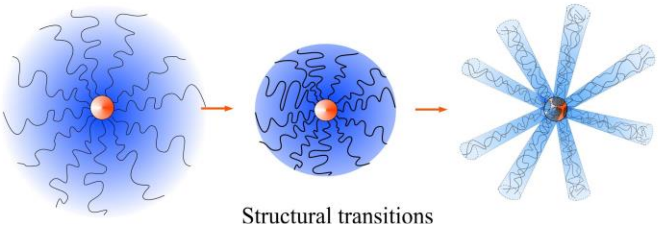
Such nanoparticles of SiO2 with hydrophobically modified polyacrylamide brushes are synthesized to increase oil recovery.[1]

The amphiphilic nature of macromolecules is taken into account by attaching the hydrophilic side group P to some fraction of monomer units of hydrophobic H backbone. The H groups have strong attraction to each other which causes the aggregation of macromolecules. On the other hand, hydrophilic P groupareattracted to solvent molecules and force the aggregates to increase their surface. It was shown that depending on the surface activity of monomer units in poor solvent, the macromolecules could form dense homogeneous spherical globules or join into several cylindrical aggregates with hydrophobic core and hydrophilic shell (rod-like structure), shown at the figure 1.



Macromolecular brush attached to a nanoparticle

Rod-like shape and internal structure



Structural transitions

Figure 1. Sperical brush of amphiphilic polymers and structural transitions in aqueous solution

Acknowledgments

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References

1. W.Pu, R.Liu, K-Y.Wang, K-X.Li, Zh-P.Yan, B.Li, L.Zhao, *Ind. Eng. Chem. Res.* **2015**, 54, 798−807.

SOME ASPECTS OF HYPERCOORDINATED 14 GROUP ELEMENTS CHEMISTRY: REACTIVITY, STRUCTURE AND PROPERTIES

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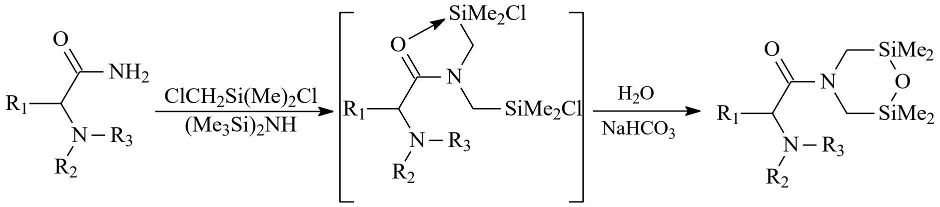
Hyper coordinate silicon, germanium and tin compounds are the focus of intense research due to the diversity of their structures, chemical properties, stereodynamic behavior and practical use in stereoselective synthesisand medical diagnostics.[1,2]

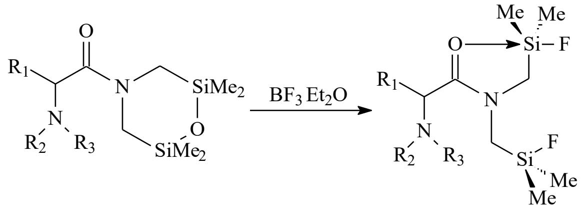
(O→Si)-chelate difluorides**4a**–**c**were synthesized by silylmethylation of amides, subsequent hydrolysis of unstable intermediates **2a**–**c** into compounds**3a**–**c** and the reaction of the latter compounds with $BF_3 \cdot Et_2O$.



1a–c **2a–c** **3a–c**

(**a**) $R_1R_2 = (CH_2)_3$, R_3 = Ms; (**b**) $R_1R_2 = (CH_2)_3$, R_3 = Ts; (**c**) R_1 = H, R_2 = Me, R_3 = Ms

Figure 1.Hydrolysis of unstable intermediates



3a–c **4a–c**

(**a**) $R_1R_2 = (CH_2)_3$, R_3 = Ms; (**b**) $R_1R_2 = (CH_2)_3$, R_3 = Ts; (**c**) R_1 = H, R_2 = Me, R_3 = Ms

Figure 2. Preparation of difluorides $R_3R_2NCH(R_1)C(O)N(CH_2SiMe_2F)_2$

The structures of compounds were confirmed by X-ray. According to IR and NMR, the O→Si coordination in solutions of these compounds was weaker than that in the solid state due to effective solvation of the Si–F bond. A permutational isomerisation was detected, and its activational parameters were determined by ^1H DNMR.

Acknowledgments

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References

1. Vad.V. Negrebetsky, S.N. Tandura, Yu.I.Baukov, *Russ. Chem. Rev.,* **2009**, *78*, 21.
2. A.A. Nikolin, Vad.V. Negrebetsky, *Russ. Chem. Rev.*, **2014**, *83*, 848.

ON THE WAY TO MOLECULAR SWITCHES: INTRAMOLECULAR STABILIZATION OF ROTAMERS IN TRANSITION METAL BIS(DICARBOLLIDE) COMPLEXES

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The bis(dicarbolide) complexes of transition metals $[3,3'\text{-}M(1,2\text{-}C_2B_9H_{11})_2]^{n-}$ are isoelectronic analogues of well-known metallocenes. Unlike the cyclopentadienyl ligand, the dicarbollide ligand contain two carbon and three boron atoms in open pentagonal face, that results in energy nonequivalence of different rotation conformers (rotamers) of bis(dicarbollide) complexes, however rotation barriers between them are rather low. Stabilization of certain rotamers can be achieved by introducing additional substituents into the closest to the metal atom belt of the dicarbollide ligands. Some examples of modification of the dicarbollide ligands and their effect on stabilization of various rotamers *via* intramolecular hydrogen bonds will be considered. The simples type of such interactions is intramolecular $CH_{carb}\ldots Hal$ hydrogen bonding between slightly acidic metallacarborane CH groups in one ligand and halogen substituents in other ligand. The $CH_{carb}\ldots Hal$ hydrogen bonds were found to be responsible for stabilization of the *transoid* conformation in the 8,8'-dihalogen derivatives of cobalt and iron bis(dicarbollides) $[8,8'\text{-}X_2\text{-}3,3'\text{-}M(1,2\text{-}C_2B_9H_{10})_2]^-$ (M = Co, Fe; X = Cl, Br, I). Another type of rotamer stabilization was found in aryl derivatives of cobalt bis(dicarbollide) $[8\text{-}Ar\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})(1',2'\text{-}C_2B_9H_{11})]^-$, where stabilization of the *transoid* conformation proceeds through intramolecular aromatic $CH_{carb}\ldots\pi$ bonds between the acidic CH groups in one dicarbollide ligand and phenyl substituents in other one.

Recently we found that the MeS substituents depending on their position can stabilize various rotamers in transition metal bis(dicarbollide) complexes $[X,Y'\text{-}(MeS)_2\text{-}3,3'\text{-}M(1,2\text{-}C_2B_9H_{10})_2]^-$ (M = Co, Fe, Ni) due to formation of intramolecular $CH_{carb}\ldots S(Me)$ hydrogen bonds. In the case of the 8,8'- and 4,4'-isomers, the *transoid* and *gauche* conformations, respectively, are stabilized by two pairs of $CH_{carb}\ldots S(Me)$ hydrogen bonds, whereas in the 4,7'-isomer the gauche conformation is stabilized by only one pair of $CH_{carb}\ldots S(Me)$ hydrogen bonds.

The addition of external transition metals (copper, silver, rhodium, palladium) to $[8,8'\text{-}(MeS)_2\text{-}3,3'\text{-}Co(1,2\text{-}C_2B_9H_{10})_2]^-$ results in disruption of weak intramolecular hydrogen bonds and appearance of stronger donor-acceptor bonds between metal and sulfur atoms of the dicarbollide ligands, that accompanies by turn of the dicarbollide ligands with transformation of the *transoid* conformation to the *cisoid* one. This process is reversible and can be used for construction of molecular switches based on transition metal bis(dicarbollide) complexes.

Acknowledgments

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METAL COMPLEXES BASED ON POLYDENTATE O-, N-, S-LIGANDS: SYNTHESIS, STRUCTURE, PROPERTIES

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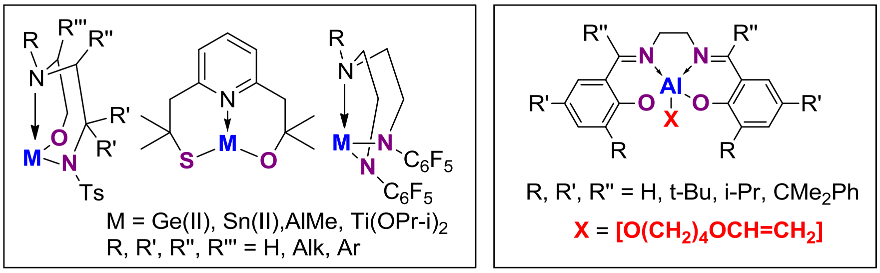
In organometallic chemistry the structure of the organic ligand determines the structure and properties of the whole molecule. The last results of our scientific group on application of novel polydentate ligands with *O*-, *N*-, *S*-coordinating atoms to the synthesis of main group (Ge, Sn; Al) and transition metal (Ti) complexes[1,2] will be reported (Figure 1). A number of these complexes were used as ligands for Pd, Mo, W derivatives, as catalysts in cross-coupling reactions, as initiators in ring-opening polymerization (ROP) of lactones. The strategy to the synthesis of macromonomers using modified Al complexes will be also presented.[3]



M = Ge(II), Sn(II),AlMe, $Ti(OPr\text{-}i)_2$

R, R', R'', R''' = H, Alk, Ar

R, R', R'' = H, t-Bu, i-Pr, CMe_2Ph

X = $[O(CH_2)_4OCH=CH_2]$

Figure 1. Types of the complexes studied.

References

1. K.V. Zaitsev, E.A. Kuchuk, A.V. Churakov, M.A. Navarsardyan, M.P. Egorov, G.S. Zaitseva, S.S. Karlov, *Inorg. Chim. Acta* **2017**, *461*, 213.
2. K.V. Zaitsev, V.S. Cherepakhin, A. Zherebker, A. Kononikhin, E. Nikolaev, A.V. Churakov, *J. Organomet. Chem.* **2018**, *875*, 11.
3. Y.A. Piskun, I.V. Vasilenko, K.V. Zaitsev, Y.F. Oprunenko, S.V. Kostjuk, *Macromol. Chem. Phys.* **2017**, *218*, 1600580.

RUTHENACARBORANES WITH DI- AND TRIPHOSPHINE LIGANDS: SYNTHESIS AND INTERPLAY BETWEEN exo-nido-, closo- AND pseudocloso- ISOMERS

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Carborane clusters of transition metals represent an interesting type of coordination compounds being similar to cyclopentadienyl (Cp) derivatives. A *nido*-$C_2B_9H_{11}^{2-}$dicarbollidedianion has similar pentagonal plane and symmetry of the frontier orbitals. It is well-known that Cp-rings may undergo slippage resulting in the formation of isomeric structures containing k^3 or k^1 -coordinatedligand.More complicated tri-dimensional structure of the carborane determines the possibility of formation of larger numbers of isomers [1, 2].

A *nido*-$C_2B_9H_{11}$ fragment may be coordinated to the transition metal center as in a k^5 manner forming *closo*- complexes, so by three agnostic hydrogen bridges giving *exo-nido*- type clusters. The investigation of an *exo-nido*- to *closo*- rearrangement of a ruthenium carborane clusters with diphosphine ligands shows the increase of the stability of an *exo-nido*- isomer with the increase of the steric bulkiness of the ligand.

The performed investigation of a series of *closo*-ruthenacarboranes with tridentate phosphine and amine ligands shows that in spite of the apparent similarity of the complexes its structural parameters are slight differ. While the diphosphine and triphosphine derivatives represent a typical *closo*-complexes, its nitrogen-based counterparts seems to have *pseudocloso* structure with the absence of strong C-C bond. The performed calculations allowed us to estimate the difference in the stability of *pseudocloso*- and *closo*- structures depending on the ligand environment.

The correlations between the structure of the complex, its electrochemical properties and the chemical shifts in ^{11}B and ^{31}P spectra was done. The possibility of application of the obtained ruthenacarboranes in the catalysis of Atom Transfer Radical Polymerzation was estimated.

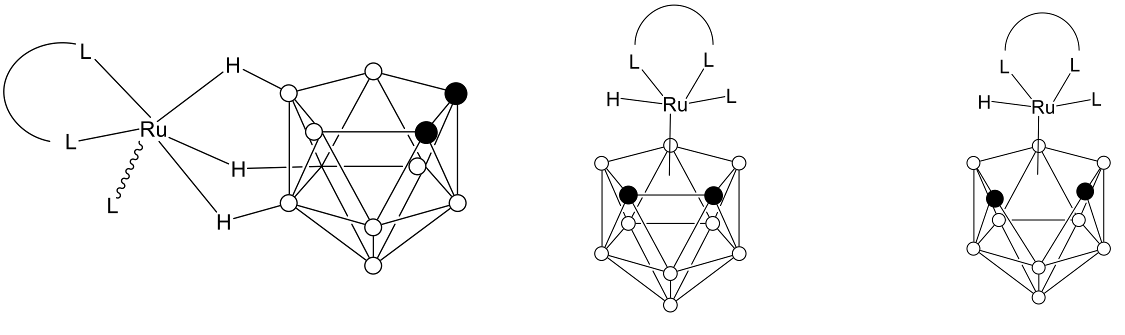

Figure 1. *Exo-nido*-, *closo*- and *pseudo-closo*-metallacarboranes

Acknowledgments

The work was supported by Russian Science Foundation (proj. 18-73-10092)

References

1. I. D. Grishin, I.T.Chizhevsky, *JOMC* **2014**, *760*, 24.
2. L. S. Alekseev et.al *JOMC* **2009**, *694*, 1727.

TRANSMETALLATION AS A SYNTETIC ROUTE TO GROUP 13 CARBENE COMPLEXES

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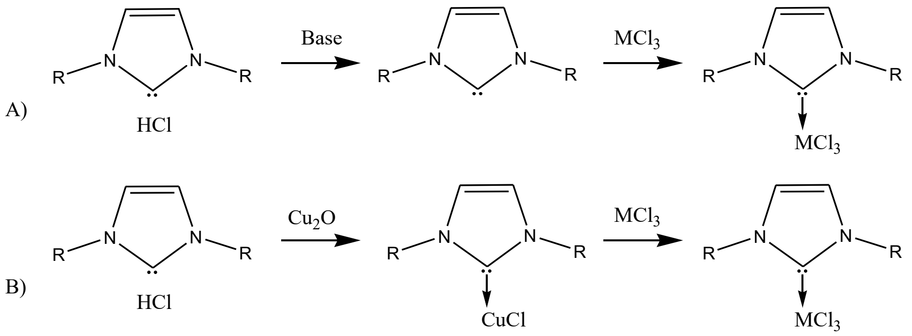
N-heterocyclic carbene (NHC) complexes of group 13 metal trihalides (NHC)MX_3 are useful precursors and catalysts in a variety of applications.[1–2] The common synthetic procedures involve preparation of free NHC and it's further reaction with group 13 trihalide (Scheme 1A). The main drawback of this pathway is using reactive free NHC, which can result in formation of side products and relatively low (40-60%) yelds.[3]

Alternative approach involves transmetallation strategy (Scheme 1B). We chose (IPr)CuCl[IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene] as the most suitable and stable NHC transfer agent. Highest yelds for transmetallation reactions were obtained in dichloromethane and excess of MCl_3 at room temperature: 92% for (IPr)$AlCl_3$ and 82% for (IPr)$GaCl_3$ with respect to(IPr)CuCl. Interesting to note, that reaction of (IPr)CuCl with $AlCl_3$ in benzene leads to formation of two-phase system. After removing solvent from heavy phase a crystalline product was isolated. According to single crystal X-ray structural analysis a sample contains (IPr)$AlCl_3$ and $[(IPr)Cu(C_6H_6)]^+Al_2Cl_7^-$, which in good agreement with NMR measurements and proposed reaction mechanism. (IPr)$AlCl_3$ and (IPr)$GaCl_3$ were characterized by NMR, IR, X-ray powder diffraction and single crystal X-ray structural analysis.



Scheme 1. Synthetic routes to (NHC)MCl_3 (M=Al, Ga).

Proposed transmetallation strategy can be used for synthesis NHC complexes of group 13 metal trihalides utilizing air-stable carbene transfer agent under mild conditions and with high (80-90%) yields.

Acknowledgments

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References

1. Z. Li, G. Thiery, M.R. Lichtenthaler, R. Guillot, I. Krossing, V. Gandon, C. Bour, Adv. Synth. Catal. 2018, 360 (3), 544.
2. T.N. Nguyen, J. A. May, Org. Lett. 2018, 20 (1), 112.
3. A. Stasch, S. Singh, H.W. Roesky, M. Noltemeyer, H.-G. Schmidt, Eur. J. Inorg. Chem. 2004, 2004 (20), 4052.

NOVEL SYNTHETIC APPROACH TO CHARGE-COMPENSATED NIDO-CARBORANE LIGANDS

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The 7,8-dicarba-*nido*-undecaborate anion due toits unique physical and chemical properties and unusual three-dimensional π-character plays an important role in the development of the metallacarborane chemistry.[1,2]Another important property of this anionic cluster is the capability to form charged-compensated compounds that can provide the ligating of transitional metal ions.

In this work we present the new synthetic approach to the obtaining of charged-compensated *nido*-carborane derivatives *via* the reactions of nucleophilic addition to its nitrilium derivatives.[3,4] The proposed method allows obtaining wide range of *nido*-carborane ligands with simple substituents as well as ligands with additional functional groups in the side-chain.

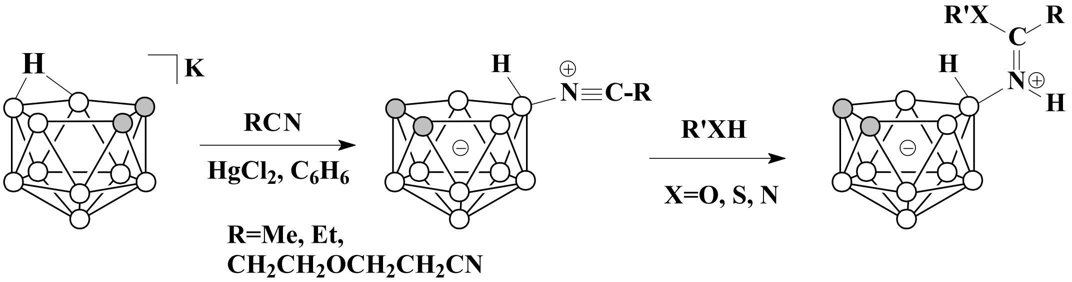

Figure 1. The synthetic rout to charged-compensated *nido*-carborane derivatives

The prepared compounds can be used for the synthesis of transitional metals half-sandwich complexes.

Acknowledgments

This work was supported by Russian Science Foundation (Grant 19-73-00229)

References

1. R.N. Grimes, *Carboranes*, Academic Press, London **2016**, 1058 p.
2. *Handbook of Boron Chemistry in Organometallics, Catalysis, Materials and Medicine*, edited by N. S. Hosmane and R. Eagling **2018**, 1400 p.
3. M. Yu. Stogniy, S. A. Erokhina, K. Yu. Suponitsky, A. A. Anisimov, I. B. Sivaev, V. I. Bregadze, *New J. Chem.* **2018**, *42*, 17958.
4. M. Yu. Stogniy, S. A. Erokhina, I. B. Sivaev, V. I. Bregadze, *Phosphorus, Sulfur, and Silicon and the Related Elements* **2019**, https://doi.org/10.1080/10426507.2019.1631312.

STABILITY AND REACTIVITY OF THE BINUCLEAR GERMYLENES BEARING N,N- AND N,O-DONOR LIGANDS

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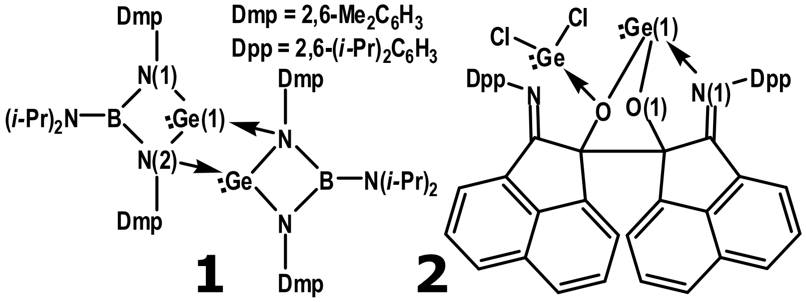
The germylenes derived from the aryl-substituted boraguanidinate and monoiminoacenaphtheneone ligands were found to form the corresponding binuclear species **1**[1-3] and **2** in the solid state (Scheme 1). In the present work we compared stability of the complexes relative to dissociation and isomerisation in the solution using DFT. The reactivity towards alkynes, isocyanates, *o*-quinones, and triethylamine was investigated. The thermodynamic parameters of the corresponding elementary reactions were calculated at the M062X/DGDZVP level in conjunction with the PCM solvation model. The most important donor-acceptor interactions were considered on the basis of electron density analysis (Figure 1).



Scheme 1

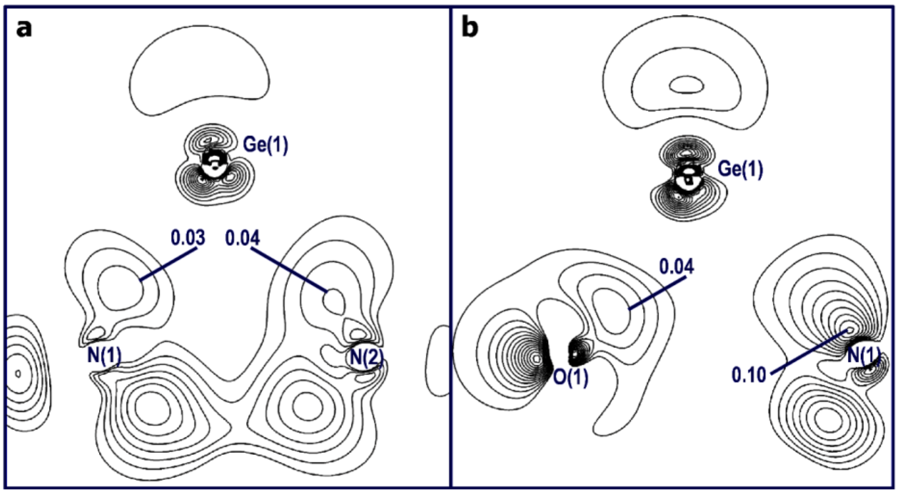


Figure 1. Deformation electron density maps in the N(1)Ge(1)N(2) plane of **1** (a) and O(1)Ge(1)N(1) of **2** (b). The contours start from 0.01 a.u. with step of 0.01 a.u. The maps are built at the same scale

Acknowledgments

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References

1. J. Böserle, M. Alonso, R. Jambor, et al., *RSC Adv.* **2016**, *6*, 19377.
2. J. Böserle, G. Zhigulin, P. Štěpnička, et al., *Dalton Trans.* **2017**, *46*, 12339.
2. J. Böserle, G. Zhigulin, S. Ketkov, et al., *Dalton Trans.* **2018**, *47*, 14880.

BRAIN AS A TARGET FOR BIOACTIVE FERROCENE-BASED COMPOUNDS

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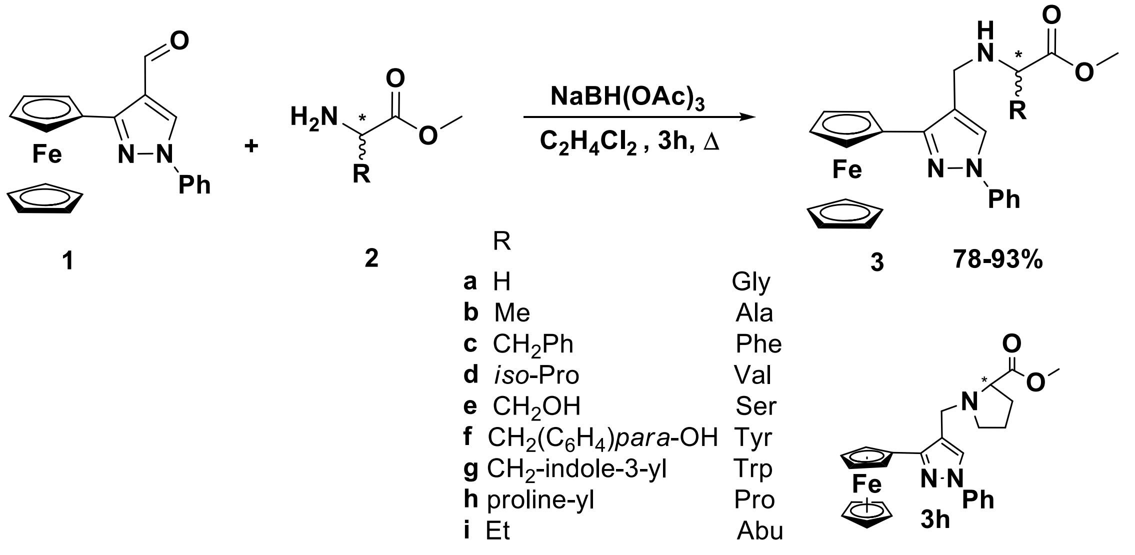
The landscape of modern organometallic chemistry has changed a lot. If synthetic studies in organometallic chemistry have been predominated during last four decades of XX century, over recent 10–15 years bio-organometallic chemistry acquired superiority, and various ferrocene-based compounds have been successfully developed in the design of promising anticancer drugs, antimicrobial or antimalarial agents, as well as tuberculostatics.

We have developed a synthetic procedure (Scheme 1) and obtained a series of ferrocenyl-substituted amino acids (including both *L*-, *D*- or racemic-forms) with pyrazole linker. Namely, glycine, alanine, phenyl alanine, valine, serine, tyrosine, tryptophan, proline, and α-amino butyric acid ones, as methyl esters.

Primary electrophysiological *in vivo* studies of the first representatives of a series of ferrocenyl amino acids, namely, ferrocenyl(phenylpyrazolyl)-glycine methyl ester (**3a**), ferrocenyl(phenylpyrazolyl)-(*D*)-alanine, (*D*)-**3b**, and ferrocenyl(phenylpyrazolyl)-(*L*)-alanine, (*L*)-**3b**, on the hippocampus (hippocampus is a key structure involved in the learning and memory processes) which is a part of a temporal lobe of the brain, have been carried out.



	R	
a	H	Gly
b	Me	Ala
c	CH_2Ph	Phe
d	*iso*-Pro	Val
e	CH_2OH	Ser
f	$CH_2(C_6H_4)$*para*-OH	Tyr
g	CH_2-indole-3-yl	Trp
h	proline-yl	Pro
i	Et	Abu

Scheme 1. Synthesis of ferrocene-modified pyrazole amino acids methyl esters.

References

1. A.N. Rodionov, L.V. Snegur, A.A. Simenel, Yu.V. Dobryakova, V.A. Markevich, *Russ. Chem. Bull., Int. Ed*. **2017**, *66*(1), 136.
2. A.N. Rodionov, L.V. Snegur, Y.V. Dobryakova, M.M. Ilyin, Jr., V.A. Markevich, A.A. Simenel. *Appl. Organomet. Chem*. **2019**, *in press*.

TRIPHENYLSILYL AND TRIPHENYLGERMYL HYDROPEROXIDES AS THE FIRST EXAMPLES OF STRUCTURALLY CHARACTERISED SI AND GE HYDROPEROXIDES

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Triphenyl silicon hydroperoxide and its isostructural germanium complex have been synthesized in good yields.[1,2] These peroxocomplexes were isolated and characterized by single crystal, powder X-ray diffraction studies, Raman spectroscopy and thermal analysis.

Triphenylsilyl and triphenylgermyl hydroperoxides exhibit 2-fold embrace motif of the hydroperoxo ligands, with each hydroperoxo group acting as a hydrogen donor and a hydrogen acceptor (fig. 1). Only two structures with localized protons of hydroperoxo (boron and tin) for p-block elements of hydroperoxo complexes are known and both exhibit the same 2-fold hydroperoxo embrace motif.[3,4]

This complexes are the first examples of structurally characterised Si and Ge hydroperoxides.

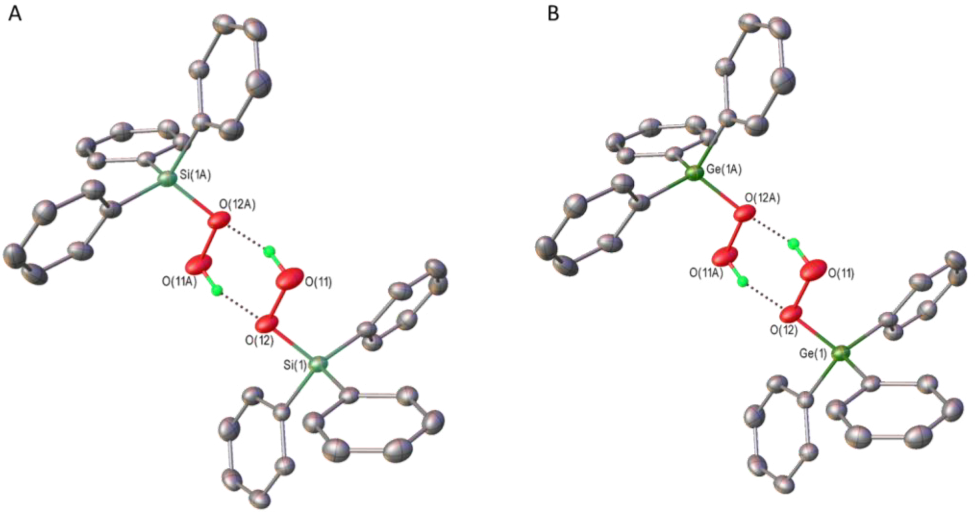

Figure 1. Hydrogenbondeddimers in the structure of Ph$_3$SiOOH (A) and Ph$_3$GeOOH (B).

Acknowledgments

We thank the Russian Science Foundation (grant 19-73-10208).

References

1. R.L. Dannley, G. Jalics. *J. Org. Chem.* **1965**, 30, 2417-2419.
1. R.L. Dannley, G.C. Farrant. J. Org. Chem. **1969**, 34, 2428-2432.
3. E. Tsurumaki, J.Sung, D. Kim, A.Osuka. *Angew. Chem.Int. Ed.* **2016**, 55, 2596-2599.
4. A.V. Churakov, S. Sladkevich, O. Lev, T.A. Tripol'skaya, P.V. Prikhodchenko. *Inorg. Chem.* **2010**, 49, 4762-4764.

N_2O AS A REAGENT IN SYNTHETIC CHEMISTRY

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The chemistry of N_2O ('laughing gas') gained a significant attention in recent years since it was identified as the most potent ozone-depleting gas emitted in the 21st century. Its concentration in the atmosphere continues to increase, and human activities contribute significantly to it. Most of anthropogenic emissions of N_2O are just destroyed by the energy-demanding decomposition into elements. However, we believe that nitrous oxide is a promising reagent. The upcoming talk will summarize our efforts to employ N_2O as a reagent in synthetic chemistry. First, the utilization of nitrous oxide an oxidant will be discussed. Furthermore, it will be shown that N_2O can be used as building block for more complex molecules and an N-atom donor for the synthesis of important organic molecules.

Acknowledgments

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References

1.Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. *Angew. Chem. Int. Ed.* **2012**, *51*, 232.
2. Tskhovrebov, A. G.; Solari, E.; Wodrich, M. D.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2012**, *134*, 1471 and *Chem. & Eng. News 2012, 90, 41*.
3. Tskhovrebov, A. G.; Vuichod, B.; Solari, E.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.* **2013**, *135*, 9486.
4. Tskhovrebov, A. G.; Solari, E.; Scopelliti, R.; Severin, K. *Inorg. Chem.***2013**, *52*, 11688 and *Chem. & Eng. News 2013, 91, 24*.
5. Tskhovrebov, A. G.; Naested L. C. E.; Solari, E.; Scopelliti, R.; Severin, K. *Angew. Chem. Int. Ed.* **2015**, *54*, 1289 and *Synfacts 2015, 11, 142.*
6. Eymann, L. Y. M.; Tskhovrebov, A. G.; Sienkiewicz, A.; Bila, J. L.; Živković, I.; Rønnow, H. M.; Wodrich, M. D.; Vannay, L.; Corminboeuf, C.; Pattison, P.; Solari, E.; Scopelliti, R.; Severin, K. *J. Am. Chem. Soc.***2016**, *138*, 15126.
7.Y. Liu, P. Varava, L. Y. M. Eymann, A. G. Tskhovrebov, O. M. Planes, E. Solari, F. F. Tirani, R. Scopelliti, A. Sienkiewicz, C. Corminboeuf, K. Severin. *Chemical Science* **2019**, *10*, 5719.

THE FIRST ALL-C-DEPROTIOTITANACYCLOBUTADIENE?

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In recent years our group was interested in the synthesis and stabilisation of all-*C*-deprotiometallacyclobutadienes (e.g. $Cp'_2M(\eta^3\text{-}Me_3SiC_3SiMe_3)$, Cp'= η^5-unsubstituted and substituted cyclopentadienyl) of group 4 metals.[1]Following up on a series of unsuccessful attempts to access such structures,[2] in one of our latest contributions to these efforts, we presented the synthesis of pure and solid $Li_2(Me_3SiC_3SiMe_3)$ (**1**), the ideal synthon for this task.[3]

The reactionof **1** and *rac*-(ebthi)$TiCl_2$in 1:1 stoichiometry eventually leads to the first all-*C*-deprotiotitanacyclobutadiene (**2**).The molecular structure unambiguously shows the four-membered metallacycle bearing two C=C double bonds and two Ti-C single bonds. With the help of a detailed quantum mechanical investigation this exotic bonding situation can be best described as open shell singlet biradical. During the formation of **2**, the formal allenediide ligand transfers an electron to the titanocene(IV), forming a titanocene(III) centre and a formal alleneylide fragment as ligand. In follow-up experiments, we investigated the insertion of simple carbonyl compounds into one Ti-C bond forming labile six membered metallacycles which undergo subsequent reaction to enynes and formal Ti oxido species.[4]

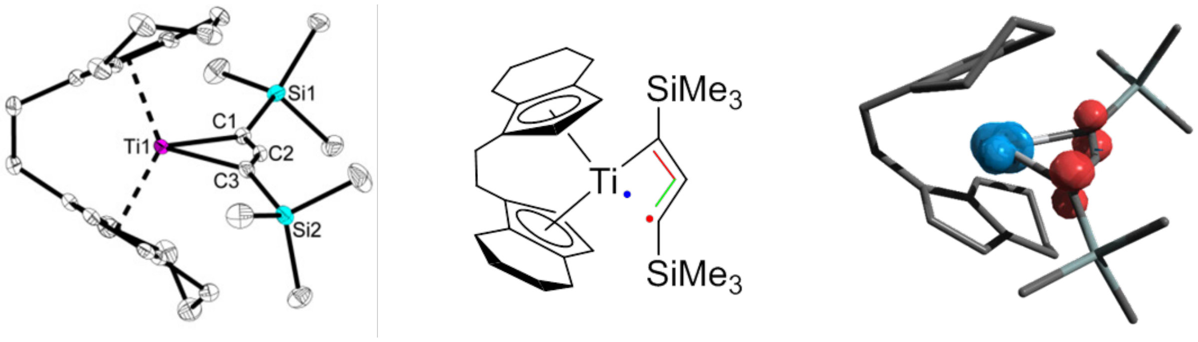

Figure 1.Molecular structure, major Lewis representation and spin density plot of **2**.

Acknowledgments

We would like to thank Prof. U. Rosenthal for his constant encouragement and fruitful discussions on this challenging research project and the DFG for financial support.

References

1. U. Rosenthal, *Eur. J. Inorg. Chem.***2019**, 3456.
2. a) F. Reiß, K. Altenburger, D. Hollmann, A. Spannenberg, H. Jiao, P. Arndt, U. Rosenthal, T. Beweries,*Chem. Eur. J.***2017**, *23*, 7891; b) F. Reiß, M. Reiß, A. Spannenberg, H. Jiao, D. Hollmann, P. Arndt, U. Rosenthal, T. Beweries, *Chem. Eur. J.***2017**, *23*, 14158.
3. F. Reiß, M. Reiß, A. Spannenberg, H. Jiao, W. Baumann, P. Arndt, U. Rosenthal, T. Beweries, *Chem. Eur. J.***2018**, *24*, 5667.
4. F. Reiß, M. Reiß, J. Bresien, A. Spannenberg, H. Jiao, W. Baumann, P. Arndt, T. Beweries, *Chem Sci.***2019**, *10*, 5319.

INVESTIGATION OF PHYSICOCHEMICAL AND CATALYTIC PROPERTIES OF ZEOLITIC IMIDAZOLATE FRAMEWORKS

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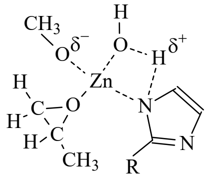
Metal-organic frameworks are currently receiving significant attention for their potential applications in gas separation and storage, sensors, and catalysis. We investigated physicochemical and catalytic properties of zinc zeolitic imidazolate frameworks (ZIFs) based on 2-methylimidazole (ZIF-8) and 2-ethylimidazole (MAF-5 and MAF-6) linkers. The main attention was focused on the effects of structure and basicity of ZIFs on their catalytic properties According to DRIFT spectroscopy using deuterated chloroform ($CDCl_3$) as a C–H acid probe, the linker nature was found to affect the basicity of ZIFs. Basicity of ZIF-8 was lower (858 kJ/mol) than MAF-5 (884 kJ/mol) and MAF-6 (872 kJ/mol) due to the difference in pK_a of conjugate acids of 2-methylimidazole and 2-ethylimidazole.

Catalytic properties of ZIFs were investigated in synthesis of 1-methoxy-2-propanol (1-MP) from propylene oxide (PO) and methanol. ZIFs were demonstrated to be used as effective heterogeneous catalysts for catalytic synthesis of 1-MP with 92.1-93.8% selectivity. Application of these materials decreased the reaction temperature to 110°C. The activity of MAF-5 and MAF-6 were higher in compared with ZIF-8 that was correlated with differences of their basicity and structure.

The reaction mechanism in the presence of ZIF-8 and MAF-5 was investigated by DRIFT spectroscopy. Experimental data point that reaction proceeds via physical adsorption of PO and dissociative adsorption of MeOH on Zn^{2+}-N active sites (pair “Lewis acid site-basic site”). (Scheme). It was suggested that the strength of basic sites of ZIFs affected the MeOH activation and, therefore, the reaction rate.



Scheme . Possible active site for adsorption of MeOH and PO

Compared with reported catalysts (metal oxides and amino-containing systems, such as amino-functionalized SiO_2), the studied ZIFs, especially MAF-5 and MAF-6, showed not only the highest conversion of PO but also the highest selectivity for 1-MP under similar reaction conditions. The conversion of PO for 7 h in the presence of metal-organic frameworks decreases in the following order: MAF-5 (90.3%) > MAF-5 (88.5%) > ZIF-8 (54.4%) > NH_2-UiO-66 (42.5%). This order is inconsistent with their basicity. The low activity of NH_2-UiO-66 is the result of the interaction strength between -NH_2 groups and carboxylic groups of the linker.

Recycling test pointed that MAF-5 and ZIF-8 materials showed good reusability for 5 cycles in catalysis, which indicates their high potential for catalytic applications.

Acknowledgments

This work was conducted within the framework of the budget project AAAA-A17-117041710082-8 for Boreskov Institute of Catalysis

INTERACTION OF THE BUCHWALD SEVEN-MEMBERED ZIRCONACYCLOCUMULENE COMPLEX WITH CARBONYL COMPOUNDS

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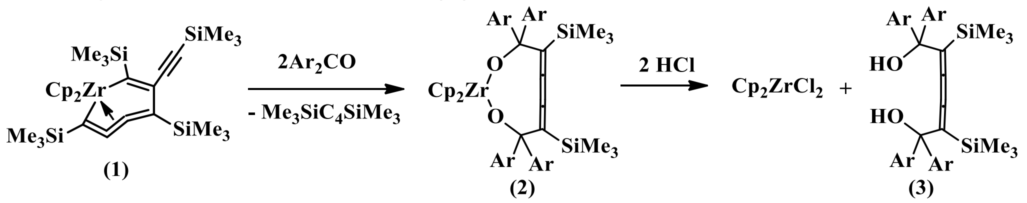
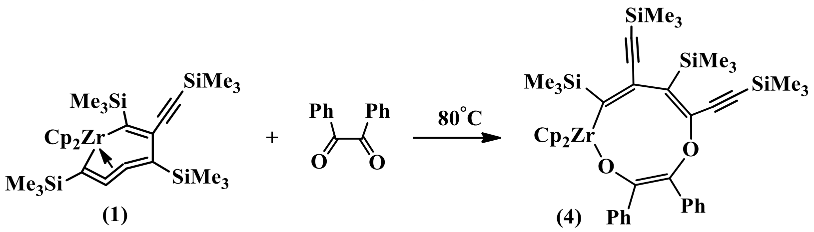
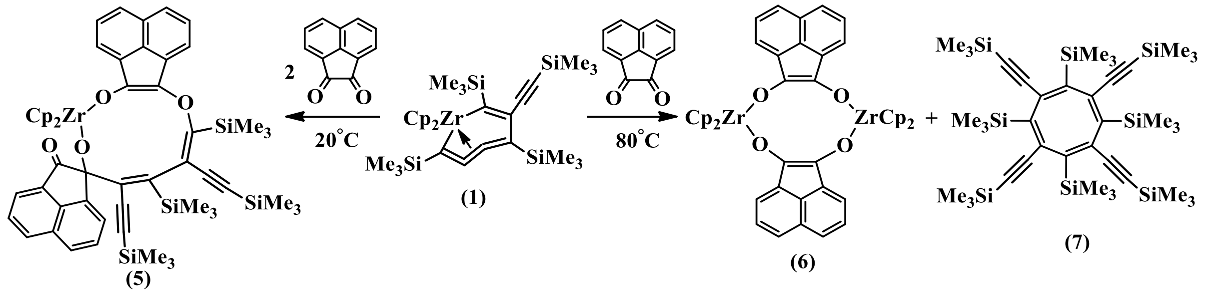
Seven-membered zirconacyclocumulene complexes of zirconocene represent an interesting but still insufficiently well-studied class of compounds. Previously, we investigated the reactions of the seven-membered zirconacyclocumulene (**1**) synthesized by Buchwald et al. (J. Am. Chem. Soc., **1993**, *115*, 10394) with nitriles and acetylenes. Here, the interaction of **1** with various carbonyl compounds is reported [1]. We have found that the reactions of **1** with diarylketones afford nine-membered dioxazirconacyclocumulenes (**2**) whose protolysis gives the corresponding *cis*-[3]cumulenic diols (**3**).



A different picture was observed in the interaction of **1** with benzil at 80°C. In this case, a nine-membered metallacycle (**4**) was obtained.



The results of the reaction of **1** with acenaphthenequinone depend on temperature. At room temperature, the eleven-membered trioxazirconacycle (**5**) was isolated, while tetraoxadizirconacycle (**6**) and octasubstituted cyclooctatetraene (**7**) were formed at 80°/C.



The mechanisms of the reactions found are discussed.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project code 19-03-00332).

References

1. V.V. Burlakov, M.V. Andreev, V.S. Bogdanov, A.F. Smol'yakov, M.Kh. Minacheva, V.B. Shur, *Organometallics* **2019**, *38*, 2636.

P*,S-BIDENTATE DIAMIDOPHOSPHITES FOR ASYMMETRIC PALLADIUM CATALYSIS

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Among phosphorus-containing ligands, diamidophosphites constitute a very promising class of chiral inducers. At the same time, they have significant differences from more widely used phosphites and phosphoramidites. For example, the nitrogen atoms bearing corresponding radicals are more bulky substituents at phosphorus than the oxygen ones. In addition, the replacement of oxygen atoms in the first coordination sphere of the phosphorus center for nitrogen ones increases the electron density on phosphorus. Diamidophosphites have balanced electronic characteristics; incorporation of the phosphorus atom into the 1,3,2-diazaphospholidine or 1,3,2-diazaphosphepine ring increases the ligand resistance to oxidation and hydrolysis. The modular structure of diamidophosphites allows one to vary in a broad manner substituents at the phosphorus and/or nitrogen atoms (thereby finely tuning the steric and electronic parameters of ligand), as well as the configuration of *P**- and *C**-stereocenters. The presence of asymmetric electron-donating phosphorus atom can significantly favor a successful chirality transfer in a catalytic cycle. Therefore, known *P*-monodentate and *P,N*- and *P,P*-bidentate diamidophosphite ligands have found successful application in the in a wide range of asymmetric metal-catalyzed transformations.

Introduction of the S donor center into the diamidophosphite composition offers new challenges, since *P*,*S*-ligands possess the following essential attributes: a) a pronounced chelating ability due to a high affinity of the thioester sulfur atom to soft complexing ions; b) the ability of such sulfur atom to become asymmetric after coordination to a metal; c) differing electronic effects of P and S donor centers and, as a consequence, different *trans*-effects of different-nature donor centers; d) differing steric demands of P and S donor centers, since the sulfide sulfur atom with two substituents imposes less steric hindrances than the phosphorus atom with three substituents; e) the C_1 symmetry favoring the asymmetric induction at the step of key catalytic intermediate.

We report the synthesis of the first *P**,*S*-bidentate diamidophosphites(Figure 1) and their application in the Pd-mediated enantioselective allylic substitution reactions with participation of various substrates and nucleophiles.

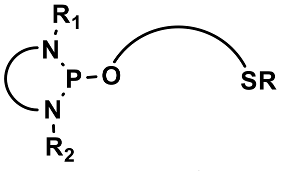

Figure 1. General structural formula of *P**,*S*-bidentate diamidophosphite ligands.

Acknowledgments

This work was financially supported by the Russian Science Foundation (Project No. 19-13-00197).

PYRAZOLATE ANIONS AS BRIDGING BIDENTATE LIGANDS IN THE CHEMISTRY OF COPPER(I) AND SILVER(I) ADDUCTS: STRUCTURES AND PROPERTIES

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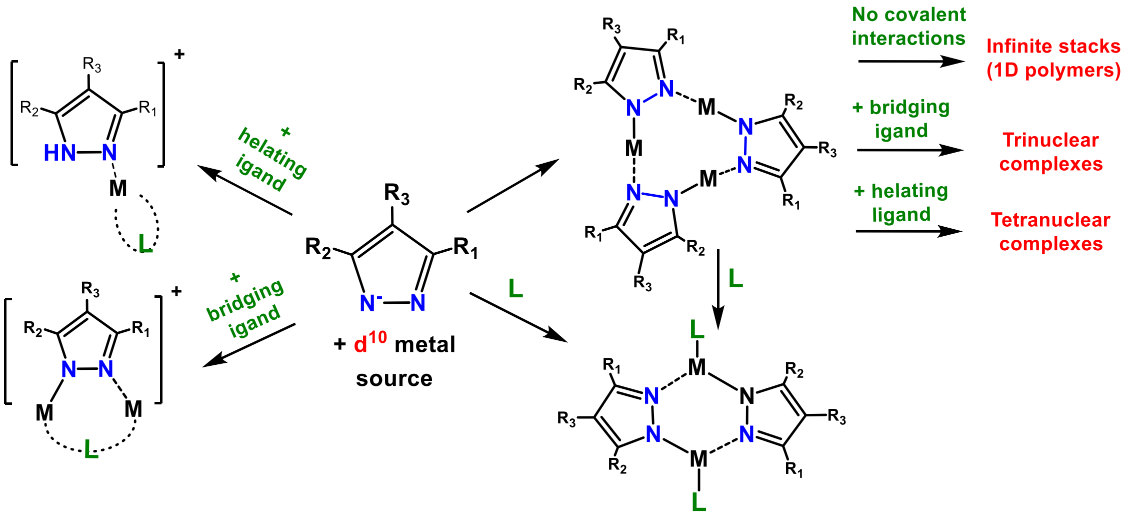
Macrocyclic copper(I) and silver(I) pyrazolate adducts represent an important class of coordination compounds used in numerous fundamental areas, such as acid-base chemistry, metallophilic bonding, supramolecular assemblies.[1,2] Pyrazolate anions can serve as bridging bidentate ligands binding with metals in a different fashion to give complexes of different structures (Scheme 1).

Additional interactions of the metal pyrazolates with nitrogen, phosphorus containing donor ligands lead to the formation of complexes of mono-, di-, tri-, tetra- or polynuclear complexes.



Scheme 1. Possible paths of group 11 metal pyrazolates formation.

Here we report syntheses, structures and study of luminescent properties with theoretical insight of the group 11 metal pyrazolate adducts.[3,4] Variation of ligand structure and metal atoms leads to the compounds possible to emit the light in a wide spectral range.

Acknowledgments

This work was partially supported by Russian Science Foundation (grant № 19-73-20262) and Russian Foundation for Basic Research (grant № 18-33-20060).

References

1. A. A. Titov, O. A. Filippov, L. M. Epstein, N. V. Belkova and E. S. Shubina, *Inorg. Chim. Acta*, **2018**, 470, 22.
2. J. Zheng, H. Yang, M. Xie and D. Li, *Chem. Commun.*, **2019**, *55*, 7134.
3. A. A. Titov, O. A. Filippov, A. F. Smol'yakov, A. A. Averin and E. S. Shubina, *Dalton Trans.*, **2019**, *48*, 8410.
1. 4.A. A. Titov, O. A. Filippov, A. F. Smol'yakov, I. A. Godovikov, J. R. Shakirova, S. P. Tunik, I. S. Podkorytov and E. S. Shubina, *Inorg. Chem.*, **2019**, *58*, 8645.

THE CYTOCHROME b6f COMPLEX: DFT MODELING OF PLASTOSEMIQUINONE OXIDATION BY THE LOW-POTENTIAL HEME OF CYTOCHROME b6

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In chloroplasts (the energy-transducing organelles of the plant cell), the cytochrome (Cyt) b_6f complex provides the connectivity between photosystems (PS) II and I.[1] This complex oxidizes plastoquinol (PQH_2) formed in PSII and reduces plastocyanin (electron donor to PSI). The two-electron oxidation of PQH_2 is the bifurcated process: one electron is delivered to the iron-sulfur protein (ISP); the second electron is transferred to the low-potential heme of Cyt b_6. In our previous work,[2] we have concluded that the first reaction is the endergonic process ($\Delta G_1 > 0$), suggesting that this step determines the overall rate of PQH_2 oxidation. In the current work, using the DFT method, we have modeled the second step of PQH_2 oxidation, the electron transfer from semiquinone to the low-potential heme of Cyt b_6 and the proton transfer to Glu78. We have demonstrated that these reactions are accompanied by a decrease in the Gibbs energy ($\Delta G_2 < 0$). The overall energy effect of the bifurcated two-electron oxidation of PQH_2 appears to be the energy-favorable process ($\Delta G_1 + \Delta G_2 < 0$); this process determines the rate of plastoquinone turnover in the intersystem electron transport in chloroplasts.

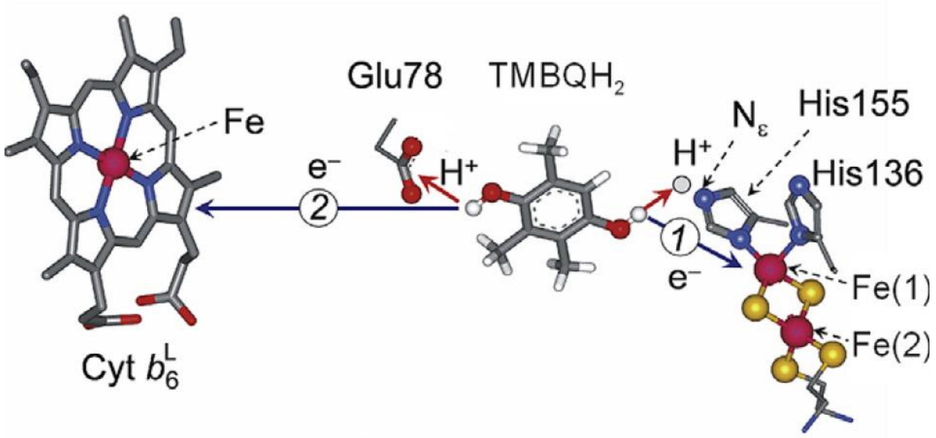

Figure 1. The two-electron oxidation of plastoquinolin the cytochrome b_6f complex.

Acknowledgments

This work was supported by RFBR (project 18-04-00214).

References

1. A. N. Tikhonov, *Plant Physiol. Biochem.* **2014**, *81*, 163.
2. L. Y. Ustynyuk, A. N. Tikhonov,*J. Organomet. Chem.* **2018**, *867*, 290.

METAL-MEDIATED INTERMOLECULAR INSERTION OF CARBONYL COMPOUNDS AND NITRILES INTO A P–P BOND OF THE CYCLIC PHOSPHINE CYCLO-(P_5Ph_5)

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The insertion of organic molecules into P–P bonds of organophosphorus compounds (OPC) is of high scientific interest, since this reactionleads to the formation of unique ligands and complexes which may have interesting properties and biological activity. A number of organic and inorganic molecules has already been tested in these reactions, i.e. isocyanates, isothiocyanates, carbon disulfide, alkenes, nitriles and isonitriles.

The P–P bonds can be cleaved homolytically with formation of phosphinyl radicals and heterolytically, when the bonds are polarized or activated through coordination to a metal atom (metal-mediated insertion).[1] The latter recently became an object of intensive studies as a potential route to novel phosphorus-rich transition metal complexes.[2]

Herein we described the reactions of the molybdenum carbonyl complex [$Mo(CO)_4$(nbd)] (nbd = norbornadiene) and cyclopentaphosphine *cyclo*-(P_5Ph_5) with small organic molecules. We have found that carbonyl compounds RR’CO, where R = R' = Me; R = R' = Ph; RR' = -$(CH_2)_7$-; R = H; R' = 4-CHO-C_6H_4, 4-Br-C_6H_4, C_2H_5, Ph and nitriles RCN, where R = Ph, *t*-Bu, 4-NC-C_6H_4, 4-Br-C_6H_4, can be inserted into a P–P bond of *cyclo*-(P_5Ph_5) leading to formation of new polyphosphorus ligands by an expansion of the phosphorus ring (Fig. 1).

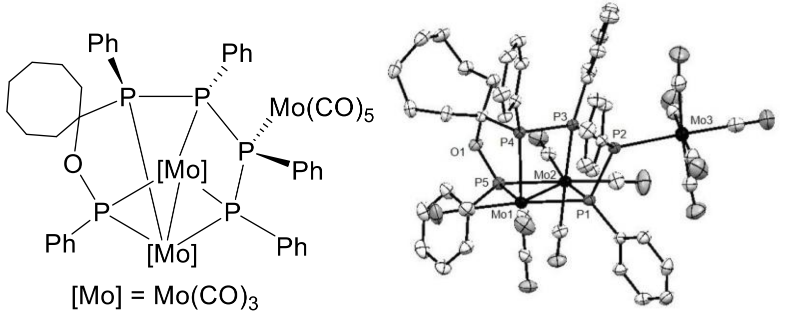

Figure 1. Structural formula and molecular structure of the trinuclear molybdenum carbonyl complex with a(PPh-PPh-PPh-PPh-C$(CH_2)_7$O-PPh)$^{2-}$ ligand (H atoms are omitted for clarity, thermal ellipsoids at 50 % probability).

Acknowledgments

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References

1. a) S. Burck, D. Gudat, M. Nieger, *Angew. Chem., Int. Ed.*, **2004**, *43*, 4801; b) N.A. Giffin, A.D. Hendsbee, J.D. Masuda, *Dalton Trans.*, **2016**, *45*, 12636; c) S.S. Chitnis, R.A. Musgrave, H.A. Sparkes, N.E. Pridmore, V.T. Annibale, I. Manners, *Inorg. Chem.*, **2017**, *56*, 4521.
2. a) M. Höhne, B.H. Müller, N. Peulecke, A. Spannenberg, H. Jiao, U. Rosenthal, *Eur. J. Inorg. Chem.*, **2017**, *23*, 3008-3014; b) D.M. Yufanyi., T.Grell, E.Hey-Hawkins, *Eur. J. Inorg. Chem.*, **2019**, 1557.

METAL-ORGANIC FRAMEWORKS BASED ON NOVEL ZN$_{12}$ CARBOXYLATE WHEELS: SYNTHESIS, STRUCTURE AND APPLICATIONS

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Metal-organic frameworks (MOFs) are one- (1D), two- (2D) or three-dimensional (3D) polymers based on building blocks consisting of metal ions or cluster/polynuclear fragments connected by bridge organic ligands. Due to their structural and functional diversity, they represent a promising class of materials and have been intensively studied during the last years[1-3].

Here we report two series of MOFs based on identical Zn_{12} carboxylate wheels formed by twelve zinc(II) cations connected by deprotonated polyatomic alcohol molecules (ethylene glycol, 1,2-propanediol, 1,2-butanediol, 1,2-pentanediol and glycerol) on the inner rimof the wheeland by dicarboxylate dianions on the outer rim of the wheel. 1,4-diazo[2.2.2.]bicyclooctane molecules and dicarboxylate dianions connect these wheels in a 3D structure: channeled in the case of 2,5-thiophendicarboxylic acid and mesoporous in the case of isophthalic acid.

All MOFs were analyzed by single-crystal X-ray diffraction and analytical methods revealing their chemical and phase purity. They demonstrate permanent porosity which was confirmed by measuring the specific surface area and pore volume for the activated compounds by gas adsorption: the obtained values were found to match the expected ones. The isotherms of CO_2, N_2, CH_4, C_2H_2, C_2H_4, C_2H_6 were measured at 0 and 25 °C, and the selectivity factors were calculated as ratio of the adsorbed volumes, as ratio of the Henry constants and by the Ideal Adsorbed Solution Theory (IAST), revealing the potential of these MOFs in separation of C_1/C_2 hydrocarbons, CO_2/N_2, CO_2/CH_4, CH_4/N_2 and C_2H_2/CO_2 gas mixtures. The separation of benzene/cyclohexane in liquid and vapor phases was also studied, and the best benzene/cyclohexane selectivity 92:1 (liquid phase) was found to outperform the known literature data. Interestingly that the trend of a preferable benzene sorption can be reversed, when alkyl chains are introduced into the framework structure. The increase of the hydrocarbon moiety of the polyatomic alcohol enhances the affinity of the corresponding porous compounds towards cyclohexane, which was never published before.The MOFs with glycerol constituent appeared to be functionalized because of pendant OH-groups and therefore demonstrate size-selective sorption of alkaline metal cations in order $Li^+ > Na^+ > K^+ > Cs^+$ as well as a notable luminescent response for cesium(I) ions and urea.

Acknowledgments

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References

1. K.Sumida, D. L. Rogow, J. A. Mason, Th. M. McDonald, E. D. Bloch, Z. R. Herm, T.-H. Bae, J. A.Long, *Chem. Rev.* **2012**, 112 (2), 724.
2. Y. Zhang, Sh. Yuan, G. Day, X.Wang, X.Yang, H.-C.Zhou, *Coord. Chem. Rev.* **2018,** 354, 28.
3. M. Yoon, R. Srirambalaji, K. Kim, *Chem. Rev.* **2012**, 112 (2), 1196.

SYNTHESIS, CHEMICAL PROPETIES AND APPLICATIONS OF PHOSPHORUS HETEROCYCLES

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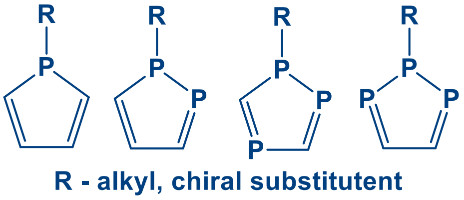
The five-membered phosphorus heterocycles (phospholes) exhibit unique properties different from the other five-membered *S, N, O, C*-heterocycles [1]. Due to low their aromaticity, phospholes are of significant interest for the preparation of highly effective catalysts, materials for light-emitting diodes and nonlinear optics etc. In contrast to furans, thiophenes and pyrroles, phospholes display cycloaddition and complexation reactions and can be used as starting materials for caged phosphines, phosphinidenes, etc. [2] Herein, we report on the synthesis and chemical properties (cycloaddition reactivity and coordination chemistry) of new 1-mono-, 1,2-di-, 1,2,3- and 1,2,4-triphospholes.



Synthesis of phospholes
Cycloaddition reactions
Coordination chemistry
Optical properties and luminescence
Application in asymmetric calalysis

A rational and highly efficient method to access lithium 2,3,4,5-tetraphenylphospholide, sodium 3,4,5-triaryl-1,2-di- and 4,5-diaryl-1,2,3-triphospholides based on the activation of white phosphorus P_4 by alkali metals and the use of commercially available reagents have been developed [3]. Alkylation of these phospholide anions proceeds with the formation of previously unknown phosphorus heterocycles - 1-mono-, 1,2-di-, 1,2,3- and 1,2,4-triphospholes with different non-chiral alkyl and chiral substituents [4]. The photophysical properties of 1-mono- and 1,2-diphospholes were studied experimentally by electron absorption and emission spectroscopy methods supported by quantum-chemical calculations in the framework of density functional theory (DFT) and non-stationary DFT (NTFP) [5]. We have examined asymmetric [4+2] cycloaddition reactions of chiral 1-alkyl-1,2-diphospholes with non-chiral dienophiles [6] as well as non-chiral 1-alkyl-1,2-diphospholes with chiral dienophile [7], which thus allows a one-step stereoselective synthesis (*de* = 80-95%), of bulky *P*-chiral tricyclic phosphines. The enantiopure *P*-chiral tricyclic phosphines show high activity and moderate enantioselectivity as ligands in Pd-catalyzed asymmetric allylic alkylation (*ee* = 52-63%) and as catalysts in organocatalytic [3+2] annelation of allenes and alkenes (*ee* = 68 %) [8].

Acknowledgments This work was supported by the Russian Foundation for Basic Research and Government of the Tatarstan Republic, research project №18-43-160025.

References

[1] F. Mathey, *Chem. Rev.*, **1988**, 88, 429. [2] A. Zagidullin et al., *Mend. Commun.*, **2013**, 23, 117. [3] I. Bezkishko et al., *J. Organomet. Chem.*, **2017**, 844, 1-7. [4] A. Zagidullin et al., *Dalton Trans*, **2018**, 47, 11521. [5] T. Burganov et al., *Dyes Pigm*, **2019**, 164, 363. [6] A. Zagidullin et al., *Eur. J. Org. Chem.* **2015**, 24, 5326. [7] A. Zagidullin et al., *Dalton Trans*, **2019**, 48, 4677. [8] A. Zagidullin et al., *Catal. Today*, **2017**, 279, 142.

SYNTHESIS AND CATALYTIC ACTIVITY STUDY OF CYANOPHENOXY- PHTHALOCYANINE SULFONATED DERIVATIVES

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Phthalocyanine molecules are ubiquitous in most areas of human activity. Effective catalysts, sensitizers, dyes and pigments, PDT applications, drugs for getting rid of alcohol addiction - and this is not a complete list of known practical ways of using compounds of this class.[1-2] This work is devoted to obtaining water-soluble complexes of phthalocyanine type with promising catalytic properties. Heterogeneous complexes of this type showed high values of catalytic activity in the oxidation reactions of sulfur-containing substrates.[3] The introduction of sulfo- groups to the periphery will expand the field of application of the studied compounds and increase their effectiveness as catalysts.

The initial cyanophenoxyphthalocyanines were obtained by template condensation in the absence of a solvent, according to the procedure described earlier.[3] The introduction of sulfo- groups to the periphery of the molecule was carried out by sulfonation of complexes with chlorosulfonic acid in the presence of thionyl chloride as a water-withdrawing agent that suppresses premature hydrolysis (**Figure 1**). The structure of the obtained complexes was confirmed by IR and NMR spectroscopy, mass spectrometric analysis. Using the standard oxidation reaction of sodium diethyldithiocarbamate the catalytic activity of phthalocyanine sulfonic acids under conditions of homogeneous catalysis were studied.

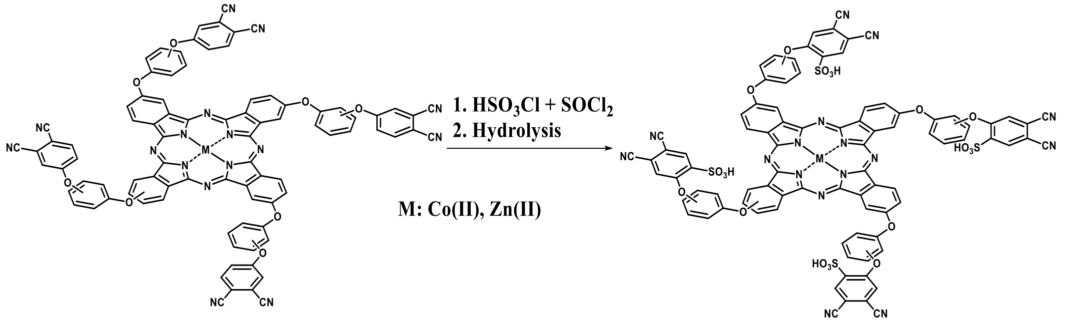

Figure 1. Introduction of sulfo- groups into cyanophenoxy- phthalocyanine complexes

Acknowledgment

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References

1. T. Birnbaum,T. Hahn,C. Martin, J. Kortus, M. Fronk, F. Lungwitz, D. R. T. Zahn, *J. Phys. Condens. Matter* **2014**, *26*, 104201.
2. R. Zhang, B. Xu, J. Wang, J. Zhao, *J. Mater. Res.,***2014**, *29*, 793–800.
3. D. A. Erzunov, A. S. Vashurin, O. I. Koifman, *Russ. Chem. Bull. Int. Ed.*, **2018**, *67*, 2250-2252.

3D-MATERIAL ON THE BASE OF CARBON NANOTUBES AND PHTHALOCYANINE

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Three-dimensional (**3D-**) structures based on single-walled carbon nanotubes (**SWCNT**) are most attractive carbon nanomaterials due to its unique morphological, electrical, adsorption and sensor properties, etc. One of the ways to obtain 3D-carbon material is covalent binding of SWCNT by using linker molecules. In this work, 3D-hybrid material (**SWCNT/SiPc-3D**) was obtained by covalent functionalization of the SWCNT surface by silicon phthalocyanine derivative (**SiPc-dyalk**) following "click-chemistry" reaction, according to the scheme:

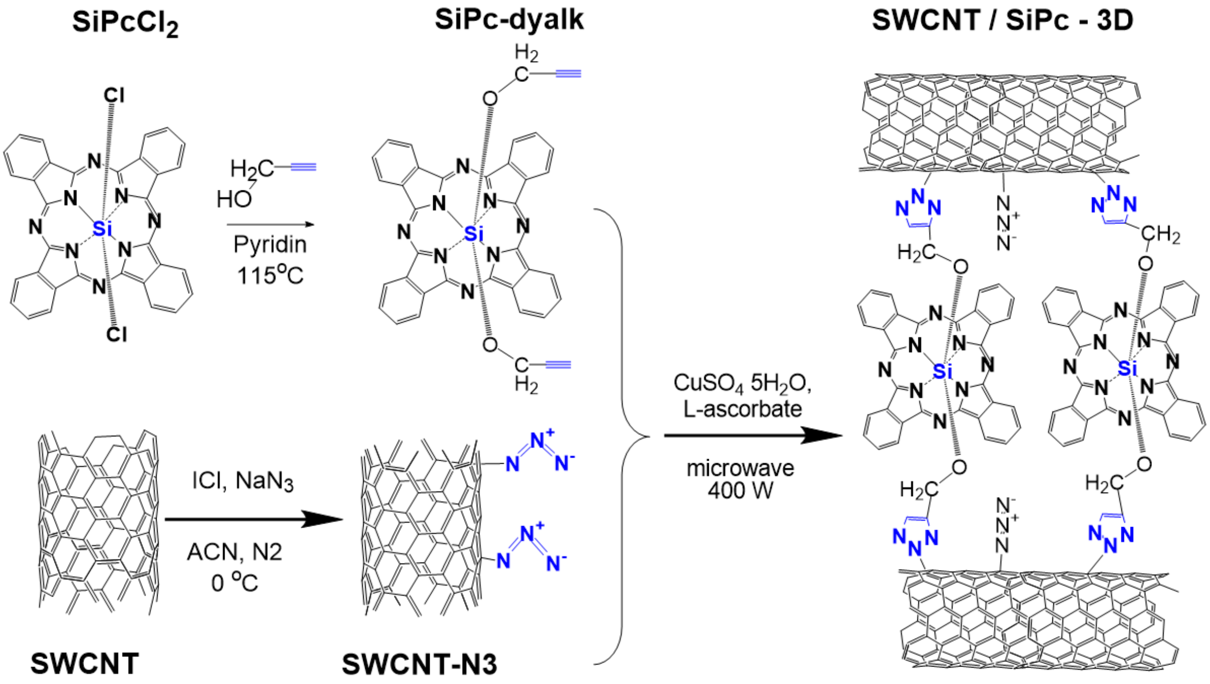

Figure 1. Synthesis scheme of 3D-material of SWCNT with SiPc derivative.

Obtained 3D-hybrids was identified and characterized by UV-vis, IR-, Raman spectroscopy, SEM, XPS, CHN analyses. It was demonstrated that SWCNT/SiPc-3D exhibits more than 10 times higher sensor responses to ammonia compared to pure SWCNT. The possibility to detect H_2S, CO_2 and H_2 using 3D-hybrids sensor layers was also shown. Additionally, sensor properties were investigated at different temperatures (25-80 °C) and relative humidity (0-75%).

Thus, the prepared 3D-hybrid structures as active layers of sensor devices increases its sensitivity and selectivity in comparing with one based on SWCNTs.

Acknowledgments

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II-VI QUANTUM DOTS INTEGRATED WITH POLYELECTROLYTE FOR PHOTOCATALYSIS IN AQUEOUS MEDIUM

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An ideal photoredox catalyst should combine both the thermodynamic and kinetic properties: it uses visible or lower-energy light to produce excited-state electrons (reductive equivalents) and holes (oxidative equivalents) with adequate potentials to form the final product. Soluble metal chalcogenide nanocrystals, or quantum dots (QDs), when properly functionalized, are in many ways ideal colloidal photoredox catalysts due to their intrinsically high catalytic surface area, the electronic structure of their cores, and the chemical tunability of both their cores and their surfaces. This work reports on the photocatalytic, photophysical properties of a number of semiconductor nanoparticles belonging to the class of II-VI quantum dots (QDs). A specific feature of the developed photocatalytic systems is using of amphiphilic polyelectrolyte coatings to stabilize QDs in aqueous medium. QDs in such integration are a flexible system for chemical design, which allows for the inclusion of cocatalyst, intermediate electron transfer links, electron donors, and acceptors interacting with QDs. QDs systems which were developed in the present work are CdS, CdSe, core-shell CdSZnS, CdSeZnS, alloys CdSZnS, CdSeZnS and similar QDs doped with transition metal atoms Mn, Cu. Photocatalytic H+ reduction under visible light irradiation was used as a model photocatalytic reaction. Polymer used in the present work are polycation - statistical copolymer 2-(methacryloyloxy)ethyltrimethylammonium methyl sulfate and stearyl methacrylate, Mn = 27000; polyanion - alternating copolymer tetramethylammonium maleate and 1-octadecene, Mn = 30,000 - 50,000. Ascorbic acid or Na_2S/Na_2SO_3 were used as sacrificial electron donors. Methylviologen was used as electron acceptor in the reaction with photoexcited QDs. Structure, morphology and chemical composition of QDs was characterized by transmission electron microscopy, time-of-flight secondary ions mass-spectrometry technique (TOF-SIMS), element-analysis. The photochemical and photophysical properties of QDs with or without cocatalyst (Ni or Pt) were examined by hydrogen evolution rate and apparent quantum yield measurements, as well as absorption and luminescent spectroscopy techniques. The dynamics of the excited states was investigated by femtosecond laser photolysis technique. We report about the mechanism and reaction rate of ultrafast interfacial electron transfer on the surface of a photoexcited QD to an electron acceptor. The fundamental laws of interfacial electron transfer with the participation of a sacrificial electron donor in the hole states of quantum dots are revealed.

Acknowledgments

The work was supported by Russian Science Foundation grant 17-13-01506

BACTERIOCHLORIN–NAPHTHALIMIDE CONJUGATES FOR SIMULTANEOUS PHOTODYNAMIC THERAPY AND FLUORESCENCE IMAGING

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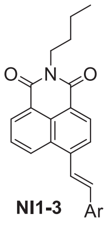
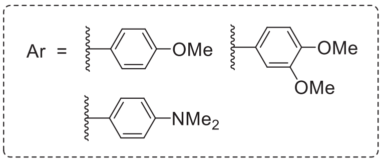
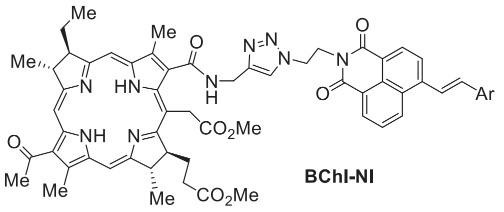
1,8-Naphthalimide derivatives are famous organic fluorophores which generally exhibit high thermo and photostability and are known to act as fluorescent brighteners and dyes for polymer fibers, laser active media, electroluminescent materials and optical memory devices. Because of its intense fluorescence, large Stokes shifts along with the relative ease of synthetic operations for targeted modification of the molecular structure, this type of compounds has found application in the construction of fluorescent chemosensors for biologically relevant cations and anions, labels or probes for proteins, cells, lysosomes and other acidic organelles. However, the emission bands of most naphthalimides are in blue and green-yellow regions. This limits their application as fluorescent probes and imaging agents in life sciences. Although it is well-known that electron-donating groups at the C-4,5-positions of naphthalene ring usually increase the fluorescence quantum yield of the compounds and cause the red shift in the spectra, the reports on 1,8-naphthalimide derivatives with emission wavelengths longer than 600 nm are very few.



NI1-3





BChl-NI

In the present work, we focused on the spectroscopical investigation of styryl-1,8-naphthalimides **NI1–3** as promising long wavelength imaging units in bifunctional conjugates for simultaneous fluorescence diagnostics and photodynamic therapy of cancer. Firstly, steady-state and time resolved photophysical properties of these compounds were studied in protic and aprotic solvents of different polarity. We have found very interesting behavior related to the interplay between fluorescence, formation of TICT states and *E*,*Z*-isomerization[1]. The observed spectral effects have been rationalized using quantum-chemical calculations, X-ray data and NMR spectroscopy. At the second step, conjugates (**BChl-NI**) of styryl naphthalimides with propargyl-15^2,17^3-dimethoxy-13^1-amide of bacteriochlorin *e* known as a highly effective natural photosensitizer (PS) in PDT have been prepared[2]. The idea was to combine the modalities of PS and fluorescent probe in one molecule where the excitation of the naphthalimide fragment is expected to produce the strong emission signal, which could be used to monitor tumor responses to treatment. Further excitation by an other light wavelength corresponding to the absorption maxima of PS would lead to formation of singlet oxygen responsible for cancer cell damage. In this work, the details of our study of optical characteristics as well as evaluation of photosensitizing activity of **BChl-NI** in solution and in living cells are presented.

References

1. P. A. Panchenko et al., *Phys. Chem. Chem. Phys.* **2017**,*19*, 1244.
2. P. A. Panchenko et al., *Phys. Chem. Chem. Phys.* **2017**,*19*, 30195.

SOLUTION NMR TECHNIQUES FOR MOLECULAR MAGNETS

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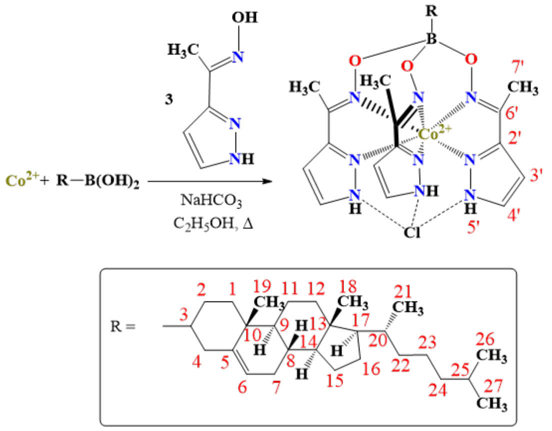
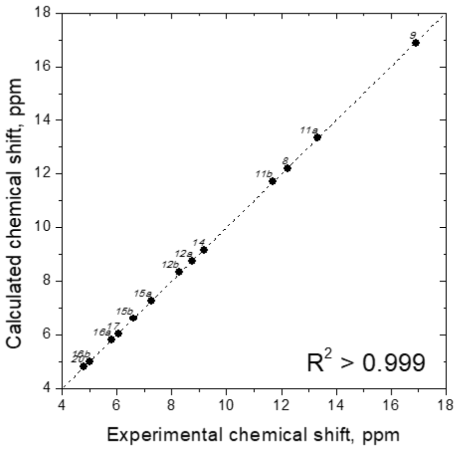
Single-molecule magnets (SMMs) are molecules able to retain their magnetization in the absence of an applied magnetic field. This behavior, which may potentially lead to a breakthrough in high-density information storage or quantum computing, is currently observed only at extremely low temperatures. The method of choice for detecting large magnetic anisotropy, which is a necessary condition for a compound to be an SMM, is ac-magnetometry. This technique, however, is quite demanding and requires accumulation of large arrays of data at different magnetic fields and at very low temperatures. If the purity of the compound is not ideal, as it is often the case with complexes of metals in unusual oxidation states, the obtained results should be interpreted with extreme care. In many cases, crystal packing effects also can dramatically change the magnetic behavior of an SMM even with a very rigid coordination geometry[1].

Large magnetic anisotropy is not only the key property of SMMs but also a parameter that defines the values of pseudocontact shift in NMR spectra of paramagnetic compounds; their analysis[2] provides an access to important magnetic parameters such as zero-field splitting energy[2] or ligand-field energy splitting[3]. To do this, one only needs a high-resolution NMR spectrometer to be available and a reasonable number of ^{1}H NMR spectra to be collected at different temperatures. The presence of impurities is not a problem, as long as they allow detecting the signals of the compound under study. Such an NMR-based approach thus paves the way to characterization of magnetic properties of unstable intermediates obtained by electro- and photo-induced switching of the molecular structure of SMMs.





Acknowledgments

The study was supported by Russian Science Foundation (Project 17-73-20369).

References

1. A.A. Pavlov, Yu.V. Nelyubina, S.V. Kats, L.V. Penkova, N.N. Efimov, A.O. Dmitrienko, A.V. Vologzhanina, A.S. Belov, Ya.Z. Voloshin and V.V. Novikov, *J. Phys. Chem. Lett.*, **2016**, 7, 4111.
2. V. Novikov, A. Pavlov, Yu. Nelyubina, M.-E. Boulon, O. Varzatskii, Ya. Voloshin and R. Winpenny, *J. Am. Chem. Soc.,* **2015**, 137, 9792.
3. A.A. Pavlov, J. Nehrkorn, Y.A. Pankratova, M. Ozerov, E.A. Mikhalyova, A.V. Polezhaev, Yu.V. Nelyubina, V.V. Novikov, V. V., *PCCP*, **2019**, 21, 8201.

COMPUTATIONAL AND THEORETICAL CHEMISTRY FOR METAL-ORGANIC FRAMEWORK RESEARCH

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Metal-organic frameworks (MOF) attract an increasing attention in various applied fields due to an extended tunability of their properties via a compositional substitution of the ligands and secondary building units[1]. The targeted functionalization of materials, generated from an extended compositional and structural space, preconditions the necessity of resorting to computations based on a theoretical background. In this talk, I will present some illustrations on how theory and computational modeling provides practical guidelines for the targeted electronic structure modification[2] of MOFs, elucidates charge carrier dynamics and recombination pathways[3], dynamics of MOF – adsorbate interactions, as well as MOF – polymer systems, thus facilitating materials optimization in relevant fields.

Acknowledgments

This work was supported by a grant from the Swiss National Supercomputing Centre (CSCS) under project ID s888.

References

1. H. Furukawa, K.E. Cordova, M. O'Keeffe, O.M. Yaghi, *Science* **2013**, *341*, 1230444.
2. M.A. Syzgantseva, C.P. Ireland, F.M. Ebrahim, B. Smit, O.A. Syzgantseva, *J. Am. Chem. Soc.* **2019**, *141*, 6271-6278.
3. M.A. Syzgantseva, N.F. Stepanov, O.A. Syzgantseva, *J. Phys. Chem. Lett.* **2019**, *10*, 5041-5046.

DIPYRROMETHENE METAL COMPLEXES: STUDY OF SPECTROSCOPIC CHARACTERISTICS AND PRACTICAL APPLICATION

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Dipyrromethene metal complexes are the simplest representatives of chromophore compounds with open-chain oligopyrrole structure. Their distinctive physicochemical and spectroscopic properties make it possible to use them in modern optical devices: laser active media, laser limiters, optical sensors, photosensitizers of singlet oxygen for the photodynamic therapy.[1]

Thanks to the achievements of chemical synthesis, to date, numerous groups of dipyrromethenes have been created. To date, the purpose of these studies is to find a simple formula for the effective production of fluorophores with predictable properties for a specific practical task.

As objects of this study are selected new coordination complexes of dipyrromethene with different ligands (Figure 1).The results have shown that alkyl- and phenyl-substituted difluoroborates of dipyrromethenes (BODIPY) are recommended as photostable liquid and solid-state laser-active media for visible and near IR-region (475-687 nm) with an efficiency of up to 90%.[2]

Substitution of halogen ("heavy" atom effect) of a dipyrromethene nucleus increases the intercombination conversion and the yield of T-states of dipyrromethenates. Such complexes are suitable for the development of sensory media for determining the oxygen concentration in the gas mixture at room temperature. Hetero-substitution of the dipyrromethene nucleus, in particular meso-aza-substitution, leads to formation of nπ*- and ππ*- states of different multiplicity, an increase in the intercombination conversion, and the change in the lifetime of T-states, which increases the sensitivity of sensory media.

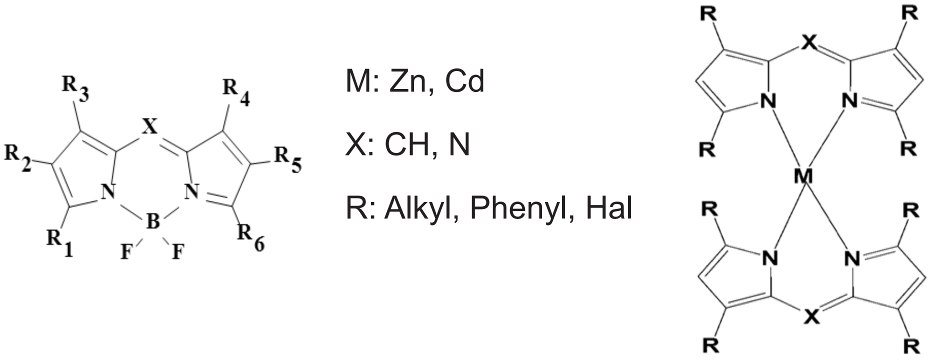

Figure 1. Structural formulas of the investigated compounds

Acknowledgments

This study was supported by the Russian Foundation for Basic Research (project no. 18-33-00284) and The Tomsk State University competitiveness improvement programme.

References

1. R.T. Kuznetsova et al., *J. Mol. Liq.* **2019**, *278*, 5.
2. R.T. Kuznetsova et al., *J. Photochem. Photobiol. A* **2018**, *354*, 147.

DIPYRROMETHENE METAL COMPLEXES: STUDY OF SPECTROSCOPIC CHARACTERISTICS AND PRACTICAL APPLICATION

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Currently, much attention is paid to obtaining sensors for biological systems. There are a large number of mechanisms for the realization of the fluorescence response, among which the effect of fluorescence enhancement caused by aggregation. Such sensors do not fluoresce in dilute solutions, but their emission flares up during aggregation. These materials are actively studied and find their application in many areas of sensory[1], however, most of these materials luminesce in the blue or green region. At the same time, the shift of the fluorescence bands to the region of the therapeutic window (650 - 1350 nm) is of great relevance in modern science.

Among all fluorescent sensors, luminescent dyes based on boron dipyrrin (BODIPY) luminophores stand out separately. This class of compounds possesses the necessary combination of physicochemical properties, namely, high quantum yields, high photostability, narrow absorption and fluorescence spectra, low toxicity, and simple modification route of the dipyrrin nucleus. And at the moment, only a few examples of modification of BODIPY structures are known, leading to a shift in the absorption and fluorescence maxima in the region of the therapeutic window.[2]

As an object of study, we took the 8-(3,5-dimethyl)-phenyl substituted BODIPY complex (Fig. 1). Earlier in our works[3], it was shown that the formation of aggregates in solid films is accompanied by a decrease in the intensity of the fluorescence band of the monomer and the appearance of a new peak corresponding to the aggregated form of the compound. But in the fluorescence spectrum of the investigated compound in a mixed solvent with a high proportion of water in the solution, we observe not one peak of the aggregated form, as expected, but 4 peaks. In this work, the concentration effects in solutions by successively increasing the dye concentration in the solution and varying the composition of the solvent (increasing the proportion of water in a binary mixture of tetrahydrofuran: water) was studied. It was shown that, in comparison to classical concepts, the dye aggregation in water is affected not only by the fraction of water, but also by the dye concentration, which allows one to obtain spectra of completely different shapes and with different peak ratios.

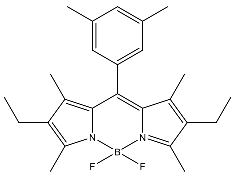

Figure 1. The structure of investigated compound

Acknowledgments

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References

1. J. Mei, N. L.C. Leung, R. T. K. Kwok, J. W. Y. Lam, B. Z. Tang, *Soar. Chem. Rev.* **2015***, 115,* 21.
2. Y. Ni, J. Wu, *Organic and biomolecular chemistry* **2014***, 12,* 23.
3. D. A. Merkushev, S. D. Usoltsev, Yu. S. Marfin, A. P. Pushkarev, D. Volyniuk, J. V. Grazulevicius, E. V. Rumyantsev, *Materials Chemistry and Physics* **2017***, 127.*

NEAR INFRARED LANTHANIDE LUMINESCENCE IN COMPLEXES WITH PERFLUORINATED MERCAPTOBENZOTHIAZOLATE LIGANDS

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Near infrared (NIR) luminescence is in demand in many modern technologies including telecommunication and bioimaging. The lanthanide ions Nd^{3+}, Er^{3+} and Yb^{3+} are natural luminescent centers which emit in the NIR range. The application of inorganic compounds of these ions has a drawback of high excitation powers that is caused by weak extinction of *f-f* transitions. To overcome this drawback these ions are usually bonded in complexes with perfluorinated antenna ligands.

To obtain efficient NIR emitters in our work we use a novel ligand–perfluorinated 2-mercaptobenzothiazole (mbt^F).[1] Recently we have synthesized the lanthanide ate-complexes with mbt^F ligands.[2] These complexes demonstrated a significant enhancement in intensity and lifetime of NIR luminescence despite the presence of numeric quenchers (C-H bounds) in their structure. In order to increase the NIR luminescence efficiency we have synthesized hydrogen-free complexes of NIR-emitting lanthanides (Fig. 1).

The use of non-solvating toluene as a solvent and perfluorinated tris(phenyl)phosphine oxide ($TPPO^F$) as a neutral hard-base ligand results in formation of highly NIR-emitting complexes of Nd and Yb, whereas the Er derivative emit both in visible and NIR range. Time-resolved luminescent studies of the complexes revealed that the lifetime of the NIR emission exceeds several tens of microseconds for Nd, Er and Yb ions. In the case of Nd derivative the value of the emission lifetime (40 μs) is among the highest ever reported for organic Nd complexes. The impact of ionizing irradiation on the photoluminescence properties of the compounds has been studied. It was found that no change in the luminescence spectra is observed after irradiation.

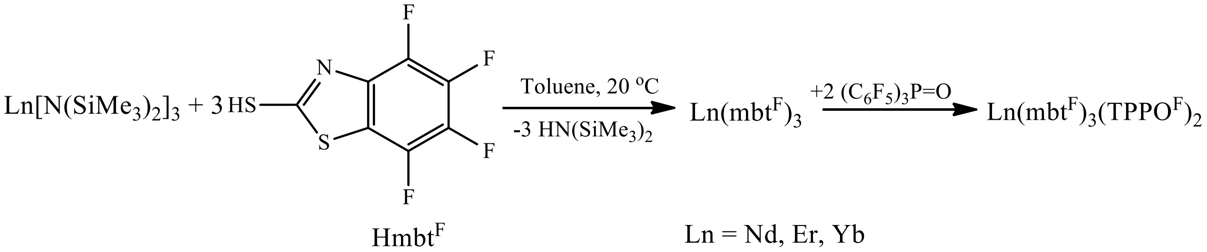

Figure 1. Synthetic scheme

Acknowledgments

This work was supported by RFBR grant № 18-33-00241.

References

1. V. A. Ilichev, L.I. Blinova, A.V. Rozhkov, T.V. Balashova, R.V. Rumyantcev, G.K. Fukin, M.N. Bochkarev, *J. Mol. Struct.* **2017**,*1148*,201.
2. V. A. Ilichev, L.I. Silantyeva, A.N. Yablonskiy, B.A. Andreev, R.V. Rumyantcev, G.K. Fukin, M.N. Bochkarev, *Dalton Trans.* **2019**,*48*, 1060.

SELECTIVE METAL COORDINATION TO POLYCYCLIC AROMATIC LIGANDS

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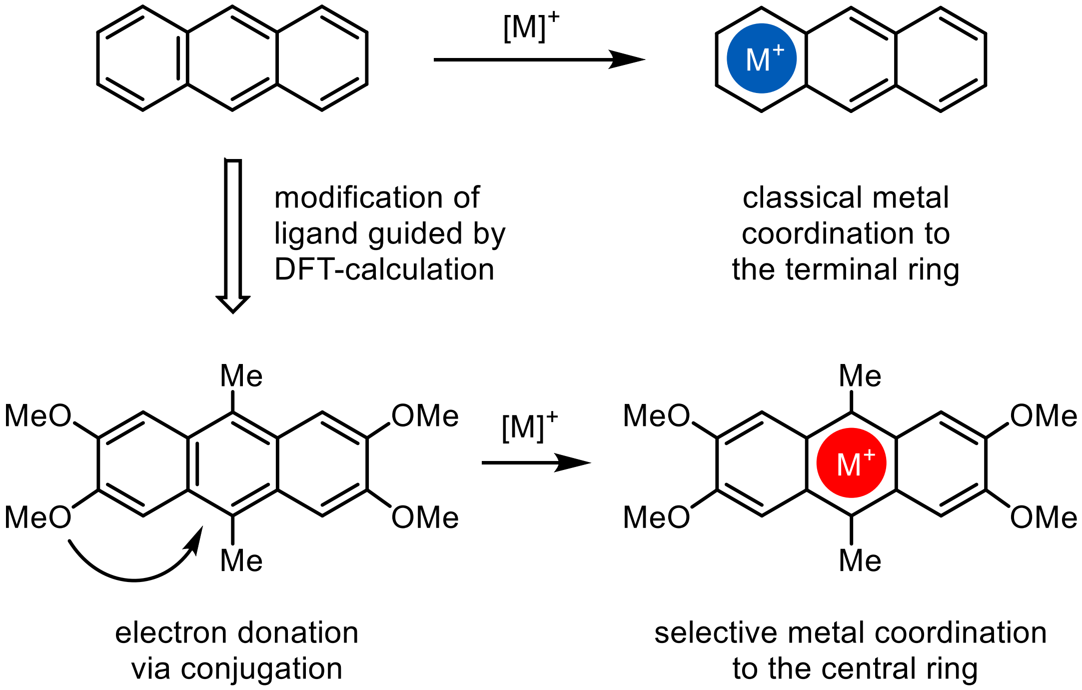
Polycyclic aromatic molecules attract a lot of attention due to their application as luminescent dyes and organic semiconductors. Their properties can be modified by selective metal coordination. Transition metals are known to coordinate only to the terminal rings of the polycyclic systems. However, we have recently developed a computationally guided approach for the coordination of organometallic fragments to the central ring anthracene. The ideas behind this approach and experimental results of its application will be presented.



Scheme 1. General approach for selective coordination of metals to polyarenes.

Acknowledgments

This work was financially supported by the Russian Science Foundation (grant 17-73-30036)

References

1. D. S. Perekalin, A. R. Kudinov, *Coord. Chem. Rev.* **2014**, *276*, 153.
2. E. E. Karslyan, A. O. Borissova, D. S. Perekalin, *Angew. Chem. Int. Ed.* **2017**, *56*, 5584.

3. POSTER PRESENTATIONS

Organoelement Compounds

CHEMISTRY OF HYDROPHOSPHORYL AND HYDROTHIOPHOSPHORYL COMPOUNDS

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Asymmetrical hydrophosphoryl and hydrotiophosphoryl compounds (HPS and HTPS) cover the field of chemistry of organic phosphorus compounds and become an interest for further research in order to find the most important biologically active drugs. In recent years, the preparation of semi-synthetic natural compounds on their basis is the most interesting in this field. These compounds are very promising and interesting because of their high reactivity, which allows them to proceed to a variety of derivatives.

The reactions between dithiophosphoric acid of dialkyl esters with orthoformate and the formation of dithiophosphorylated formals have been studied previously.

In order to synthesize new derivatives of asymmetric HPS and HTPS, we carried out the phosphorylation and thiophosphorylation reactions of orthoformate triethyl ester. This reaction proceeds under milder conditions without the presence of any catalysts at a moderate temperature with the release in equimolar amount of ethyl alcohol and obtaining the corresponding phosphorylated formals with asymmetric radicals under the phosphoryl group.

The resulting preparations became the new organophosphorus monomers for obtaining various amino derivatives in the field of chemistry of organophosphorus compounds.

For the next step we carried out the reaction of interaction of asymmetric phosphorylated formals with monoethanolamine vinyl ether. The reaction proceeds with the breaking of the bond between the atoms of the C-O-C group of phosphorylated formals and the N-H groups of the monoethanolamine vinyl ether; the corresponding new heteroatom-containing Schiff bases are formed as a result of the substitution reaction.

It is known that compounds containing azomethine group with more bulky phosphoryl and thiophosphoryl radicals are among the biologically active substances. The composition and individuality of the obtained compounds are confirmed by elemental analysis, TLC, and IR-spectroscopy.

In this regard, we will continue scientific research in the field of chemistry of asymmetric hydrophosphoryl-, hydrotiophosphoryl compounds and heteroatom-containing Schiff bases.

THE SYNTHESIS OF 1,3-OXAZOLIDINES AND 1,4-DIHYDRO-2H-3,1-BENZOXAZINES CONTAINING (η^6 ARENE)TRICARBONYLCHROMIUM GROUP

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The synthesis of transition metal complexes with N,O-heterocyclic ligands, such as 1,3-oxazacycloalkanes, is interesting both for applied and fundamental chemistry. The most perspective method for the synthesis of such π-complexes is the direct reaction of aromatic derivatives of 1,3-oxazolidines and 1,4-dihydro-2H-3,1-benzoxazines with $(NH_3)_3Cr(CO)_3$. As known, interaction of oxazolidines with carbonyl complexes leads to the opening of the heterocycle and the formation of n-donor type coordination compounds. We found that $CH_3C(O)$-, t-$C_4H_9OC(O)$-; a good protecting group is also a phenyl group. The complexation reaction with $(NH_3)_3Cr(CO)_3$ gives high yields of π-arene derivatives (Figure 1).

In the case of benzoxazines, due to the presence of conjugation, the process leads to the formation of π-complexes with absence of protective groups at the nitrogen atom (Figure 2).

The obtained products after isolation and purification were characterized using HPLC, UV-, IR-, ^{1}H NMR-spectroscopy, mass-spectrometry and X-ray diffraction.

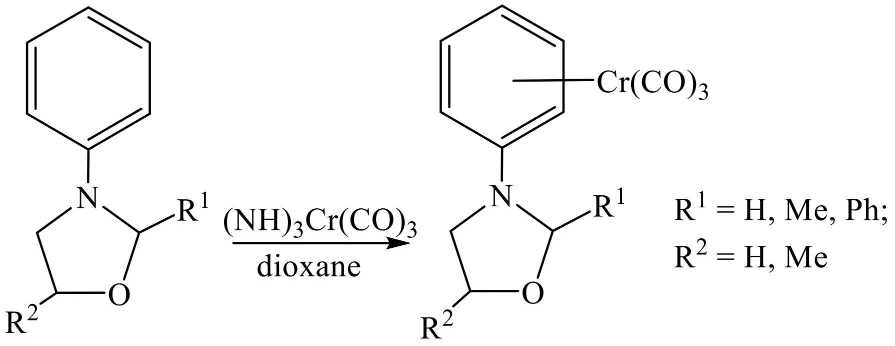

Figure 1. Reaction of phenyl-containing N-substituted 1,3-oxazolidines with $(NH_3)_3Cr(CO)_3$

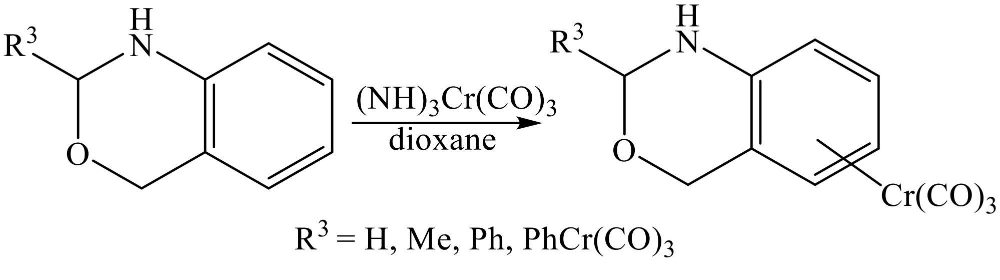

Figure 2. Reaction of1,4-dihydro-2H-3,1-benzoxazines with $(NH_3)_3Cr(CO)_3$

NOVEL BASE-INITIATED CASCADE REACTIONS OF HEMIINDIGOS TO PRODUCE DIPOLAR γ-CARBOLINES AND INDOLE-FUSED PENTACYCLES

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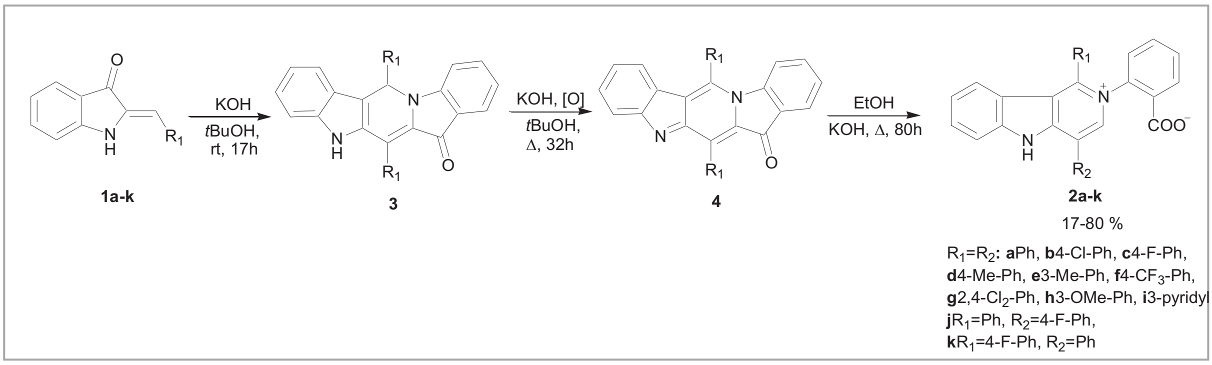
In a continuation of our research into transformations[1] of 2-arylideneindoxyls (hemiindigos) **1** we developed novel continuous-flow cascade reactions for producing 1,4-diaryl-disubstituted dipolar γ-carbolines **2** bearing a carboxylate group and their two indole-fused pentacyclic precusors **3, 4**. The γ-carboline skeleton is widely used in the design of agents against various diseases and represents a basic core of many clinically successful drugs. The synthetic utility and potential applications of **3, 4** were demonstrated by the initial antimycobacterial activity studies. The conjugated system of **3**, **4** resembles the ring system of rimino-compounds including antileprotic and antimycobacterial drug clofazimine possessing unprecedentedly high activity against drug-resistant and dormant tuberculosis.The promising *in vitro* antimycobacterial activity of **3**, **4** against both *Mycobacterium tuberculosis* H37Rv and isoniazid-resistant human isolate CN-40 was identified. It is believed that just the ring system of both rimino-compounds and **3**, **4** is responsible for the unique mechanism of their action. We hope the new scaffold we have found will be useful indeveloping lead agents against multidrug-resistant/dormant tuberculosis.

Scheme 1



R_1=R_2: **a**Ph, **b**4-Cl-Ph, **c**4-F-Ph, **d**4-Me-Ph, **e**3-Me-Ph, **f**4-CF_3-Ph, **g**2,4-Cl_2-Ph, **h**3-OMe-Ph, **i**3-pyridyl
jR_1=Ph, R_2=4-F-Ph,
kR_1=4-F-Ph, R_2=Ph

References

1. V. S. Velezheva, P. J. Brennan, V. Y. Marshakov, D. V. Gusev, I. N. Lisichkina, A. S. Peregudov, L. N. Tchernousova, T. G. Smirnova, S. N. Andreevskaya and A. E. Medvedev. *J. Med. Chem.* **2004**, *47*, 3455.

CARBORANE CONJUGATES OF β- ANDMESO-MALEIMIDE-SUBSTITUTED PORPHYRINS AND CHLORINS: SYNTHESIS AND BIOLOGICAL PROPERTIES

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Chemical modifications of tetrapyrrole-containing compounds are aimed at improving their characteristics as antitumor photosensitizers. Among the various porphyrin/chlorin derivatives that have been studied over the years, conjugates with boron polyhedra which were initially prepared as compounds for boron neutron capture therapy (BNCT), have demonstrated promising efficacy in PDT cellular and animal models. In this contribution we present a panel of new *β*- and *meso*-maleimide functionalized *meso*-arylporphyrins and chlorins. The selective reactivity of porphyrin/chlorin maleimides toward thiols was demonstrated using mercapto carboranes and cysteine, as a result, corresponding succinimide derivatives were obtained. Prepared porphyrins and chlorins demonstrated a remarkable ability to produce singlet oxygen (quantum yields > 70%). Peripheral substituents provided no steric hindrance for the formation of stable complexes with albumin, a major biological carrier. It was shown that new compounds were nontoxic in the dark whereas illumination of cells loaded with a cell permeable porphyrins and chlorins triggered rapid generation of superoxide anion radical concomitantly with a decrease of mitochondrial membrane potential and then the loss of the plasma membrane integrity and cell death.

The combination within one molecule porphyrin, carborane and maleimide structural moieties resulted in new compounds which are particularly pertinent to the development of anticancer agents with manifold activities such as photosensitizers and beyond.

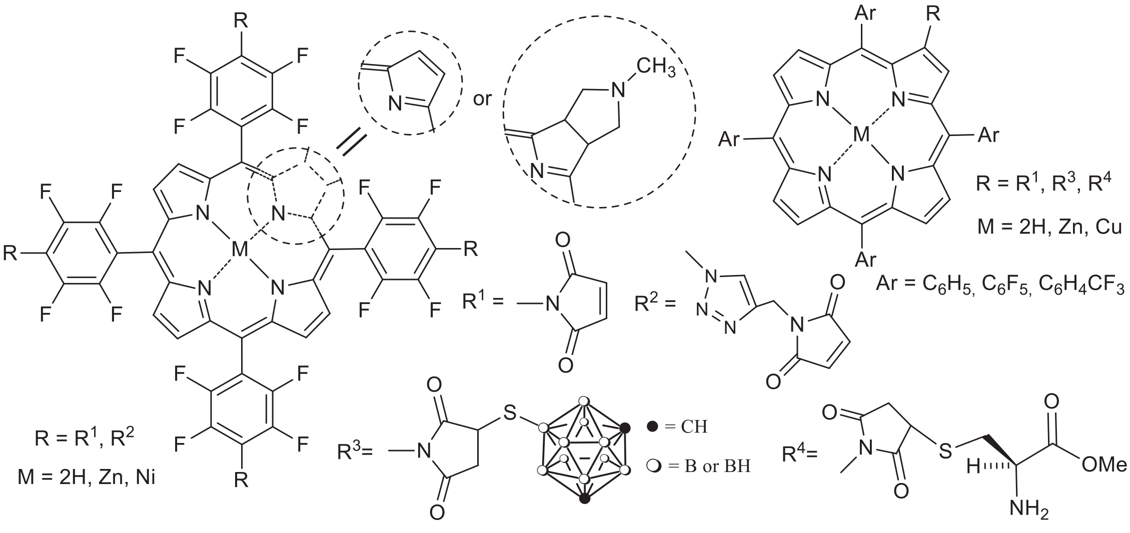

Figure 1. Structures of synthesized compounds

X-RAY DIFFRACTION ANALYSIS OF HYBRID MATERIALS BASED ON CARBON NANOTUBES AND NANOSIZED WO_3, CuO

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Carbon nanotubes and hybrid materials based on them due to a wide range of unique physical and chemical properties are extremely relevant objects in various fields of science and industry, including in the field of nanoelectronics. One of the most promising classes of such functional materials are multi-wall carbon nanotubes (MWCNTs) with nanoscale coatings of metal oxides, for example with such as coatings of tungsten oxide, tungsten carbide and copper oxide.

Earlier, in the Hybrid Nanomaterials Laboratory of the G.A. Razuvaev Institute of Organometallic Chemistry of RAS hybrid materials based on MWCNTs were synthesized by the method of deposition from the vapor phase of organometallic compounds. Coatings deposited on them during the pyrolysis of tungsten hexacarbonyl and copper formate.

The obtained materials were investigated by the powder X-ray diffraction method. The method allows us to determine qualitatively the phase composition of nanoshealths, and also to estimate the coherent-scattering regions, that is, to estimate the particle sizes of the nanophase.

Analysis of the samples was conducted on the Shimadzu XRD-7000 diffractometer (CuKα, λ = 1,54Å). All X-ray experiments were performed under the identical condition.

Acknowledgments

The reported study was funded by RFBR according to the research project № 18-33-00776.

THE EFFECT OF THE METALLOALKOXYSILOXANE FILLER STRUCTURE ON THE RESISTANCE OF THE POLYIMIDE COMPOSITES TO ATOMIC OXYGEN

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At the present time polymeric materials are widely used in the construction of modern spacecraft. One of the most used polymers in this area is polyimide (PI) due to its thermal properties but in its initial form, its operation in near-earth orbits showed low resistance to atomic oxygen (AO) and ultraviolet radiation. The solution to this problem may be filling the polyimide matrix with particles resistant to AO. A common way to obtain composite materials is the sol-gel method, in which the formation of filler particles occurs *in situ*. One of these fillers is silicon dioxide, its precursors are silicon alkoxides, metal alkoxides and silicates, the hydrolytic processes of which occur in the polymer bulk in a humid environment and in the presence of a catalyst and this impedes the widespread use of this method. The use of highly reactive precursors as metalloalkoxysiloxanes promote formation of inorganic structures in the polymer under normal humidity conditions[1].

This work is aimed at creating composites and studying the properties of the materials obtained, in which organosoluble PI is used as a matrix and metalloalkoxysiloxanes (M-siloxanes) of the general structural formula $M[O\text{-}Si(R)(OEt)_2]_n$, where M = Fe, Zr, Hf, and R = $-CH_3$, $-C_6H_5$ are used as precursors of particles.

When studying the properties of PI-based composites it was shown that they have a higher AO resistance than the initial polymer and when it is *in situ* filled the mass erosion coefficient decreases by more than an order of magnitude. It is established that the chemical structure of the alkyl group of M-siloxane refers to the factors of directional regulation of the material properties. The “change” of the phenyl substituent at the silicon atom with methyl substituent increases the resistance of the composites to AO. In addition, the resistance of the material can be varied by changing only the type of central metal atom (Fe, Zr, Hf). With the same “organosilicon environment” of M-siloxanes, the mass loss of composites based on them after AO irradiation decreases in the series: Zr-siloxane – Fe-siloxane – Hf-siloxane. The morphology of the initial samples and samples after exposure to oxygen plasma was studied by scanning electron microscopy.

Acknowledgments

This work was supported by RFBR (№18-03-00514) and Ministry of Science and Higher Education of the Russian Federation.

References

1. Tebeneva N.A., Tarasenkov A.N., Buzin M.I., et al.*Russian Chemical Bulletin* **2016***, 65, 4*, 1097.

PREPARATION OF FUSED HETEROCYCLIC COMPOUNDS VIA IODINE EXCHANGE

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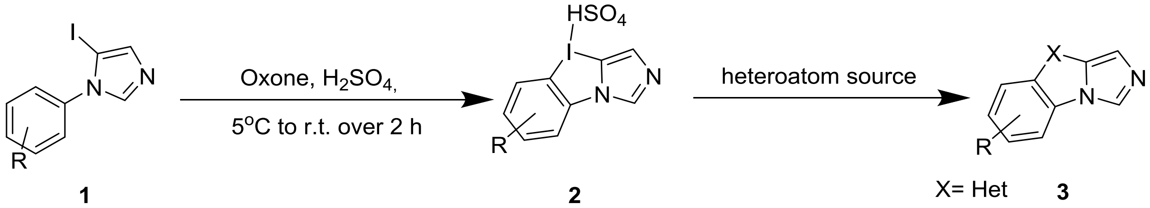
Diaryliodonium salts have a broad range of synthetic applications[1]. Cyclic iodonium salts are also extremely important reagents for the preparation of fused heterocycles[2] which are widely applying in organic electronics[3,4] and as biological active compounds[5]. Dibenziodolium salts can be readily prepared from the commercially available *o*-aryliodobenzenes via the simple oxidation[2]. Nevertheless, the preparation of cyclic iodonium salts containing heteroaryl moiety as C-ligand had been less discussed. In 2016 Shafir reported the route for the preparation of 1-aryl-5-iodoimidazoles containing a wide range of substituents[5]. These compounds are promising substrates for the formation of cyclic imidazolyl(aryl)iodonium salts, which can be applied for the synthesis of fused heterocycles.

Herein, we developed experimental procedure for the preparation of cyclic imidazolyl(aryl)iodonium salts by the oxidative ring-closure reaction of 1-aryl-5-I-imidazoles using cheap and available H_2SO_4/Oxone[6]. Furthermore, we demonstrated the synthetic applicability of prepared reagents in the iodane/heteroatom-exchange with the formation of merit heterocyclic systems.



Scheme 1

In summary, we developed a versatile approach to the preparation of imidazolyl-containing fused heterocycles via the formation of cyclic iodonium salts followed by iodine/heteroatom-exchange.

Acknowledgments

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References

1. A. Yoshimura, V.V. Zhdankin, Chemical reviews. **2016,** 116(5), 3328-3435.
2. N. Chatterjee, A. Goswami, *European Journal of Organic Chemistry*. **2017**, 21, 3023-3032.
3. X. Chen, H. Liu, L. Xia, T. Hayat, A. Alsaedi, Z. A. Tan, *Chemical Communications*. **2017**.
4. S. Dey, *Small.* **2019**, 15(21), 1900134.
5. Y. Wu, S. Izquierdo, P. Vidossich, A. Lledós, A. Shafir, *Angewandte Chemie International Edition*. **2016**, 55(25), 7152-7156.
6. P. S. Postnikov, O. A. Guselnikova, M. S. Yusubov, A. Yoshimura, V. N. Nemykin, V. V. Zhdankin, *The Journal of organic chemistry*. **2015**, *80*(11), 5783-5788.

A WAY TO NEW ORTHO-CARBORANE ARYLAZO DERIVATIVES

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The reaction of the diazonium salt of *ortho*-carborane $[3\text{-}N_2\text{-}1,2\text{-}C_2B_{10}H_{11}]BF_4$ with Grignard reagents has been described in the literature[1]. However, in our hands, the reaction with aromatic Grignard reagents in tetrahydrofuran instead of the expected aryl derivatives leads to arylazo derivatives of *ortho*-carborane (Figure 1). 3-Bromo and 3-$Br(CH_2)_4O$-*ortho*-carboranes were isolated as by-products.

The obtained compounds were characterized by NMR and mass spectroscopy, and the structures of the azo coupling products were determined by X-ray diffraction (Figure 2).

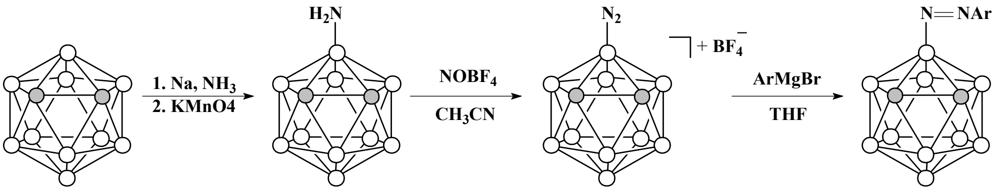

Figure 1. The synthetic route to arylazo *ortho*-carborane.

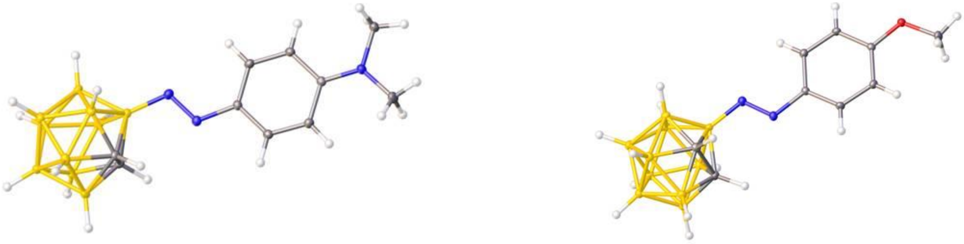

Figure 2. Some examples of X-ray structures of arylazo *ortho*-carboranes.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grants 18-33-00336 and 18-33-20115).

References

1. D. Zhao, I Z. Xie, *Chem. Sci.*, **2016**, *7*, 5635.

SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS VIA C–H ACTIVATION FOR ORGANIC LIGHT-EMITTING DEVICES

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Polycyclic aromatic hydrocarbons (PAHs) have found widespread applications in optoelectronics, bioimaging, and catalysis.[1] Of our special interest is the use of PAHs in the OLED technology. Significant recent impetus in synthesis of PAHs was gained by C–H activation of aromatic compounds by the cyclopentadienyl rhodium complexes $[(C_5R_5)RhCl_2]_2$.[2] In the present work, we demonstrated crucial influence of substituents in the cyclopentadienyl ring on chemoselectivity of oxidative coupling of aromatic carboxylic acids with internal alkynes. In particular, the use of the pentamethyl complex $[Cp^*RhCl_2]_2$ as a catalyst leads to isocoumarins as a result of incorporation of one alkyne molecule, while the parent non-methylated derivative $[CpRhI_2]_n$ facilitates decarboxylation of the acid and annulation of two alkyne molecules to give the naphthalene moiety.

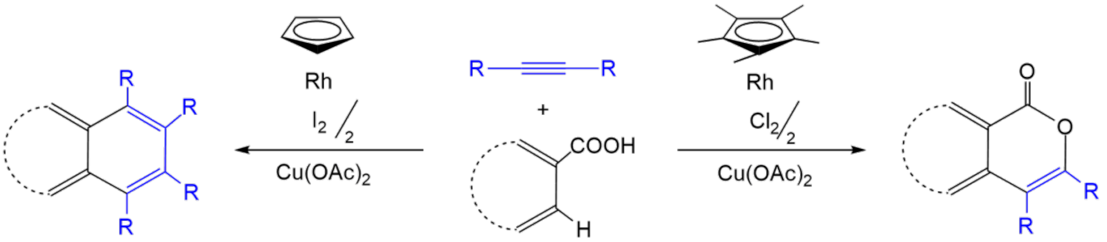

Figure 1.Synthesis of isocoumarin and naphthalene derivatives

The compounds prepared have rich optical properties with strong Stokes shifts of fluorescence emission. They were used for the OLED manufacturing as emissive layers.

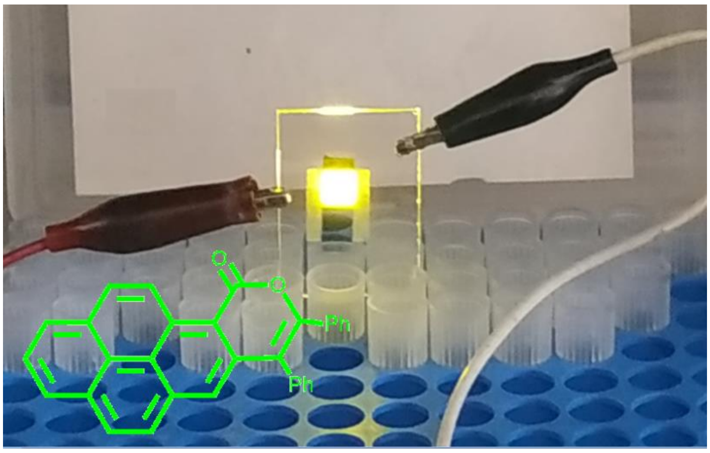

Figure 2. Working OLED structure based on 7,8-Diphenyl-10H-phenaleno[1,9-gh]isochromen-10-one

Acknowledgements

This work was supported by the Russian Science Foundation (Grant No. 17-73-30036).

References

1. J. E. Anthony, *Chem. Rev.* **2006**, *106*, 5028.
2. D. A. Loginov and V. E. Konoplev, *J. Organomet. Chem*. **2018**, *867*, 14.

STRUCTURAL-ENERGIES PROPERTIES OF ISOSTRUCTURAL ACETYLENE ALCOHOLS C_{15}, C_{20} AND THEIR SOLUTIONS

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Acetylene alcohols C_{15}, C_{20} of saturated and unsaturated series with isostructural methyl groups, bordered of fragments from four carbon atoms of alkyl chain, are prototypes of bioorganic compounds. That is whey an establishment structural-thermodynamic properties of these compounds allows to receive the important information on specific interactions, followed, specifically, from heat of mixing in case of binary solutions, and move to a determination of the value of these interactions. In this lecture we substantiate a insufficiently of the existing notion on H-network of liquid structures, tacked into consideration H-bonds and nonspecific interactions and ignored, for example, the interactions, which are realized in liquid methane with the energy about 2.0 kJ mol^{-1}. It is not quite notions about network of H-bonds which can display at clean type in water, analogical compounds of VI group elements and liquid ammonia. We use the ideas, expounded[1] at which takes into consideration: -substantiated refusal from sp^3-hybridization in CH_4 and molecules of elementorganic, organic compounds with alkyl ligand; - formation of specific interaction by essential nondivaided $2s^2$ electron pair of carbon atom, turned up at pentacoordinated state; - additional orbital dative type of interaction in electron structure of main group elements of compounds with saturated and unsaturated hydrocarbon chine [1, 2]; - employment of all bond vacancies of molecules at interaction in liquid and solid state; - enthalpy and entropy of evaporation are interconnected with number and energy of specific intermolecular interactions [3].

It is discussed first established experimental date of thermodynamic properties of vaporation process of acetylene alcohols C_{15}, C_{20} their solutions, isofitol and dihydrolinalool, values of which are not depended from number of CH_2-groups of chain and fragments (three, four), bordered of isostructural CH_3-groups , took part at a distribution of electron density in molecule. Fulfilled structural-energies discussing of thermodynamic properties and structures of liquid compounds with network of stable specific interactions, formed of OH- and end CH_3-groups and weak stable interactions, formed of isostructural CH_3-groups, which lead to the determination of values of energies of this bonds.

It was showed, that a positive deviation on isotherms of vapour pressure and negative on dependences of $\Delta H^0(T) = f(x)$, $\Delta S^0(T) = f(x)$ of solutions of the binary system C_{15} – C_{20} is conditioned by decreasing of the energy of H-bonds and stable specific interactions with participation of pentacoordinated carbon atom of end CH_3-group at a formed solvate structures. Supplementary contribution at destabilised effect of formed intermolecular interactions at the solutions bring a structural breach, prompted of different length of alkyl chains of interacted molecules of C_{15} and C_{20}.

We determined the values of the energies of H-bonds, a stable and week specific interactions, formed of pentacoordinated carbon atom of end and isostructural methyl groups correspondingly of isostructural alcohols C_{15}, C_{20}, their solutions and isofitol, dihydrolinalool.

Reference

1. Alexei K. Baev // 28th International Conference on Solution Chemistry. Debresen. Hungary. 2003. P. 79.
2. Baev A.K., Korolkov D.V., Book of Abstract the XVth FECHEM Conference on Organometallic Chemistry. University of Zurich. Svizeland. (2003) 350.
3. A.K. Baev. Specific Intermolecular Interactions of Organic Compounds. Springer. Hiedelberg, Dordrecht, London, New York. 2012. 434 p.

GENERALIZATION OF THE FOUNDERIC NEW IDIES AND CREATION OF THEORY SPECIFIC INTERACTIONS OF ORGANIC COMPOUNDS

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My scientist Prof. S.A. Schukarev, of the follower of D.I. Mendeleev, wrote at 1965 year (Sc. Petersburg, Univ.): “In the present time the science about substance survive special moment, in principle similar with that, which the history of human culture passed 100 years ago, at epoch of discovery by D.I. Mendeleev of the Periodical system chemical elements. Then invisible hypothetical atoms … roused at the eyes of the thinking humanity as deep at own maintenance reality on the height of new generalization, and appeared possibility to foretell the properties of still not open elements.” Using in this lecture wide specter thermodynamic investigations of organically compounds, we substantiate the necessity to proposal a new, non-stereotypic ideas, secured expose of the nature of specific intermolecular interactions and penetration in more deep of their understanding and apprehension for substantiation and development of theory types of this interactions, establish of values energetic parameters at which scientists required so march. Ander specific interactions follow to understand the interaction by bonding vacancies’ of atoms contacted molecules. Basis of substantiation of this interactions are thermodynamic

1. Pentacoordinated carbon atom forms specific intermolecular interactions at wide range values[1] energies, more tree-time overstepping of energy hydrogen bond 10.99 kJ .mol[1] of H_2O;
2. Novel kind of intramolecular interaction - rivers dative bond between carbon atom C alkyl ligand R and central atom A in complex AR_k C(2e)→A(0e), in its electron structure is consist;
3. Substantiated refusal from sp^3(c)-hybridization model of electron configuration of carbon atom;
4. Existence of essential no divided $2s^2$(c)-electron pair,
5. All bonding vacancies of a molecule must take part at a formation of specific intermolecular interactions;
6. Enthalpy (entropy) vaporization (sublimation) is interconnected with a number and energy of formed molecule of specific interactions [2].

investigations of phase reorganization of the processes vaporization and sublimation of alkyl compounds of the elements II – VI groups, another organic compounds and investigations[2] of condition compounds in gas phase, determination the energetic parameters of specific interactions monomer forms, law- governed nature of their changing and with all that this implies. Substantiated dimirisation at gas phase of alkyls aluminum with high dissociations energy dimer $Al_2(CH_3)_6$ и $Al_2(C_2H_5)_6$ correspondingly, are incontestable evidence participation pentacoordinated carbon atom at quality bonding vacancies at formation specific interactions[1]. It was established, that at mane atomic ketones and acetylene alcohols with fragments from four carbon atoms of chain, turned upon by isostructural methyl groups, prototypic proteins, vetch discussed at lecture.

References

1. A.K. Baev, Russ. J. Coordin. Chem. **1996,** 22. 399.
2. A.K.Baev. Specific Intermolecular Interactions of Organic Compounds. Springer. Hiedelberg, Dordrecht, London, New York. **2012**. 434

DEVELOPMENT OF NEW CHELATORS FOR RADIOPHARMACEUTICALS

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Radiopharmaceuticals are products containing one or more radionuclides. It is used for the treatment and diagnosis of cancer. The main component of pharmaceuticals is chelator, which binds a radioactive metal ion into a stable complex, so that it can be delivered to the desired molecular target in the body[1,2].

The currently existing chelators are limited mainly by derivatives of the azacrown-ether DOTA and the acyclic ligand DTPA, but they have some disadvantages. The aim of this work is to develop optimal macrocyclic and acyclic chelators suitable for use as components of radiopharmaceuticals with bismuth and copper. The idea of the work is to insert hard fragments into the chelator's structure, which increases the rate of complex formation and increases its stability[3].

In this work ligands with picolinate and carboxyl chelating groups were synthesized (Figure 1).

The complexation of ligands **1** and **2** with bismuth and copper was studied using NMR- and IR-spectroscopy, mass-spectrometry, elemental and X-ray diffraction analysis. The results obtained revealed differences in the properties of macrocyclic (**1**) and acyclic (**2**) chelators.

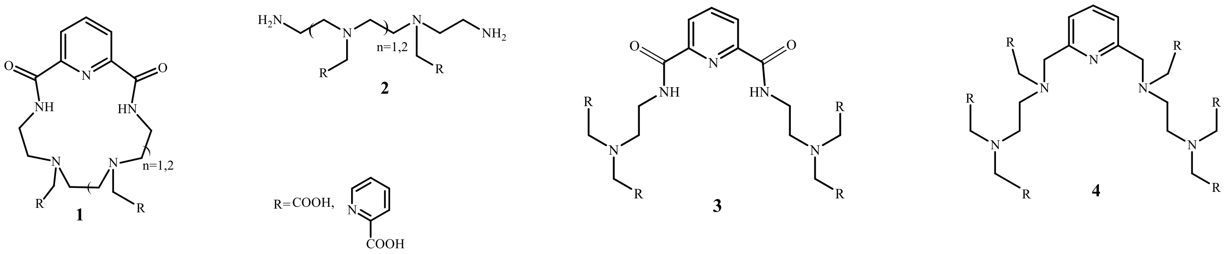

Figure 1. Synthesized chelators

Acknowledgments

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References

1. C. Ramogida, C. Orvig, *Chem. Commun.*, **2013**, *49*, 4720.
2. M. Jamous, U. Haberkorn, W. Mier, *Molecules* **2013**, *18*, 3379-3409.
3. А. Д. Зубенко, А. А. Бахарева, О. А. Федорова, *Успехи в химии и химической технологии*, **2018**, *32,* 35-37.

SYNTHESIS AND STRUCTURE OF GADOLINIUM COMPLEXES IN AQUEOUS SOLUTION OF CARBOXYLATE PHOSPHABETAINES

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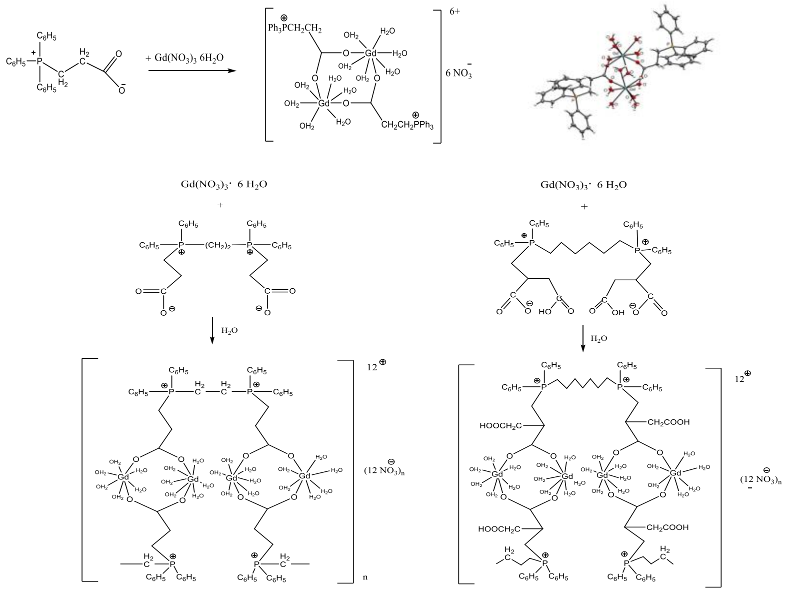
Gadolinium complexes are commonly used to improve the contrast of images obtained by Magnetic Resonance Imaging. Unfortunately, gadolinium ion is highly toxic in its hydrated form $[Gd(H_2O)_8]^{3+}$, its complexation with an organic ligand reduces this toxycity and form thermodynamically very stable compounds [1]. Earler we showed that a series of new mononuclear and heteronuclear complexes of carboxylate phosphonium betaines with biologically important metals (Zn(II), Cd(II), Hg(II) and Cu(II)) were obtained in aqueous media at ambient temperature. X-ray single crystal diffraction showed that carboxylate phosphonium betaines exhibit versatile complexation abilities, producing monomeric, dimeric and tetrameric homonuclear and mixed metal complexes [2]. In this work we have studied the formation of colorless gadolinium complexes with mono- and diphosphonium betaines in aqueous solution.



The structure of the complexes have been established by chemical, physical, and physicochemical methods. The thermal stability was studied by synchronous thermogravimetry and differential scanning calorimetry (TG-DSC).

Acknowledgments

The work is performed according to the Russian Government Program of Competitive Growth of KFU.

References

1. T. J. Volg, W. Pegios, Mc. Mahon, *American J. of Roentgenology.* ***1992***, *158, 887.*
2. I. Galkina, A. Tufatullin, D. Krivolapov, Yu. Bakhtiyarova et al. *CrysEngComm.* ***2013***, *16, 9010.*

SYNTHESIS AND STRUCTURE PHOSPHONIUM SALTS, BASED ON 3-(DIPHENYLPHOSPHINO)PROPIONIC AND Ω-HALOALKYLCARBOXYLIC ACIDS

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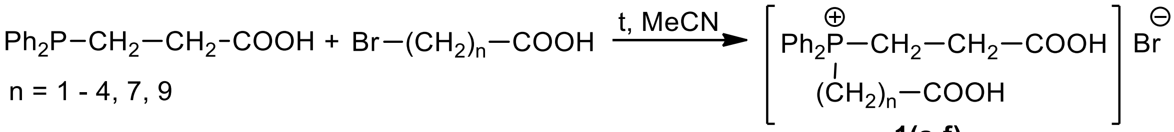
Carboxylate phosphabetaines and phosphonium salts are of particular interest in the chemistry of organoelement compounds. These compounds can exhibit biological and catalytic activity[1] and act as ionic liquids.[2] In previous work, we presented a method for the synthesis of carboxylate phosphonium salts, based on tertiary phosphines and ω-haloalkylcarboxylic acids.[3]

In this work, we synthesized new phosphonium salts **1(a-f)** based on 3-(diphenylphosphinopropionic and ω-haloalkylcarboxylic acids (Scheme 1). The reaction proceeds in acetonitrile with boiling in a water bath.



$$Ph_2P-CH_2-CH_2-COOH + Br-(CH_2)_n-COOH \xrightarrow{t,\ MeCN} \left[\underset{(CH_2)_n-COOH}{\overset{\oplus}{Ph_2P}}-CH_2-CH_2-COOH \right] \overset{\ominus}{Br}$$

n = 1 - 4, 7, 9

1(a-f)

Scheme 1.

All compounds synthesized in good yields and characterized by IR-, NMR-spectroscopies and elemental analysis. X-ray analysis was performed for one compound **1a**.

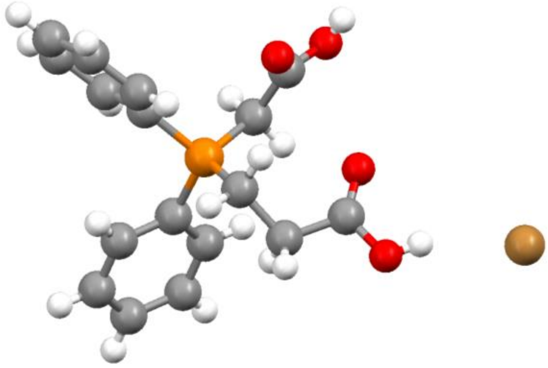


Figure 1. X-ray analysis of phosphonium salt **1a**

Decarboxylation is observed for many phosphonium compounds with α-arrangement of the carboxylic group.[4] However, in this study we were able to obtain new phosphonium salts with carboxylic group, located in α-arrangement.

Acknowledgments

This work was funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (№. 4.5888.2017/8.9)

References

1. D. Xu, H. Wei, Y. Zhen, Y. Gao, *Org. Chem. Front.* **2019**, 6, 1981.
2. D. Wei-Lia, J. Bia, L. Sheng-Liana, L. Xu-Biaoa, *Appl. Catal. A-Gen.* **2014***,* 470, 183.
3. S. R. Romanov, A. F. Aksunova, Yu. V. Bakhtiyarova, I. V. Galkina, Phosphorus Sulfur, **2016**, 191, 1637
4. Yu. V. Bakhtiyarova, R. I. Sagdieva, I. V. Galkina, R. A. Cherkasov, *Russ. J. Org. Chem.* **2007**, 43, 215.

NOVEL DONOR-ACCEPTOR LUMINOPHORES BASED ON TRIPHENYLAMINE

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The development of novel organic luminophores and materials based on them, which are emitting light in the long wavelength ranges of the visible spectrum, seems to be an extremely urgent task at the moment because of their wide range of applications. One approach to obtaining such luminophores is the use of long π-conjugated blocks in combination with strong electron-withdrawing groups. The application of this approach can significantly reduce the LUMO energy levels of the obtained molecules and, as a result, leads to a narrowing of the bandgap with a significant bathochromic shift of both the absorption and luminescence spectra. However, an excessive increase in the length of the conjugation, on the one hand, leads to a significant increase in crystallinity, and, on the other hand, leads to the appearance of effects of internal quenching of luminescence due to nonradiative transitions of internal conversion and vibrational relaxation. A way to circumvent these limiting factors is to use a donor-acceptor concept. This strategy can allows, with a minimum number of aryl and heteroaryl units, to efficiently shift the luminescence spectrum to the long wavelength region without a strong loss in solubility, due to the intramolecular charge transfer from the donor to the acceptor part of the molecule.

In this paper, we report the synthesis of novel triphenylamine-based donor-acceptor luminophores with various electron-withdrawing groups. The complex of physicochemical methods was used to study the optical and thermal properties, as well as the phase behavior of the obtained luminophores. All compounds demonstrate effective luminescence both in dilute solutions and in an individual form. In addition, various polymer films and composite materials based on the developed luminophores were obtained.

Acknowledgments

This study was supported by a grant from the Russian Foundation for Basic Research (project no. 18-29-17073)

MODEL OF SELECTIVITY ON METHYL NONANOATE OF 1-OCTENE HYDROCARBOMETHOXYLATION CATALYZED BY $Pd(PPh_3)2Cl_2$ / PPh_3 / p-TOLUENESULFONIC ACID SYSTEM

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Three isomeric esters are formed in the mild conditions in 1-octene hydrocarbomethoxylation catalyzed by $Pd(PPh_3)_2Cl_2$ / PPh_3 / p-toluenesulfonic acid (TsOH) system. The main of them is methyl nonanoate which can used as a half-product in the medicinal substance synthesis. Kinetic models and models of selectivity frame necessary foundation for hydrocarbalkoxylation process technologies.

The kinetic experiments were conducted in the periodic reactor in toluene medium at 378 К and P_{CO}=2 MPa. The procedures of experiments and analyses of the reaction mass were described earlier.[1]

Five serieses of monofactor experiments on the effects of methanol, $Pd(PPh_3)_2Cl_2$, PPh_3 and TsOH concentrations and CO pressure on 1-octene hydrocarbomethoxylation were conducted. The methyl nonanoate concentrations (C_1) dependences on the general concentration of three products ($C_1+C_2+C_3$) of reaction in each experiment were constructed. In each experiment these dependences had a linear character with correlation coefficient from 0.992 to 1.00. The differential regioselectivity in each experiment was calculated as tangent of straight slop angle C_1 on ($C_1+C_2+C_3$). The reaction regioselectivity was practically constant in examined interval $C(Pd(PPh_3)_2Cl_2)=(0.1\text{-}1.5)\cdot10^{-2}$ M and became equalized 63.5±2.4 %. According to PPh_3 concentration increasing from 0 to $4.8\cdot10^{-2}$ M the regioselectivity was increasing and got to 81.1 %. TsOH concentration rise in interval $(0.6\text{-}6.0)\cdot10^{-2}$ M invited regioselectivity decreasing from 77.0 to 58.7 %. According to CH_3OH concentration increasing from 0.03 to 0.60 M the regioselectivity passed through the minimum. At P_{CO} increasing from 1.0 to 5.0 MPa regioselectivity was decreasing non-linearry from 77.6 to 68.9 %.

For the first time the model of regioselectivity on methyl nonanoate was obtained as equations system – regioselectivity dependences on CO pressure, methanol, PPh_3 and TsOH concentrations. The model workes at the total reaction way up to the high conversions of 92.5%. The explanation to arranged dependences was given in the limits of exhibitions about 1-octene acid-catalyzed isomerization to 2-octene, hydride many-route mechanism of esters formation, electronic and steric effects in palladium catalytic complexes which contained PPh_3 and CO ligands.

Acknowledgments

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References

1. V.A. Aer'yanov, S.A. Batashev, N.T. Sevostianova, V.M. Zarytovsky, *Catalysis in Industry* **2005**,*2*, 25.

MAGNESIUM AND ZINC CYANOPHENOXY-PHTHALOCYANINE COMPLEXES. STYNTHESIS AND SPECTROSCOPIC-LUMINESCENT PROPERTIES

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The unique structure of phthalocyanine molecules opens up opportunities for research chemists to create, on the basis of these data complexes, devices of new generation and applications with promising applied properties. One of the most important field of application of materials based on phthalocyanine macrostructures is medicine. Due to the complexation of the phthalocyanine ligand with the luminescent-active metal atom, it becomes possible to obtain highly effective fluorescent biological markers for various deviations in the human body. Based on this, this work describes the synthesis and study of the spectral-luminescent properties of cyanophenoxy-substituted peripheral complexes of phthalocyanines with zinc and magnesium as central atoms.

The synthesis was carried out by fusing substituted phthalonitrile with anhydrous acetate of the corresponding metal at a temperature of about 180 °C (**Figure 1**). The resulting alloy was filtered and washed with chloroform to get rid of polymer-type impurities. Further purification was carried out using column chromatography on silica gel M60 using a mixture of chloroform-acetone as an eluent (gradiently increasing the concentration of acetone from 0 up to 5 vol.%). The structure of the compounds obtained was confirmed by IR, NMR and electronic absorption spectroscopy, mass spectrometry and elemental analysis.

For the complexes obtained, electronic absorption spectra were recorded in a number of organic solvents, extinction coefficients were determined, and the aggregation parameters in these media were studied. The quantum yields of the synthesized phthalocyaninates relative to unsubstituted zinc phthalocyanine were calculated.

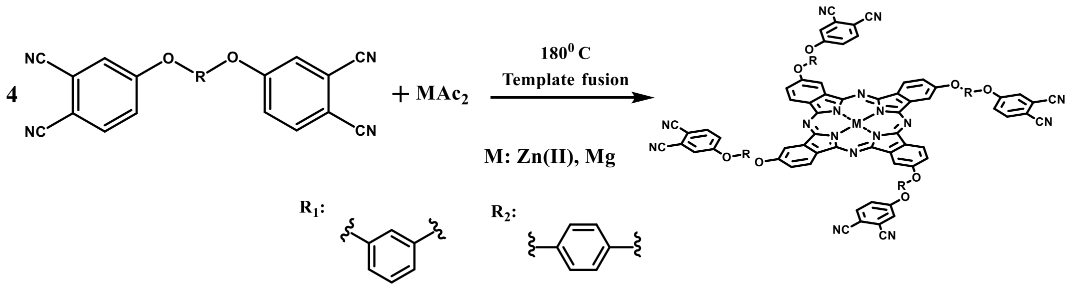

Figure 1. Template synthesis of cyano- substituted Mg and Zn complexes

Acknowledgments

The work was supported by Russian Federation President grant SP-541.2019.4.

ANION EFFECT ON THE CUMENE HYDROPEROXIDE DECOMPOSITION IN THE PRESENCE OF CU(II) 1,10-PHENANTHROLINATES

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The systems based on hydroperoxides (ROOH) and transition metals compounds are widespread initiator ones for the radical processes of organic compounds oxidation. Transition metals salts decrease the activation barrier of the ROOH decomposition reaction and contribute to the radicals formation in the system at temperatures close to room temperature. Metal reactivity can be regulated by using of compounds that capable to selection and catalyst binding. The use of Cu(II) complex compounds [1, 2] has proved to be successful in this direction. The purpose of this work is study of catalytic activity of complexes of 1,10-phenanthroline (Phen) with Cu(II) salts (CuX_2, X: $NO_3^–$, $SO_4^{2–}$,$CH_3COO^–$, $Cl^–$) in the cumene hydroperoxide decomposition reaction.

Kinetic studies of cumene hydroperoxides decomposition in the presence of of Phen with CuX_2 were carried out in conditions of the ROOH excess in the system at 313 K. Reactions were carried out in water : ethanol (1:1) mixture in a thermostated glass reactor in an inert atmosphere. The ratio of CuX_2 and Phen was 1:2. The kinetic curves of ROOH decomposition in the presence of CuX_2 - Phen complexes are presented on Fig. 1. Introduction of indicated amount of $Cu(NO_3)_2$ with Phen (Fig. 1, curve 1) not lead to ROOH decomposition.

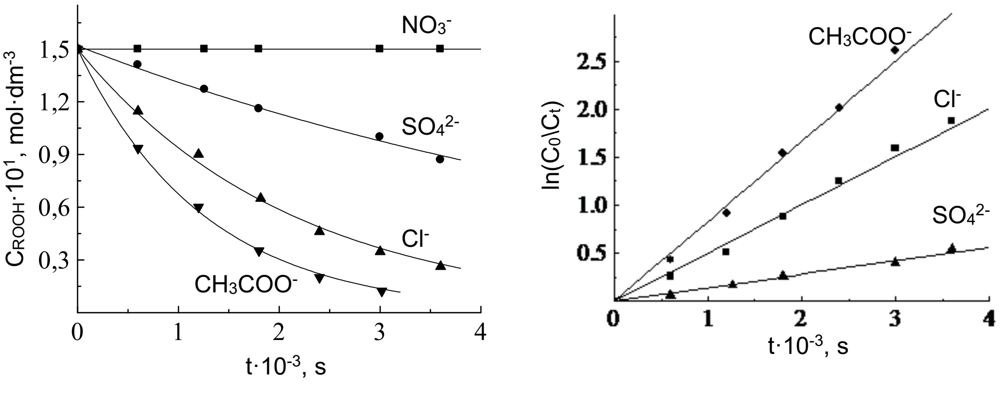

Figure 1. The kinetic curves of cumene hydroperoxide decomposition in the presence of Phen with $Cu(NO_3)_2$ (1), $CuSO_4$ (2), $CuCl_2$ (3), $Cu(CH_3COO)_2$ (4). ($[ROOH]_0$ = $1{,}52\cdot10^{-1}$ mol·dm^{-3}, $[CuX_2]_0 = 4\cdot10^{-3}$ mol·dm^{-3}; $[Phen]_0 = 8\cdot10^{-3}$ mol·dm^{-3})

The kinetic curves anamorphous were linear in the corresponding first-order coordinates (Fig. 1). The value of the reaction effective rate constants increase in the following row of anions: $SO_4^{2–} < Cl^– < CH_3COO^–$. This indicates that reactivity of the CuX_2 - Phen system depends on the salt anion nature.

References

1. T. Punniyamurthy, L. Rou, *Coordin. Chem. Rev*. **2008**, 252, 134.
2. G. B. Shul'pin, J. Gradinaru, Yu. N. Kozlov, *Org. Biomol. Chem*. **2003**, 1, 3611.

RESEARCH OF THE REACTION OF OXIDATION OF THIOLS IN THE PRESENCE OF METAL COMPLEXES

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The study of chemical and biochemical reactions occurring in the presence of a transition metals, is gaining popularity. Typically, such reactions are a model for the study of enzymatic processes.

Actively ongoing research related to the study of intracellular signal transduction and oxidative modification of sulfur-containing compounds, especially thiols different nature.

The method of ATR-FTIR spectroscopy was used to study the oxidation of *L*-cysteine in the presence of hydrated ions or complexes of transition metals Cu(II) and Fe(III) depending on the pH and the nature of the anion in the solution.

It has been found that the oxidation of *L*-cysteine to *L*-cystine in the presence of transition metal salts of Cu(II) and Fe(III), proceeds rapidly with metal reduction to Cu(I) and Fe(II). In this case, the yield of *L*-cystine is 24-37%.

Introduction of chelate complexes of Cu(II)[1] in the reaction of oxidation of *L*-cysteine resulted in a decrease of the reaction rate. This made it possible to establish intermediate reaction products (Fig.1) and to assign their characteristic absorption frequencies. It is interesting that the oxidation of *L*-cysteine in the presence of salts containing the anions SO_4^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ also proceeds rather slowly for 24 hours and leads to *L*-cystine with a yield of up to 99%.

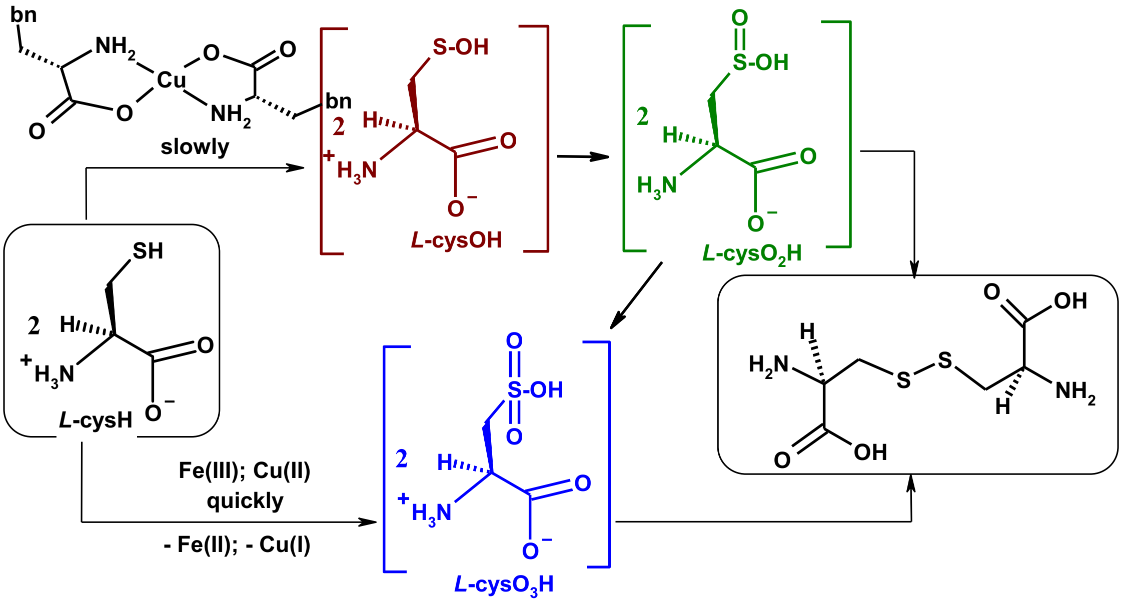

Figure 1. The found intermediates of *L*-cysteine oxidation in solution

References

1. Berestova T.V., Kuzina L.G., Amineva N.A., Faizrakhmanov I.S.; Massalimov I.A., Mustafin A.G., *J. Mol. Struct.*, **2017**, *1137*, 260.

NEAR INFRARED LANTHANIDE LUMINESCENCE IN COMPLEXES WITH PERFLUORINATED MERCAPTOBENZOTHIAZOLATE LIGANDS

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Polyaminoboranes, inorganic polymers that are valence isoelectronic to ubiquitous polyolefins, can be accessed through metal complex catalysed dehydropolymerisation of primary amine boranes.[1] Recent studies from our group and others were mainly focussed on mid-to-late transition metal catalysts.[2] In contrast, examples for early transition metal complexes that catalyse the selective formation of polyaminoboranes are comparably rare.[3] In view of the above mentioned analogy between C-C and B-N and thus polyolefins and polyaminoboranes it is however highly desirable to extend the field of available catalysts to early transition metal complexes as well. Along with this, several questions such as control of molecular weights and polymer stereochemistry become of interest.

In this contribution, we present a rare example of a group 4 metal complex $[(Cp_2ZrCl)_2(\mu\text{-}Me_3SiC_3SiMe_3)]$ (**1**) for catalytic dehydropolymerisation of methylamine borane ($H_3B{\cdot}NMeH_2$).[3] Comparisons with other related precatalysts and mechanistic studies suggest that the dinuclear motif of the precatalyst is essential for efficient dehydrogenation and polymer growth at the metal complex (Figure 1).

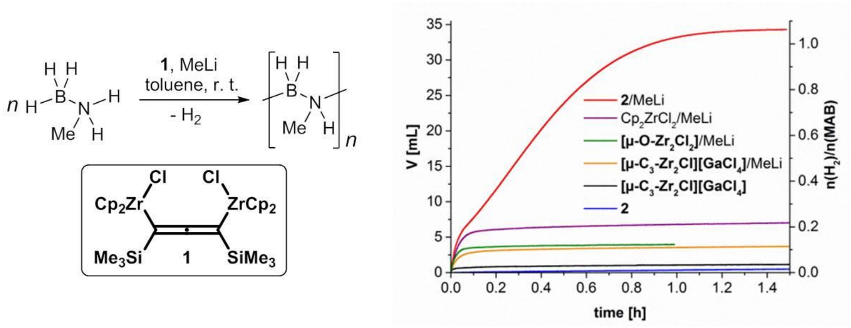

Figure 1. Zirconocene catalysed dehydropolymerisation of $H_3B{\cdot}NMeH_2$.

Acknowledgments

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References

1. a) D. Han, F. Anke, M. Trose, T. Beweries, *Coord. Chem. Rev.* **2019**, *380*, 260; b) H. Johnson, T. Hooper, A. Weller, *Top.Organomet.Chem.* **2015**, 153.
2. *Selected recent examples:* a) G. M. Adams, D. E. Ryan, N. A. Beattie, A. I. McKay, G. C. Lloyd-Jones, A. S. Weller, *ACSCatal.* **2019**, 3657; b) D. A. Resendiz-Lara, N. E. Stubbs, M. I. Arz, N. E. Pridmore, H. A. Sparkes, I. Manners, *Chem. Commun.* **2017**, *53*, 11701; d) F. Anke, D. Han, M. Klahn, A. Spannenberg, T. Beweries, *Dalton Trans.* **2017**, *46*, 6843; e) A. Glüer, M. Förster, V. R. Celinski, J. Schmedt auf der Günne, M. C. Holthausen, S. Schneider, *ACS Catal .***2015**, *5*, 7214.
3. T. Jurca, T. Dellermann, N. E. Stubbs, D. A. Resendiz-Lara, G. R. Whittell, I. Manners, *Chem. Sci.* **2018**, *9*, 3360.
4. M. Trose, M. Reiß, F. Reiß, F. Anke, A. Spannenberg, S. Boye, A. Lederer, P. Arndt, T. Beweries, *Dalton Trans.* **2018**, *47*, 12858.

SYNTHESIS OF HYBRID POLYMERIC MATERIALS WITH BODIPY AND THEIR USE AS SENSORS

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Measurement of fluorescence parameters serves as one of the promising investigation methods in modern science, including analytical chemistry, molecular biology and material science. The BODIPY fluorescent probes are attracting considerable interest in this area. They exhibit high fluorescence quantum yields and extinction coefficients whilst possess severe photostability. Furthermore, they generally have narrow excitation and emission bands, which are situated invisible region and could be precisely shifted via structural modification. Due to this unique combination of properties, BODIPY dyes are effectively utilized as selective ion sensors[1], for environment polarity measurement[2], as active components of thermo responsive polymers[3], pH sensitive membrane materials[4] and in some other precise responsive technologies[5,6], such as environmental sensors in biochemical studies[7]. Functional hybrid materials are of high interest in this exact area, since use of dye solutions is not technologically convenient in many cases. Pure and modified silicon dioxide materials are noteworthy among other polymers due to the combination of high achievable optical transparency, chemical inertness, thermal stability and ease of precise alteration of morphological characteristics. Organic polymers such as polymethylmethacrylate (PMMA), polysulfone (PSU), polyvinyl chloride(PVC) and ethyl cellulose can also be used.

This study describes the synthesis and fluorimetric characterization of pH/polarity sensitive BODIPY dyes. Five BODIPY dyes with different substituents at *meso*-position were investigated in thin films and bulk polymeric materials.

Hybrid materials have been obtained. The dependences of spectral properties of dyes depending on the matrix were obtained. Dependence of quantum fluorescence yield on viscosity of sol-gel systems in different matrixes is obtained. The possibility of using hybrid materials as sensors on pH, the polarity of the medium, as well as their stability under the influence of intense UV radiation has been studied.

Acknowledgments

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References

1 K. Rurack, et al. *J. Am. Chem.Soc.* **2000**, 122, 968
2 M. V. Shipalova, A. V. Bobrov, et al. *Journal of Mol. Liq.* **2019**, *283*, 688
3 D. Gong, et al., *Sensors Actuators B Chem*. **2017**, 252, 577
4 M. Hecht,et al.*J. Analyst*. **2013**, 138, 325
5 Y. S. Marfin, et al. *J. Fluoresc* **2014**, 24, 1613
6 M. L. Vetter, et al.*J. ChemBioChem* **2014**, 15, 1317
7 R.-H. Yeh, et al.*J. Biol. Chem*. **2002**, 277, 11527

TOWARDS AUTOMATIC PROCESSING OF ESI-MS DATA: THE CASE STUDY OF THE PALLADIUM CHLORIDE PRE-CATALYST

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Nowadays, there is a strong demand for high throughput experimentation (HTE) and screening (HTS) in the industry and academia. The automation of experiments together with the state of the art machine learning approaches allows performing a wide-scale search for new compounds and reactions[1]. However, HTE and HTS require a fast and reliable approach to automatically analyze acquired big data and, ideally, to interpret the data on the fly. Mass spectrometry (MS) with automatic analysis of spectra can play an essential part in this paradigm[2].

MS plays an essential role in chemical experimentation. With the development of electrospray ionization (ESI) it became a conventional tool for analysis of complex reaction mixtures making simultaneous detection and (to some extent) quantitative analysis of multiple compounds possible. Nevertheless, some spectra are hard to analyze on the fly and require a significant amount of man-hours for the interpretation. As a model example, $PdCl_2$ in acetonitrile exhibits a rather complex ESI-MS spectrum. At the same time, $PdCl_2$ is a conventional catalyst precursor in many cross-coupling and functionalization reactions which are of significant interest for the community. Hence, the application of automated methods could advance the research process of these catalytic reactions. Currently, such approaches are more common in the so-called “omics” research, while the application in chemistry is comparably less developed[3,4]. Thus, the main goal of the present work is to estimate the utility of available free software for the automated analysis of ESI-MS spectral data on a model case of $PdCl_2$ solution in acetonitrile.

Our method will be based on the application of recently developed methods for analyzing MS data[5]. The majority of such approaches is based on easy to apply Python[6]. The data will be analyzed automatically by processing MS. The result will consist of an automatic pipeline where compounds will be identified, and mass spectra will be interpreted and plotted on demand for the end-user. Consideration of the model case of $PdCl_2$ is our first step towards the automated processing of real-time ESI-MS data of Pd-catalyzed reactions, which will enable performing HTE and HTS for complex homogeneous catalytic systems.

References

1.J.M. Granda, L. Donina, V. Dragone, D.L Long, L. Cronin, *Nature*, **2018**, *559,* 7714
2. J. Lin, C. Masui, R. Lieu, K. Zhang, *Spectroscopy* **2019**,*17*, 3.
3. M. Katajamaa, M. Orešič, *Journal of chromatography* **2007** *1158*,1-2.
4. Z.Lai, H. Tsugawa, G. Wohlgemuth, S. Mehta, M. Mueller, Y. Zheng, A. Ogiwara, J. Meissen, M. Showalter, K. Takeuchi, T. Kind, *Nature methods* **2018**, *15,* 53.
5. M. Strohalm, D. Kavan, P. Novák, M. Volný, V. Havlíček, *Analytical Chemistry* **2010**, *82*, 11
6. L. Y. Geer, S. P. Markey, J. A. Kowalak, L. Wagner, M. Xu, D. M. Maynard, W. Shi, S. H. Bryant, *Journal of Chemical Information and Modeling* **2019** *59*, 4

“CLICK” SYNTHESIS AND ELECTROCHEMICAL BEHAVIOUR OF REDOX-ACTIVE PYRIDYLPHENYLENE DENDRIMERS

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Redox-active dendrimers are well-defined hyperbranched macromolecules whose ability to electron-transfer process determines their applications in redox catalysis, ion-sensing and molecular electronics. Among different types of the dendritic structures, the shape-persistent rigid dendrimers possess their own unique properties since they have constant shapes and prevent backfolding of the peripheral functional groups. Recently, we combined the redox properties of ferrocenyl groups with the explicit shapes of pyridylphenylene dendrimers into novel organometallic macromolecules.[1]

In the present study, we demonstrate the superior synthetic protocol to be both efficient and clean. It comprises the copper-catalyzed azide-alkyne cycloaddition between ethynyl-terminated pyridylphenylene dendrimers and azidomethylferrocene. Six novel ferrocenyl-containing dendrimers of 1-3 generations were prepared and characterized (^{1}H, ^{13}C NMR, GPC and MALDI-ToF) in this way (Figure 1).

The redox properties of the resulting dendrimers were studied using the cyclic voltammetry technique (CV). The strong adsorption onto the Pt electrode occurs during CV and makes it possible to fabricate the stable modified electrodes coated with dendrimer. The resulting electrodes are stable towards washing with organic solvents and proved to be able to recognize transition-metal ions.

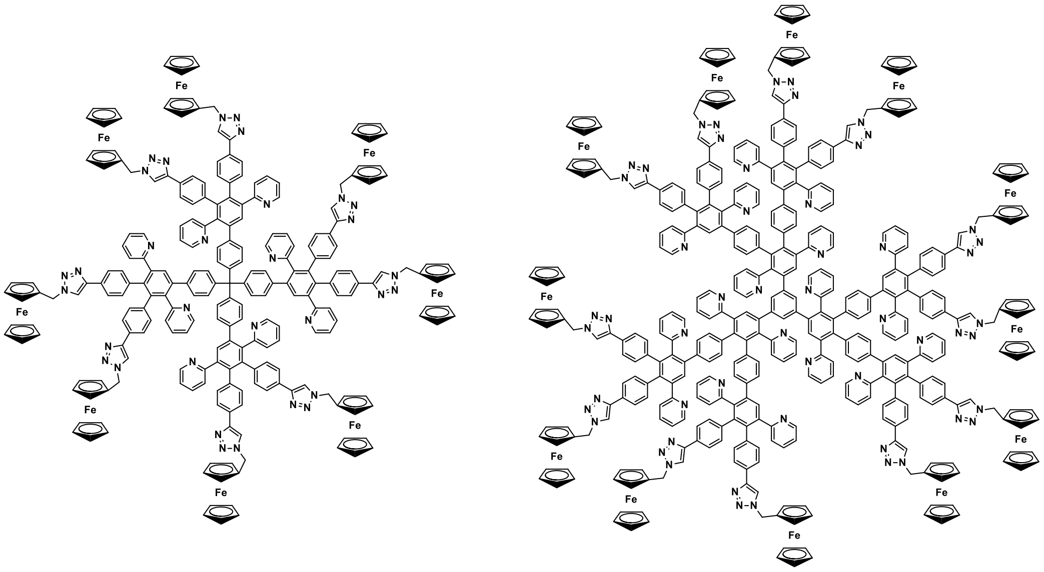

Figure 1. Redox-active pyridylphenylene dendrimers of the first two generations.

Acknowledgments

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References

1. E. S. Serkova, A. A. Chamkin, K. L. Boldyrev, V. V. Novikov, A. S. Peregudov, Z. B. Shifrina, *Polymer* **2019**, *173*, 34.

TWO SYNTHETIC PATHWAYS FOR THE PREPARATION OF THE 4-PYRIDYL-TERMINATED IRON(II) CAGE COMPLEXES WITH NON-EQUIVALENT CAPPING GROUPS: TRANSMETALLATION VS DIRECT TEMPLATE CONDENSATION

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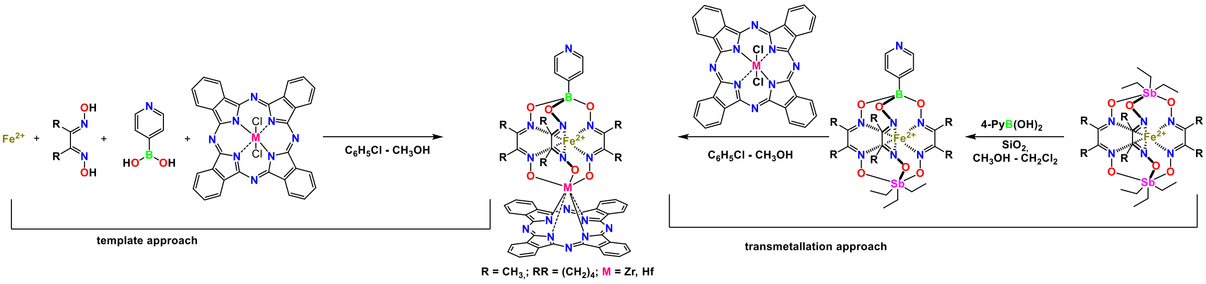
Cage metal complexes (clathrochelates[1]) with terminal reactive, donor or biologically relevant group(s) are prospective, chemically robust, three-dimensional molecular platforms and macrobicyclic building blocks for the design of new types of (photo)electronic devices, modern functional materials and prodrugs as well.

Ditopic metallophthalocyaninato-capped[2,3] macrobicyclic iron(II) dioximates can be prepared by a transmetallation of their labile triethylantimony-capped macrobicyclic precursors using the metal(IV) phthalocyaninates as Lewis acids (*transmetallation approach*). Recently, we succeeded in the synthesis of these hybrid compounds using the metallophthalocyaninato-capped iron and nickel(II) tris-pyridineoximates[4] using an efficient synthetic pathway based on a direct *one-pot* template condensation of 2-substituted pyridineoximes with zirconium and hafnium(IV)phthalocyaninates on the corresponding metal(II) ion as a matrix (*template approach*). Both of these approaches allowed us to obtain the new 4-pyridyl-terminated iron(II) cage complexes with non-equivalent capping groups by Scheme 1.



Scheme 1.

The above complexes were characterized using elemental analysis, UV-Vis, MALDI-TOF MS, IR,^{1}H and ^{13}C{^{1}H} NMR spectra and by the single crystal X-ray diffraction as well.

Acknowledgments

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References

1. Ya.Z. Voloshin, I.G. Belaya, R Krämer, *Cage metal complexes: clathrochelates revisited,* Springer, Heidelberg, **2017**.
2. Y. Z. Voloshin, O. A. Varzatskii, S. V. Korobko, V. Ya. Chernii, S. V. Volkov, L. A. Tomachynski, V. I. Pehn'o, M. Yu. Antipin, Z.A. Starikova, *Inorg. Chem*. **2005**, *44*, 822
3. G.E. Zelinskii, S.V. Dudkin, A.S. Chuprin, A.A. Pavlov, A.V. Vologzhanina, E.G. Lebed, Y.V. Zubavichus, Y. Z. Voloshin, *Inorg. Chim. Acta* **2017**, *463*, 29.
4. S. V. Dudkin, S. A. Savkina, A. S. Belov, Y. Z. Voloshin, *Macroheterocycles* **2018**, *11*, 418.

SYNTHESIS OF NEW LIPOPHILIC AMINOPHOSPHINE OXIDES BY THE PUDOVIK REACTION

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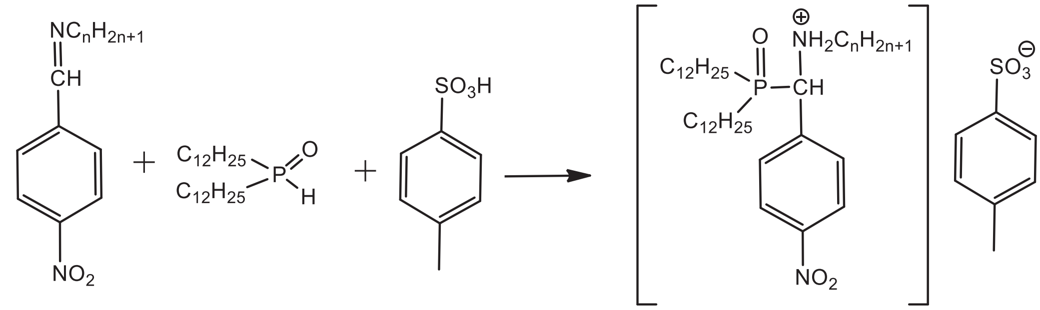
We have developed a new approach to the directed synthesis of physiologically active substances based on the Pudovik reaction. Amination of p-nitrobenzaldehyde with long chain aliphatic amines provides condensation products - imines, the phosphorylation of which in the presence of a salt-forming agent / catalyst (p-toluenesulfonic acid) in benzene leads to the formation of the corresponding α-aminophosphin oxides.



n = 12 (**1**), 14 (**2**), 16 (**3**), 18 (**4**)

Figure1. Scheme of Pudovic reaction

It was found that compounds 1-4 potentially have a wide spectrum of biological effects. In particular, a study of the biological activity of compound **2** showed that for a 1% solution in ethanol, the maximum growth inhibition zone was 22 mm for *S. Aureus*, 17 mm for *B. Cereus*, 16 mm for *Salmonella*.

Compound **2** was isolated in the form of crystals; its molecular structure is shown in Figure 2.

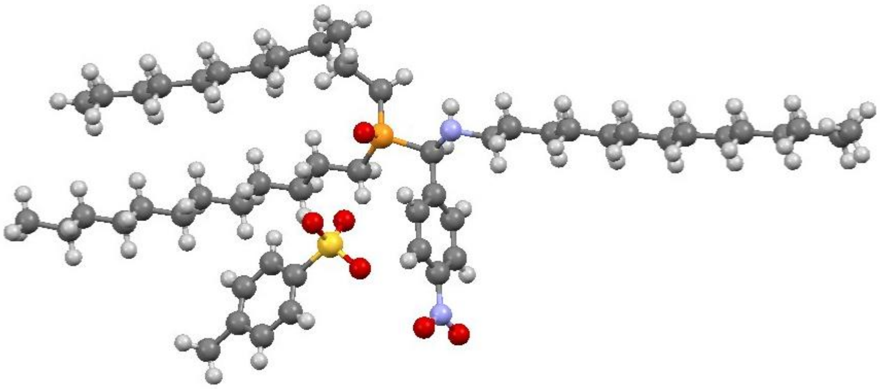


Figure 2. The molecular structure of compound 2 obtained by X-ray diffraction analysis

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MEMBRANE EXTRACTION OF RARE-EARTH METAL IONS BY NEW BISPHOSPHORYLDIAMINES AND BISPHOSPHORYLDIAZAPODANDS

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We have studied the processes of membrane transport of Nd (III), Sm (III), Gd (III) and Sc (III) by the diaminophosphoryl carriers I–VI of the general formula $[R_2P(O)CH_2NH]_2Z$, where R = C_8H_{17} (I-III), $CH_3C_6H_4$ (IV-V), R = C_6H_5 (VI); Z = $(CH_2)_4$ (I), $(CH_2)_6$ (II) $(CH_2)_3O(CH_2)_2O(CH_2)_3$ (III, V),$(CH_2CH_2O)_2CH_2CH_2$ (IV, VI).The influence of principal parameters of the three-phase extraction process, including the concentration of rare-earth metal, the extracting agent concentration in the membrane, and the nature of the membrane on the flow permeability, characterizing the efficiency and selectivity of membrane transporters, was established.

It has been established that the replacement of donor alkyl groups at the phosphoryl center with acceptor p-tolyl groups in carriers III and V leads to a decrease in ion flows. The flows of transmembrane transfer of metals induced by I-V are presented in table.

№	Flow $J_i \cdot 10^5$ mol/m^2 min			
	Nd(III)	Sm(III)	Gd (III)	Sc (III)
I	9.9 ± 0.1	7.5 ± 0.7	3.3 ± 0.1	3.7 ± 0.4
II	**129.3 ± 6.1**	**93.2 ± 9.3**	**54.8 ± 2.9**	**28.3 ± 3.3**
III	66.0 ± 6.3	64.1 ± 6.2	3.2 ± 0.2	66.2 ± 6.7
IV	31.7 ± 4.2	38.1 ± 3.8	26.5 ± 1.9	1.3 ± 0.1
V	29.8 ± 1.9	26.3 ± 2.6	24.0 ± 1.9	6.1 ± 0.7

It was found that the flows for diphosphorylated diamine II are superior to those for phosphorylated diazapodands III-V, which indicates a greater contribution of the PCH_2N fragment of carrier molecules to the transport of substrates than polyester oxygen atoms.

Using the IR spectroscopy method, the participation of P = O and C-O-C groups of carrier molecules in complexation with rare-earth metal ions is proved.

The procedure for conducting experiments on the active transport of neodymium, samarium, and gadolinium ions using carrier II was optimized. The active process of these metals was studied and permeability for different membrane solvents was calculated.

This work funded by the subsidy allocated to Kazan Federal University for the state assignment in the sphere of scientific activities (№ 4.5888.2017/8.9)

COPPER (I) BROMIDE COMPLEXES BEARING PHOSPHOLANYLPYRIDINES

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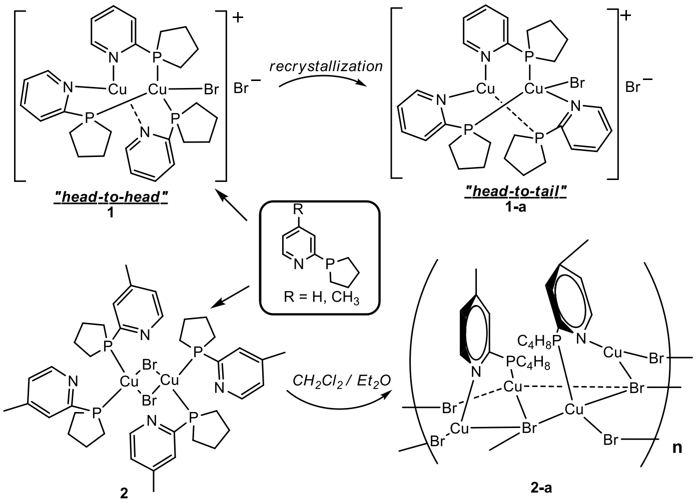
Polynuclear copper (I) halide phosphine complexes attracted considerable attention due to their diverse structures, photoluminescence properties and wide applications in material science [1, 2]. Recently we demonstrated a series of polynuclear copper (I) iodide complexes based on the novel P,N-hybrid ligands – P-pyridylphospholanes [3]. Herein we represent synthesis and structural features of P-pyridylphospholanes complexes with CuBr.



Scheme 1

Interaction of CuBr with P-pyridylphospholane in the ratio 2:3 led to formation of binuclear cationic $[L_3Cu_2Br]Br$ complex (**1**) whereas the same metal:ligand ratio between P-pyridylphospholane and CuI gave neutral $[L_3Cu_2I_2]$ complex with butterfly-shaped metal-halide core [3]. Noteworthy that complex **1** has “head-to-head” structure and its recrystallization from ethanol the “head-to-tail” isomer (**1-a**) was isolated. Reaction of CuBr with ligand excess resulted to a neutral $[L_4Cu_2Br_2]$ complex **2**. After crystallization of **2** using vapor diffusion of diethyl ether into its CH_2Cl_2 solution, a 1-D coordination polymer **2-a** with unique $(CuBr)_n$ chain was obtained.

Acknowledgments

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References

1. S. Naik,J. Mague, et.al.,*Inorg.Chem*. **2014**, 53, 3864
2. K. Chen, J. Shearer, V.J.Catalano, *Inorg. Chem*. **2015**, 54, 6245
3. E.I. Musina, A.V. Shamsieva, I.D. Strelnik, et.al., *Dalton.Trans*. **2016**, 45, 2250

INTRAMOLECULAR ELECTRON TRANSFER IN COPPER (II) COMPLEXES WITH ARIL-IMIDAZO-1,10-PHENANTHROLINES

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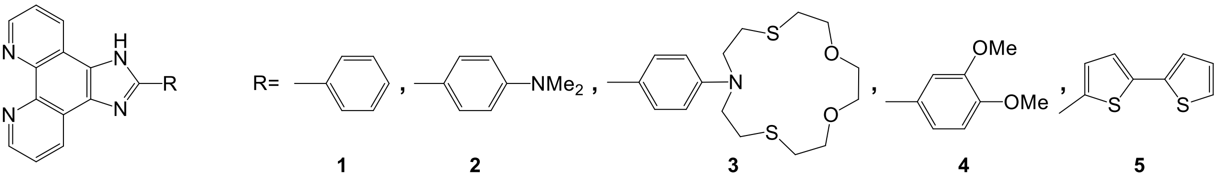
1H-imidazo[4,5-f][1,10]phenanthrolines containing phenyl- (1), 4-(N,N-dimethylamino)phenyl- (2), 4-(azadithiacrown-ether)phenyl- (3) 3,4-dimethoxyphenyl- (4) and 2,2'-bithiophen-5-yl- (5) were synthesized and their Cu(II) complexes were studied to determine the effect of substituent, geometry of complex and solvent nature on the spectral and redox properties of the copper complexes. It was found that in case of 4-(N,N-dimethylamino)phenyl- and 4-(azadithiacrown-ether)phenyl substituents the formation of $L_2 \cdot Cu^{2+}$ complex of pseudo-tetrahedral geometry causes the appearance of an intense metal-to-ligand charge transfer (MLCT) band at the visible region and induces a positive shift in the reduction potential providing the occurrence of autoreduction of Cu(II). Density functional theory (DFT) and its extension to time dependent density functional theory (TD-DFT) were performed to study the molecular structure, electronic and spectroscopic properties of copper with the 4-(N,N-dimethylamino)phenyl-1H-imidazo[4,5-f][1,10]phenanthroline ligand (2). The calculation results are in agreement with those obtained from optical measurements. Electrochemical study showed that the autoreduction is observed when Cu^{2+}/Cu^{+} transfer and oxidation of ligand occur at the closed electrochemical condition.



1 2 3 4 5

Acknowledgements

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SYNTHESIS AND CHARACTERIZATION OF NOVEL TRANSITION METAL OXO- CLUSTERS

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While the coordination chemistry of monometallic complexes and the surface properties of extended metal particles are well understood, the control of metal nanocluster formation has remained challenging. Discrete metal nanoclusters constitute unique molecular architectures between the regimes of monometal coordination compounds and larger particles.[1-2] The synthesis of metal nanoclusters has direct ramifications for the understanding of nanoparticle growth, materials design, metal-catalyzed reaction mechanisms, and biological processes.

Starting with simple bivalent iron and cobalt amide precursors we envisioned synthesis of unprecedented pyridonate oxo-clusters. Structural characterization (XRD), reactivity tests and catalytic investigations have been performed.

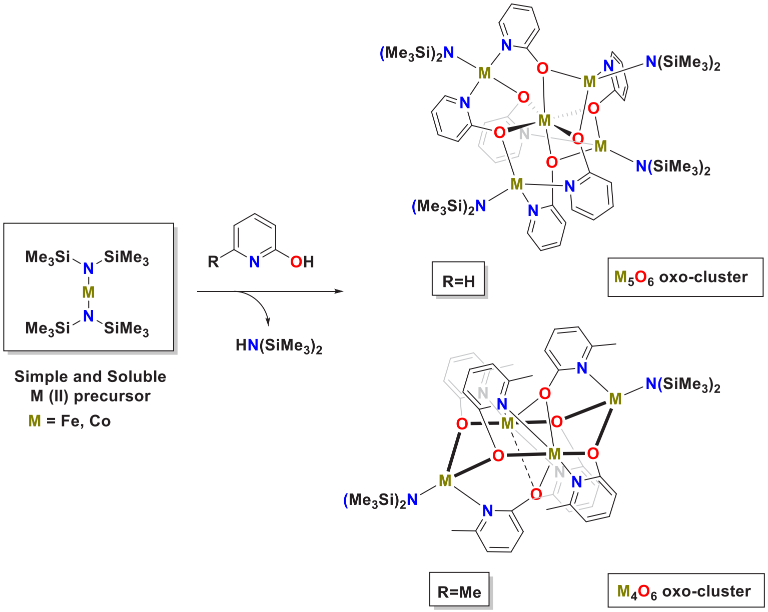

Figure 1. Synthesis of Fe and Co oxo-clusters

References

1. I. Chakraborty, T. Pradeep, *Chem. Rev.* **2017**, *117*, 8208.
2. P. Braunstein, L. A. Oro, P. R. Raithby, *Metal Clusters in Chemistry*, Wiley-VCH, Weinheim, **1999.**

BINUCLEAR COMPLEXES $(BATH)_2GD_2(PIV)_6$•XSOLV: THE EFFECT OF THE STRUCTURE ON TERMAL BEHAVIOR AND MAGNETIC AND LUMINESCENT PROPERTIES

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Solution chemistry methods were developed, resulting in the controllable formation of single-phase single crystals of binuclear complexes $(bath)_2Gd_2(piv)_6\cdot 2EtOH$ (**1a**·2EtOH, triclinic, *P-1*), $(bath)_2Gd_2(piv)_6\cdot 2EtOH$ (**1b**·2EtOH, Monoclinic, *C2/c*), and$(bath)_2Gd_2(piv)_6\cdot H_2O$[1] (**1c**·$H_2O$, Monoclinic, *I*2/a), where piv is $(CH_3)_3CCO_2^-$ and bath is 4,7-diphenyl-1,10-phenanthroline. **1a**·2EtOH, **1b**·1.5EtOH, and **1c**·$0.75H_2O$ were characterized by single-crystal X-ray diffraction. For complexes **1** the scattering spectra, the absorption spectra, as well as the photoluminescence (PL) spectra at 300 and 77 K were studied, the luminescent properties were analyzed, the quantum yields of the PL of singlet S_1 and triplet T_1 levels were calculated at 300 and 77 K, as well as the energy S_1 and T_1 levels, which amounted to 27742, 27746 and 27771 cm^{-1} and 20100, 20899 and 19954 cm^{-1} for **1a**·2EtOH, **1b**·2EtOH and **1c**·H2O, respectively. For complexes **1** the magnetic properties were investigated by SQUID magnetometry in the temperature range of 2-300 K, the main magnetic characteristics are obtained, the nature of the magnetic coupling between gadolinium(III) ions in **1** was determined, a theoretical interpretation of the magnetic behavior in the temperature range of 2-300 K is proposed, Zeeman splitting was taken into account in the calculations.In addition, EPR spectra indicate that Gd(III) ions interact with each other, and half-field EPR signals characteristic for dimers are observed. The spectra can be simulated using relatively weak exchange coupling (J~1-3 cm^{-1}) and broad distribution of D tensor components, which noticeably vary from one complex to another. The affect of the molecular and crystalline structure of binuclear complexes $(bath)_2Ln_2(piv)_6$•xSolv, where x = 0-2 and Solv is H_2O or EtOH, on the features of their thermal behavior below the decomposition temperature, and the optical and magnetic properties are considered.

Acknowledgments

This study was supported by the Russian Foundation for Basic Research (Project No. 19-03-00252).

References

1. I.G. Fomina, Zh.V. Dobrokhotova, V.O. Kazak, G.G. Aleksandrov, K.A. Lysenko, L.N. Puntus, V.I. Gerasimova, A.S. Bogomyakov, V.M. Novotortsev, and I.L. Eremenko, *Eur. J. Inorg. Chem.*, **2012**, *22*, 3595.

PD-CATALYZED ENANTIOSELECTIVE ALLYLIC SUBSTITUTION WITH DIASTEREOMERIC DIAMIDOPHOSPHITE-THIOETHER LIGANDS FROM GLUTAMIC AND TARTARIC ACIDS

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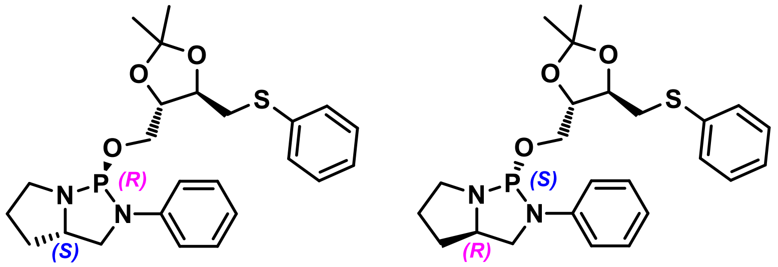
Novel diastereomeric *P**,*S*-diamidophosphites (S_C,R_P)-**1** and (R_C,S_P)-**1** (Figure 1) were obtained *via* direct phosphorylation of ((4*S*,5*R*)-2,2-dimethyl-5-((phenylthio)methyl)-1,3-dioxolan-4-yl)methanol by (5*S*)- or (5*R*)-3-phenyl-2-chloro-1,3-diaza-2-phosphabicyclo[3.3.0]octanein toluene in the presence of an excess of Et_3N as a base. In turn, the phosphorylating reagents are easy to produce using natural (*S*)- and unnatural (*R*)-glutamic acids, respectively. Stereo individual ligands (S_C,R_P)-**1** and (R_C,S_P)-**1** are readily purified by flash chromatography, are freely soluble in convenient organic solvents, are capable of long-term storing in a dry atmosphere, and can be produced in gram-scale quantities. Their structure was confirmed by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy techniques(including ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC two-dimensional NMR spectroscopy) and elemental analysis.



(S_C,R_P)-**1** (R_C,S_P)-**1**

Figure 1. Novel*P**,*S*-bidentate diamidophosphite ligands.

The results of their preliminary testing in palladium catalyzed allylation reactions (using [Pd(π-allyl)Cl]$_2$ as the precatalyst) are presented on Figure 2 (quantitative conversion took place in all cases).

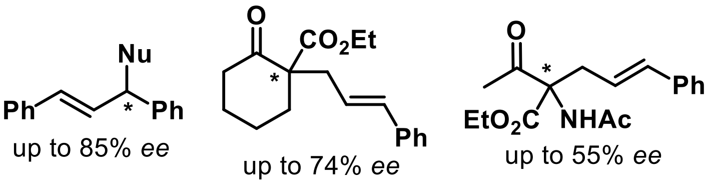


Figure 2. Enantioselectivity in Pd-catalyzed allyl substitution using novel *P**,*S*-diamidophosphites.

Acknowledgments

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OXIDATION OF HYDRIDE AND P-TOLYLSILOXANES: DEVELOPMENT OF CATALYTIC APPROACHES

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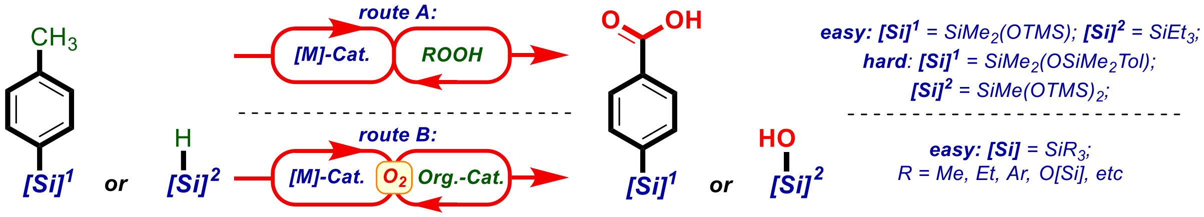
Organosilicon chemistry was the slower developing field of chemistry compared to organic chemistry. So, much methods for obtaining [Si]-derivatives, functionalized ones, in particular, still are time-consuming, require harsh conditions, stoichiometric amounts of toxic and expensive reagents producing waste (some of them are commercially unavailable) which provokes Si–O-, Si–C- and other bonds destruction. Sometimes these methods are of low functional group tolerance.[1]

On the other side, functionalized siloxanes are believed to widen the fields of applicability of such compounds. So, developing of "green" and commercially available systems for functionalization of siloxanes is an actual task. Green chemistry, is thought, will became the only suitable approach for selective synthesis of siloxanes with complex structures.

Two target types of compounds were chosen for elaboration of suitable method: siloxanols and *p*-carboxyphenylsiloxanes. They can be obtained *via* oxidation of easily accessible hydride siloxanes and *p*-tolylsiloxanes.

Well proven peroxide and metal combination was the first system to be tried for these oxidations (Scheme 1, *route A*).[2,3] After optimizing the conditions we concluded, that this system allows simple compounds to be oxidized with high conversions (such as triethylsilane and *p*-tolylpentamethyldisiloxane), but requires more harsh conditions for more complex ones.

Then O_2 was chosen as the most abundant, eco-friendly and mild oxidant in combination with transition metal and organic catalyst. After optimizing the conditions we found out that this approach is applicable for oxidation of both hydride and *p*-tolylsiloxanes of varios structures in good conversions and yields (Scheme 1, *route B*).[4,5]



Scheme 1

Acknowledgments

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References

1. Abakumov, G. A.; Piskunov, A. V.; Cherkasov, V. K. et al. *Russ. Chem. Rev*. **2018**, *87* (*5*), 393−507.
2. Arzumanyan, A. V.*; Goncharova, I. K.; Novikov, R. A. et. al. *Synlett*. **2018**, *29* (*4*), 489−492.
3. Goncharova, I. K.; Arzumanyan, A. V.*; Milenin, S.A.; et. al. *J.Organomet. Chem*. **2018**, *862*, 28−30.
4. Arzumanyan, A. V.*; Goncharova, I. K.; Novikov, R. A. et.al. *Green Chem*. **2018**, *20* (*7*), 1467−1471.
5. Goncharova, I. K.; Silaeva, K.P.; Arzumanyan, A.V.* et.al. *J. Am. Chem. Soc*. **2019**, *141* (*5*), 2143-2151.

METAL ORGANIC FRAMEWORKS BASED ON 1,2,3-TRIAZOLE-4,5-DICARBOXYLATES OF REE: KINETIC ASPECTS OF ENERGY TRANSFER BETWEEN LANTHANIDES

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Metal organic frameworks based on coordination compounds of lanthanides have recently become objects of increased attention. Due to having volume pores in the structure of such compounds, different guest molecules can be introduced inside the framework. This presence may lead to the change of luminescent character of lanthanide ions, which can be used as a sensory response.

Previously in our work a sensory material based on a 3D MOF of structure $[Tb_{0.9}Eu_{0.1}(TDA)(H_2O)_3]*H_2O$ was made, which is able to quantitatively determine the content of water in heavy water, acetonitrile and dioxane[1]. The change of sensory response is based on the presence of energy transfer from resonance level of terbium to the resonant level of europium.

In order to study the kinetics of luminescence sensitization three series of mixed-metal compounds with different ration of lanthanides were synthesized: $[Ln1_xLn2_{1-x}(TDA)(H_2O)_3]*H_2O]$(Ln1, Ln2 – Eu, Tb(**1**), Eu, Gd(**2**), Tb, Gd(**3**)) and theirs spectroscopic and kinetic properties were examined.

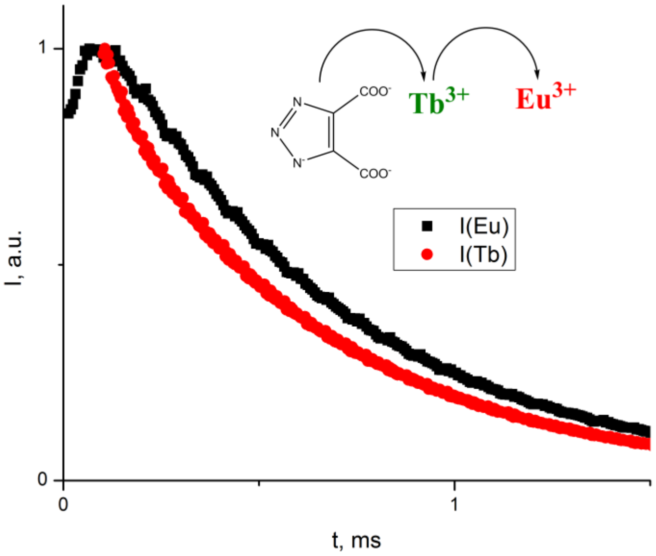

Figure 1. Decay curves of europium and terbium luminescence and the scheme of excitation transfer in sample $[Tb_{0.95}Eu_{0.05}(TDA)(H_2O)_3]*H_2O$

Acknowledgements

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References

1. V.E. Gontcharenko, A.M. Lunev, I.V. Taydakov, V.M. Korshunov, A.A. Drozdov, Yu.A. Belousov, IEEE Sensors Journal **2019**, *17*, PP. 7365-7372

MOLECULAR DYNAMICS OF THE PALLADIUM-MEDIATED CARBON-HETEROATOM BONDS FORMATION

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Cross-coupling reactions catalyzed by transition metal complexes are an effective and universal method for the synthesis of organic and organoelement compounds.[1] The key step in the cross-coupling process is the reductive elimination, i.e. transformation of the M(II) complex to the M(0) complex according to formation of carbon-carbon or carbon-heteroatom bond (Figure 1). Based on the analysis of potential energy profiles along the reaction coordinate, the mechanism of reductive elimination leading to the formation of a C-C bond was considered in detail in the literature.[2]

However, quantum molecular dynamics gives a more detailed, and in some cases a completely new mechanisms of the individual stages of the catalytic processes, since it is a more realistic model of a reacting chemical system.

The dynamics of palladium(II) complexes for a number of substituents X and R (Figure 1) at various temperatures (300, 400, 600, and 800 K) was performed by ADMP molecular dynamics using PBE1PBE/def2SVP D3BJ level of theory. Correlations between the values of activation energies of reaction and the rate of reductive elimination during molecular dynamics modeling were founded. For example, the formation of the Si-C bond occurs at the initial points of the molecular dynamics trajectory even at a temperature of 300 K, which is consistent with the low activation energy of this reaction (5.6 kcal/mol for R = Eth). Moreover, elimination can proceed not only by the synchronous mechanism, but also by the asynchronous one, in which X-Pd bonding is maintained despite the formation of the C-X bond.

The possibility of tandem metal complex catalysis was established for the first time, that is, realization of different catalytic events sequentially on the same metal atom. For example, for the SiH_3 group, after the reductive elimination step resulting in Si-C bond, the oxidative addition step takes place for Si-H bond, that is, the initial stage of the hydrosilylation process occurs after reductive elimination stage.

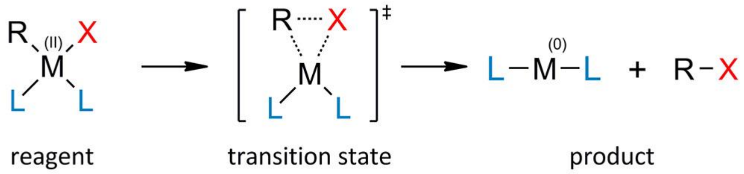

Figure 1. Scheme of C-X coupling reaction on metal (II) complexes. R = Me, Ph, Vin, Eth; X = $B(OH)_2$, NH_2, PH_2, OMe, SMe, SeMe, TeMe, SiH_3, F; L = PH_3.

Acknowledgments

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References

1. I. P. Beletskaya, V. P. Ananikov, *Chem. Rev.* **2011**, *111*, 1596.
2. V. P. Ananikov, D. G. Musaev, K. Morokuma, *Organometallics* **2005**, *24*, 715.

ON THE MERCURY POISONING TEST SELECTIVITY: FROM AMALGAMATION OF PALLADIUM(0) TO REDOX-TRANSMETALLATION OF P,C-PALLADACYCLE

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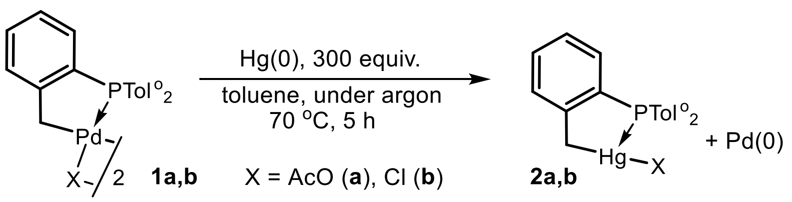
For a hundred years (from 1918[1]) suppression of Pd-catalyzed reactions by metallic mercury was explained only by an amalgamation of Pd(0) particles. Later Jones suggested that the catalysis inhibition may indicate the presence of a molecular Pd(0) intermediate.[2] Recently we conducted the systematic investigation of the Hg(0) reactions with azapalladacycles,[3] and have shown that all *C,N*-precatalysts react with Hg(0) through redox-transmetallation to form corresponding organomercurials.

Herein we report our studies of the mercury(0) reactions with palladacycles containing highly-protected *P,C*-donor ligands. We have chosen as examples well-known cyclopalladated derivatives of tris-*ortho*-tolylphosphine, namely μ-acetate (**1a**) and μ-chloride (**1b**) *P,C*-dimers. In contrast to all *C,N*-dimers, the *P,C*-dimers **1a,b** do not react with Hg(0) at room temperature due to effective Pd(II) protection by strong *P,C*-chelated ligand. However, at high temperature, the complete conversion of the cyclopalladated dimers **1a,b** into the benzylmercurials **2a,b** was observed. The structure of isolated organomercurial **2b** was confirmed by ^{1}H, $^{13}C\{^1H\}$, $^{31}P\{^1H\}$, and $^{199}Hg\{^1H\}$ NMR spectroscopy, X-ray diffraction studies, and DFTcalculation.

The highest stability to the mercury(0) impact was observed in the case of thecyclopalladated phosphite dimer $[\{(\kappa^2P,C\text{-}L)Pd(\mu\text{-}Cl)\}]$ (**3**) ($L^- = 2,4\text{-}^tBu_2C_6H_4$), known as the Bedford's precatalyst. Even after its very long boiling in toluene with a 330-fold excess of Hg(0), we did not find traces of the expected arylmercurial $[(\kappa^2P,C\text{-}L)HgCl]$. The extremely high stability of the *ortho*-palladated *phosphite* dimer **3** compared to its cyclopalladated *phosphine* analog **1b** can be explained by the greater π-acidity of its *P*-donor, the lower σ-basicity of the *ortho*-palladated carbon atom, and the more electron-deficient palladium center.



Scheme 1. Redox-transmetallation of the cyclopalladated μ-acetato- and μ-chloride *P,C*-dimers **1a,b**

Acknowledgments

This work was supported by the Russian Foundation of Basic Researches (project no. 18-03-01026a) and the Ministry of Science and Higher Education of the Russian Federation.

References

1. C. Paal, W. Hartmann, *Ber. Deutsch. Ber. Dtsch. Chem. Ber*. **1918**, *51*, 711.
2. N.T.S. Phan, M. van der Sluys, C.W. Jones, *Adv. Synth. Catal*. **2006**, *348*, 609.
3. O.N. Gorunova, I.M. Novitskiy, et al, *Organometallics* **2018**, *37*, 2842.

THE FEATURES OF THE INTERACTION BETWEEN PENTAPHENYLANTIMONY WITH PYRIMIDINE-4(3H)-ONE DERIVATIVES

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As we know, a wide range of biological activity is typical for pyrimidine derivatives. For example, pyrimidine-4(3*H*)-one derivatives exhibit antimycotic, antitumor, and antiviral activities. On the other hand, some of the arylantimony derivatives show similar function. The inclusion of the ligand with pyrimidine cycle in the arylantimony (V) compounds allows expanding the range of their practically important properties. The presence of different functional groups in the pyrimidine ring provides the structural variety of the obtained compounds.

It has been shown that interaction of pentaphenylantimony with 2-[(6-aminopyrimidine-4(3*H*)-one-2-yl)sulfonyl]acetic acid leads to the substitution of the hydrogen atom for the Ph_4Sb-fragment in the carboxylic group with the formation of complex **1**.

The carboxylic and hydroxyl groups take part in the reaction between pentaphenylantimony and 2-[(6-hydroxo-5-nitrosopyrimidine-4(3*H*)-one-2-yl)sulfonyl]acetic acid by the way of the substitution of the hydrogen atom for the Ph_4Sb-fragment. The product of the reaction is binuclear complex **2** with the bridging ligand. According to the X-ray analysis, the antimony atoms in compounds 1 and 2 have a distorted trigonal-bipyramidal coordination (Figure **1**).

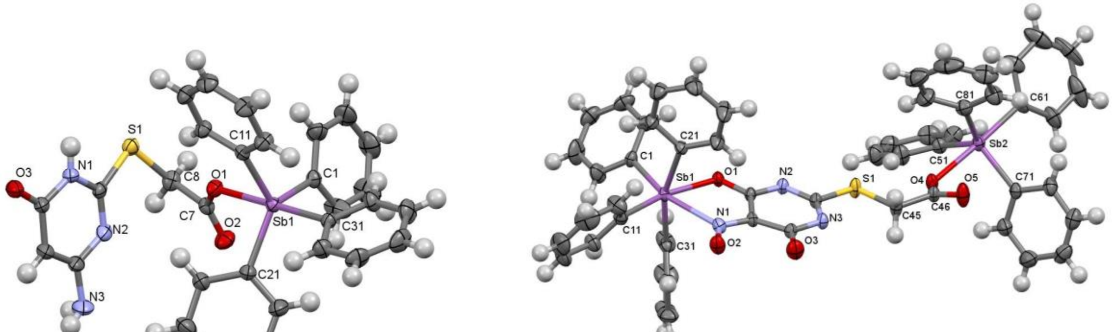

Figure 1. Molecular structures of compounds **1** and **2**

Acknowledgments

The reported study was funded by RFBR, project number 19-33-90061

References

1. E.R.T. Tiekink, *Crit. Rev. Oncol. Hematol*. **2002**, *42*, 217.
2. I.I. Ozturk, C.N. Banti, M.J. Manos, A.J. Tasiopoulos, N. Kourkoumelis, K. Charalabopoulos, S.K. Hadjikakou, *J. Inorg. Biochem*. **2012**, *109*, 57.
3. M.I. Ali, M.K. Rauf, A. Badshah, I. Kumar, C.M. Forsyth, P.C. Junk, L. Kedzierski, P.C. Andrews, *Dalton Trans*. **2013**, *42*, 1, 16733.

SYNTHESIS OF NEW BIS(STYRILASAGETEROCYCLES)

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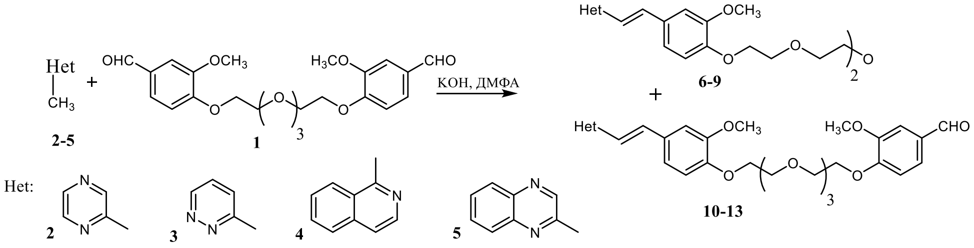
Azaheterocycles conjugated to styryl fragments are widely used in various fields of science. These compounds are in demand for research in medicine, for example, as fluorescent markers of biological cells, in electronics, in optical systems for storing and recording information, etc. The presence of a double C = C bond in such chromophores allows them to easily undergo phototransformation. This ability makes it possible to use styryl heterocycles as optical brighteners, laser paints, scintillators, nonlinear optical materials and electroluminescent materials.

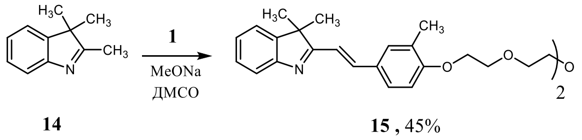
The aim of this work is to obtain new bis-styryl derivatives of azaheterocycles for further study of their photochemical and biological properties.

A number of monostyril and bis-styryl derivatives of azaheterocycles 6–13 were synthesized by condensation of the aldol type methyl derivatives with benzaldehyde derivatives 1 under mild conditions in the presence of the main KOH agent (Scheme 1).



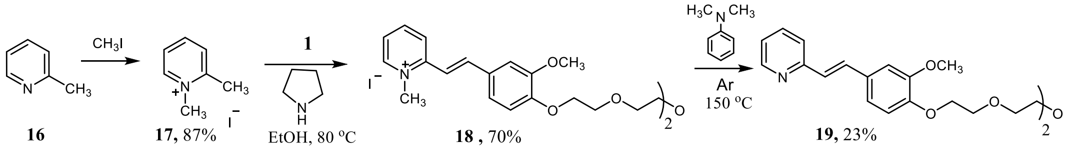
Scheme1.

The bisstyryl derivative of indolenin 15 was obtained by condensation of reagents in DMSO in the presence of sodium methylate (Scheme 2).



Scheme 2.

The conditions for producing bis (styrylheterocycles) 10–13.15 were unsuitable for the synthesis of bis (styrylpyridine) 19. To obtain 19, a three-stage synthesis was proposed (Scheme 3).



Scheme3.

Thus, synthesis routes were proposed and mono- and bis-styryl derivatives of azaheterocycles not described previously were obtained.

Acknowledgments

This work was supported by the Russian Science Foundation (grant No. 19-43-04127). The structure of compounds was established with the support of the Ministry of Science and Higher Education of the Russian Federation using the scientific equipment of the Center for the Study of the Structure of Molecules of INEOS RAS.

SINTHESIS OF HYDROPHOBIC GLUTATHIONE-CAPPED GOLD NANOCLUSTERS AND IT'S APLICATION IN CHEMILUMINESCENSE

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In recent time, metallic nanoclusters attract a great attention because of their outstanding physical properties. Gold nanoclusters (GNCs) stand out from others due to their perfect stability and biocompatibility. Therefore, GNCs are widely used in biosensing and bioimaging. In this study, we tried to use GNCs for hydroperoxide sensing. It is well known, that enhanced level of H_2O_2 in human cells is one of the diagnostic characters of oncogenesis. Thus, selective sensing of H_2O_2 can have great significance in cancer diagnostics and therapy. Such selectivity can be provided by using remarkably selective peroxyoxalatechemilumenescentreaction (PO-reaction) between aromatic oxalates and H_2O_2 in the presence of activators (commonly, polyaromatic compounds).Recently, it has been demonstrated that glutathione-capped GNCs can serve as activators of PO-reaction in water-ethanol mixtures [1]. However, it is known that oxalated are unstable in water solution. Therefore, both oxalate and activator should be placed into hydrophobic surroundings.

We synthesized glutathione-capped GNCs according to previously published protocol [2] and confirmed size distribution and structure of the GNCs by electrophoresis, fluorescent spectroscopy, spectrophotometry, RFA and ^{1}H-NMR spectroscopy. We have also demonstrated extremely high catalytic activity of GNCs in model reaction between p-nitropenol and $NaBH_4$. Obtained clusters possessed high solubility in water and were not soluble in organic solvents.

To use these GNCs in PO-reaction, we hydrophobized them by modification of carboxylic group of glutathione by octylamine, using carbodiimide method. Successes of modification was confirmed by ^{1}H-NMR spectroscopy. Modified clusters had good solubility in methanol and DMF. Emulsion of pluronic L61 was used as a hydrophobic medium for PO reaction according to [3]. We demonstrated for the first time that the hydrophobized glutathione-capped GNCs could serve as activator of PO-reaction in polymeric emulsions.

Acknowledgments

The authors express their gratitude to the Russian Foundation for Basic Research for financial support of this work (grant No. 18-03-01234a)

References

1. Y. Negishi, K. Nobusada, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, 127, 5261.
2. L. Zhang, N. He, C. Lu, *Anal. Chem.* **2015**, *87*, 1351.
3. A.V. Romanyuk, N.S. Melik-Nubarov, *Polymer Science - Series B*, **2015**, 57, 360.

TERTIARY PHOSPHINES ARE EFFECTIVE CATALYSTS FOR THE A- / BIS-ADDITION OF DIALKYLPHOSPHITES AND DIARYLPHOSPHINE OXIDES TO ALKYNES

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The addition of P(O)H compounds to carbon-carbon multiple bonds of activated alkenes and alkynes is one of the most versatile P-C bond forming methods in organophosphorus chemistry.

Recently, our group showed that the addition of dialkyl phosphites to alkenes during PBu_3 catalysis gives the corresponding phosphonates and phosphinates in high yields in a short reaction time.[1]

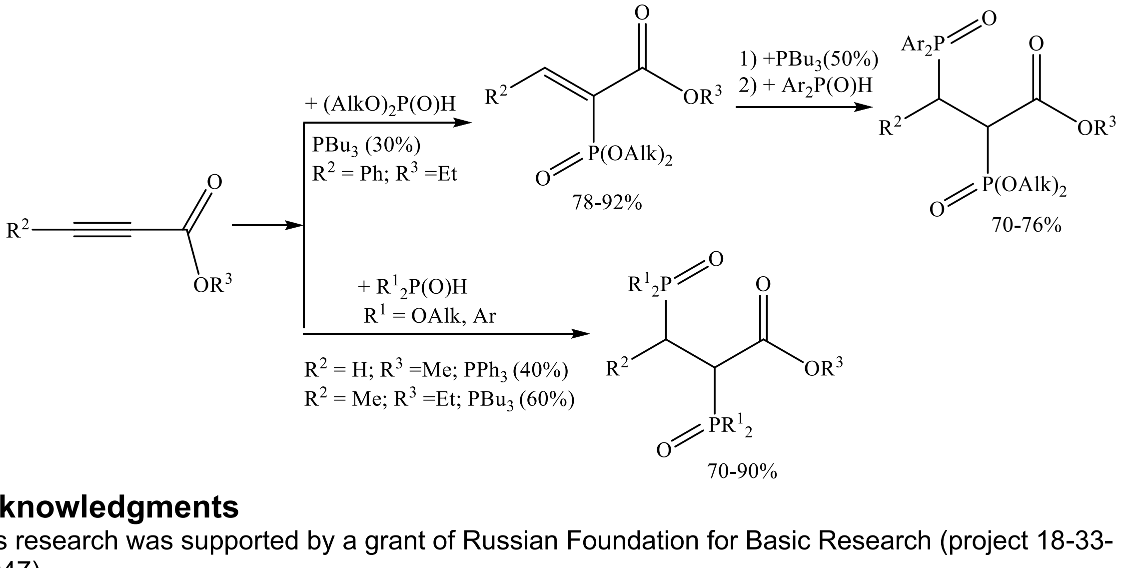
An efficient PBu_3-catalyzed addition of the P (O) -H bond to ethyl phenyl propiolate has also been developed.[2]

These data has prompted us to examine the potential catalytic activity of tertiary phosphines for vicinal bishydrophosphorylation of activated alkynes. It was established that diarylphosphinites are more reactive in phosphine-catalyzed bishydrophosphorylation reaction than dialkylphosphites.

The best results were provided when the reactions were performed using nucleophilic aliphatic phosphine PBu_3 as a catalyst.

Polar solvents such as MeCN, DMF and DMSO can significantly facilitate the reactions, and the best results were obtained using acetonitrile as a solvent.

The use of tri-n-butylphosphine as a catalyst in the reactions of highly reactive methyl propiolate was not useful. The use of less nucleophilic triphenylphosphine turned out to be more effective.



Acknowledgments

This research was supported by a grant of Russian Foundation for Basic Research (project 18-33-00047).

References

1. A. V.Salin, A. V. Il'in, F. G. Shamsutdinova, A. R. Fatkhutdinov, V. I. Galkin, D. R. Islamov, O. N. Kataeva, Curr. Org. Synthesis, **2016**,.13, 132-141.
2. A.V.Salin, A.V. Il'in, F.G. Shamsutdinova, A.R. Fatkhutdinov, V.I. Galkin, D.R. Islamov, O.N. Kataeva, Tetrahedron Letters*,* **2015**, 6282-6286.

MODIFICATION OF EPOXY COATINGS WITH FUNCTIONAL SILOXANES

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Epoxy resins are among the most widely used high performance materials due to their excellent properties, such as excellent moisture, solvent and chemical resistance, good adhesive strength, high modulus and tensile strength, ease of cure and processing [1]. Besides the composite industry, epoxides have a leading role in the protective coating industry. However, their short comings are low fracture energy, low thermal stability, poor hydrophobicity, weathering and impact strength, which restrict their wide application in the field of coatings and paints. Now more and more often, silicone compounds are used as epoxy modifiers to improve these properties [1, 2]. One of the most popular modified silicones are epoxy functional siloxanes [1, 3]. They have been well-known and used for a lot of various applications since many years. The high reactivity of the oxirane ring of epoxides makes it possible to obtain a wide range polymer materials, as well as to increase the compatibility of the organosilicon modifier with the polymer matrix and to prevent its leaching when used in marine coatings.

The present work considers the preparation of various organosilicone epoxy composite materials using epoxysiloxanes of various molecular weights with terminal or internal epoxy groups and their use in anticorrosion-antifouling marine coatings.

The synthesized epoxysiloxanes were used to obtain coatings based on the primer-enamel EpoxyCoat 5250, manufactured by "VDM "Pigment". The compositions were applied to previously purified metal substrates, followed by curing at 20°C.

Analysis of experimental data showed that there is a significant increase in the water contact angle with an increase in the amount of epoxysiloxanes in the coating. So an increase in the content of epoxysiloxanes up to 5-10%$_{\text{mass}}$ (depending on the structure of the corresponding epoxysiloxane) in a composition based on primer-enamel EpoxyCoat 5250, the water contact angle increases significantly to (100-101)°, compared to the initial value of 84°. The increase in the number of epoxysiloxanes in the composition is above 5-10%$_{\text{mass}}$ does not lead to significant changes in the hydrophobic properties of the coatings.

Acknowledgments

This work was supported by state assignment of the Ministry of Education and Science of the Russian Federation (project no. 11.5362.2017/8.9) and the integrated program for the development of high tech production of the Ministry of Education and Science (contract no. 03.G25.31.0237).

References

1. M. A. Il'ina, L. N. Mashlyakovskii, A. S. Drinberg, E. V. Khomko, A. V. Garabadzhiu, *Russ. J. Appl. Chem.* **2019**, *52*, 530.
2. M. Lejars, A. Margaillan, Ch.Bressy, *Chem. Rev.* **2012**, *112*, 4347.
3. J. J. Chrusciel, E. Lesniak, *Prog. Polym. Sci*. **2015**, 41, 67.

ELECTROCHEMICAL SYNTHESIS, PROPERTIES AND REACTIVITY OF ORGANONICKEL SIGMA-COMPLEXES OF TYPE [NiBr(aryl)(L)]

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Complexes of transition metals have proven themselves as active catalysts for various processes, including cross- and homo-coupling reactions of organic halides, chlorophosphines, as well as the process of ethylene oligomerization. However, methods for producing such compounds are often associated with the use of environmentally unsafe and expensive compounds.[1] Based on this, a universal method was developed for the preparation of nickel-based complexes with various heterolytic imine ligands (Figure 1). The resulting nickel complexes contain an organic fragment sigma-linked to the nickel atom, this Ni-C bond exhibits catalytic properties in various catalytic processes.[2]

This work presents the electrochemical synthesis of new nickel-organic complexes, the study of their electrochemical properties and reactivity with various organic substrates.

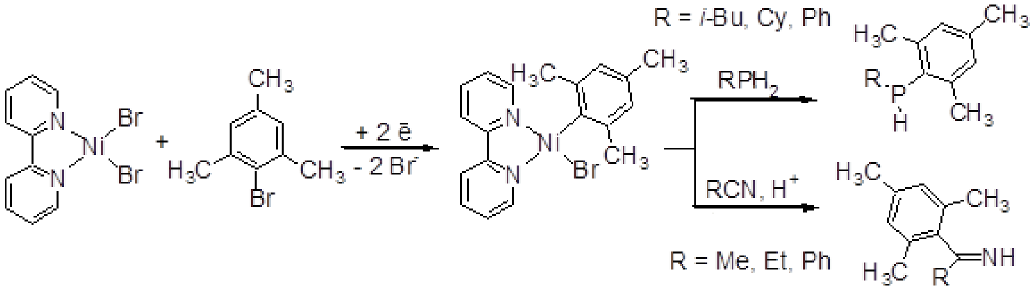

Figure 1. Electrochemical synthesis and reactivity of organonickel sigma complexes

Acknowledgments
The reported study was funded by RFBR according to the research project no. 18-33-00177.

References

1. Z. N. Gafurov, O. G. Sinyashin, D. G. Yakhvarov, *Pure Appl. Chem*. **2017**, *89*, 1089.
2. D. G. Yakhvarov, E. A. Trofimova, I.H. Rizvanov, O. S. Fomina, O. G. Sinyashin, *Electrochem.* **2011**, 47, 1180.

SYNTHESIS OF THE CARBORANE COMPLEXES OF RUTHENIUM (II) WITH H3-PHOSPHORUS-CONTAINING AND H3-NITROGEN-CONTAINING LIGANDS

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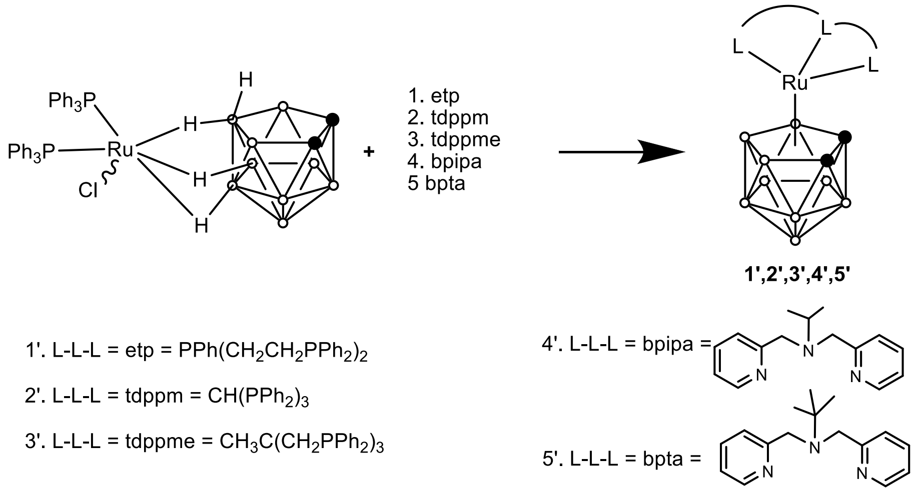
Carborane complexes of transition metals, in particular, ruthenacarboranes - an important area of modern chemistry of coordination compounds. Compounds of this type have an unusual structure - they are formed by non-classical electron-deficient multicenter bonds, which determines the importance of their study from a fundamental point of view. In addition, ruthenium carborane clusters have wide prospects of practical application in various fields of chemistry, catalysis, and medicine. At the moment, a huge number of metalcarboranes containing bidentate ligands have been obtained and studied, while similar complexes containing tridentate ligands are poorly understood.

This work presents the synthesis of new carborane complexes of ruthenium (II) with η^3-triphosphine and η^3-trinitrogen ligands. The process was carried out in accordance with the scheme 1. The interaction of the original exonido-5,6,10-[RuCl(PPh$_3$)$_2$]-5,6,10-(μ-H)$_3$-10-H-7,8-C$_2$B$_9$H$_8$ with bis-(2-(diphenylphosphino)ethyl)phenylphosphine (etp), tris-(diphenylphosphino)methane (tdppm), tris-(diphenylphosphinomethyl)ethane (tdppme) in boiling toluene (110 °C) leads to the formation of new compounds with yields of 43.0, 57.1, and 62.4%, respectively. A similar interaction of the initial complex with N,N-bis-(pyrid-2-ylmethyl)-tert-butylamine and N,N-bis-(pyrid-2-ylmethyl)-isopropylamine in benzene at 60 °C leads to the formation of new clusters with yields 72.0 and 63.9%, respectively. The resulting complexes are isolated in pure form. The purity of the products was confirmed by HPLC. The structure was confirmed by NMR spectroscopy, IR-spectroscopy, time-of-flight mass spectrometry, and for **1'–4'** by X-ray diffraction analysis.



Scheme 1. Obtaining ruthenium (II) carborane complexes **1'-5'**

Acknowledgments

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NOVEL IMIDAZOLE-BASED LIGANDS FOR TRANSITION METAL COMPLEXES

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The ability of some transition metal complexes to exist in two spin states and to switch between them under an applied stimulus (temperature, pressure or light irradiation) is behind many concepts of high-density data storage, switching, sensing and development of many molecular devices and materials. Earlier, a series of mononuclear homo- and heteroleptic complexes of iron and cobalt with tridentate nitrogen-containing ligands was obtained in our laboratory and their capability of spin-transition was proven.[1]

Polynuclear complexes are more forward-looking systems for the molecular design of spin-transition compounds. However, in order to obtain them, sophisticated organic ligands that can predictably bind two metals are required. We consider that systems based on 4,5-di(2-hydroxyphenyl) imidazoles are likely to be promising ligands for binuclear spin-transition complexes of iron and other metals, the structure of which is shown in Figure 1.Therefore, the aim of this work was to develop a synthetic route (Figure 2) to 4,5-disubstituted imidazoles and metal complexes based on them.

Thus, we synthesized a series of new 4,5-disubstituted imidazoles - precursors of ligands of binuclear metal complexes.

All compounds have been identified by NMR and IR spectroscopy as well as by elemental analysis.

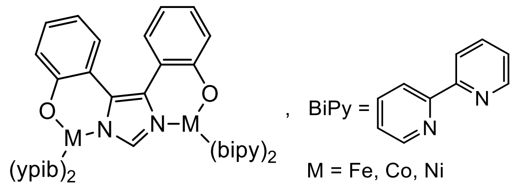

Figure 1. Binuclear imidazole-based complexes

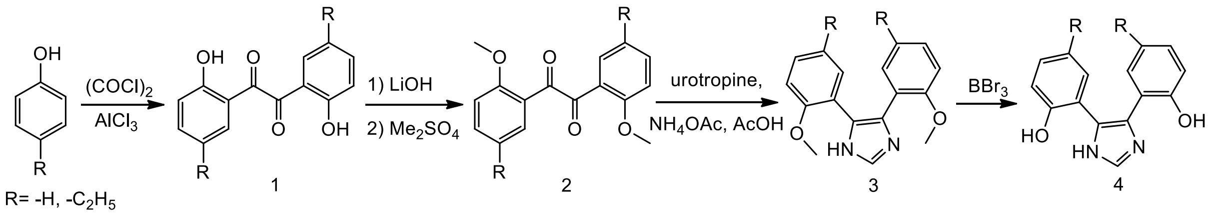

Figure 2. Synthetic route for novel imidazole-based ligands

References

1. Y. Nelyubina, et all, Magnetochemistry 2018, 4(4), 46.

COBALTOCENIUM ACETYLSALICYLATE: SYNTHESIS AND STUDY OF INTERACTIONS WITH DNA USING CIRCULAR DICHROISM

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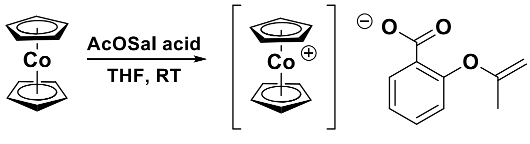
Cobaltocenium salts,in contrast to ferrocene compounds, have been studied to a much lesser extent. Although cobaltocenium salts, like ferrocenes, have an 18-electron structure, high stability, and reversible redox chemistry. Moreover, cobalt, being a biogenic metal, performs important functions in aliving organism. So, vitamin B_{12}, containing cobalt, is involved in the synthesis of hemoglobin. Cobaltocene compounds have only recently become the items of research in the field of biology, medicine, and bioelectrocatalysis.

We have proposed an available method for the synthesis of cobaltocenium acetylsalicylate (**1**) byoxidizing cobaltocene with acetylsalicylic acid (Scheme 1). This method allows obtaining the product with an acceptable yield in analytically pure form. The interaction of the water soluble salt **1** with double-stranded DNA was studied by the circular dichroism (CD) method.

The chiral DNA molecule in the CD spectra is recorded in the form of a sinusoidal curve (see Fig. 1, the more intense black curve). The observed changes in the positions and intensities of the Cotton effects were interpreted as conformation changes in double-stranded DNA. A decrease in the intensity of the curves both in the positive and in the negative regions was found in the CD spectra when the achiral cobaltocenium salt **1** in increasing concentrations was added to the sodium salt of calf thymus DNA in phosphate-buffered saline. Moreover, the maxima and minima of these curves also monotonously shift the bathochromic and hypochromic, respectively. Local changes in DNA conformation can be caused by the interaction of positively charged cobaltocenium cations with negatively charged phosphorus DNA fragments and/or the partial intercalation of metallocenium compounds between pairs of nucleic base.



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Scheme 1. Synthesis of cobaltocenium acetyl salicylate (**1**).

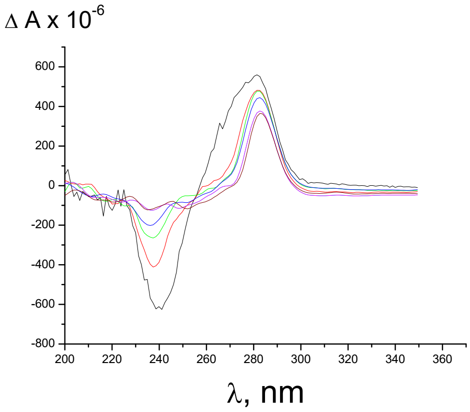

Fig. 1. CD profiles of the titration of the 5μM of dsDNA(black) by cobaltocenium acetyl salicylate (**1**) in increasing concentrations (colored lines).

Acknowledgement

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References

1. L.V. Snegur,M.V. Kaverin, K.K. Babievsky, *Russ.Chem. Bull., Int. Ed.* **2019**, *68*(9), 1787.

DFT ANALYSIS OF THE UNPRECEDENTED REACTIVITY OF SOME ORGANOARSENIC AND ORGANOANTIMONY COMPOUNDS TOWARDS CARBON-CARBON MULTIPLE BONDS

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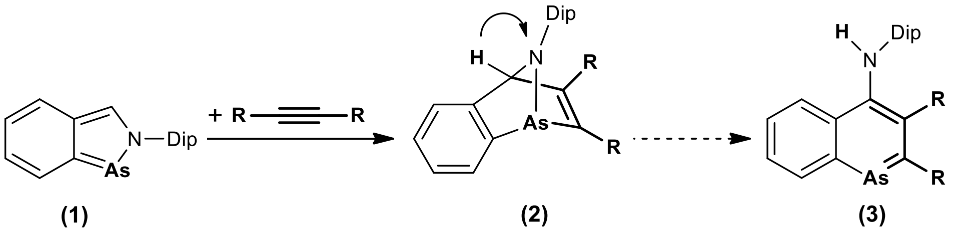
The new benzazaarsole and *N,C,N*-chelated stibinidene demonstrate unusual reactivity towards alkynes and maleimides, respectively. The 1*H*-2,1-benzazaarsole (**1**) works as a 1,3-diene in the reaction with alkynes RC≡CR (R = CO_2Me, C_5F_4N) leading to 1-arsa-1,4-dihydro-iminonaphthalenes (**2**) which undergo unexpected facile C*H*→N*H* proton shift (Scheme 1) thus producing extremely rare stable 1-arsanaphthalenes (**3**). DFT analysis reveals, however, a very high activation barrier for the direct proton migration. The reaction mechanism appears to include subsequent addition of the alkyne and **1** molecules. The intermediates providing a substantial decrease in the energy barriers accompanying the **2** → **3** transformation have been found on the basis of quantum chemical calculations and the detailed reaction mechanism has been suggested.[1]

The first example of reversible activation of a C=C bond in selected maleimides by a low-valent antimony compound ArSb (Ar = C_6H_3-2,6-(CH=N*t*Bu)$_2$) has been studied with DFT. This process is ligand-assisted, demonstrating the non-innocent behavior of the *N,C,N*-pincer fragment. The geometries of reactants, products and transition states (TS) were optimized and the corresponding changes of enthalpies and Gibbs free energies were calculated. The replacement of the Me or Ph group with *t*Bu in maleimide results to a relative destabilization of both the reaction product and the corresponding TS, the DFT results being in accord with the experimental data.. QT AIM analysis predicts the Sb-C interaction, corresponding to the new bond formed on the maleimide addition, to be weak which provides the facile dissociation.[2]



Scheme 1

Acknowledgments

This work was supported by the RFBR (project 19-03-00755).

References

1. V. Kremláček, M. Erben, R. Jambor, A. Růžička, J. Turek, E. Rychagova, S. Ketkov and L. Dostál, *Chem. Eur. J.* **2019**, *25*, 5668.
2. M. Kořenová, M. Hejda, M. Erben, R. Jambor, A. Růžička, E. Rychagova, S. Ketkov, L. Dostál, *Chem. Eur. J.* **2019**, doi:10.1002/chem.201902968.

SYNTHESIS OF NOVEL DIPHOSPHONIUM SALTS BEARING 1,4-DIHYDROXYNAPHTHALENE FRAGMENT

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Recently, much attention was focused in the literature on the antitumor activity of quinones, including various naphthoquinones.[1] Phosphonium salts are most effective compounds for the targeted delivery to the mitochondria of tumor cells because they have a sufficiently high lipophilicity and delocalized positive charge on the phosphorus atom.[2]

Recently, we have shown that 1,2-naphthoquinones easily react with tertiary and secondary phosphines to form phosphorus zwitter-ionic species with a P-C bond, which can be used for the synthesis of arylphosphonium salts.[3,4] In this work, 2-methyl-1,4-naphthoquinone was involved in the reaction with tertiary phosphines. It turned out that the reaction with triphenylphosphine proceeds rather slowly (7 days) and the product of double phosphorylation of quinone is formed (Figure1). The reaction occurs under mild conditions (CH_2Cl_2, r. t.) with high regioselectivity. Changes of the chemical shift and multiplicity of the signal of the phosphorus atom in the ^{31}P-NMR spectra of the reaction mixtures indicate the formation of phosphonium compounds with new two P-C bonds as sole reaction products. The reactions of menadione with anisylphosphines bearing electron donating methoxy groups proceed in a similar way. The zwitterions were converted to diphosphonium salts after treatment with dry HBr. The structure of one of the obtained diphosphonium salts was proved by XRD analysis.

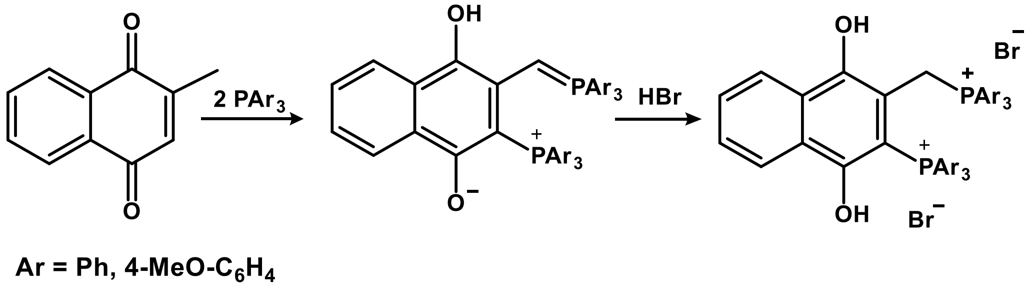

Figure 1. Synthesis of diphosphonium salts

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (project no. 18-33-00224 mol_a).

References

1. K. D. Badave, A. A. Khan, S. Y. Rane, *Anti-Cancer Agents Med. Chem.* **2016**, *16*, 1017.
2. J. Zielonka, J. Joseph, A. Sikora, M. Hardy, O. Ouari, J. Vasquez-Vivar, G. Cheng, M. Lopez, B. Kalyanaraman, *Chem. Rev.* **2017**, *117*, 10043.
3. N. R. Khasiyatullina, V. F. Mironov, A.V. Bogdanov, D. B. Krivolapov, I. A. Litvinov, *Mendeleev Commun*. **2011**, *21*, 346.
4. V. F. Mironov, N. R. Khasiyatullina, D. B. Krivolapov, *Tetrahedron Lett*. **2015**, *56*, 7132.

CROSS-COUPLING OF SECONDARY PHOSPHINE SELENIDES WITH MERCAPTOALCOHOLS IN THE CCL$_4$/ET$_3$N SYSTEM

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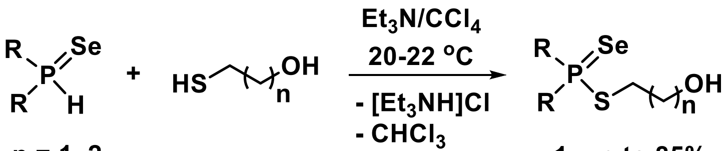
Chalcogenophosphinic esters and thioesters are widely used as ligands for metal complex catalysts, intermediates for drug design, flame retardants and RAFT agents for the controlled styrene polymerization. An oxidative cross-coupling of secondary phosphine chalcogenides with HS- or HO-compounds can be used as a convenient method for the synthesis of these demanded building blocks. At the same time, the fundamental question of chemoselectivity in the oxidative cross-coupling of secondary phosphine chalcogenides with multifunctional compounds containing both HS- and HO-groups has remained open until the present work.

Using available secondary phosphine selenides (easily obtained by the Trofimov-Gusarova reaction[1]) as well as 2-mercaptoethanol or 3-mercaptopropanol, we showed for the first time that, at an equimolar ratio of reactants, their cross-coupling proceeds chemoselectively under mild conditions (20–22 °C, Et_3N/CCl_4) and leads to the selenophosphinic acid thioethers **1** in a yield of up to 85% (Scheme 1).

However, a change in the ratio of the starting reagents (secondary phosphine selenide : 2-mercaptoethanol = 3:1) allows to implement the oxidative cross-coupling simultaneously on both functional groups of 2-mercaptoethanol under the same conditions (20–22 °C, Et_3N/CCl_4) and obtain *O,S*-diselenophosphinates **2** in a yield of up to 70% (Scheme 2).

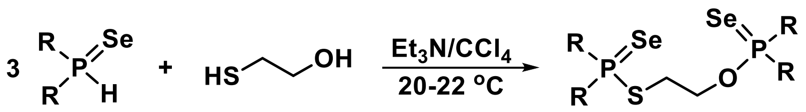
Thus, the oxidative cross-coupling of secondary phosphine selenides with mercaptoalcohols in the Et_3N/CCl_4 system opens up convenient routes for the synthesis of the in-demand selenophosphinic acid thioesters, or mercaptoethanol double selenophosphorylation compounds containing both thioester and ester groups.



n = 1, 2

1, up to 85%

Scheme 1



2, up to 70%

Scheme 2

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grant no. 18-33-00120 mol_a).

References

1. B. A. Trofimov, N. K. Gusarova, *Mendeleev Commun.* **2009**, *19(6)*, 295.

THE FIRST NC$_{SP3}$N PINCER LIGAND IN THE COORDINATION CHEMISTRY OF LANTHANIDES AND SYNTHESIS HOMOLEPTIC STABLE COMPLEXES

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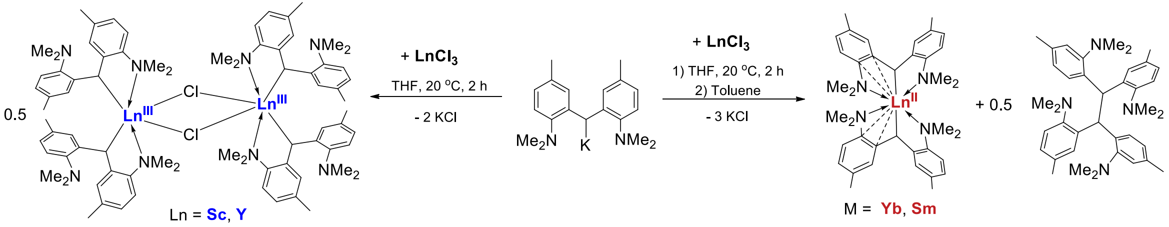
Alkyl complexes of rare-earth metals possess a unique complex of properties and have undoubted interest for catalysis. Studies over the past three decades have vividly demonstrated that the stability and reactivity of alkyl derivatives of rare earth metals are determined by the nature of the auxiliary ligand environment. However, the modification of the coordination environment of the metal center can be achieved not only by replacing the auxiliary ligand (spectator ligand), but also by varying the nature of the alkyl group itself. In our study 2,2'-methylenebis(N,N,4-trimethylaniline) 2,2'-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH$_2$ was used as potentially tridentate alkyl ligand.

A series of alkali metal alkyl complexes containing tridentate diphenylmethanido ligand [2,2'-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]Li(TMEDA) (**1**$^{\mathbf{TMEDA}}$), [2,2'-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]Na(THF)$_3$ (**2**$^{\mathbf{THF}}$), {[2,2'-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]K(THF}$_2$ (**3**$^{\mathbf{THF}}$) and [2,2'-(4-MeC$_6$H$_4$NMe$_2$)$_2$C(SiMe$_3$)]K (**5**) were synthesized and structurally characterized. Smaller Li and Na ions form monomeric complexes **1**$^{\mathbf{TMEDA}}$ and **2**$^{\mathbf{THF}}$ featuring η^4-CCCN-coordination of [2,2'-(4-MeC$_6$H$_4$NMe$_2$)$_2$CH]$^-$ ligand, while larger K affords dimeric complex **3**$^{\mathbf{THF}}$ in which two different types of metal-ligand bonding μ-η^5-pentadienyl:κ^2-NN and μ-η^3-CNN:η^6-arene are realized.

Further salt metathesis reaction of **1–3** with LnCl$_3$ (M = Sc, Y) lead to the formation of dimeric bis(alkyl) complexes {[2,2'-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH]$_2$Ln(μ^2-Cl)}$_2$ (Ln = Y (**4**), Sc (**5**)). Analogues salt metathesis reactions of **3** with YbCl$_3$ or SmCl$_3$ accompanied by spontaneous reduction of the Ln(III) ions to divalent state giving homolepticbis(diphenylmethanido) complexes [2,2'-(4-MeC$_6$H$_4$-NMe$_2$)$_2$CH]$_2$Ln^{II} (Ln = Yb^{II} (**6**), Sm^{II} (**7**)).



XRD study revealed that in Ln(III) complexes of Y and Sc diphenylmethanido ligands are bidentate (κ^2-C,N), while in case of Ln(II) derivatives diphenimethanido ligands become tridentate and bounded to Ln(II) ions via κ-N-η^4-CCCN coordination mode.

Acknowledgements

This work was supported by the Russian Science Foundation (project No. 17-73-20262).

References

[1] D. O. Khristolyubov, D. M. Lyubov, A. V. Cherkasov, G. K. Fukin, A. S. Shavyrin, A. A. Trifonov,*Organometallics*, **2018**, *37*, 1627.

METHANOLYSIS OF ARYL(ALKYL) HYDROSILANES AND AHPC OF THEIR DEHYDROCONDENSATION PRODUCTS

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Hydride nature of hydrogen in compounds of $R^1_nR^2_{(3-n)}SiH$ (where R^1-CH_3; R^2-C_6H_5; n=0÷2) kind allows their use as reducing and even hydrogenant agents[1]. The presence of electron withdrawing substituents in triorganosilanes, for example, $CF_3CH_2CH_2$[2] and a phenyl group[3], increases the covalence of the Si – H bond. Thus, the reducing ability of $R^1_nR^2_{(3-n)}SiH$ decreases with the decrease in the effect of a negative charge at hydrogen in Si-H bond.

Derivatives of silicon, comprising a Si-H bond, readily enter the dehydrocondensation reaction with water, alcohols, acids, amines, etc. One of the catalysts for the dehydrocondensation of $R^1_nR^2_{(3-n)}SiH$ by alcohols is the Speir catalyst, although triorganosilanes easily reduce H_2PtCl_6 to a free metal.

We have studied the dehydrocondensation reaction with methanol in the presence of a Speir catalyst of a series of triaryl(alkyl)silanes:

$$R^1_nR^2_{(3-n)}SiH + CH_3OH \rightarrow R^1_nR^2_{(3-n)}SiOCH_3 + H_2$$

GLC and ^{29}Si and ^1H NMR spectroscopy showed that the rate of triorganosilanes dehydrocondensation with methanol decreases in the following order:

$$C_6H_5(CH_3)_2SiH > CH_3(C_6H_5)_2SiH > (C_6H_5)_3SiH$$

Unlike methyl-containing silanes, triphenylsilane dehydrocondensation was performed in toluene. The dearylation compounds - diphenyldimethoxysilane (~ 10%) and an equimolar amount of benzene were found in the composition of methanolysis products.

Alkoxysilanes were separated from spongy platinum by filtration, and toluene was removed under vacuum.

Then, triaryl(alkyl)methoxysilanes were subjected to acidohydrolytic condensation (AHPC) with glacial acetic acid in the presence of a catalytic amount of concentrated sulfuric acid and symmetric hexaorganodisiloxanes were produced by the reaction:

$$2R^1_nR^2_{(3-n)}SiOCH_3 + CH_3C(O)OH \rightarrow [R^1_nR^2_{(3-n)}Si]_2O + CH_3C(O)OCH_3 + CH_3OH$$

When n=0,~80% of hexaphenyldisiloxane and ~20% of octaphenyltrisiloxane were obtained.

With an increase in the number of phenyl groups in triorganomethoxysilanes, their activity to AHPC decreases, this is also proved by GLC and 29Si and 1H NMR spectroscopy.

References

1. Orlov I.F.,Bogatkin R.A., Sergeeva Z.I., Voronkov M.G. Zhurnal Obshchei Khimii, 1963, 35, 1934.
2. Shevchenko I.V., Kovalev I.F., Arbuzova V.A, Voronkov M.G., Khudobin Yu.I., Kharitonov I.P. Doklady AN SSSR, 1970, 192, 842.
3. Voronkov M.G. Kovalev I.F.,Shevchenko I.V.., Khudobin Yu.I. Izvestiya AN SSSR, Ser. Khimiya,1973, 2479.

SILVER ION STABILIZATION OF CYTOSINES IN THE STRUCTURE OF NUCLEIC ACIDS: A THEORETICAL STUDY USING THE COMBINED QM/MM METHOD

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Cytosines bound by silver ions along the axis of the DNA helix can be used as building blocks to create solution stable nanostructures [1-2]. At pH values close to neutral, the N3 positions of cytosines are deprotonated, and when the silver salt $AgNO_3$ is added, specific complexation with Ag + ions and the formation of C-Ag + C type crosslinks occur. Such crosslinks lead to an increase in the melting temperature of DNA, which in turn causes an increase in thermodynamic stability.

In this work, we studied the profile of the isomer dissociation reaction (in cis- and trans- configurations) of cytosine pairs stabilized by silver ions using the combined QM/MM method in the CP2K software package. Using the method of thermodynamic integration along the path of molecular dynamics along the reaction coordinate, the profiles of the free energy change were obtained.

It was shown that in the case of monomeric complexes with silver ions for both isomers there is a configuration on the profile with a lower energy value in comparison with equilibrium configurations. Relative to this profile, the energy barriers of dissociation for the cis and trans configurations are significantly different. Regarding the main minimum, the cis-configuration seems preferable to the trans-configuration, since it has a larger energy barrier relative to dissociation. For cytosine dimers stabilized by silver ions, the free energy profile change does not contain a secondary minimum, which is apparently determined by the significant contribution of the bases stacking interaction and ion metalophilic interactions.

Acknowledgments

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References

1. Alberti, P.; Bourdoncle, A.; Saccà, B.; Lacroix, L.; Mergny, J. L. DNA Nanomachines and NanostructuresInvolvingQuadruplexes. Org. Biomol. Chem. 2006, 4 (18), 3383–3391.
2. Day, H. A.; Huguin, C.; Waller, Z. A. E. Silver CationsFold I-MotifatNeutral PH. Chem. Commun. 2013, 49 (70), 7696–7698.

FUNCTIONAL ARYLOXYCYCLOTRIPHOSPHAZENES FOR DENTISTRY

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The improvement of wellbeing is currently remaining one among the most important problems. First of all, it concerns the human health. For many years the problems in the field of restorative dentistry have been topical due to the need to develop new materials with improved performance properties.[1,2] One of the few ways to improve the properties of dental materials is to modify the binder. The use of various modifiers has contributed to a decrease in the viscosity of the dental composition[3], as well as a decrease in shrinkage during polymerization.[4] In addition, the modification of the binder can increase adhesion.[5]

A modifier consisting of the mixture of cyclotriphosphazenes containing 4-allyl-2-methoxyphenoxy and β-carboxyethenylphenoxy moieties has been developed in this work (Fig. 1). The synthesized compounds were characterized by ^1H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry. The optimal conditions to combine the modifier with the starting dental mixture consisting of bis-GMA and TGM-3 were revealed by DSC method. Properties of the cured modified compositions were evaluated for the compliance with requirements ISO 4049:2009. It was found that these compositions possess the increased adhesion to a dental tissue and cure depth, and the decreased water sorption and water solubility. It was also noticed that the values of elastic modules, destructive compressive stress, and microhardness were also increasing along with the increased content of the modifier in the composition. The values of these parameters are very important, since the restorative materials of the said type are subjected to regular mechanical loads during chewing of food. Taking into account everything presented hereinabove, it can be concluded that the developed dental composition can be practically applied as a high-quality, highly adhesive restorative material.

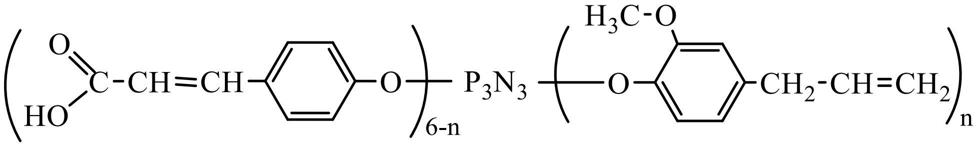

Figure 1. The developed modifier of dental compositions

Acknowledgments

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References

1. O Tao, DT Wu, HM Pham, N Pandey, SD Tran. *Applied Sciences.* **2019**, 9(2), 317.
2. Chi M, Qi M, Lan A, Wang P, Weir MD, Melo MA. *International Journal of Molecular Sciences*, **2019**, 20(2), 278.
3. R. Srivastava, J. Liu, C. He, Y. Sun, *Mat. Sci. Eng*. **2018**; 88, 25.
4. J. He, S. Garoushi, E Säilynoja, P.K. Vallittu, L. Lassila. *Dent Mater*. **2019,** 35(4), 627.
5. V.V. Kireev, E.M. Chistyakov, S.N. Filatov, A.S. Tupikov, D.V. Panfilova, A.I. Chetverikova. *Russ.J. App.l Chem.* **2015**, 88(5), 866.

DIELS-ALDER REACTION BETWEEN 2,5-DIMETHYLTHIOPHENE AND N-PHENYLMALEIMIDE AT HIGH PRESSURE

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It is known that 2,5-dimethylthiophene is highly aromatic and does not enter into the Diels-Alder reaction. However, in this work, we were able to introduce 2,5-dimethylthiophene (**1**) into the cycloaddition reaction with N-phenylmaleimide (**2**) (Scheme 1). The reaction was carried out in a barostat (Figure 1). The reaction mixture was kept in a fluoroplastic cell of barostat at the pressure of 8000 atmospheres and the temperature of 120 °C within 3 days. The resulting mixture was separated by column chromatography on silicagel. As shown in Scheme 1, the isolated products were a 1:1 cycloadduct, 3,6-dimethyl-N-phenylphthalimide (**3**) (34%), and a 1:2 cycloadduct, 1,4-dimethylbicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic acid bis(phenylimide) (**4**) (30%). The structures of the products were determined by ^{1}H and ^{13}C NMR spectrometry.

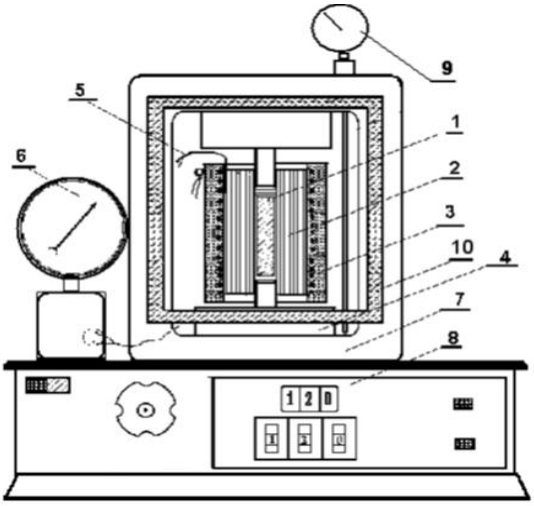
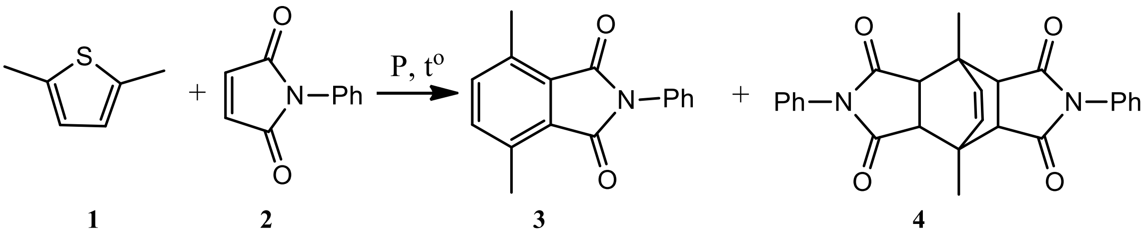


Figure 1.Barostat (1 – fluoroplastic cell, 2- high pressure unit, 3 – electric heater, 4 – press plunger, 5 – chromel-copel thermocouple, 6 – manometer, 7 – barostat frame, 8 – temperature regulator, 9 – pressure indicator, 10 – glass door).



Scheme 1. The Diels-Alder reaction between 2,5-dimethylthiophene and N-phenylmaleimide.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project No 18-33-00063).

CATALYTIC ACTIVITY OF NOVEL LANTHANIDE CYMANTRENECARBOXYLATES WITH FERROCENE PHOSPHINE OXIDO LIGAND IN POLYMERIZATION PROCESSES

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It is known that cymantrene (CymH = (η^5-C_5H_5)Mn(CO)$_3$) derivatives can serve as polymerization catalysts.[1] At the same time, carboxylate complexes of the lanthanides can influence the stereoregularity of the process.[2]

Earlier we have shown that cymantrenecarboxylate complex of neodymium [$Nd_2(CymCO_2)_6(DMSO)_4$] can be the catalyst of stereoregular polymerization of dienes.[3] Continuing our research in the field of organometallic carboxylates, we obtained a new series of heteroleptic organometallic *3d-3d´-4f*-complexes [$Ln^{III}(CymCO_2)_2(DppfO_2)_2$]Cl·*Solv* (Ln = Nd(**1**), Dy(**2**), Ho(**3**), and Er(**4**); DppfO$_2$ is the Fe(η^5-$C_5H_4P(O)Ph_2)_2$ ligand; *Solv* are the lattice solvent molecules). Both kinds of ligands in the unique bulky cations [$Ln(CymCO_2)_2(DppfO_2)_2$]$^+$ are bidentate (Fig.1, left).

All the constituents of the obtained complexes can potentially affect the polymerization processes. Activities of complexes **1** and **3** in the polymerization of methyl methacrylate and styrene in the presence of benzoyl peroxide, as well as under UV-light or thermal activation in the presence of CCl$_4$, are studied and discussed.

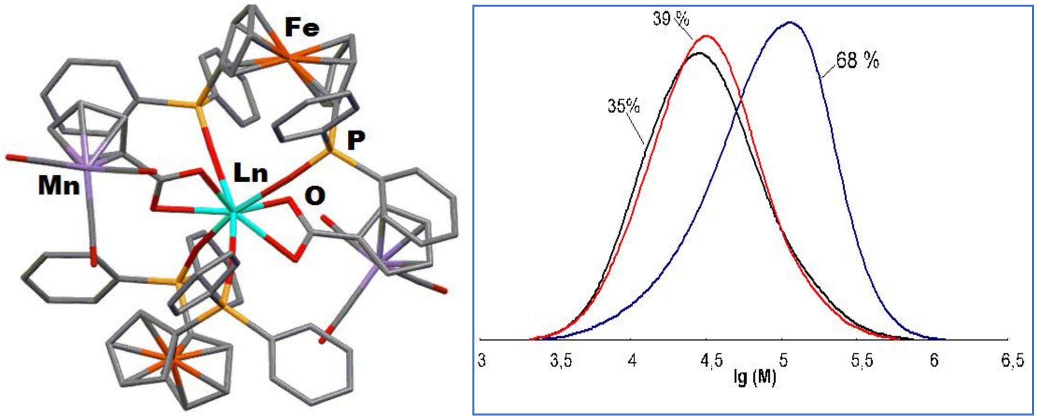

Figure 1. Structures of bulky cations in compounds **1**-**4** (left) and the curves of the molecular weight distribution of polystyrene samples synthesized in the presence of **1** (0.05 mol.%) and CCl$_4$ (0.25 mol.%) at 110°C (right).

Acknowledgments

The work was supported by the Russian Science Foundation (project 16-13-10407) and Russian Foundation for Basic Research (project 17-03-00498).

References

1. M.V. Pavlovskaya, E.V. Kolyakina, E.S. Kotlova et al., *Russ. J. Appl. Chem.*, **2011**, *84 (10)*, 1813.
2. Z. Zhang, D. Cui, B. Wang, B. Liu, Y. Yang, *Struct. Bond.*, **2010**, *137*, 49.
3. P.S. Koroteev, Zh.V. Dobrokhotova et al., *Russ. Chem. Bull., Int. Ed.*, **2012**, *61 (6)*, 1069.

REACTIONS OF ZIRCONACYCLOPENTADIENE COMPLEXES OF ZIRCONOZENE WITH ACENAPHTHENEQUINONE

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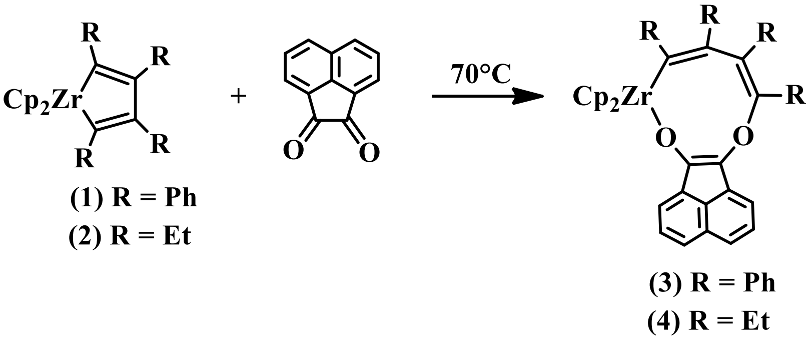
Zirconacyclopentadiene complexex of zirconocene are interesting for the synthesis of various unsaturated organic and organoelement compounds. Their reactions with a wide range of different reagents have been studied. However, there is no information about the behavior of zirconacyclopentadienes towards carbonyl compounds. Here, we report on the interaction of a number of zirconacyclopentadiene complexes with acenaphthenequinone.

We have found that the heating of tetraphenyl and tetraethyl substituted zirconacyclopentadiens (**1**) and (**2**) with acenaphthenequinone in benzene at 70°C results in the formation of nine-membered dioxazirconacycles (**3**) and (**4**).

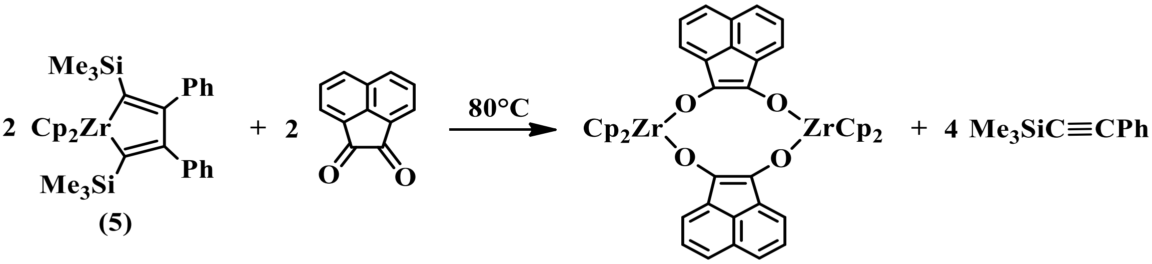


(1) R = Ph
(2) R = Et

(3) R = Ph
(4) R = Et

The both compounds were isolated from the mixture in the analytically pure state and their structure was determined by an X-ray analysis.

The interaction of phenyl(trimethylsilyl) substituted zirconacyclopentadiene (**5**) with acenaphthenequinone proceeds quite differently. In this case, a tetraoxadizirconacycle (**6**) and free phenyl(trimethylsilyl)acetilene are produced. The structure of **6** was also established by an X-ray diffraction study.



(5)

(6)

Acknowledgments

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VARIOS METHODS OF ACTIVATION OF TITANIUM COMPLEX WITH SALIGENIN LIGAND TO OBTAIN UHMWPE

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As a result of this work, the catalytic activity of non-metallocene complex of titanium (IV) (Figure 1) was studied during the polymerization of ethylene. Also the oxidation state of the transition metal in this complex after activation it by aluminum (Et_2AlCl, $Et_3Al_2Cl_3$, $EtAlCl_2$, Et_3Al) and magnesium (Bu_2Mg) organic compounds or their binary mixtures was determined. The activation process of complex was studied by EPR and NMR spectroscopy.

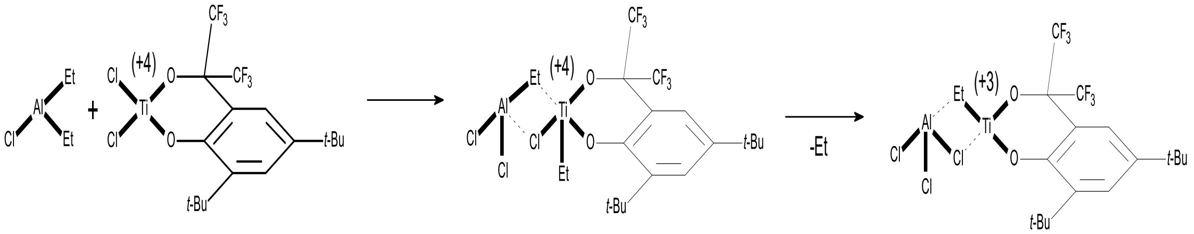

Figure 1. Scheme of activation complex by Et_2AlCl.

The maximum activity in ethylene polymerization was 4200 kg PE/mol $Ti^{-1}\cdot h^{-1}\cdot atm^{-1}$. It was found that with prolonged interaction of the titanium complex (IV) with organoaluminum compounds, the activity of the system is increasing more than two times, due to the reduction of the complex to titanium (III). Depending on the choice of aluminum organic activator, it becomes possible to control the molecular weight of polyethylene, so in the series of $Et_2AlCl < Et_3Al_2Cl_3 < EtAlCl_2$ there is a significant increase in the molecular weight of the formed PE. Obtained UHMWPE reaches M_w up to $7.2\cdot10^6$ Da and has very low bulk density, less than 0.1 g/cm^3. That is one of the crucial prerequisites for solid-state formation of tapes from UHMWPE nascent powder. All UHMWPE powders with M_w higher than $1.6*10^6$ Da were transformed into tapes by solid-state method described by Ozerin.[1]

Acknowledgments

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References

1. A.N. Ozerin, S.S. Ivanchev, S.N. Chvalun, V.A. Aulov, N.I. Ivancheva, N.F. Bakeev // Polym. Sci. Ser. A. **2012**, 54, 950–954.

COBALT-CATALYZED ALKYLATION OF INDOLES WITH METHYL 3,3,3-TRIFLUORO-2-DIAZOPROPIONATE

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The selective incorporation of the fluorine functionalities in biologically relevant compounds has become an essential tool in drug discovery process.[1] The metal-carbene C–H insertion starting from diazo compounds (including methyl 3,3,3-trifluoro-2-diazopropionate) has proved to be the most efficient approach to solve this task.[2,3] In the present work, we developed new family of catalytic systems based on the cobalt complexes for the regioselective CF_3-functionalization of *N*-(pyrimidin-2-yl)indole at the 2- or 3-positions. In particular, we found that 2,2'-bipyridyl and 1,10-phenanthroline Co(III) complexes $[CpCo(N,N\text{-ligand})I]^+$ selectively catalyze alkylation of N-(pyrimidin-2-yl)indole with methyl 3,3,3-trifluoro-2-diazopropionate to give C3-substituted indole derivative. It should be noted that this reaction proceeds without participation of directing group (pyrimidinyl substituent) because required vacant coordination sites at cobalt atom are blocked by N,N-ligand. In contrast, similar reaction catalyzed by the (carbonyl)iodide complex $Cp^*Co(CO)I_2$ leads to C2-substituted indole as a result of chelation-assistance of pyrimidinyl group.

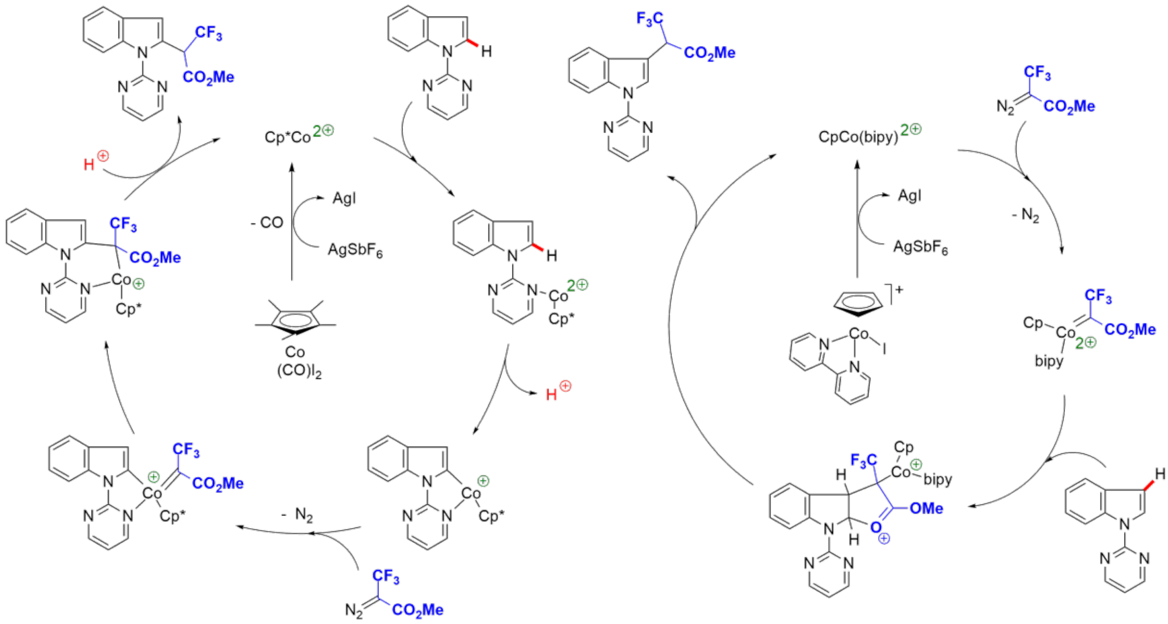

Figure 1. Two reaction pathways

Structure of the catalysts as well as mechanisms of catalytic reactions will be also discussed.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (Grant No. 16-29-10672).

References

1. S. Fustero, V. A. Soloshonok, H. Liu, et al., *Chem. Rev.* **2014**, *114*, 2432.
2. D. V. Vorobyeva, S. N. Osipov, *Synthesis* **2018**, *50*, 227.
3. D. V. Vorobyeva, M. M. Vinogradov, Y. V. Nelyubina, D. A. Loginov, A. S. Peregudov, S. N. Osipov, *Org. Biomol. Chem.* **2018**, *16*, 2966.

NEW TYPE OF HOVEYDA-GRUBBS CATALYSTS FOR ROCM REACTIONS OF OXABICYCLOHEPTENES WITH ALKENES

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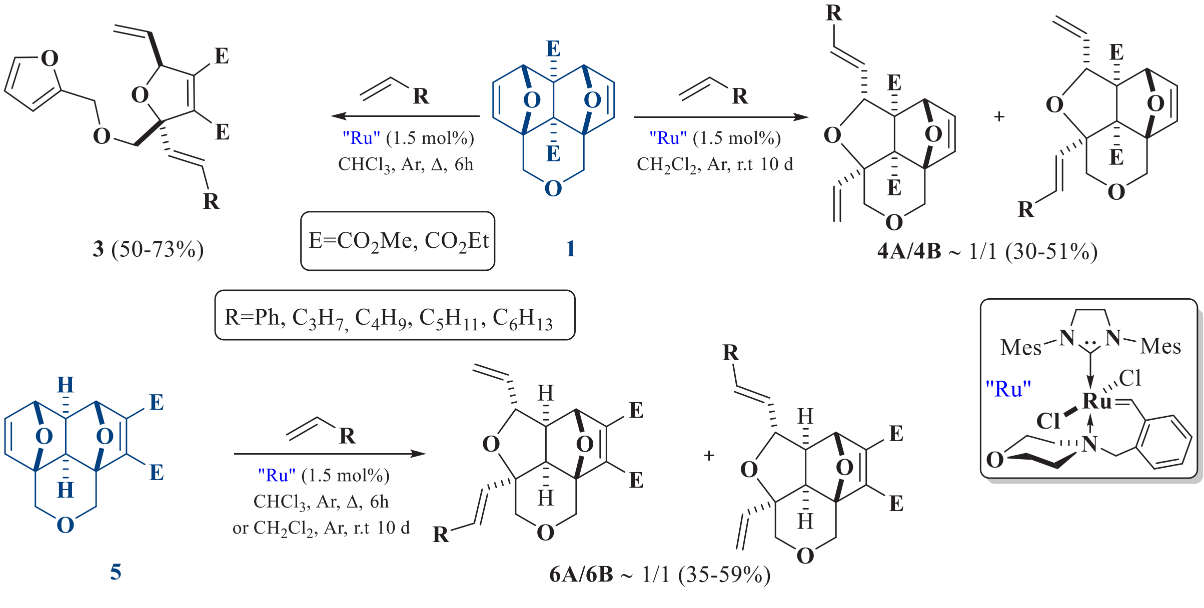
This work is devoted to the study of the catalytic activity of the new Hoveyda-Grubbs catalysts in ROCM (ring-opening cross metathesis) reactions [1]. Oxabicycloheptene systems 1 and 2 were rested as model objects for this study [2,3].

It has been shown, that the ROCM reaction of «pincer» adducts (1) with styrene is carried out at room temperature and leads to ring opening products 4 as a pair of distereoisomers in the ratio of 1: 1. Under heating, the same reaction is accompanied by the retro-Diels-Alder reaction leading to dihydrofurans 3. In the case of «domino» adducts (5) we obtained ring opening products 6 both under heating and at room temperature.



Acknowledgments

Funding for this research was provided by the Russian Science Foundation (RSF), project № 18-13-00456)

References

1. K. B. Polyanskii, F. I. Zubkov, et al. Beilstein *J. Org. Chem*. 2019, in press.
2. E. A. Kvyatkovskaya, Fedor I. Zubkov et al. *J. Org. Chem*. 2018, 83, 4840–4850.
3. K. K. Borisova, et al. *Chem. Commun*. 2018, 54, 2850-2853.

DIVALENT YTTERBIUM, SAMARIUM AND CALCIUM COMPLEXES COORDINATED BY NHC LIGANDS – VERSATILE CATALYSTS FOR HIGHLY REGIO- AND CHEMOSELECTIVE HYDROPHOSPHINATIONS

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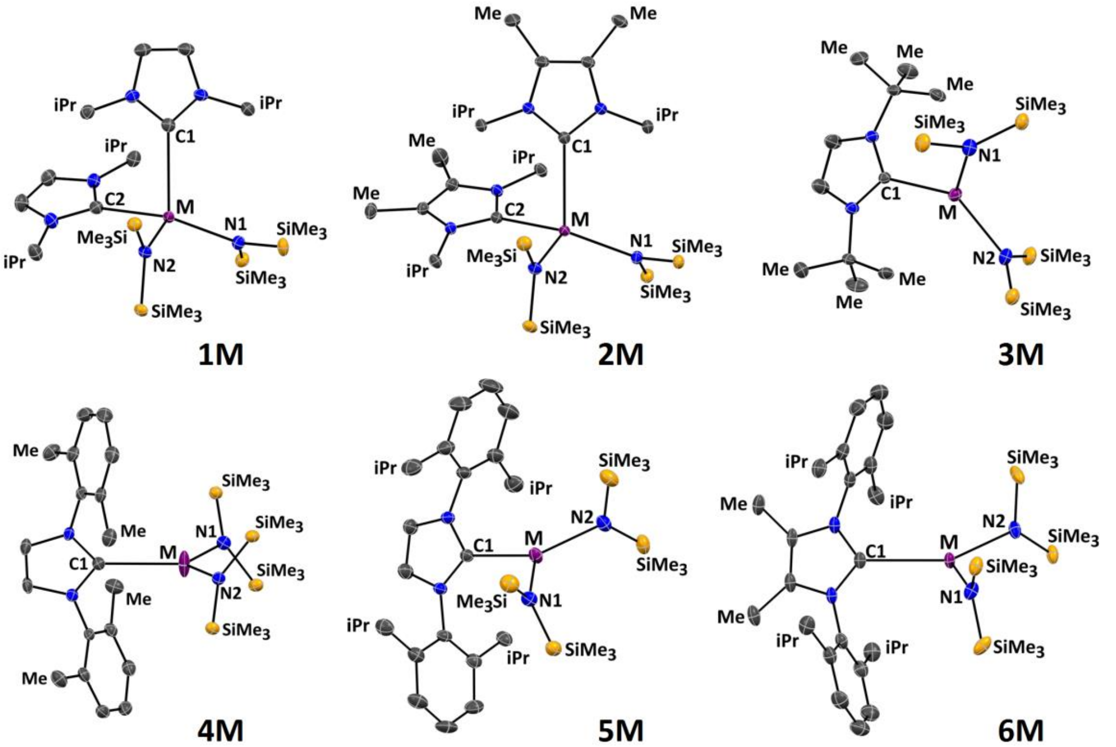
The formation of C–P bonds via single-step intermolecular hydrophosphination reactions of unsaturated substrates is a simple, atom-efficient route to a wide range of phosphorus-containing compounds. Addition of PH_3 to alkenes and alkynes offers considerable potential in the synthesis of primary, secondary and tertiary phosphines.

A series of novel amidocomplexes of Ca, Sm(II), Yb(II) coordinated by NHC ligands has been prepared and tested as catalysts for the intermolecular hydrophosphination of styrene, 2-vinylpyridine and phenylacetylene with PH_3 (Figure 1). The reactions of styrene with PH_3 proceed under mild conditions in quantitative yields allowing chemo- and regioselective way to a variety of primary, secondary and tertiaryphosphines. Crucial effect of the Lewis base coordinated to the metal center on catalytic activity in styrene hydrophosphination with PH_3 was demonstrated.[1]



1M 2M 3M

4M 5M 6M

Figure 1. Single-crystal X-ray structures of complexes $[(Me_3Si)_2N]_2M(NHC)_n$ (M = Ca, Yb,Sm)

Acknowledgments

The authors thank Russian Science Foundation (Grant № 17-73-20262)

References

1. I. V. Lapshin, I. V. Basalov, K. A. Lyssenko, A. V. Cherkasov, A. A. Trifonov. *Chem. Eur. J.*, **2019**, *25*, 459.

RUTHENIUM (II) MIXED-LIGAND COMPLEXES WITH 2-ARYLBENZIMIDAZOLES AND 4,4`-DICARBOXY-2,2`-BIPYRIDINE: SYNTHESIS, OPTICAL AND ELECTROCHEMICAL PROPERTIES

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Polypyridyl ruthenium (II) complexes are used as sensitizers in DSSC. Such complexes contain two types of ligands: “donor” ligands, which are responsible for the absorption of light, and a ligand with “anchor” groups (for example, carboxyl, phosphoryl, or sulfone groups), that are covalently bonded to the surface of a semiconductor. Ruthenium complexes absorb light in the visible and near infrared ranges, have suitable redox potentials for cell operation. However, they do not have good stability, which reduces the functioning time of the cell. The introduction of a cyclometalated fragment (a five-membered cycle with a metal-carbon covalent bond) into the complex increases the stability of the complexes. Introduction of various substitutes into C^N ligand affect electron structure of molecule, and, consequently, photophysical and electrochemical properties.

Ruthenium (II) complexes with 4,4`-dicarboxy-2,2`-bipyridine dimethyl ether and derivatives of 1-phenyl-2-arylbenzimidazole were selected as objects of study in this work. The synthesis of complexes involves two stages. The first stage is cyclometalation. The corresponding 2-arylbenzimidazole, potassium hexafluorophosphate and sodium hydroxide were added to the $[Ru(p\text{-cymene})Cl]_2Cl_2$ dimer complex. The resulting complexes were purified by column chromatography. After that, an anchoring ligand (4,4`-dicarboxy-2,2`-bipyridine dimethyl ether) was introduced, the product was purified by column chromatography and recrystallization. All obtained ligands and complexes were characterized by ^1H NMR spectra. Single crystals for X-ray diffraction analysis were obtained for some complexes.

A series of complexes with general formula $[Ru(dmdcbpy)_2L]PF_6$ is obtained, where L = 1-phenyl-2-aryl-benzimidazole with -F, $-CF_3$, -Cl, -CN, $-NO_2$, $-CH_3$, -OMe, $-NMe_2$ and -H substitutes in 2-aryl ring.

The complexes were characterized by electron absorption spectroscopy (ESP), luminescent spectroscopy and cyclic voltammetry (CV). According to CV, an increase in the electron-donor properties of substituents in 2-arylbenzimidazole from $-NO_2$ to -OMe leads to a decrease in the redox potential (Ru^{3+}/Ru^{2+}). Moreover, it leads to a red-shift (in general) of absorption and luminescence bands. Nevertheless, complexes with the substituents possessing strong acceptor nature, do not show expected photophysical properties – spectral bands were not shifted to the UV region.

DERIVATIVES OF CLOSO-DECABORATE ANION WITH PENDANTE POLYAMINE GROUPS

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Derivatives of $[B_nH_n]^{2-}$ (n = 10,12) anions with oxonium and thionium cyclic substituents are promising compounds for the preparation of closo borates with pendant functional groups.[1,2] Biological polyamines (spermine, spermidine, putrescine, etc.) are important for metabolism and fairly common biologically active molecules in living systems.

We have studied the interaction of the 1,4-dioxane derivative of the $[B_{10}H_{10}]^{2-}$ anion with biologically active polyamines (putrescine, cadaverine, spermine) in ethanol. It was shown that, as a result of the reactions, the cyclic substituent unfolds with the addition of the polyamine fragment to the boron cluster through an alkoxyl spacer chain.

The introduced polyamine groups will allow the resulting *closo*-borates to bind to various polyanionic targets in the cell (DNA, RNA, phospholipids, charged sections of proteins, etc.)

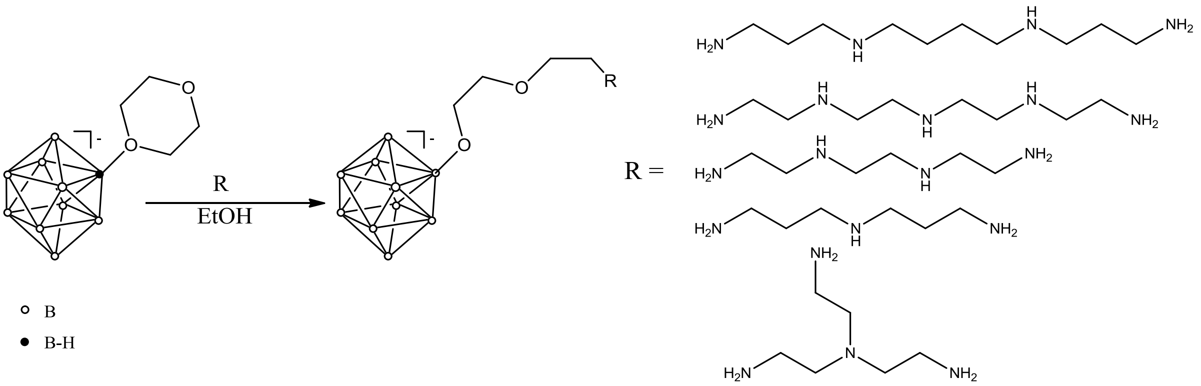

Figure 1. The interaction of oxonium derivatives of the *closo*-decaborate anion with polyamines

References

1. Matveev E.Yu., Akimov S.S., Kubasov A.S. et al. *Rus. J. Inorg. Chem.* 2017, **62**, 6, 808.
2. Laskova J., Kozlova A., Ananyev I. et al. *J. Organomet. Chem.*, 2017, **834**, 64.

AMIDO RARE EARTH COMPLEXES COORDINATED BY TRIDENTATE AMIDINATE LIGAND. THE SYNTHESIS, STRUCTURE AND CATALYTIC ACTIVITY

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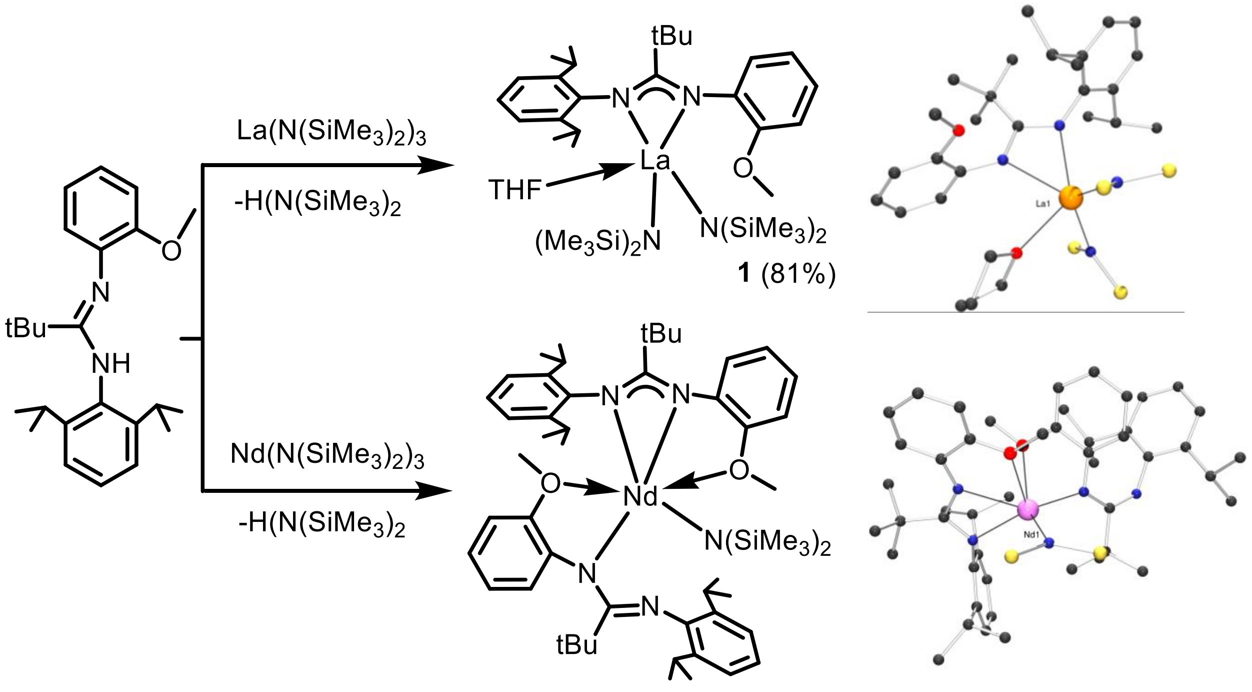
Synthetic polyisoprene is the most important elastomer and is widely used in the creation of artificial rubbers and compositions based on them. Optimization and development of new catalytic systems of isoprene polymerization, is of both fundamental and applied interest for the creation of materials with desired rheological properties.

In order to create new effective catalysts for the polymerization of isoprene (Scheme 1), we obtained new mono- and bis (amide) complexes of Nd and La with a tridentate amidinate ligand. Both complexes found a great activity and efficiency of isoprene polimerisation.



Scheme 1

Acknowledgments

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DEVELOPMENT OF MOLECULAR MATERIALS BASED ON PORPHYRIN DERIVATIVES OF METALS WITH HIGH-PERFORMANCE OPTOELECTRONIC AND MAGNETOCALORIC PROPERTIES

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The design and preparation of new conjugated organometallic molecules is one of the research topics in Molecular Materials Science. A planar structure and an ideal aromatic system inherent in porphin molecules and their numerous derivatives. However of great interest for application as molecular materials are porphyrins predominantly in the form of metallic derivatives (MPs) due to the advent of new unique properties by combination of metal ion and macrocycle electronic systems in one molecule. These are the high charge-carrier mobility, p-channel, n-channel, and ambipolar charge-transport associated with the tunable HOMO and LUMO energy levels,1 electron donor ability favoring photoindused electron transfer (PET), strong light absorption from the ultraviolet to the near-IR region, and high reactivity of axial positions in the molecule. Metal porphyrins are studied and applied as catalysts2, chemical probes for ions, VOCs, gases, optical chemosensors3, semiconductors, and functional dyes for organic solar cells and photodynamic therapy.4 In this review, we will summarize the MPs, axially bonded with anions (X) and heterocyclic molecules (L) as well as their technical applications. This review highlights the potential of MPXLs in optoelectronics and provides important perspective for advances of MPXLs catalysts. We will discuss the progress of MPXLs according to their applications, including solar energy conversion, optical sensing, magnetic refrigeration and hyperthermia.

This work was carried out under partial financial support from the Russian Foundation for Basic Research (Project No. 18-43-370022-r-a) and from the Program of the State Academies of Sciences (Subject No. 0092-2014-0002 and 0092-2014-0003).and with the help from the Centre for Joint Use of Scientific Equipment “The Upper Volga Region Centre of Physicochemical Research”

References

1. D. Zhu, Molecular materials and devices: an interdisciplinary field of research, *Mater. Chem. Front.*, **2018**, 2, 10.
2. Handbook of Porphyrin Science. V. 21. Catalysis, World Scientific Publishing Co Pte Ltd, Singapore, **2012**.
3. T. Lomova, Axially coordinated metal porphyrins in Science and Applications. URSS, Moscow, **2018**.
4. F.B ian , J. Jiang , Recent Advances in Phthalocyanine-Based Functional Molecular Materials, in: D.M.P. Mingos (Ed.) 50 Years of Structure and Bonding – The Anniversary Volume, Structure and Bonding 172, Springer International Publishing Switzerland, 2016.

FACILE ACCESS TO ALDEHYDES FROM CALCIUM CARBIDES AS SUSTAINABLE CARBON SOURCE

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Acetylene is one of the primary building blocks in synthetic organic and industrial chemistry. Several highly valuable processes have been developed based on this simplest alkyne and the development of acetylene chemistry has had a paramount impact on chemical science over the last few decades. However, the practical implementation of high-pressure acetylene chemistry can be very challenging, owing to the risk of explosion and the requirement for complex equipment; special safety precautions need to be taken to store and handle acetylene under high pressure, which limit its routine use in a standard laboratory setup. Calcium carbide is a stable and inexpensive acetylene precursor that is available on the ton scale and it can be handled with standard laboratory equipment.[1]

One of the well-known areas in acetylene chemistry is acetaldehyde production, which is an important chemical.[2] Until the 1960s, acetaldehyde was produced commercially from acetylene. The acetylene was first treated with sulfuric acid and mercuric sulfate, and in a consecutive step oxidized to acetic acid by molecular oxygen. Later, acetaldehyde was mainly produced from ethylene. Currently, efficient procedure is based on Wacker process through the direct oxidation of ethylene to acetaldehyde with a $PdCl_2/CuCl_2$ catalyst in water in the presence of air or other oxidants.[3] The disadvantages of ethylene and acetylene processes are high pressure operation and toxic catalysts.

Ethanol is another raw material for acetaldehyde. For the production of acetaldehyde, ethanol can either be dehydrogenated or oxidized in the presence of oxygen.[2,3]

We propose a scheme for the synthesis of acetaldehyde from calcium carbide without the use of high pressure and toxic catalysts. In this scheme, the resulting alcohol is recycled, which significantly reduces production costs and waste.

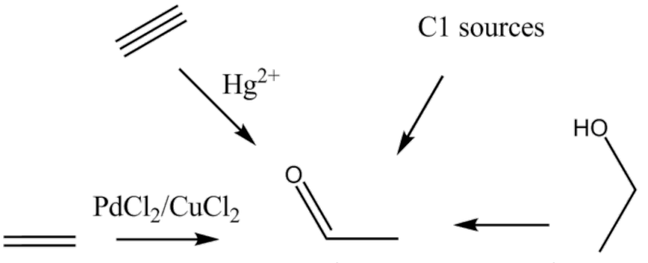

Figure 1. Industrial routes for the synthesis of acetaldehyde

References

1. K. S. Rodygin, G. Werner, F. A. Kucherov, V. P. Ananikov, *Chem. Asian J.* **2016**, *11*, 965.
2. A. Segawa, A. Nakashima, R. Nojima, N. Yoshida, M. Okamoto, *Ind. Eng. Chem. Res.* **2018**, *57*, 11852.
3. C. Angelici, B. M. Weckhuysen, P. C. A. Bruijnincx, *Chem. Sus. Chem.* **2013**, *6,* 1595.

UNRAVELING STRUCTURAL, ORBITAL, AND SPECTRAL PROPERTIES OF D0 ORGANOMETALLICS: EFFECTIVE COMPUTATIONAL ROUTE

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The diverse titanium(IV) complexes represent a major class of compounds widely used in many fields of modern molecular science. At the same time, intriguing is that structure–property relationship in such an amazing organometallic family retains enigmatic. Modeling of geometry and excited states of complicated organometallic complexes is a difficult task. There is a particular problem of modeling charge-transfer (CT) transitions, a class of electronic transitions of particular importance in chemistry and biochemistry. Whereas ligand-to-metal charge transfer (LMCT), excited states play a significant role in molecular photonics, the theoretical and experimental knowledge on properties of LMCT excited states, unlike MLCT, metal-centered, ligand-centered or other excited states accounts unsystematic, silent data. Attempts to model the structures of simple group IV metallocenes were previously made, however, the calculated structural parameters deviated significantly from the crystallographic values.

In this work, we applied for the first time a wide set of quantum chemical methods at different levels of theory to geometry determination and modeling electronic absorption spectra of the structurally complicated d^0 metallocene complex in the gas and liquid phases using titanocene dicarbonyl as an example.The performance of density functional theory (DFT), Hartree-Fock (HF), and respective time-dependent (TDHF, TDDFT) methods for computing geometry, molecular orbitals, and electronic excitation spectrum of d^0-titanocene dicarboranyl as the reference model was analyzed.[1] The HF methods and most of the applied DFT methods reproduce the crystal structure with appropriate accuracy; much scarce are the methods capable of modeling ligand-to-metal charge-transfer (LMCT) excitations in the d^0-organometallics with acceptable accuracy. Upon transfer of a complex from gas to solution, the compression of the sandwich fragment and activation of the metal–carbon σ-bonds in group IV metallocenedicarboranyls were deduced.[2]

The sophisticated organometallic structure $M(\eta^5:\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$(M = Ti, Zr,Hf) and their LMCT electronic excitation spectra in gas and in typical organic solvents were systematically modeled for the first time using the methods at different levels of theory. From amongst the seventeen functionals, based on the different approximations, the functional B3LYP outperformed the others in its description of the LMCT excitations. The worst spectral fit with the experiment was obtained with the TDHF and TDDFT/M06-HF methods.

Acknowledgments

Financial support from FASO (the state contract 0089-2019-0003) and RFBR (project 18-03-00359) is gratefully acknowledged.

References

1. G. V. Loukova, A. A. Milov, V. P. Vasiliev, V. I. Minkin, *High Energy Chem*. **2018**, *52*, 384.
2. G. V. Loukova, A. A. Milov, V. P. Vasiliev, *Russ. Chem. Bull., Int. Ed*. **2018**, *67*, 2323.

TRIS(PYRAZOLYL)METHANE AND TRIS(PYRAZOLYLMETHYL)AMINE –VERSATILE LIGANDS FOR DESIGN OF LN(III) COMPLEXES FEATURING MAGNETIC AND LUMINESCENT PROPERTIES

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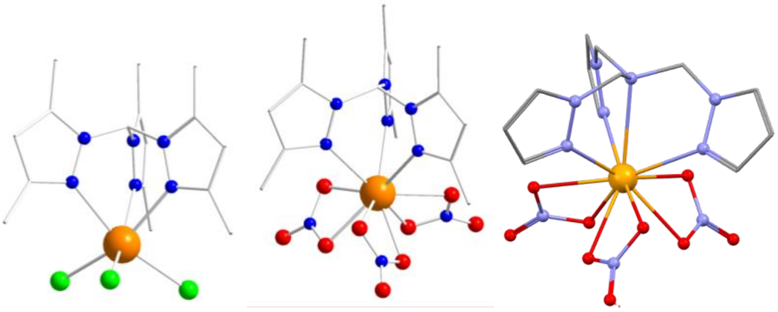
Using neutral tris(3,5-dimethyl-pyrazolyl)methane (Tpm) and tris((pyrazolyl)methyl)amine (Tpa) as neutral ligands, a series of Ln(III) $[Ln(Tpm)X_3]$ (Ln = Eu, Tb, Dy, Er, Yb; $X^- = Cl^-, NO_3^-$; Fig. 1) and $[Ln(Tpa)(NO_3)_3]$ (Ln = Eu, Tb, Dy, Er, Yb; Fig. 1). It was shown that the observation of a slow relaxation of the magnetization of these derivatives induced by the field strongly depends on the nature of the anion. NO_3^- fragments are suitable for stabilization of the oblate electron density of Dy^{3+}, while Cl^- generate an equatorial crystalline field necessary for the slow relaxation of “elongated” Er^{3+} ions. It has also been demonstrated that Tpm and Tpa ligands are an appropriate coordination environment for Eu^{3+}, Tb^{3+}, and Dy^{3+} ions luminescence sensibilization.



$[Ln(Tpm)Cl_3]$, $Ln(Tpm)(NO_3)_3]$ и $[Ln(TPA)(NO_3)_3]$

Figure 1. Molecular structures of complexes $[Ln(Tpm)Cl_3]$, $Ln(Tpm)(NO_3)_3]$ and $[Ln(TPA)(NO_3)_3]$

Acknowledgments

This work was financially supported by the Russian Science Foundation (grant 17-73-30036)

References

1. J. Long, D. M. Lyubov, T. V. Mahrova, A. V. Cherkasov, G. K. Fukin, J. Guari, Ju. Larionova and A. A. Trifonov, *Dalton Trans.* 2018, **47**, 5153.

CARBORANYL TETRAZOLES AS HIGH ENERGY COMPOUNDS: SYNTHESIS AND A COMPUTATIONAL STUDY

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The large positive heats of formation of nitrogen rich compounds make them promising targets for the preparation of high energetic materials. Among polynitrogen heterocycles tetrazoles possess remarkable thermochemical characteristics. Icosahedral carboranes as new energetic materials also attract the growing interest during last years, since the carborane polyhedron possesses rather high thermal and chemical stability, and has a high enthalpy (ΔH_f = 42 kcal/mol) of formation. These characteristics were the basis for including the structural fragments of carboranes in the creation of the high-energy systems. So, the design of monomolecular structures containing various energetically active components, namely tetrazoles and carboranes are of great interest in the search for the high-energy materials. In this contribution an efficient method for the preparation of carboranyl-substituted tetrazoles and their energetic characteristics will be presented. A variety of carboranyl substituted tetrazoles were prepared by the triflic acid catalyzed regioselective alkylation of 5-R-1H-tetrazoles with readily available allylcarboranes.

The energetic properties of 22 carboranyl tetrazoles were evaluated using quantum chemical calculations (DFT 6-311+G*). The theoretical values of total energy, entropy, dipole moments, diagonal tensor elements of polarizability (Pxx, Pyy, Pzz), HOMO and LUMO energies, for above compounds in gaseous phase were found. Theoretical terahertz frequencies for potential high-energy density materials (HEDMs) were computed which allows the opportunity for the remote detection of these compounds. According to the results of calculations the most promising HEDMs among studied compounds were found. Based on the calculated frontier molecular orbital energy gap these energetic materials are even less impact sensitive than classical diaminotrinitrobenzene (DATB) and trinitroaniline (TNA). Thus our results demonstrated that carboranes containing nitrogen rich units are perspective for their potential applications as HEDMs.

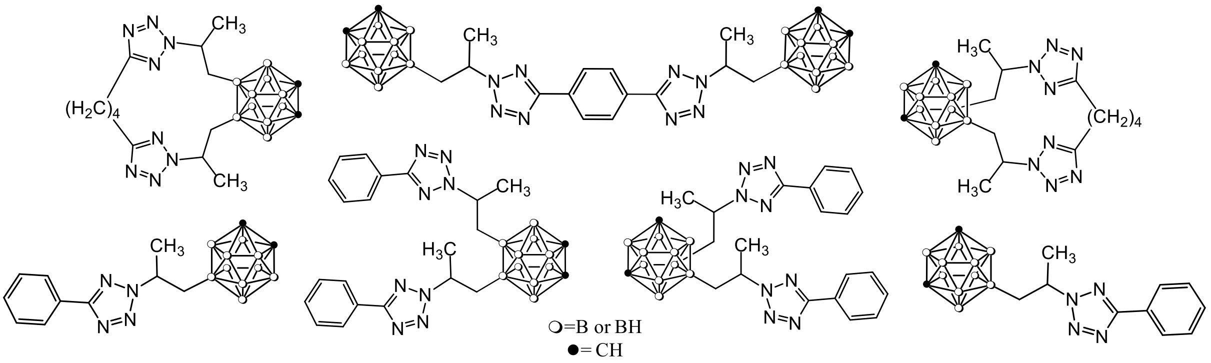

Figure 1. Prepared carboranyl tetrazoles

MOLECULAR STRUCTURE OF ZIRCONIUM CARBOSILANES

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Introduction

Modern computer methods for calculating non-empirical and semi-empirical quantum chemistry make it possible to predict with high probability the structure of compounds, energy, and other equally important characteristics of molecules.

The purpose of this work is to calculate the thermodynamically stable molecular structures of zirconium carbosilanes synthesized in GNIIChTEOS[1,2], and to optimize their geometric structure.

The development of clear ideas about the structure and molecular organization can lead to optimization of the conditions for the synthesis of zirconium carbosilanes, which are designed to form high-temperature components of ceramic composite materials (reinforcing fibers, coatings, matrices, etc.) and to stabilize their high-strength ultrafine ceramic structure above 1300 °C. Therefore, the study of the molecular structure of zirconium carbosilanes seems to be very relevant.

Experimental

The calculation of the ground, intermediate, and transition states of the previously synthesized[2] zirconium carbosilanes was carried out using the Gaussian 98 software package.

Modeling, preliminary calculation of thermodynamically stable structures and their optimization were carried out within the HyperChem software package using molecular mechanics (force field MM +) and the semi-empirical PM3 method.

The molecular structure was optimized, and the electronic and thermodynamic characteristics were calculated in the Gaussian software package in the Hartree-Fock approximation using a valence-split basis that is optimal for these compounds. The correlation corrections were taken into account according to the Density Functional Theory (DFT) in the B3LYP approximation.

Conclusion

The most probable molecular structures of previously synthesized zirconium carbosilanes was determined by computer chemistry methods.

References

1. P. A. Storozhenko, G. I. Shcherbakova, et al. *Inorg. Mater.* **2006**, *42*, 1159.
2. G. I. Shcherbakova, P. A. Storozhenko, et al. *Inorg. Mater.* **2011**, *47*, 535.

BIS(ARENE)CHROMIUM 1-(1-(N-PHENYLPROPIONAMIDO)ETHYL)-1-HYDROFULLERIDES

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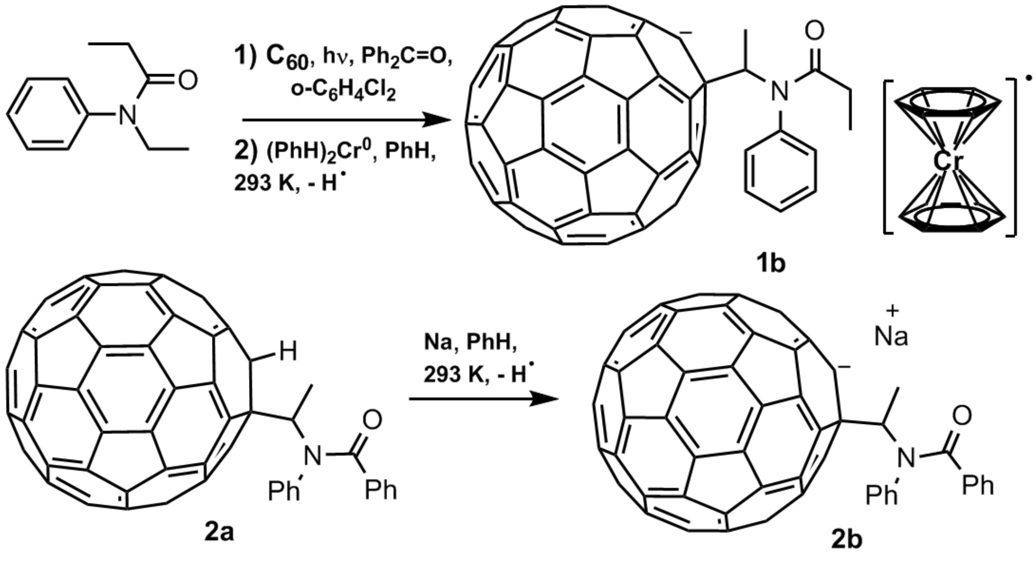
Bis(benzene)chromium reacts with 1-(1-(N-phenylpropionamido)ethyl)-1,2-dihydrofullerene (**1a**), in toluene at 293 K to form salt bis(benzene)chromium 1-(1-(N-phenylpropionamido)ethyl)-1-hydrofulleride (**1b**). Sodiumreacts with 1-(1-(N-phenylbenzamido)ethyl)-1,2-dihydrofullerene (**2a**), in toluene at 293 K to form salt sodium1-(1-(N-phenylbenzamido)ethyl)-1-hydrofulleride (**2b**). Fullerides **1b**, **2b** are stable at 313K, and insoluble in hexane, sparingly soluble in PhMe, soluble in THF. NIR spectrum of fullerides **1b, 2b** in THF at 290 K indicates absorption bands in 985 - 997 and 645 - 665 nm range typical for anions [1-(1-(N-phenylpropionamido)ethyl)-1-hydrofulleride]$^-$ and [**2a**$_{\text{-H}}$]$^-$. The reaction of fullerides **1b, 2b** with HCl gaveinitial **1a, 2a** correspondingly. Fullerene **1a** was obtained by irradiation of fullerene C$_{60}$, N-ethyl-N-phenylpropionamide and benzophenone in o-dichlorobenzene solution using luminescent UV lamp 370 nm 10x10w in an evacuated and sealed pyrex ampoule at 313 – 323 K. After solvent evaporation in vacuo column chromatography over silica gel with toluene as eluent gave first unreacted [60]fullerene, some impurities and then, fullerene **1a** as amorphous brown solid in 39% yield. Fullerene **1a** is insoluble in hexane, soluble in CHCl$_3$ and THF. The UV/vis spectrum of **1a** in decaline at 290 K show absorption bands at 706, 639, 434, 325, 256, 208 typical for 1,2 [60]fullerene derivatives. All reactions were carried out under an inert atmosphere.



Acknowledgments

The work was performed using the instrumental base of the Analytical Center of the G.A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences and in the framework of the Russian state assignment.

PERFLUOROCARBON EMULSION WITH PORPHYRINOIDS IN PHOTODYNAMIC THERAPY

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Hypoxia is a major factor that limits the efficacy of photodynamic therapy and perfluorocarbon emulsions with photosensitizers soluble in the fluorocarbon phase would possess the following advantages such as a high oxygen capacity and its ability to accumulate in inflammation areas. Porphyrinoids (porphyrins, chlorins, bacteriochlorins) are widely used as photosensitizers in photodynamic therapy of cancer. The solubility in the fluorocarbon phase was achieved by introduction of perfluoroaliphatic substituents to the photosensitizer structure. The number of porphyrins, chlorins and bacteriochlorins were synthesized and their optical parameters (light absorption, ROS generation) and photodynamic activity were compared. In emulsionform porphyrinoids cause the death of human tumor cells HCT116 (colon carcinoma) and MCF7 (breast carcinoma) in submicromolar concentrations (5-20 μM) upon photoexcitation in "red" light region. Dark cytotoxicity of emulsions during 72 h cell incubation was not detected. Emulsions without photosensitizers were inert *in vitro*. The mechanism of cell death was photo-induced necrosis. Necrosis was visualized by staining propidium iodide cells in confocal microscopy. The leader fluorinated chlorin in aqueous solution (control without fluorine phase) caused photoinduced necrosis in normoxia, but not in hypoxia. The leader fluorinated chlorin in a fluorocarbon emulsion initiated photoinduced necrosis in both normoxia and hypoxia.

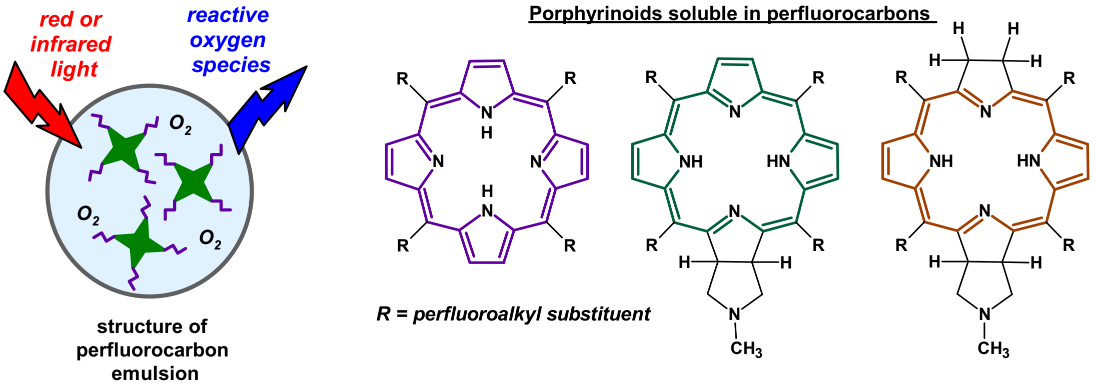

Figure 1. Construct of perfluorocarbon emulsion with porphyrinods and their chemical structures

Acknowledgments

This work was supported by RFBR (№18-315-00432). NMR studies, spectral characterization, elemental analysis were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

SYNTHESIS OF DERIVATIVES OF ANION $[B_{10}H_{10}]^{2-}$ WITH BIOLOGICALLY ACTIVE PENDANTE GROUPS

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Presently, one of the most urgent tasks for ^{10}B neutron capture therapy of malignant tumors is the development of methods for the synthesis of compounds containing cluster boron anions $[B_nH_n]^{2-}$ (n = 10,12) with biologically active fragments attached to ensure drug delivery to the cell. It is known that the interaction of derivatives of the $[B_nH_n]^{2-}$ oxonium type anion with nucleophiles reveals a cyclic substituent followed by attachment of a pendant functional group.[1,2] Use of biogenic compounds (amino acids, nucleotides, carbohydrates, etc.) as nucleophilic reagents their derivatives allows you to get a wide range of compounds, promising for use in ^{10}B-NCT.

We have studied the interaction of the 1,4-dioxane derivative of the *closo*-decaborate anion with amino acids (glycine, cysteine, serine) under various conditions. It was shown that as a result of the reactions, the oxonium substituent is opened with the addition of an amino acid fragment to the boron cluster through a spacer group (shown by the example of glycine):

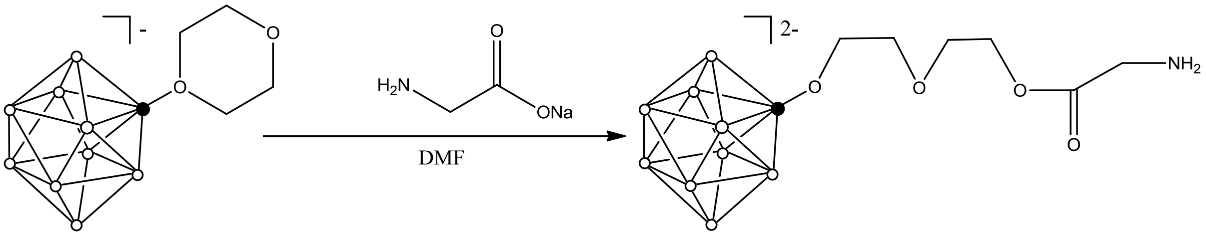

Figure 1. Opening of a cyclic substituent in derivatives of a closo-decaborate anion by amino acids

References

1. Matveev E.Yu., Akimov S.S., Kubasov A.S. et al. *Rus. J. Inorg. Chem.* 2017, **62**, 6, 808.
2. Laskova J., Kozlova A., Białek-Pietras M. *J. Organomet. Chem.,* 2016, **807**, 29.

NEW TRIPODAL LIGANDS ON THE TRIPHENYLPHOSPHINE OXIDE PLATFORM AS ANCESTORS OF ATRANE-TYPE LANTHANIDE COMPLEXES

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Tripodal ligands on the triphenylphosphine oxide platform with various donor groups in the side arms are known to produce complexes with multiply charged cations of *f*-block elements due to preorganized propeller conformation[1–3]. These potentially tetradentate ligands show the rich structural and reaction chemistry. To date, however, these ligands are found to coordinate to Ln(III) only in bi- and tridentate modes.

We have synthesized a series of novel functionalized phosphine oxides: [2-FG-$(CH_2)_nOC_6H_4]_3PO$ (FG = $Ph_2P(O)$, CO_2H, tetrazol-1-yl, 3-Ph-triazol-5-yl; n = 1, 3), promising as receptors and ligands for applications in catalysis, biomedicine, designing molecular containers, etc.

For the first time, we revealed the formation of atrane-type lanthanide complexes with tetradentate coordination of the ligands in solutions.

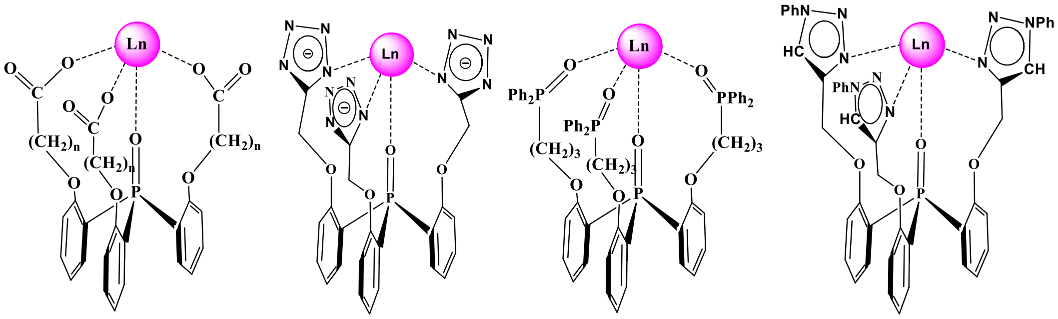

Figure 1. Visualization of core structure of “lanthanatrane” complexes in solutions according to IR, multinuclear (^1H, ^{13}C, and ^{31}P) NMR, and DFT data.

Acknowledgments

This work was supported by RFBR (project no. 17–03–00800). Spectral studies were performed with the financial support from the Ministry of Science and Higher Education of the Russian Federation using the equipment of the Center for molecular structure studies of INEOS RAS.

References

1. I. Yu. Kudryavtsev, T. V. Baulina, M. P. Pasechnik, S. V. Matveev, A. G. Matveeva, *Phosphorus, Sulfur, Silicon Relat. Elem.* **2014**, *189* (7–8) 946.
2. A. G. Matveeva, I. Yu. Kudryavtsev, M. P. Pasechnik, A. V. Vologzhanina, T. V. Baulina, A. V. Vavina, G. Ya. Sukat, S. V. Matveev, I. A. Godovikov, A. N. Turanov, V. K. Karandashev, V. K. Brel, *Polyhedron* **2018**, *142*, 71.
3. A. N. Turanov, A. G. Matveeva, I. Yu. Kudryavtsev, M. P. Pasechnik, S. V. Matveev, M. I. Godovikov, T. V. Baulina, V. K. Karandashev, V. K. Brel, *Polyhedron* **2019**, *161*, 276.

SYNTHESIS OF NEW BULKY PHOSPHITE AND PHOSPHORAMIDITE LIGANDS AND THEIR APPLICATION IN ASYMMETRIC HYDROGENATION

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Enantioselective homogenous hydrogenation catalyzed by chiral transition metal complexes has become one of the most wide-spread methods for obtaining of optically active organic compounds, more commonly utilizing complexes based on Ru, Rh or Ir and including phosphorous-containing chiral ligands. Tetrahydro-1*H*-benzodiazepinones represent a novel, currently developed class of bioactive compounds displaying antiasthmatic, antitumor, and neuroprotective activities. New bulky phosphite and phosphoramidite (**L1** - **L4**) ligands were synthesized and tested in the asymmetric Rh-catalyzed hydrogenation of a series of substrates, including dimethyl itaconate, α- and β-dehydroamino acid derivatives and in the Ir-catalyzed hydrogenation of 2-methylindole (Figure 1).[1] In Ir-catalyzed asymmetric hydrogenation of a series of 4-R-1,3-dihydro-2*H*-1,5-benzodiazepin-2-ones up to 74% *ee* was achieved.[2,3]

The structure of obtained compounds was determined based on one- and two-dimensional NMR spectroscopy data (^{1}H, ^{13}C, ^{31}P, ^{1}H-^{1}H COSY, ^{1}H-^{1}H ROESY, ^{1}H-^{13}C HSQC and ^{1}H-^{13}C HMBC).

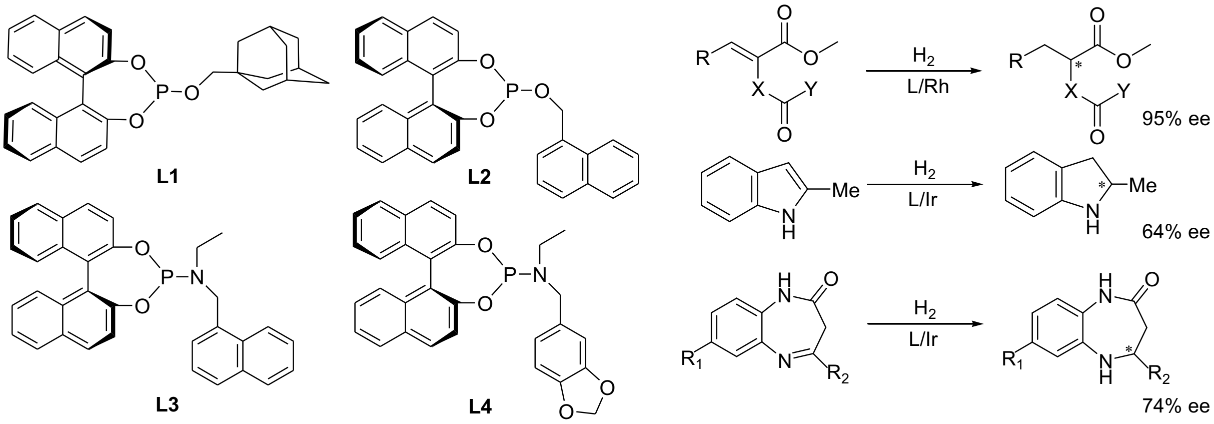

Figure 1. Structures of ligands **L1**-**L4** and schemes of Rh- or Ir-catalyzed hydrogenation of different substrates.

Acknowledgments
This work was supported by RFBR grant № 17-03-00483.

References

1. M. V. Sokolovskaya, S. E. Lyubimov, I. S. Mikhel, K. P. Birin, V. A. Davankov, *J. Organomet. Chem.* **2018**, *861*, 230.
2. M. V. Sokolovskaya, S. E. Lyubimov, I. S. Mikhel, K. P. Birin, V. A. Davankov, *Russ. Chem. Bull.* **2018**, *67*, 260.
3. S. E. Lyubimov, M. V. Sokolovskaya, I. S. Mikhel, K. P. Birin, V. A. Davankov, *Russ. Chem. Bull.* **2019**, *68*, 1429.

SYNTHESIS AND CYTOTOXICITY OF NOVEL DAUNORUBICIN DERIVATIVES

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Anthracyclines is the most effective and well-known chemotherapeutic agents used for cancer treatment. However, a broad range of adverse effects, including cardiotoxicity and multidrug resistance (MDR), seriously limit their application. To eliminate these drawbacks, many hundreds of their analogs were prepared, but negative properties remained until now[1].

To date, the synthesis of hybrid (bivalent, chimeric) molecules containing two pharmacophoric groups in one compound is one of promising approaches to design new pharmaceuticals (antitumor including)[2]. Depending on the type of spacer used for this purpose (cleavable or non-cleavable), this approach can provide double mechanism of action and considerable deceleration of MDR development for new drug. In the context of approach to the synthesis of hybrid molecules showing cancerolytic properties on the basis of daunorubicin cancerostatic and two natural aldehydes that display bactericide properties, piperonal and its dimethoxy derivative, recently we prepared conjugates considerably superior to the initial anthracycline in the scope of therapeutic action[3].

Taking into account the relative simplicity of synthesis based on reductive amination of aromatic aldehydes[4] and high cancerolytic activity of prepared compounds, we considered promising to obtain a series of hybrid molecules containing both fragments of closely related piperonal analogs and spacers of fundamentally different types.

In this study, we have prepared 21daunorubicin conjugates with different piperonal derivatives and tested their anticancer activity. Thereby we have revealed that conjugates with non-cleavable (amine) spacer show larger efficiency than those ones with cleavable (amide) spacer.Its elongation to the 1,2,3-triazole linker does not increase anticancer activity.

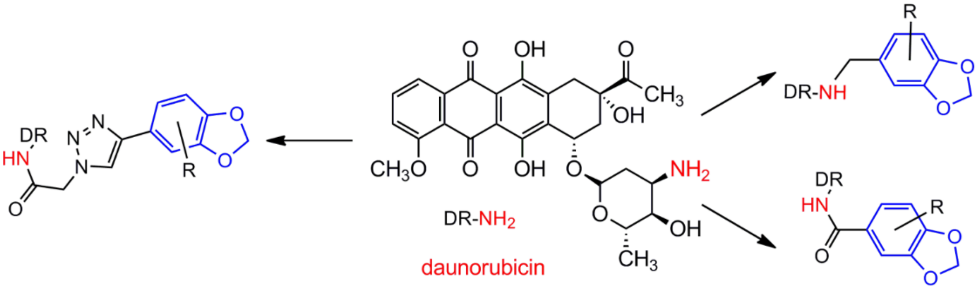

Figure 1. Novel daunorubicin derivatives (R = OCH_3, Br, NO_2)

Acknowledgments

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References

1. A. A. Moiseeva, *INEOS OPEN.* **2019**, *2(1)*, 9.
2. A. N. Tevyashova, E. N. Olsufyeva*et al.*, *Russ. Chem. Rev.* **2015**, *84(1)*, 61.
3. V. K. Brel, O. I. Artyushin *et al.*, *Pat. RU 2642068*. **2018**.
4. O. I. Artyushin, E. V. Sharova *et al.*,*Russ. J. Gen. Chem.* **2017**, *87(6)*, 1323.

CHARGE-COMPENSATED RHODACARBORANES AS CATALYSTS FOR ANNULATION OF ARYLCARBOXYLIC ACIDS WITH ACETYLENES

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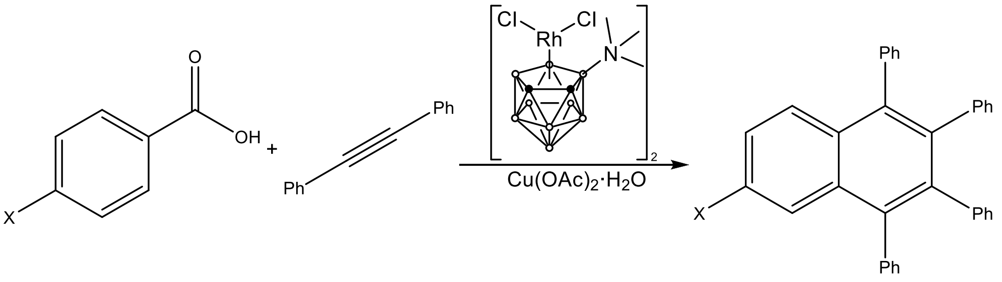
Charge-compensated metallacarboranes are perspective catalysts in wide range of organic reactions such as olefin hydrosylilation[1], cyclopropanation[2] and radical polymerization[3].

Previously we demonstrated that $[1,1\text{-}Br_2\text{-}8\text{-}SMe_2\text{-}1,2,8\text{-}IrC_2B_9H_{10}]_2$ catalyzes the oxidative coupling of benzoic acid with diphenylacetylene yielding 1,2,3,4-tetraphenylnaphtalene as well as products of di- and trimerization of alkyne[4]. In this work we report the annulation of arylcarboxylic acids catalyzed by $[1,1\text{-}Cl_2\text{-}4\text{-}NMe_3\text{-}1,2,3\text{-}RhC_2B_9H_{10}]$. In presence of this complex arylcarboxylic acids react with tolan and copper acetate (II) as an oxidant to give the corresponding tetraphenylsubstituted benzoannulated derivatives in moderate yields.



X=H
OMe
Cl

Acknowledgements

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References

1. Zakharkin L.I., Agahanova T.B. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 1208.
2. O. Tutusaus, S. Delfosse, A. Demonceau, A. F. Noels, R. Nucez, C. Vicas, F. Teixidor, *Tetrahedron Lett.* **2002**, 43, 983-987.
3. O. Tutusaus, S. Delfosse, S. Simal, A. Demonceau, A. F. Noels, R. Nucez, C. Vicas, F. Teixidor, *Inorg. Chem. Commun.* **2002**, 5, 941-945.
4. A.P. Molotkov, M.M. Vinogradov, A.P. Moskovets, O. Chusova, S.V. Timofeev, V.A. Fastovskiy, Y.V. Nelyubina, A.A. Pavlov, D.A. Chusov, D.A. Loginov, *Eur. J. Inorg. Chem.* **2017** 4635–4644.

MONOSUBSTITUTED PILLAR[5]ARENES CONTAINING PHOSPHORYL FRAGMENT AS HOSTS FOR SOME METAL CATIONS

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Heavy metal pollution is the result of many human activities, such as mining and metallurgy. The volume of heavy metal emissions into the environment is continuously increasing as a result of industrial activity and technological development, which poses a serious threat to the environment and public health due to their toxicity and accumulation in the food chain. In this regard, the identification of heavy metals is of paramount importance. There are some examples of the application of cyclophanes (calix[n]arenes and thiacalix[n]arenes, cucurbit[n]urils, cyclodextrins) in the separation and extraction of heavy metals. Unlike these metacyclophanes, classical paracyclophanes are rather difficult to functionalize, however, in the last decade, the pillar[n]arene class of paracyclophanes has become widespread. The advent of the pillar[n]arenes has provided an opportunity to fully realize and demonstrate the interesting properties of these paracyclophanes which can be functionalized through their free phenolic groups.

In the course of the study, monosubstituted pillar[5]arenes containing phosphonate and 1-aminophosphonate fragments were synthesized. The structure of the obtained macrocycles was confirmed by a complex of physical methods of NMR ^{1}H, ^{13}C and IR spectroscopy, individuality of compounds by measuring the melting point and TLC, and composition by elemental analysis and mass spectrometry. It was shown that the synthesized macrocycles are capable to bnd some metal cations.

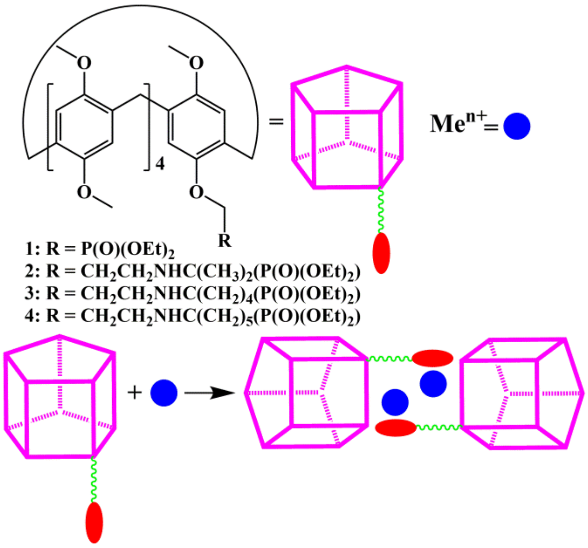

Figure 1. Schematic representation of the binding of the studied metal cations by monophosphorylated pillar[5]arenes.

Acknowledgments

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ELECTROCHEMICAL PROPERTIES OF N-SUBSTITUTED α-DIPHENYLPHOSPHINOGLYCINES

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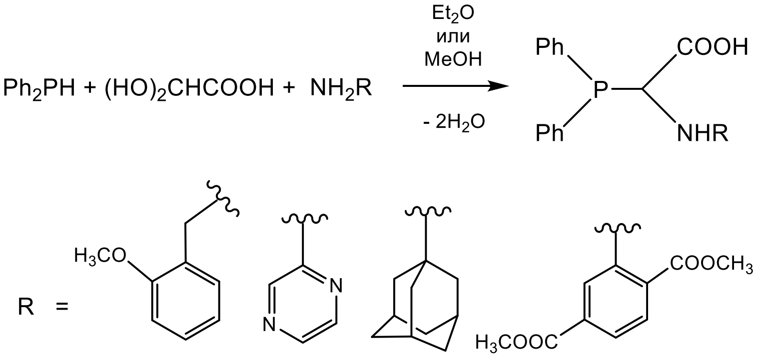
[b] *Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, Kazan, Russia.*

Shell High Olefin Process is the most popular technology to produce linear olefins.[1] Recently we have shown that *N*-substituted α-phosphino-α-aminoacids can be used for creation of efficient systems for catalytic ethylene oligomerization based on nickel complexes.[2] However, the use of low stable [Ni(COD)$_2$] (COD – cyclooctadiene-1,5) as precursor for formation of active catalyst has some limitations. Thus, the electrochemical generation of active catalyst starting from nickel (II) derivatives is of high interest. This requires the investigation of the electrochemical properties of these organophosphorus ligands based on α-phosphino-α-aminoacids.

The electrochemical properties of the *N*-substituted α-diphenylphosphinoglycines: *N*-(2-methoxybenzyl) diphenylphosphinoglycine (**1**), *N*-(pyrazin-2-yl) diphenylphosphinoglycine (**2**), *N*-(1-adamantyl) diphenylphinoglycine (**3**), and *N*-(2,5-dimethoxycarbonylphenyl) diphenylphosphinoglycine (**4**) obtained by three-component condensation of diphenylphosphine, glyoxylic acid hydrate, and the corresponding amine have been studied by cyclic voltammetry on a glassy carbon electrode (Figure 1).[3]



1 **2** **3** **4**

Figure 1. Reaction of three-component condensation .

It was found that compounds **1-4** are stable at cathodic potentials and can be used for *in situ* generation of active catalyst for ethylene oligomerization and polymerization processes.

Acknowledgments

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References

1. (a) W. Keim*, Ind..Appl..Homog.Catal*. **1988**. 335; (b) W. Keim, *Angew. Chem. Int*. Ed. **1990**, 29, 235
2. N. Peulecke, D.G. Yakhvarov, J.W. Heinicke, *Eur.J.Inorg.Chem*. **2019**, 1507-1518.
3. О.С. Софьичева, Ю.А. Кислицын, А.А. Нестерова, А.Б. Добрынин, Д.Г. Яхваров, *Электрохимия*. **2019**,inprint

TERPENYLAMMONIUM SALTS IN CATALYTIC AND STOICHIOMETRIC REACTIONS WITH DIBENZYLIDENEACETONE-PALLADIUM (0) COMPLEXES

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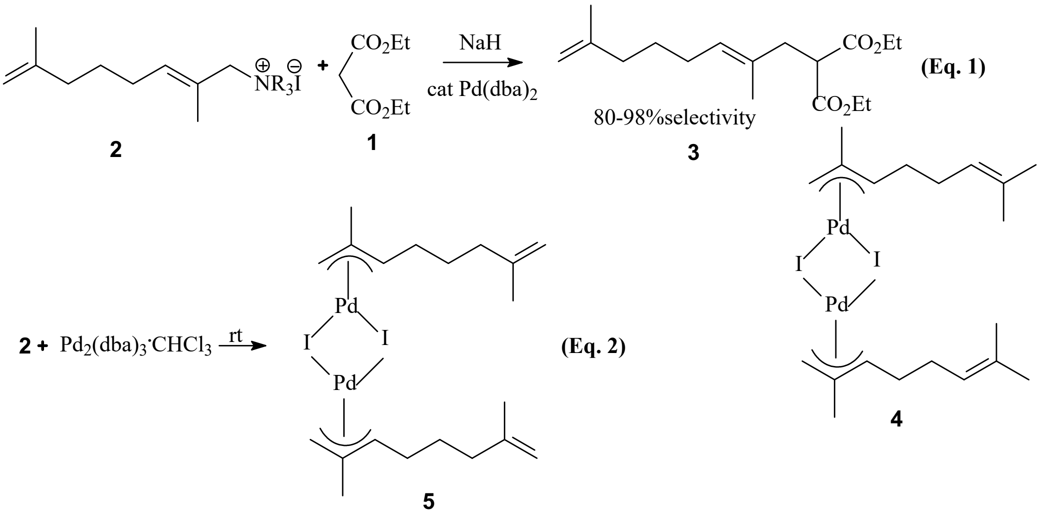
We found that allyl alkylation of malonic ester **1** with terpenylammonium salts **2** catalyzed by Pd(dba)$_2$ without of phosphorus ligand and in the presence of NaH occurred with the predominant formation of a normal substitution product S$_N$2 type (2,7-dimethyl-2,7-octadien-1-yl)malonate (**3**) in accordance with Equation 1 (Scheme). Optimization of the experiments showed that yields were 28-96% and selectivity 80-96%. From the experiments with moderate yields, we isolated mixture of salt **2** and salt with isomerized N-(2,7-dimethyl-2,6-octadien-1-yl)ammonium cation. This mixture we used again in reaction of Equation 1. Malonate **3** in this case was formed in the mixture with yellow crystalline substance. X-Ray analyses of yellow crystals showed that this is complex **4**. Structure of molecule in the crystal showed coordinating square Pd$_2$I$_2$ is nonplanar, bendalong the line I(1)…I(2) is14.0°. We tested the reaction of salt **2** with Pd$_2$(dba)$_3$ at room temperature and after 30-45 min prepared thermally unstable complex **5** by data of X-Ray analyses (Equation 2, Scheme). Earlier for preparing of bis(η^3-allylpalladium chloride) from Pd$_2$(dba)$_3$, were geranyl was complexed to palladium like η^3-allyl manner used geranyl chloride[1]. So we found that for the synthesis of bis(η^3-allylpalladium halides) from dibenzylideneacetone-palladium (0) complexes may use allylammonium salts.



References

1. AJ. Muzart, J.P. Pete, Bull. Soc. Chim. Fr.II, 1983, 56-58.

SYNTHESIS OF O-TRIMETHYLSILYL-N-(PHENYLSULFONYL)ACETIMIDATE

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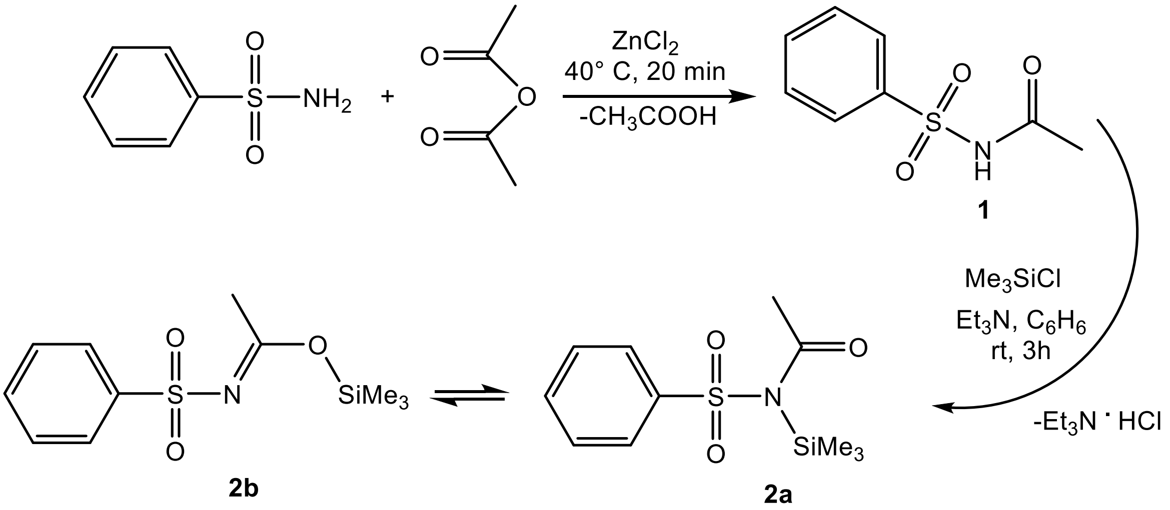
N-acetylbenzenesulfonamide **1** was obtained by acylation of benzenesulfonamide with acetic anhydride in the presence of catalytic amounts of $ZnCl_2$ without solvent in 90% yield. The treatment of compound **1** by trimethylchlorosilane lead to the formation of O-TMS-N-(phenylsulfonyl)acetimidate **2b.** This reaction runs at room temperature using benzene as a solvent and triethylamine as an acceptor of hydrogen chloride. According to results of quantum chemical calculations (B3LYP/6-311G*), imidate **2b** is on 7.9 kcal/mol more stable than its amide tautomer **2a**. Structure of compound **2b** was confirmed by NMR spectroscopy and X-Ray analysis (Fig.1).



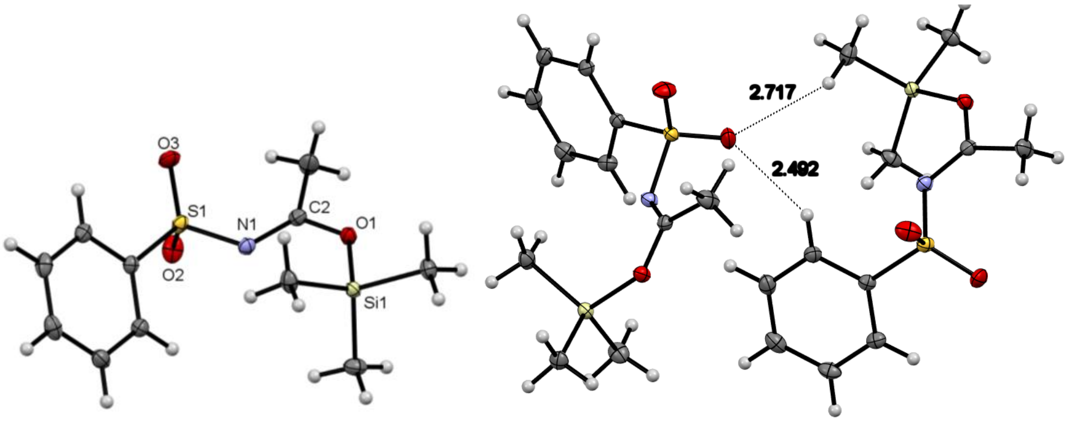


Fig 1. Molecular structure and short contacts between molecules of O-TMS-N-(phenylsulfonyl)acetimidate **2b**

Acknowledgments

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THE STUDY OF METHYL(R)CYCLOSILOXANES (R=H, VINYL, PHENYL) WITH 1D- ^{1}H, ^{13}C, ^{29}SI AND 2D-HSQC, DOSY NMR

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Cyclic siloxanes are often formed as undesirable impurities in the industrial production of linear polysiloxanes.

We studied cyclosiloxanes of the general formula -$(MeRSiO)_n$-, R = H, Me, Ph, n=3-6 by NMR spectroscopy. Cyclosiloxanes with different substituents on silicon are mixtures of spatial isomers. The number of signals depends on the size of the cycle. Possible structures of isomers are considered and the theoretical number of signals which should be observed in the spectra is determined.

So, for the trimer, there must be two isomers and three signals in each ^{1}H, ^{13}C и ^{29}Si spectrum. Tetracyclosiloxane has four isomers, all of which should be represented by six signals in the spectra. The four isomers of the five-membered cycle must be represented by ten signals. In a six-membered cycle, theoretically there should be eight isomers and twenty signals in the spectra.

In the ^{1}H, ^{13}C and ^{29}Si real spectra of cyclosiloxanes, characteristic narrow signals are observed. The largest range of chemical shifts is observed in the ^{29}Si spectra. The number of lines in spectra was less than theoretical due to the superposition of signals of different isomers. But using 2D-HSQC (^{1}H-^{13}C, $^{1}J_{CH}$) and HSQC (^{1}H-^{29}Si, $^{n}J_{SiH}$) we were able to observe all the cross-peaks, the number of which coincided with the theoretical number of lines, including twenty cross-peaks of 6-cyclosiloxane (R = Ph). Thus, we determined the complete sets of chemical shifts ^{1}H, ^{13}C и ^{29}Si of all isomers of 3-, 4-, 5-, 6-cyclic siloxanes.

In the DOSY spectra, the difference in molecular weights of the mixture 3-, 4-, 5-, 6-cyclic siloxanes is clearly visible.

ADENINE AND GUANINE PERRHENATES

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Perrenate ion is readily available from the $^{188}W/^{188}Re$ generator and it is interesting in nuclear medicine for diagnostic and therapeutic applications[1]. In recent years, neutral hosts of a complex structure with internal cavities containing nitrogenous bases have been developed[2]. In case of effective binding with perrhenate anions, they can be promising suppliers of rhenium to cells of various organs and tissues. Purine nitrogen heterocyclic molecules are important elementary molecular components in modeling the creation of similar hosts for ReO_4^-.

Two new perrhenates with adenine and guanine cations (isothermal evaporation of solutions of magnesium perrhenate and nitrogenous bases in HCl) were synthesized as single crystals in this study. An X-ray diffraction study was performed (automatic diffractometer Bruker KAPPA APEX II). Crystallographic data: $H_2Gua(ReO_4)_2$ (**I**): a = 5.2014(2), b = 15.7463(6), c = 14.9004(5) Å, β = 92.908(2)°, at 100 K, Z = 4, space gr. $P2_1/n$, $R1$ = 0.0199; $H_2Aden(ReO_4)_2$ (**II**): a = 16.0078(8), b = 5.0950(2), c = 16.2841(9) Å, β = 116.078(2)°, at 100 K, Z = 4, space gr.$P2_1/c$, $R1$ = 0.0176.

In both compounds, the nitrogenous base molecules are twice protonated. All nitrogen atoms are protonated in **I**, and the nitrogen atom in the *para*-position to the amino group is not protonated in **II**. The NH and NH_2 groups in both compounds are proton donors in hydrogen bonds, and the oxygen atoms of perrhenate ions act as proton acceptors. One bond between the amino group and the perrenate ions in structure **I** is bifurcate. The oxygen atom of the guaninium cation in structure **I** does not participate in hydrogen bonds. In structure **I**, each cation is linked by hydrogen bonds with six anions, and in **II** - with four.

The crystal packing in structures **I** and **II** can be represented as consisting of cationic and anionic columns. In both structures, each cationic column is surrounded by 6 anionic ones and each anionic one is surrounded by 3 cationic ones. In both structures, there is no π-stacking interaction. The study showed that the similar nature of cations and the similar composition of compounds lead to the formation of crystalline packings of the same type, despite some differences in the system of hydrogen bonds.

References

1. W. A. Volkert and T. J. Hoffman, *Chem. Rev.*, **1999***, 99,* 2269- 2292.
2. A. Ravi, A. S. Oshchepkov, K. E. German, G. A. Kirakosyan, A. V. Safonov, V. N. Khrustalev, E. A. Kataev, *Chemical Communications.* **2018**, *54(38),* 4826-4829.

ACTIVATION OF C–H BONDS OF AROMATIC HYDROCARBONS UNDER THE ACTION OF DI-N-BUTYLHAFNOCENE

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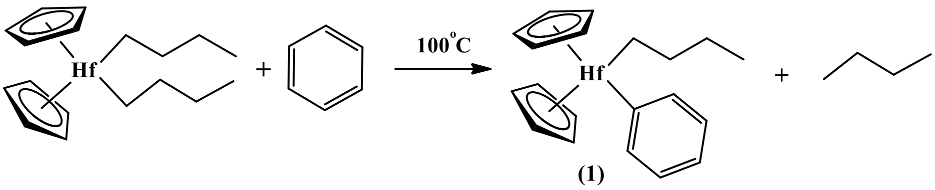
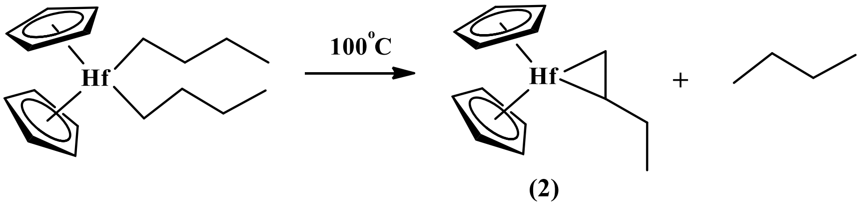
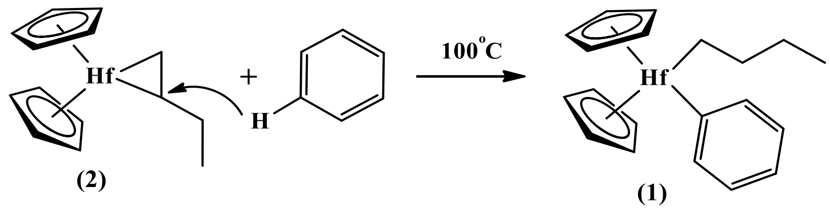
A remarkable feature of di-*n*-butylhafnocene $Cp_2Hf^nBu_2$ synthesized for the first time in our group is that, unlike the corresponding zirconium analogue $Cp_2Zr^nBu_2$, it is quite stable at room temperature under Ar and begins to decompose, generating hafnocene, only at 100°C [1, 2]. We have found that the heating of di-*n*-butylhafnocene at 100°C in the benzene solution leads to activation of C–H bonds of benzene and the formation of *n*-butyl(phenyl)hafnocene $Cp_2Hf(^nBu)Ph$ (**1**) and *n*-butane.



If benzene in this reaction is replaced by benzene-d_6, the resulting **1** contains the deuterium atom at the β-carbon atom of the *n*-butyl group. Apparently, in the course of the reaction, the starting $Cp_2Hf^nBu_2$ eleminates *n*-butane and the arising butene complex Cp_2Hf(1-butene) (**2**) reacts further with the benzene molecule to give the end compound **1**.





When $Cp_2Hf^nBu_2$ is heated in toluene, the hydrogen transfer from the *o*-, *m*- and *p*-positions of the toluene species to the 1-butene complex occurs and, as a result, three isomeric *n*-butyl(tolyl)hafnocenes $Cp_2Hf(^nBu)C_6H_4Me$ are formed.

Acknowledgments

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References

1. V.V. Burlakov, V.S .Bogdanov, K.A. Lyssenko, P.V. Petrovskii, T. Beweries, P. Arhdt, U. Rosenthal, V.B. Shur. Izv. Akad. Nauk, Ser. Khim. **2008**, 6, 1294. [Russ. Chem. Bull., **2008**, 57, 1319].
2. V.V. Burlakov, T. Beweries, V.S. Bogdanov, P. Arhdt, W. Baumann, P.V. Petrovskii, A. Spannenberg, K.A. Lyssenko, V.B. Shur, U. Rosenthal. *Organometallics* **2009**, 28, 2864.

PEROXO COMPLEXES AS MODELS OF METALLOENZYMES

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Metal peroxide complexes have a huge role in the oxidative transformation of organic substrates by metal enzymes.[1] Nonetheless, it must be stressed aryl- and alkyl-peroxide complexes are much less recognized than hydroperoxide complexes. Accordingly, this field of science is the subject of advanced research. Being analogues of metal hydroperoxide complexes, in some cases, their affinity for biological targets is an order of size greater.[2] Thus, such compounds are key ones in a wide range of biological oxygen-centric processes. Our research group develop methods for producing stable peroxide complexes, as well as study the stability of obtained coordination compounds in comparison with the initial ligands and search for criteria that affect the stability of the obtained compounds.

An approach to the creation of synthetic analogues of active centres of metal enzymes is proposed. This is one of the rapidly developing areas of modern chemistry, located at the junction of bioorganic chemistry, coordination chemistry, and biochemistry. The obtaining of stable i.e. secreted and stable during storage under standard conditions peroxide complexes could open the door to several new applications for such an important class of compounds as peroxides.

Acknowledgments

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References

1. K. Ray, F. F. Pfaff, B. Wang, W. Nam, *J. Am. Chem. Soc.*, **2014**, 136(40), 13942-13958.
2. Special thematic issue. Bioinorganic Enzymology, *Chem. Rev.*, **1996**, 96, 2237-2238.

EPOXY-POSS AS A MODYFIER FOR EPOXY COMPOSITIONS

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Creation of epoxysilicon compositions is a well-known method of improving the properties of both types of polymers, aimed at eliminating their inherent disadvantages and imparting new properties. It is known that the introduction of organosilicon compounds in epoxy compositions allows to adjust their heat resistance, regulate their stress-strain properties and a number of other characteristics.

The main directions of the formation of epoxy-organosilicon compounds are: mixing of non-interacting components, each of which forms a separate phase; obtaining interpenetrating networks while curing each of the components in a mixture or by forming a joint network structure by reacting between groups belonging to an epoxy and organosilicon compounds.

At the present study the effect of an epoxy-containing organosilsesquioxoxane (epoxy-POSS) on the thermomechanical and deformation-strength properties of an epoxy composition based on bisphenol A epoxy oligomer cured by isomethyltetrahydrophthalic anhydride in the presence of an accelerator was investigated. The curing of the samples was carried out at temperature of 160 °C for 5 hours.

Epoxy-POSS was obtained by complete acidohydrolytic polycondensation of a mixture of glycidoxypropyltrimethoxy- (2 mol), dimethyldimethoxy- (6 mol) and methylphenyldimethoxy- (9 mol) silanes with glacial acetic acid (18 mol) in the presence of catalytic amounts of concentrated hydrochloric acid (36%). POSS was studied by ^{1}H and ^{29}Si NMR spectroscopy. The completeness of alkoxysilane condensation and the correspondence of its composition to the ratio of the starting reagents were determined by the integral intensities of the characteristic chemical shifts and Fischer titration. According to the obtained data, the content of epoxy groups in epoxy-POSS is about 2.2 mass. %.

By thermomechanical analysis it was found that introduction of the modifier to epoxy composition in the amount of 5-10 mass. % leads to decrease in elastic deformation while maintaining the values of glass transition temperatureat the level of 135-140 °C. A further increase in the content of epoxy-POSS in the composition causes an increase of deformability, decrease of glass transition temperature and the degree of curing by 5-7% in comparison with the unmodified epoxy composition. Obviously, this is due to the creation of steric difficulties in curing due to the significant size of the modifier macromolecules. It should be noted that, regardless of the epoxy-POSS content, thermomechanical curves showed a decrease in deformability of cured modified compositions above the glass transition temperature. It may be caused by increasing of mobility of macromolecules segments and post-curing of the samples at higher temperatures.

It was found that introduction of epoxy-POSS in the epoxy composition led to an increase of tensile stress of the cured samples by 15-20%, elongation in tension– by 30-40%. Cured epoxysilicon compounds also showed less reduction in hardness losses when exposed to aggressive substances such as acids, alkalis and water.

THE USE OF (α-FERROCENYLALKYL) CARBONATES IN THE SYNTHESIS OF FERROCENE CONTAINING AMINO ACIDS

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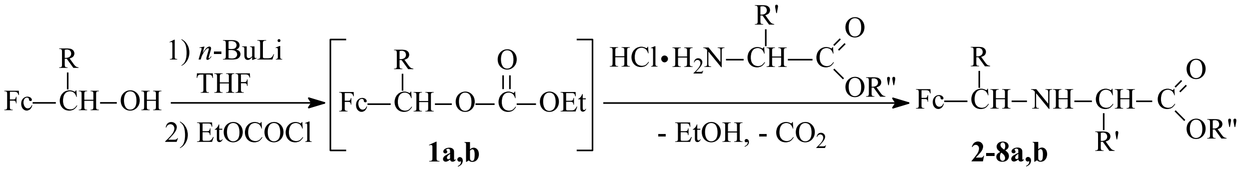
Ferrocene-containing amino acids have biological activity and can be used to treat neurodegenerative diseases. [1] Therefore, the ferrocenylalkylation of amino acids and their derivatives is an attracting synthetic problem.

Recently we have disclosed a method of ferrocenylalkylation based on the *in situ* formation of *α*-ferrocenylalkyl carbonates and their use as the ferrocenylalkylating agents. [2] Proceeding of the reaction under neutral conditions is the main advantage of this method, which is important for the alkylation of compounds labile in acid media. Herein we report the preparation of ferrocene containing amino acids *via* the ferrocenylalkylation using (*α*-ferrocenylalkyl) carbonates.



R = CH_3 (**a**), Ph (**b**)

Carbonates **1a,b** were generated by the known method[4] and they were decomposed in the presence of amino acid ester (R” = Me, Et, Pr*ⁱ*) hydrochlorides affording previously undescribed ferrocene-modified esters of glycine **2a,b**(R” = Me), alanine **3a,b** (R” = Prⁱ), phenylalanine **4a,b** (R” = Prⁱ), leucine **5a,b** (R” = Et), **6a** (R” = Me), serine **7a** (R” = Me) and tyrosine **8a** (R” = Me) in 11-54% yields. The structure of the obtained compounds was proved by ^{1}H, ^{13}C NMR methods using (in the case of diastereomers) correlation methods (^{1}H, ^{1}H-COSY, HMQS).

Acknowledgments

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References

1. A. N. Rodionov, L. V. Snegur, A. A. Simenel, Yu. V. Dobryakova, V. A. Markevich, Russ. Chem. Bull. **2017**, 66, 1, 136–142
2. E. V. Shevaldina, A. D. Shagina, V. N. Kalinin, A. B. Ponomaryov, A. F. Smol’yakov, S. K. Moiseev, J. Organomet. Chem., **2017**, 1-7, 836-837

ORGANOMETALLIC CHEMISTRY OF NEW CARBON MATERIALS: DFT INVESTIGATION

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Organometallic chemistry of new carbon materials (NCM) such as both pristine and defected graphenes, carbon nanotubes and fullerenes with group 6 (Cr, Mo, W) and group 8 (Fe, Ru, Os) metals M^0, clusters M_n and complexes with organometallic groups OMG (metal tricarbonyls and MCp^+) was systematically investigated by quantum chemistry methods. Structure, electronic properties (charge distribution, HOMO-LUMO gap) and thermodynamic data of dynamic processes in such systems (rotation, rearrangements, ligand inversions etc.) were calculated by DFT.

For graphene model metal localizes over six-membered ring (Figure 1) thus preferring η^6-hapticity in pristine graphene molecule. M^0 can situated on different positions over graphene sheet and rapidly moves across graphene surface with low activation barrier (η^6,η^6-IRHR, E_a ~ 8-10 kcal/mol). Such mobility means that pristine graphene is not a good support for bare metal atoms and has little prospect for SAC catalysis which demands uniform distribution and strong binding of catalytically active metal.

OMG ML_n such as $M(CO)_3$ (M = Cr, Mo, W) and MCp^+ (M = Fe, Ru, Os) groups intramolecularly move rapidly across all types of NCM from one ring to another with surrounding metal ligands L (inter-ring haptotropic rearrangement η^6,η^6-IRHR or η^6,η^5-IRHR for fullerenes) much faster than in small polyaromatic ligands (E_a ~ 15-20 kcal/mol vs 30-40 kcal/mol for naphthalene and fluorenyl anion). For second metal of triad barrier reaches minimum.

Metal clusters migrate much slowly on graphene than M^0 do and thus in some cases being introduced in small and narrow carbon nanotubes with high distortions or in open fullerenes with restricted metal motion inside polyaromatic ligand, can be considered as suitable for SAC.As well graphenes possessing different types of defects (*e.g.* single vacancy SV or Stone-Wales SW) could play positive role in catalysis because of thermodynamic stability for metal localized inside defect, especially for SV and absence of haptotropic rearrangement to surrounding defect six-member rings outside SV (IRHR outside E_a ~ 35-40 kcal/mol).

In contrast all kinds of metallic particles could migrate inside SW defect between five-membered rings, from five- to seven-membered ring, between seven-membered rings and even outside SW to surrounding six-membered rings with activation barriers depending on metal group, metal nature M^0 and clusters size M_n (E_a ~ 9-15 kcal/mol).A number of catalytic hydrogenations, mainly of industry important acetylene and ethylene were investigated by DFT on SAC catalysts with metal strongly and uniformly bonded to the NCM in defect or inside carbon nanotube/open fullerene as mini-reactors.

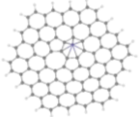

Figure 1. η^6-Localization of Fe^0 triplet on model graphene molecule

THE LACKING RUTHENIUM CLUSTER CP$_4$RU$_4$(CO)$_4$

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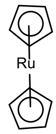
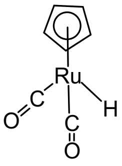
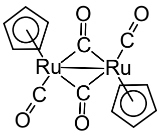
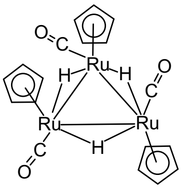
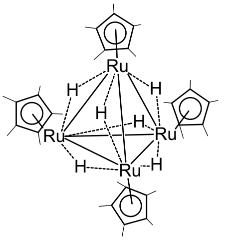
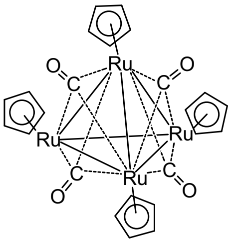
The method for preparation of widely used in organometallic synthesis dimer $[CpRu(CO)_2]_2$ from the thermal reaction of cyclopentadiene with $Ru_3(CO)_{12}$ was described almost 50 years ago[1]. Among the reaction products mononuclear complexes and their dimers are mentioned in the literature. However, it is known that harsh reaction conditions can lead to the decay of $Ru_3(CO)_{12}$ cluster and the formation of complexes of various nuclearity. Therefore, in preparing $[CpRu(CO)_2]_2$ by the reaction of $Ru_3(CO)_{12}$ with cyclopentadiene in boiling heptane we studied products in more detail.

Thorough silica gel chromatography of product mixture with various eluents allows to isolate besides rutenocene Cp_2Ru, dimer $[CpRu(CO)_2]_2$, the new tetranuclear complex $Cp_4Ru_4(\mu_3\text{-}CO)_4$. The structure of the complex was established by single-crystal X-ray study. This tetra-nuclear complex is unstable in chlorine-containing solvents. That is probably why it was not detected earlier by means of standard chromatography. The new cluster $Cp_4Ru_4(\mu_3\text{-}CO)_4$ fills a vacant place in the range of known ruthenium cyclopentadienyl complexes (see table). Its formation confirms the general tendency of ruthenium carbonyls to form polynuclear cluster compounds.

A similar previously described iron complex[2] $Cp_4Fe_4(\mu_3\text{-}CO)_4$ is of interest for obtaining new types of chelating ligands containing organometallic cluster skeleton[3].

Cp_2Ru	$HCpRu(CO)_2$	$[CpRu(CO)_2]_2$	$H_3Cp_3Ru_3(CO)_3$	$H_6Cp^*_4Ru_4$	**$Cp_4Ru_4(\mu_3\text{-}CO)_4$**
					

References

1. A. P. Humphries S. A. R. Knox, *J.C.S. Chem. Comm.*, **1973**, 326.
2. R. B King, *Inorganic Chemistry,* **1966**, *5*, 2227.
3. H.-F. Dai, C.-H. Chen, W.-Y. Yeh, *Organometallics,* **2011***, 30***,** 3438.

THE BIOLOGICAL DECOMPOSITION OF AROMATIC HYDROCARBONS AS A WAY TO IMPROVE OF ECOLOGY

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Abstract. In this paper, methods for controlling compounds that are harmful to the physiological state of all organisms, such as polycyclic aromatic hydrocarbons, are identified. The most effective methods for their biodegradation by bacteria, as the best mineralizers of organic matter, are determined.

Polycyclic aromatic hydrocarbons (PAHs) are a large class of very diverse organic compounds whose molecules consist of three or more aromatic-political rings that form different configurations.

Today it is known that these compounds are very common in the environment and adversely affect the physiological state of all organisms, from bacteria to the human body, factors of mutagenicity, teratogenicity and carcinogenicity. PAHs, which are available as natural components in coal and oil, are also formed as a result of incomplete combustion of organic compounds, and therefore are found in rather high concentrations in fossil fuel processing products. The main mineralizers of organic matter are bacteria. The ability to quickly adapt to new environmental conditions, a fairly wide range of enzyme systems, allow them to use various organic compounds as an energy source and thereby destroy toxic, carcinogenic and mutagenic substances, which also include aromatic hydrocarbons. In science, many studies have been conducted on the selection and selection of strains and associations of bacterial cultures that can use various aromatic compounds as the sole source of carbon and energy. Biological products based on immobilized active strains - oil product destructors have been created. The ability of these biological products to decompose oil in soil and water is determined.

PAHs entering the environment can bind to compounds, such as humic, commonly found in soils and bottom sediments. The formation of xenobiotic complexes with macromolecular organic matter requires a more detailed study of the chemical structure of these substances in order to find possible approaches to their mineralization. The interaction of PAHs and their metabolites with macromolecular organic matter in soils and water bodies by the type of chemical bond can be either covalent (ethers, carbon-carbon bond) or non-covalent (hydrophobic sorption, electrochemical and hydrogen bonds) Depending on the nature of the PAH bond with another organic matter and changes the mineralization rate of such complexes. Further study of microorganisms that are capable of decomposing sufficiently stable organic compounds, such as oil hydrocarbons, in particular, the selection of cultures of destructors, the study of their physiology, metabolic pathways, etc. can significantly accelerate the removal of hazardous substances from the environment and thereby reduce the risk of environmental degradation.

References:

1.Laborde A. L., Gibson D. T., Appl. and Environ. Microbiol., **1977**, 34, 783-790.
2. Mahaffey W. R., Gibson D. T., Cerniglia C. E. Ibid., **1988**, 54, 2415-2423.
3. Ortega-Calvo J.J., Alexander **1994**, 60, 2643-2646.

ADVANCED ANALYSIS OF THERMOCHEMICAL PROPERTIES OF METALLIC ALKANES OF I-IV GROUPS OF MENDELEEV'S TABLE

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It has been shown,[1,2] that the changes of thermodynamic functions Ψ^o (ΔG^o, ΔH^o, ΔS^o), which describe processes of vaporization (vap), combustion (c), formation (f) and entropy (s) can calculated on the equation (1), in which *i* and *f* are stoichiometric coefficients, *N* is a number of valence electrons and *n* is a number of lone electron pairs (*g*) of heteroatoms in investigated molecules.

$$\Delta_{vap,c,f,s}\Psi^o = i \pm f*(N - ng) \qquad (1)$$

After painstaking analysis of the structure of metallic alkanes of first four groups of Periodic table, we believe that the equation (1) necessary to represent in modified form (2).

$$\Delta_{vap,c,f,s}\Psi^o = i \pm f*N \qquad (2)$$

The process of combustion of alkanes with atoms of lithium, zinc, cadmium, mercury, bor, germanium, aluminium, gallium, stannum and lead in condensed and gas phase (50 compounds) may be presented by the general equation (3).

$$C_aH_bMet_c\ (s, g) + (4a + b)/2\ O_2 \rightarrow aCO_2\ (g) + b/2H_2O\ (l) + Met_{c(+1)}O_{c(\pm 1)}\ (s) \qquad (3)$$

Here Met are Li, Zn, Cd, Hg, B, Al, Ga, Ge, Sn, Pb; *a*, *b*, *c* are stoichiometric coefficients before gaseous (g), solid (s) and liquid (l) reagents and products. The necessary thermodynamic data for metal oxides are taken from monograph.[3]

The 30 equations with the values of free energies, the heats of combustion, formation, entropies and atomization of all metallic alkanes were calculated in the range of equation (2). The heat of atomization gave a possibility to calculate the strengths of some bonds in these compounds.

Acknowledgments

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References

1. V.V. Ovchinnikov, Am.Chem.Soc.J. **2013**, *3*, 11.
2. V.V. Ovchinnikov, Chem. J. **2013**, *2*, 59.
3. M.Kh. Karapetyanz , M.L. Karapetyanz , The basic thermodynamic constants of inorganic organic chemistry, Chemistry, M.: **1968**.

SYNTHESIS OF BIS-NHC-SILVER(I) IONIC COMPLEXES WITH 13 GROUP METAL HALIDES

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Complexes of N-heterocyclic carbenes with silver (I) are of interest as antibacterial and anticancer effects were found for them.[1] Since it was shown that the Ag-C bonding has a high lability, these compounds can be used in carbene-transfer reactions for synthesis of metallorganic catalysts for Suzuki cross-coupling, Heck cross-couplingand cyanation of aryl halides.[2]

For our research we chose chloro[1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene]argentum(I) (IPrAgCl). Choosing the optimal conditions for synthesis we obtained abis-carbene silver (I) complex with 13-group metals tetrahalides as a counterion $(IPr)_2\,Ag^+MCl_4^-$ (M = Al, Ga, In). These compounds were caracterised by NMR-, IR- spectroscopy, powder X-ray diffraction and single crystal X-ray diffraction analysis. As an example, structure of $(NHC)_2Ag^+AlCl_4^-$ shown in Figure 1.

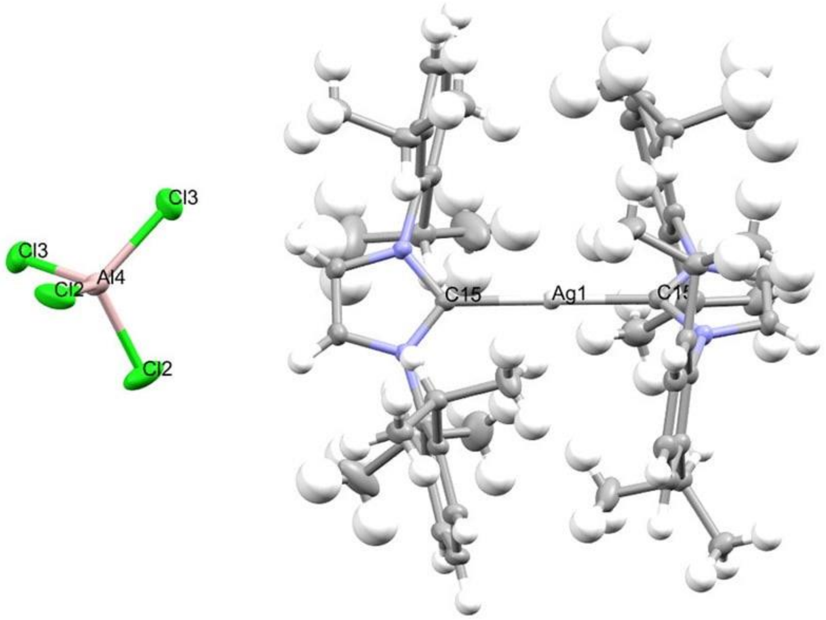

Figure 1. Structure of $(NHC)_2Ag^+AlCl_4^-$ in the solid state.

Acknowledgments

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References

1. Melaiye, A., R. S. Simons, A. Milsted, F. Pingitore, C. Wesdemiotis, C. A. Tessier, and W. J. Youngs, *J. Med. Chem.*, 47, **2004**, 973.
2. A. Martínez, J.L. Krinsky, I. Peñafiel, S. Castillón, K. Loponov, A. Lapkin, C. Godard, C. Claver., *Cat. Sci. Tech*. 5, **2015**, 310-319.

DEVELOPMENT OF NEW RECEPTORS FOR HEAVY METAL CATIONS

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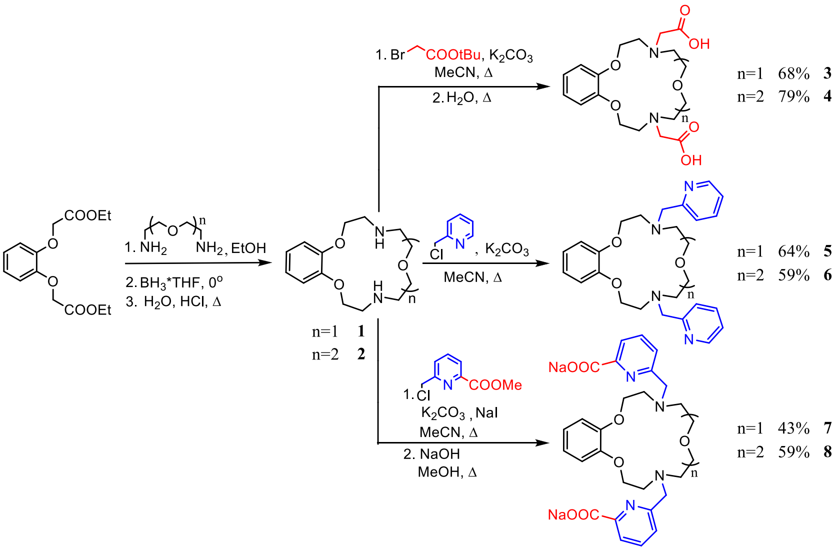
Chemical sensors are a significant part of our lives. They are used in many fields, such as biochemistry, clinical and medical sciences, analytical chemistry and ecology.[1] Receptor binding the metal cation is an important structural unit of chemosensors. Currently, the search for new sensors that can quickly and efficiently work in aqueous media is an extremely urgent task. Therefore, the aim of this work is to create receptors based on azacrown compounds containing a structurally rigid fragment that limits the steric mobility of the ligand, contributing to the fast binding of the metal cation. In order to increase the stability of the complexes and selectivity of the receptors, various chelating groups were introduced into the macrocycles.

The following synthesis scheme (Scheme 1) was proposed for benzoazacrown compounds and their derivatives. As a result, a series of ligands with various sizes of macrocyclic cavity and different nature of pendant arms (carboxyl, pyridyl and picolinate groups) was obtained.



Scheme 1. Synthesis of ligands

The study of the complex formation of synthesized compounds **3**-**8** with Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}cations was carried out by potentiometric titration, NMR spectroscopy, mass spectrometry and X-ray analysis. It was found that all ligands are capable of forming stable complexes even under acidic conditions, and the complex geometry dramatically dependent on the metal ion size.

Acknowledgments

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References

1. P. A. Panchenko, Y. V. Fedorov, V. P. Perevalov, G. Jonusauskas, O. A. Fedorova, *J. Phys. Chem. A* **2010**, *114*, 4118–4122.

CARBORANE COMPLEXES OF RUTHENIUM (II) WITH DIPHOSPHINE LIGANDS: SYNTHESIS AND USE IN CATALYSIS

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Ruthenium carborane clusters are of a great interest not only due to their unique structure with non-classical covalent bonding but because of their high catalytic activity in Atom Transfer Radical Polymerization, Kharasch addition and other essential processes. The capability of mentioned complexes to catalyze polymerization process is govern by reversible redox process accompanied by the halogen atom transfer. Subsequently, coordination-unsaturated particles are generated, which are subsequently capable of directly participating in catalytic processes.

In this work, new ruthenium (II) metal carboranes containing labile nitrile and phosphine ligands are obtained. Chlorine-containing ruthenium (III) complexes were used as starting compounds. The obtained complexes were characterized by means of NMR and IR spectroscopy and mass spectrometry. A single-crystal X-ray diffraction study unambigously confirmed closo-structure of the obtained complexes and the presence of acetonitrile molecule as a ligand. The performed electrochemical investigation of the obtained ruthenacarboranes testified its ability to undergo reversible oxidation to Ru(III) species.

It was found that the dissolution of the obtained clusters in weakly polar solvents in the presence of atmospheric oxygen is accompanied by the dissociation of nitrile ligands and the formation of the corresponding oxygen-containing complexes.

The assumption of lability of nitrile ligands is confirmed by studies of the reactivity of complexes. It was shown that the obtained nitrile complexes are capable of oxidative addition of hydrogen chloride.

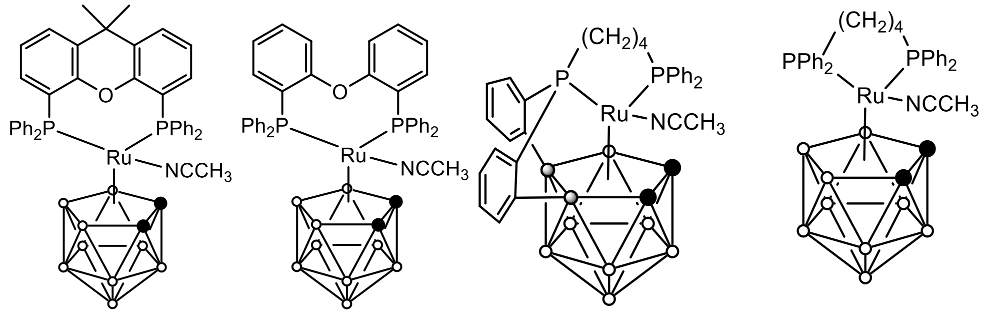

Figure 1. complexes containing labile ligand

Acknowledgments

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REGULARITIES OF DIRECT SYNTHESIS OF METHYLCHLOROGERMANES

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The direct synthesis of methylchlorogermanes from germanium metal and methyl chloride was studied in the presence of a copper catalyst at various temperatures (350-450°C). The influence of the zinc content in the reaction mass (RM) on the results of process was also studied.

It is shown that with an increase of copper content in RM productivity is growing almost exponentially, reaching 850 g/kg· hour at 50% concentration of Cu. The selectivity to Me_2GeCl_2 has a maximum at mass concentration of Cu 13–16%, while the Me_2GeCl_2 mass concentration in the reaction products is ~95%, and the productivity of the process for the mixture of methylchlorogermanes is ~275 g/kg·h.

The reaction products in addition to Me_2GeCl_2 were also included $GeCl_4$, Me_3GeCl and $MeGeCl_3$. The ratio of the molar amount of methyl groups to the molar amount of chlorine groups (Me:Cl) was about 1, which indicates insignificant losses of the methyl radical during direct process and possible disproportionation of products. Based on this assumption, the following direct synthesis model was proposed:

- Me_2GeCl_2 is produced during the main reaction $Ge + 2\ MeCl = Me_2GeCl_2$ (1)
- all Me_3GeCl is produced by the reaction: $2\ Me_2GeCl_2 = MeGeCl_3 + Me_3GeCl$ (2)
-- all $GeCl_4$ is formed by the reaction: $2\ MeGeCl_3 = GeCl_4 + Me_2GeCl_2$ (3)
- the remaining $MeGeCl_3$ not accounted for by reaction (2) is formed in the pyrolysis process: $Ge + 3\ MeCl = MeGeCl_3$ +by-products and off gases (4)

The thorough experiment allowed us to analyze the composition of the reaction products during the induction period. In the start of synthesis, a significant amount of Me_3GeCl is formed. Then the yield of $MeGeCl_3$ increases. The induction period is completed within ~1 hour from the start of synthesis and the process reaches a stable mode with high selectivity to Me_2GeCl_2, while the molar ratio Me:Cl is ~0.98÷0.99. This suggests that in the direct synthesis copper is consistently involved in the following processes: methylation of germanium (in the process of formation of CuCl) → chlorination of germanium (during the reaction of CuCl with Ge in the formation of the surface active site of the reaction) → catalysis of disproportionation reactions. The participation of copper in the processes of methylation and chlorination should take place throughout the synthesis of Me_2GeCl_2, but it was not possible to find it out experimentally against the background of the significant production of Me_2GeCl_2.

The proposed model was also tested for direct synthesis on a copper-zinc catalyst. It was shown that the dependence of productivity on the mass ratio Zn:Cu has a pronounced maximum (~264 g/kg·h) at a value equal to ~0.1. It was found that the presence of zinc in the contact mass leads to an increase in the losses of the methyl group, presumably by reaction (4). At a ratio of Zn:Cu=0.1, the ratio of Me:Cl in the reaction products is 0.84, versus 0.98 in the absence of zinc.

1-(2,7-DIMETHYL-2,7-OCTADIEN-1-YL) – BENZIMIDAZOLE AND 1-(2,7-DIMETHYL-1,7- OCTADIEN-3-YL) BENZIMIDAZOLE AS FUNGICIDES

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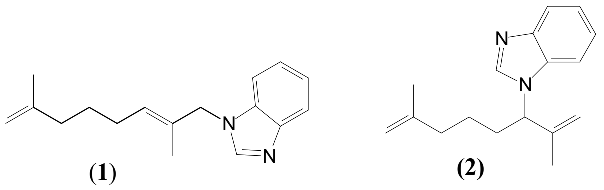
Compounds **1** and **2** (figure1), related to the terpene derivatives of benzimidazole of an irregular structure, are formed upon telomerization of isoprene with benzimidazole,[1, 2] and are environmentally friendly insecticides (juvenoids).[3] A priority trend in the production of modern pesticides is the use of drugs with binary activity. So, the drug Celest Top consists of a mixture of an insecticide (Thiamethoxam), and two fungicides (Diphenoconazole and fludioxonil). However, thiamethoxam belongs to neonicotinoids, the use of which is currently prohibited in the USA and the EU, due to the death of bees. So it seems promising to use compounds that have binary activity and do not have a harmful effect on the environment. The present investigation is the detection of fungicidal activity in compounds with insecticidal action, in order to obtain environmentally friendly binary pesticides. Laboratory tests for *in vitro* fungicidal activity were carried out by treating the nutrient medium with compounds **1**, **2** and their 1: 1 mixture[4] and then using the treated nutrient medium to grow phytopathogenic fungi in it. The results were evaluated as a percentage reduction in the growth of fungal cultures in the treated medium compared to untreated. Tests for the fungicidal activity *in vivo* were carried out on plants in greenhouses[4, 5]. Data *in vitro* show that benzimidazole **1** is a more active fungicide than **2**. When using compound **1**, the inhibition of fungal cultures growth up to 80-90% is observed for pyriculariosis, rhizoctoniosis, helminthosporiosis, cercosporella rot, cinnamon and citrus late blight, alternariosis, and septoriosis. Benzimidazole **2** shows moderate activity to all tested fungal cultures. A mixture of compounds **1** and **2** (1:1) have a synergistic effect: in the case of pyriculariosis, cinnamon and citrus late blight, the growth of fungi is suppressed by 100%. When tested *in vivo* on plants benzimidazole **2** is more active: it inhibits the development of pyriculariosis by 90%, and brown rust of wheat by 50%, while benzimidazole **1** has a fungicidal effect only for brown rust of wheat (reduces growth by 75%). A 1:1 mixture of benzimidazoles **1** and **2** works synergistically: it inhibits the development of pyriculariosis by 90%, brown rust in wheat by 75% and nay such harmful fungal diseases as potato late blight and powdery mildew of barley, for which the components of the mixture *in vivo* do not show activity at all.



(1) (2)

Figure 1.

References

1. Petrushkina EA, Bregadze V.I. Orgamometallic Chem. in the USSR 1991, 4(2), 229.
2. A. Petrushkina E.A., Gavrilenko V.V., Oprunenko Yu.F., Akhmedov N.G. Russ. J. Gen. Chem. 1996, 66(11),1815
3. Petrushkina E.A.. Polonic N.B. Ivanova G.B. Pestic. Sci.1999, 55(6), 650.
4. EP 0551048 A1, 1993
5. US 5,246,954 A, 1993; EP 0486409 A1, 1992.

SYNTHESIS AND INVESTIGATION OF STRUCTURE OF m-CRESOLESULFONIS ACID SALTS WITH NH_4^+, K^+, Rb^+ AND Cs^+ CATIONS BY X-RAY STRUCTURAL AND VIBRATIONAL SPECTROSCOPY METHODS

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Earlier in our work we have investigated molecular and crystal structure of m-cresolsulfonic (2-hydroxy-4-methylbenzene sulfonic) acid as well as proton conductivity [1]. It was shown that proton conductivity of m-cresolsulfonic acid increased up to 10^{-3} S/cm at relative humidity ab. 60 rel. %. IR spectroscopic studies of aromatic sulfonic acids were demonstrated that the bands belonging to the vibrational transitions of the proton hydrate complex and sulfo group are of high intensity, as a result of which they are quite easily detected against the background of less intense bands of the phenyl group and its organic substituents. The interpretation of vibrational spectra is noticeably more complicated when OH-substituents are included in the H-bond system. The easiest way to determine the vibrational frequencies of the OH group attached to the aromatic ring – from the spectrum of the corresponding alkali metal salt.

In this work, we study the effect of substitution of acid proton of sulfogroup in 2-hydroxy-4-methylbenzene sulfonic acid on alkali metal cations and ammonium on a change in the structure of the hydrogen bond network and proton conductivity upon wetting.

Salts of 2-hydroxy-4-methylbenzene sulfonic acid with alkali metal cations (K, Rb and Cs) and ammonium were obtained by the neutralization reaction with the corresponding hydroxides during slow evaporation without access CO_2. All synthesized salts are anhydrous.

According to DSC, the decomposition of salts begins after 247 (NH_4^+), 279 (K^+) and 348°C (Cs^+ and Rb^+ salts), respectively.

The crystalline structures of the salts of 2-hydroxy-4-methylbenzene sulfonic acid with cations NH_4^+, K^+, Rb^+ and Cs^+ were determined by X-ray diffraction.

In the IR spectra of all salts there is a very intense band of stretching vibration ν (OH) of the phenolic group in the region 3106–3121 cm^{-1}. The IR spectrum of ammonium salt is generally completely similar to the spectra of alkali metal salts.

A study of water sorption with increasing relative humidity (RH) showed that the amount of adsorbed water in salts does not exceed 0.8 mass %, which is less than 0.1 mole at RH 95 rel. % and room temperature.

Using the method of impedance spectroscopy, it was shown that the salt conductivity does not exceed 10^{-9}–10^{-8} S/cm.

Acknowledgments

This work was performed in accordance with the state task, state registration No AAAA-A19-119061890019-5. The work has been performed using the equipment of the Multi-User Analytical Center of IPCP RAS.

References

1. A.V. Pisareva, G.V. Shilov, A.I. Karelin, Yu.A. Dobrovolsky, R.V. Pisarev *Russ. J. Phys. Chem. A.* **2010**, *84*, 444.

TWO NEW POLYMORPHS OF CIS-PERINONE: CRYSTAL STRUCTURES, PHYSICAL AND ELECTRIC PROPERTIES

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The crystal structures of two polymorphs of *cis*-perinone (bisbenzimidazo[2,1-*b*:1',2'-*j*]benzo[*lmn*][3,8]phenanthroline-6,9-dione, Pigment Red 194) (figure 1) were solved from single crystals obtained solvothermally from 1,2-dichlorobenzene or n-butanol at 220 °C. Both crystal structures (space group $P2_1/c$) derive from stacking of flat molecules arranged due to π-π interaction[1].

The melting points of these two polymorphs are 471 °C and 468 °C and the optical band gap $E_{bg}^{(1)} = 1.94$ eV and $E_{bg}^{(2)} = 1.71$ eV. One of the polymorphs demonstrates drift and hopping mechanisms of electric conductivity, whereas the other one is dominated by the drift conductivity. The direct current (DC) electric conductivity of the samples are $\sigma_{DC}^{(1)} = 4.77 \times 10^{-13}\ \mathrm{S/m}$ and $\sigma_{DC}^{(1)} = 6.84 \times 10^{-10}\ \mathrm{S/m}$ at room temperature. The significant difference in DC conductivities could be explained by the dependence of the mobility and concentration of charge carriers on the samples' structure[2].

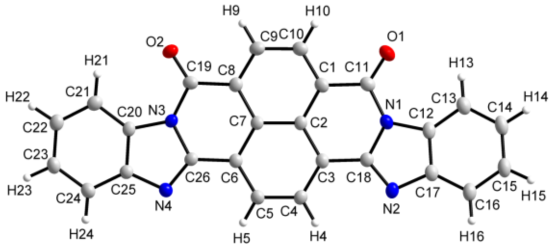

Figure 1. Cis-perinone

Acknowledgments

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References

1. M. Stępień, E. Gońka, M. Żyła, and N. Sprutta, "Heterocyclic Nanographenes and Other Polycyclic Heteroaromatic Compounds: Synthetic Routes, Properties, and Applications," Chem. Rev., vol. 117, no. 4, pp. 3479– 3716, Feb. 2017/
2. F. Cervantes-Navarro and D. Glossman-Mitnik, "Density functional theory study of indigo and its derivatives as photosensitizers for dye-sensitized solar cells," J. Photochem. Photobiol. A Chem., vol. 255, pp. 24–26, 2013.

STUDY OF THE CATION-DEPENDENT RESONANCE ENERGY TRANSFER IN THE CROWN-CONTAINING BISCHROMOPHORIC SYSTEM BASED ON 4-ALCOXY- AND 3,4-DIMETOXYSTYRIL-1,8-NAPHTHALIMIDE

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At the moment, the direction of development and research of optical FRET (Förster Resonance Energy Transfer) sensors for metal cations is actively developing in supramolecular chemistry. This type of sensor is well established for measuring the concentration of metal ions in biological systems *in vitro*, because they have properties of ratiometric measurements[1]. The aim of this study is the research of cation-dependent resonance energy transfer in a crown-containing bischromophore system based on 4-alcoxy- and 3,4-dimethoxystyryl-1,8-naphthalimide (figure 1). Compound 1 was obtained by a click reaction between a crown-containing propargyl derivative and 3,4-dimethoxystyrylnaphthalimide. Azadithia-15-crown-5-etheris characterized by binding to heavy metal cations, was used as a receptor[2].

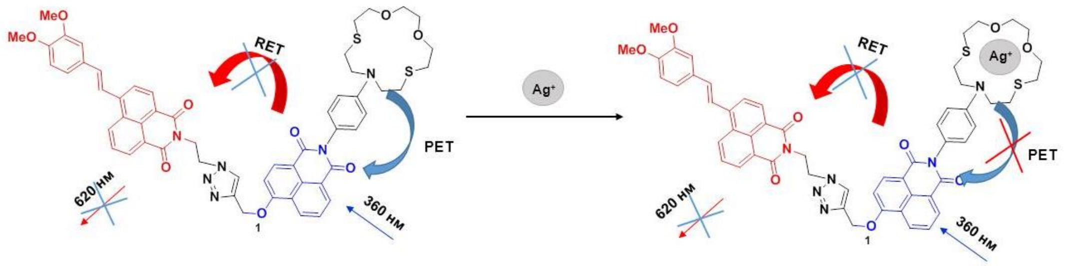

Figure 1

As a result of the study of resonance energy transfer in the presented conjugate 1, it was found that the system has an intramolecular cation-dependent energy transfer, and its efficiency during complex formation varies from 50 to 100%.Using optical spectroscopy methods, it was shown that in the free ligand due to photo-induced electron transfer (PET), energy transfer is suppressed, and therefore, fluorescence quenching. The binding of the silver cation inhibits the PET process and leads to an increase in fluorescence by 620 nm due to energy transfer from the alcoxy-naphthalimide donor to the styryl fragment (acceptor). It was found that the fluorescence of the styryl acceptor is also cation-dependent.

This work was supported by the Russian Foundation for Basic Research (grant No. 18-33-20111), studies of the spectral and luminescent properties are supported by science and higher education in the Russian Federation using scientific equipment. Central Research on Building Molecule.

References

1.Gollavelli, G., & Ling, Y.C. Magnetic and fluorescent graphene for dual modal imaging and single light induced photothermal and photodynamic therapy of cancer cells // Biomaterials. 2014.№ 35(15), C 4499 – 4507.
2. L.D Lavis., R.T. Raines // ACS Chem. Biol. 2008. № 3, C. 142 – 155.

CYCLOHEXADIENYL RHODIUM COMPLEXES. SYNTHESIS AND REACTIVITY

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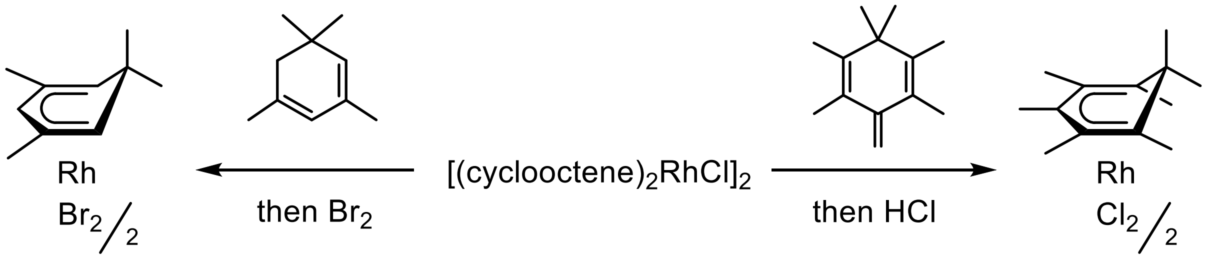
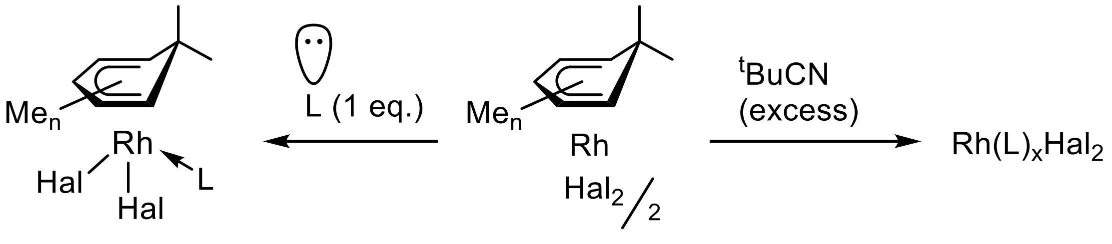
Activation of C-H bond by the rhodium (III) complexes is powerful method for synthesis of various heterocycles. The classic catalyst for such reaction is cyclopentadienyl rhodium complex $[(C_5Me_5)RhCl_2]_2$. In order to search more active and selective catalyst, we decided to explore analogous rhodium complexes **1** and **2** containing cyclohexadienyl ligand.

Compounds of this type have not been previously described, therefore we developed the first methods of their synthesis. It is based on the substitution of the labile cyclooctene ligands in the commercially available complex $[(cyclooctene)_2RhCl]_2$ by cyclohexadiene $Me_4C_6H_4$ or cyclohexatriene $Me_6C_6{=}CH_2$ and the subsequent reaction of intermediates $[LRhCl]_2$ with Br_2 or HCl.



1, 66% **2**, 92%

Compounds **1** and **2** are convenient precursors for the preparation of other cyclohexadienyl complexes. For example, their stoichiometric reactions with 2-electron ligands give adducts **3a–f**. At the same time, the excess of the strong ligand ^tBuNC unexpectedly leads to the displacement of the cyclohexadienyl ligand. Apparently, such process blocks the catalytic activity of complexes **1** and **2** in CH-activation reactions.



3a-**f**, 80-90% Hal = Cl, Br L = Py, $P(OEt)_3$, PPh_3

Acknowledgments

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References

1. R.A. Pototskiy, O.I. Afanasyev, Y.V. Nelyubina, D.A. Chusov, A.R. Kudinov, D.S. Perekalin, J. *Organomet. Chem.* **2017**, *835*, 6.
2. R.A. Pototskiy, A.A. Lisov, Y.V. Nelyubina, D.S. Perekalin, *J. Organomet. Chem*. **2018**, *862*, 71.

ROTAXANE STRUCRURES BASED ON MONOPHOSPHORYLATED PILLAR[5]ARENES

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Chemistry of macrocyclic compounds is one of the rapidly developing areas of modern organic chemistry. Presently, several thousands of macrocyclic compounds have been synthesized, which have become widespread due to the high availability of parents compounds, the possibility of synthesis of ligands based on them for highly selective ion and molecular recognition, ion-selective membranes, electrodes, sensors and nanocontainers for targeted drug delivery. In addition, in the past few years, the attention of researchers has again been chained to mechanically interlocked molecules (rotaxanes and pseudorotaxans) and supramolecular polymers, which can be explained by their potential application as molecular machines and materials. Mechanically interlocked molecules are molecular architectures consisting from two or more components which mechanically bind due to their own topology.

Among the variety of macrocyclic compounds the special attention attracted macrocyclic platform of pillararene opened in 2008 by T. Ogoshi and T.-A. Yamagishi. Pillar[5]arenes as a new type of macrocyclic «hosts» became one of the most popular paracyclophanes since their first synthesis.

Special interest is the creation of polyfunctional compounds because of their potential application in molecular recognition of various substrates. Organophosphorus compounds are one of the most interesting typifier of such polyfunctional compounds. Hydrophosphoryl and (amino)phosphonate derivatives attracted special attention, because they have potential application in different areas of daily life (act as substrates or enzyme inhibitors, involved in protein metabolism, widely used as antibiotics, as well as herbicides).

Thus, under this research work a number of novel phosphorylated pillar[5]arenes were synthesized. The structure of the new synthesized derivatives was fully proved by NMR ^{1}H, ^{13}C, IR spectroscopy, elemental analysis and mass spectrometry (MALDI-TOF).

Acknowledgments

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SYNTHESIS OF NEW FUNCTIONALIZED ARYL AND HETARYL AMINOMETHYLENEBISPHOSPHONIC ACIDS VIA SILICON-ASSISTED METHODOLOGY

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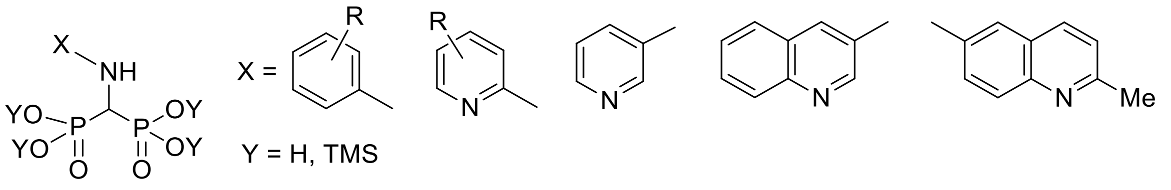
Functionalized methylenediphosphonic acids and their derivatives with aromatic and heterocyclic moieties are well-known biomimetics of hydroxy- or aminocarboxylic acids and natural pyrophosphates, and some of them such as zoledronic, risedronic, and minodronic acids are widely used in medicine. These substances demonstrate the properties of herbicides, pesticides, antibiotics, antiviral and antitumor agents and enzyme inhibitors.

The organosilicon applied synthesis of functionalized organophosphorus acids is a convenient method for creating P-C bonds; recently this methodology has been successfully developed and became modern trend in organophosphorus chemistry.[1-3]

The convenient synthesis of new functionalized aryl and hetaryl aminomethylenebisphosphonic acids has been developed *via* silicon-assisted methodology. New functionalized aminomethylenebisphosphonic acids containing aryl, pyridine and quinoline moieties were obtained using unique reaction of tris(trimethylsilyl) phosphite with *N*-formyl derivatives of corresponding (het)arylamines and trimethylsilyl triflate as a catalyst under mild conditions. Intermediates – tetra(trimethylsilyl) aminomethylenebisphosphonates formed, were converted to the target acids by further treatment with methanol excess. The catalytic schemes of target substances formation are proposed.



R = H, 4-F, 4-Cl, 5-Cl, 5-Br, 5-I, 4-Me, 5-Me, 6-Me, 2-MeO, 4-MeO; yields 84-92%.

Figure 1. New functionalized aryl and hetaryl aminomethylenebisphosphonic acids and their derivatives.

Acknowledgments

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References

1. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *J. Organomet. Chem.*, **2018**, *867*, 149.
2. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *J. Organomet. Chem.*, **2018**, *871*, 36.
3. A.A. Prishchenko, R.S. Alekseyev, M.V. Livantsov, O.P. Novikova, L.I. Livantsova, V.S. Petrosyan, *Inorg. Chim. Acta*, **2019**, *484*, 319.

QUANTUM CHEMICAL INVESTIGATION OF DIPYRROMETHENE COMPLEXES WITH D-ELEMENTS

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The need for modern technologies in the use of various optical devices leads to study new organic luminophores. One of them dipyrromethenes can form stable complexes with ions of d-elements such as Zn(II) and Cd(II). An advantage of complexes of d-metals with dipyrromethenes is high sensitivity of the photonics characteristics to changes in the chromophore structure and nature of the solvent as well as easier “self-assembly” of these complexes.

Experimental investigation complemented with theoretical-computational studies accompaniment lead to deeper understanding of electronic structure, pathways of electronic transitions, and specific spectral-luminescence features to develop more efficient optical sensors and triplet photosensitizers. Therefore, the purpose of the present work is theoretical research of photophysical and photochemical processes occurring in zinc and cadmium dipyrromethenates and depending on their structure, nature of the solvent and the characteristics of the exciting radiation. In order to optimize the compounds in ground and excited states as well as to investigate their electronic structures, schemes of excited energy dissipation, several TD-DFT functionals accompanied with various basis sets were used.

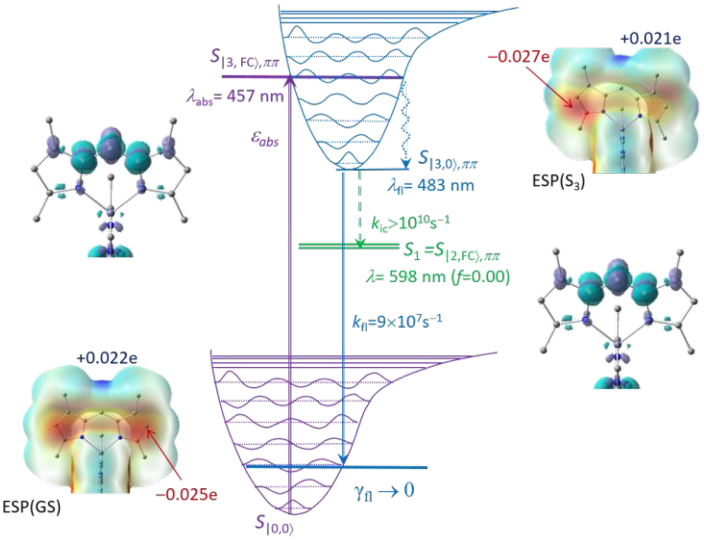

Figure 1.Internal conversion k_{ic} from S_3 for [Zn(dpm)$_2$]. Wavelets mean vibrational modes of ground (violet) and optical active excited (blue) states on their potential energy surface (PES). Electron density redistributions are obtained as a difference (EDD) between the active excited and ground states where dark lilac area points density increasing. ESP is mapped between red negative and blue positive maxima.

Acknowledgments

This study was supported by the Russian Foundation for Basic Research (project no. 18-33-00284) and The Tomsk State University competitiveness improvement programme.

FLUORINE-CONTAINIG ENAMINONES AS EUROPIUM (III) COMPLEXONATES

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Luminescent complexes of fluorine-containing β-diketones with europium (III) are actively used in biological microassay in particular in time-resolved immunofluorescence assay (IFA)[1,2]. Relatively low stability constants of REE β-diketonates limit the scope of application of the secompounds in IFA, for instance, the possibility of creating stable conjugates with proteins. Structural analogues of β-diketones - fluorine-containing β-enaminones were obtained with the aim of the evoluation of the luminescence-spectral properties of their complexes with Eu^{3+} in comparison with diketones. Trifluoromethylbenzofuranyl-containing enaminones were prepared through intermediate haloenonones in a two-stage using thionyl chloride or phosphorus tribromide as halogenating reagents. In the course of the reaction, regioisomers of haloenones were isolated, which further allowed to obtain and study enaminones of various structures[3].

The luminescence-spectral properties of the obtained enaminones and their complexes with europium (III) in aqueous solutions were studied.

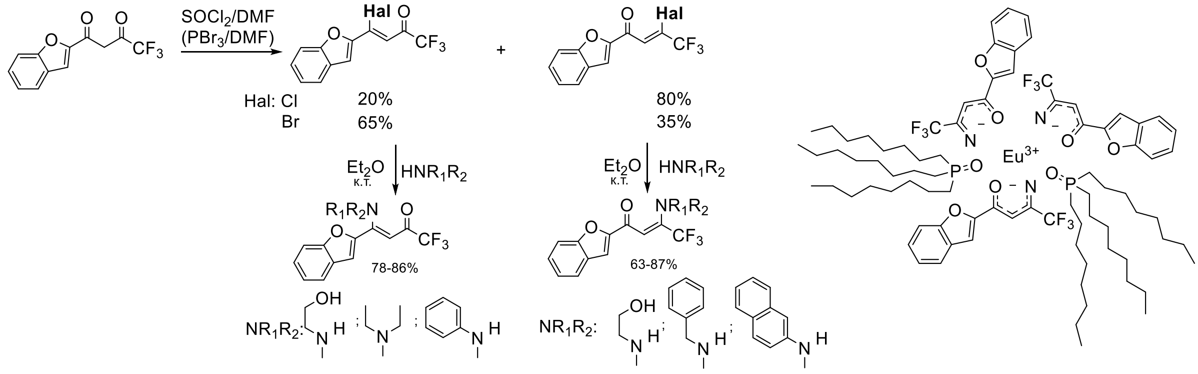

Figure 1.

References

1.D.E.Pugachov, T.S.Kostryukova, G.V.Zatonsky, S.Z.Vatsadze, N.V. Vasil'ev, *Chem. Heterocycl. Compd.* **2018**, 54, 528.
2. K. Binnemans, *Chem. Rev.* **2009**, 109, 4283.
3. D.E. Pugachov, G.V. Zatonsky, N.V. Vasil'ev, *Fluorine notes* **2019**, 125, 9.

BIS(ALKYL) RARE-EARTH (III) COMPLEXES SUPPORTED BY AMIDINATE-TYPE LIGANDS

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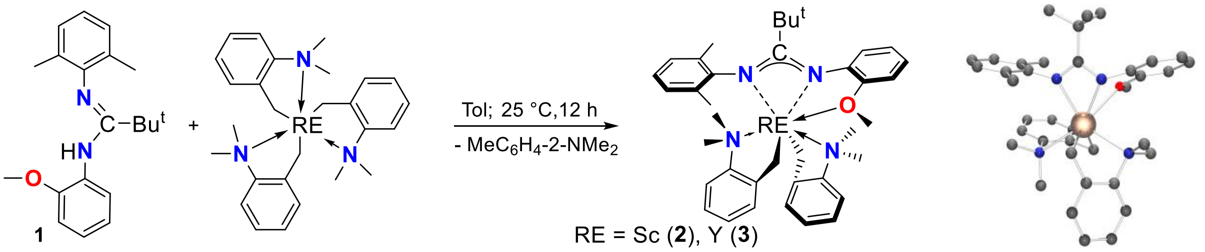
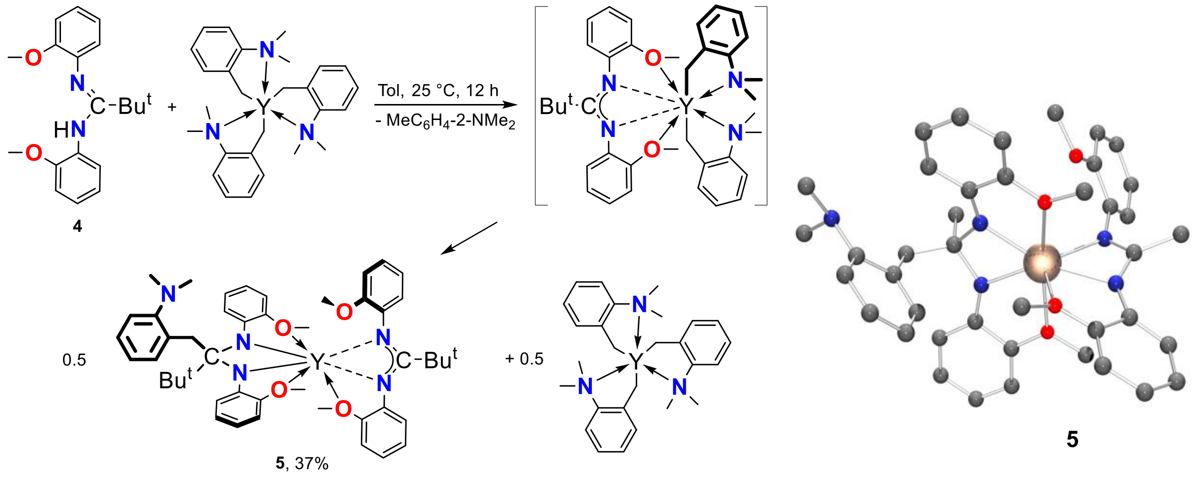
Two different synthetic approaches are successfully used for the preparation of bis(alkyl) rare-earth complexes. The first one is the alkane elimination reaction of tris(alkyl) rare-earth species LnR_3(R = Me_3SiCH_2, $CH_2C_6H_4$-2-NMe_2) with one equivalent of the protio form of the ligand LH (Scheme 1). The second one is based on the alkylation reactions of dihalo complexes $LLnX_2$ (X = Cl, Br, I) with appropriate alkyl derivatives of alkaline or alkaline-earth metals.[1,2]



Scheme 1. Synthesis of bis(alkyl) complexes **2**,**3**.

The σ-bond metathesis reaction of amidine (2-MeO-C_6H_4)N=C(Bu^t)-NH(C_6H_4-2-OMe) (**4**) with equimolar amount of Y{$CH_2C_6H_4$-2-NMe_2}$_3$ in toluene is completed by the addition of N,N-dimethylaminobenzyl group to C=N bond of the amidinate fragment, and disproportionation, leading to formation of novel bis(amide)amidinate complex [(2-OMe-C_6H_4N)$_2$C(Bu^t)$CH_2C_6H_4$-2-NMe_2]Y[(2-OMe-C_6H_4N)$_2$C(Bu^t)] (**5**):



Scheme 2. Synthesis of bis(amide)amidinate complex **5**.

Acknowledgments

This work was financially supported by the Russian Foundation for Basic Research (Project 18-43-520036).

References

1. A. A. Trifonov, D. M. Lyubov, *Coord. Chem. Rev.* **2017**, *340*, 10.
2. K. R. D. Johnson, P.G. Hayes, *Chem. Soc. Rev.* **2013**, *42*, 1947.

FIRST EXAMPLE OF INTERMOLECULAR HOMO-COUPLING OF ALKYNYL PHOSPHINS WITH THE FORMATION OF METALLACYCLOPENTADIENES

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The creation of effective methods for the homo-coupling of P-containing alkynes and the preparation of functionalized heterocyclopentadienes is important for the development of new materials for supramolecular chemistry and molecular electronics. Currently, there are no methods for intermolecular homo-coupling of 1-alkynylphosphines and phosphoroxides. Only one example is known that demonstrates the use of the $Ti(OPr^i)_4$-Pr^iMgX reagent for the intermolecular coupling of 1-alkynylphosphonates.[1]

We found that the reaction of aryl-substituted 1-alkynylphosphines with 1 equivalent of Cp_2ZrCl_2 and 1.2 equivalent of Mg in the presence of 1 equivalent of $EtAlCl_2$ in THF at room temperature for 3 hours leads to the selective formation of the products of homo-coupling with good yield(Figure 1). The selectivity of the reaction decreases markedly when using catalytic amount of Cp_2ZrCl_2.The reaction does not proceed in the absence of $EtAlCl_2$.We believe that in the absence of a strong Lewis acid, a zirconocene complex with alkynylphosphine is formed due to the interaction of zirconium and phosphorus atoms. This prevents the further conversion of alkynylphosphine. The addition of organic aluminum halide leads to the formation of a complex of alkynylphosphine with $EtAlCl_2$.Thus, aluminum halide acts as a protective group.

Unfortunately, alkyl substituted alkynylphosphines under the reaction conditions gave a complex mixture of dimerization products. However, we hope to improve the selectivity of the reaction at lower temperatures and with the use of other polar solvents.

Thus, the first positive results were obtained on the homo-coupling of 1-alkynylphosphines, that paves the way for the synthesis of new P-containing compounds for supramolecular chemistry and molecular electronics.

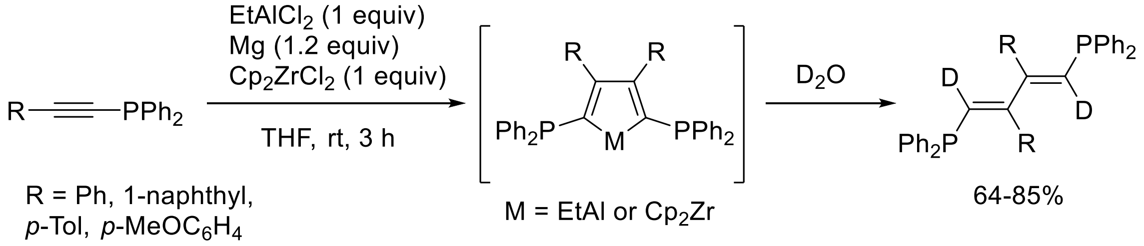

Figure 1. Homo-coupling of 1-alkynylphosphines.

Acknowledgments

The study was carried out with a grant from the Russian Science Foundation (project No. 19-73-20128)

References

1. A.A.Quntar, O.Baum, A.Shibli, V.M.Dembitsky, M.Srebnik, *Angew. Chem. Int. Ed. Engl.* **2003**, *42*, 4777.

A GENERAL BENZYLIC C-H ACTIVATION AND C-C COUPLING REACTION AT ZIRCONOCENES MEDIATED BY C-N BOND CLEAVAGE IN TERT-BUTYLISOCYANIDE – UNUSUAL FORMATION OF IMINOACYL COMPLEXES

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In recent years our group was interested in the reactivity of metallacyclopropenes of the type $Cp'_2M(\eta^2\text{-}Me_3SiC_2SiMe_3)$($Cp'$= η^5-unsubstituted and substituted cyclopentadienyl) of group 4 metals towards nitriles and isocyanides. We were able to reveal a previously unknown redox disproportionation of an isocyanide stabilized decamethyltitanocene acetylide complex.[1] Furthermore, we have found that the aryl substituted CN-Xy (Xy = 2,6-dimethylphenyl) shows a series of unusual multiple and highly selective alkyne–isocyanide C-C and C-N couplings at elevated temperatures in the presence of the *ansa*-bridged *rac*(ebthi)Zr(η^2-$Me_3SiC_2SiMe_3$) (**1**).[2]

In our recent work we investigated the reactivity of the aryl substituted *tert*-butylisocyanide and **1** (Figure 1). In a first step a simple end-on coordination of the isocyanide leading to complex **2** occurs. In the presence of methylated arenes (Ar'-CH_3), an excess of *tert*-butylisocyanide and at elevated reaction temperatures this compound is converted into zirconocene-2-iminoacyl cyanide complexes **3a-e** with elimination of the alkyne. These complexes are formed by coupling with a benzyl fragment through C-H bond activation of a methyl group of the methylbenzene. The dimeric cyanidebridged zirconocene complex **4** is formed as a side-product of this process.[3]

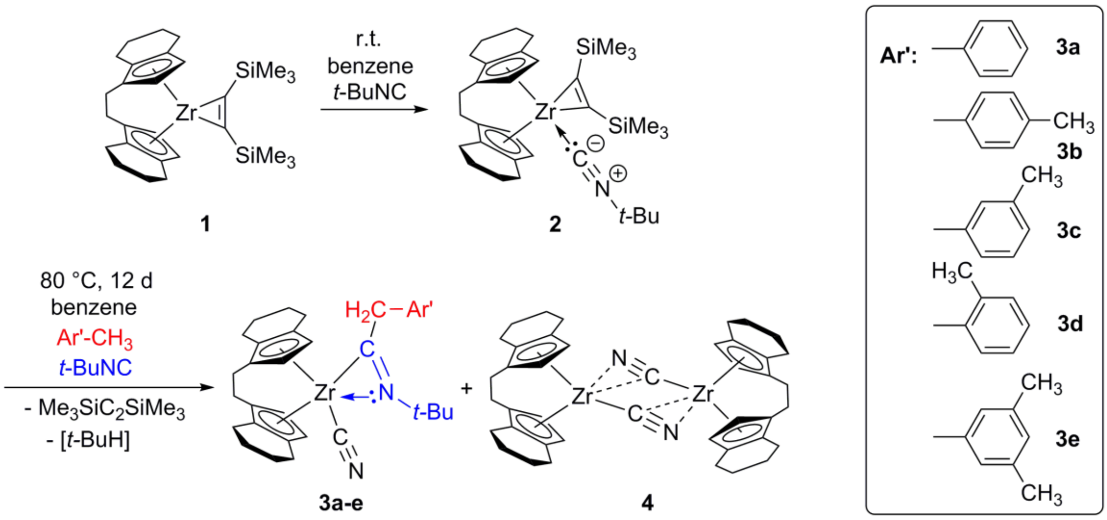

Figure 1. Reaction sequence of the general methylarene activation process.

References

1. F. Reiß, K. Altenburger, D. Hollmann, A. Spannenberg, H. Jiao, P. Arndt, U. Rosenthal, T. Beweries, *Chem. Eur. J.* **2017**, *23*, 7891-7895.
2. K. Altenburger, P. Arndt, L. Becker, F. Reiß, V. V. Burlakov, A. Spannenberg, W. Baumann, U. Rosenthal, *Chem. Eur. J.* **2016**, *22*, 9169-9180.
3. P. Arndt, M. Reiß, A. Spannenberg, C. Schünemann, F. Reiß, T. Beweries, *Dalton Trans.* **2019** *accepted article*.

TERTIARY PHOSPHINES IN REACTIONS WITH SUBSTITUTED CINNAMIC ACIDS

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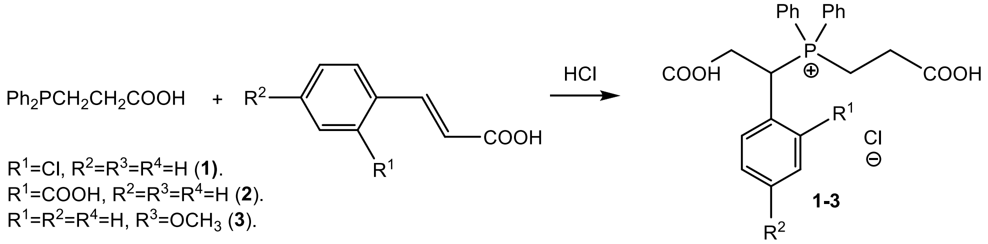
Phosphonium salts and carboxylate phosphabetaines have very wide practically useful properties. Phosphonium saltsare used as ionic liquids, attract interest as Lewis acidic catalysts and phase-transfer catalysts. Phosphabetainesare widely used as medications.

In previous works[1] we described the syntheses of dicarboxylatephosphabetaines on the basis of 3-(diphenylphosphonio)propanoic acid and different unsaturated monocarboxylic acids. Interesting that the direct reaction of 3-(diphenylphosphino)propanoic acid with orto-substituted cinnamic acids doesn't allow to obtain phosphabetaine and contributes the formation of phosphinoxide. This happens, probably, because of orto-effect. To solve this problem in the present work we offer new synthesis method that includes adding the hydrochloric acid.

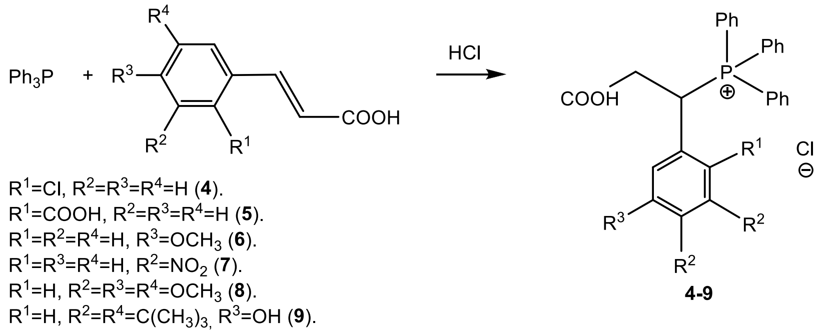


R^1=Cl, R^2=R^3=R^4=H (**1**).
R^1=COOH, R^2=R^3=R^4=H (**2**).
R^1=R^2=R^4=H, R^3=OCH_3 (**3**).

1-3

The reactions we carried out by boiling in chloroform with adding two drops of hydrochloric acid.

The reaction of triphenylphosphine with any substituted cinnamic acids also leads to the formation of triphenylphosphinoxide. Therefore, we decided to use the same method.



R^1=Cl, R^2=R^3=R^4=H (**4**).
R^1=COOH, R^2=R^3=R^4=H (**5**).
R^1=R^2=R^4=H, R^3=OCH_3 (**6**).
R^1=R^3=R^4=H, R^2=NO_2 (**7**).
R^1=H, R^2=R^3=R^4=OCH_3 (**8**).
R^1=H, R^2=R^4=$C(CH_3)_3$, R^3=OH (**9**).

4-9

All phosphonium salts were synthesized in good yield. The composition and structure were confirmed by elemental analysis and NMR and IR spectroscopy.

References

1. Yu. V. Bakhtiyarova, R.R. Minnullin, M.V. Morozov, D.I. Bakhtiyarov, D.R. Islamov, A.B. Dobrynin, O.N. Kataeva, R.A. Cherkasov, V.I.Galkin, I.V. Galkina, *Phosphorus, Sulfur Silicon Relat. Elem.* **2016**, *191*, 1633-1636.

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THEORETICAL AND EXPERIMENTAL-THEORETICAL APPROACH TO THE STUDY OF THE TOPOLOGY OF ELECTRON DENSITY IN {$YB^{2+}_2(\mu_2$-$OCH(CF_3)_2)_3(\mu_3$-$OCH(CF_3)_2)_2$ $YB^{3+}(OCH(CF_3)_2)_2(DME)_2$}

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A recent study showed that an experimental-theoretical approach based on the use of whole-molecule aspherical scattering factor («molecular invariom») can be used to obtain topological characteristics of the electron density of Sb[1] and Cr[2] complexes.

The lanthanide fluoroalkoxides can be used as emission materials[3]. And their properties are determined by the crystal structure.

In order to understand how adequately the approach of «molecular invariom» describes the topological characteristics of electron density in the coordination sphere of lanthanide atoms, complex {$Yb^{2+}_2(\mu_2$-$OCH(CF_3)_2)_3(\mu_3$-$OCH(CF_3)_2)_2$ $Yb^{3+}(OCH(CF_3)_2)_2(DME)_2$} (**1**) was studied. Both approaches to the study of electron density (DFT and «molecular invariom») showed good convergence of geometric characteristics in complex **1** with X-ray diffraction data.

The main topological characteristics obtained during the study are in good agreement with each other. The maximum differences in the values of $\rho(\mathbf{r})$ and $\nabla^2\rho(\mathbf{r})$ between DFT and «molecular invariom» are 0.009 a.u. for $\rho(\mathbf{r})$ and 0.045 a.u. for $\nabla^2\rho(\mathbf{r})$ for the coordination sphere of ytterbium.

An experimental-theoretical study of intramolecular non-valence fluorine interactions in these complexes allows localization of a smaller number of them compared to a theoretical one (table 1). Probably, this difference is due to the optimization of geometry in a theoretical study.

Table 1. Interaction F…X (X = F, H, O) in **1**.

Interaction	Number of interactions		E, kcal/mol		∑ E, kcal/mol	
	DFT	Invariom	DFT	Invariom	DFT	Invariom
F...F	24	11	0.65 ÷ 4.11	0.53 ÷ 1.67	55.22	10.93
F...H	24	13	0.23 ÷ 2.25	0.33 ÷ 1.54	26.14	11.86
F...O	14	6	0.48 ÷ 2.23	0.86 ÷ 1.66	16.93	7.26

Acknowledgments

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References

1. G.K. Fukin, E.V. Baranov, A.V. Cherkasov, R.V. Rumyantcev, E.A. Kozlova, L.S. Ohlopkova, A.I. Poddel'sky, *Izv. Akad. Nauk, Ser. Khim.*, **2019**, 9, 1650.
2. G.K. Fukin, E.V. Baranov, A.V. Cherkasov, R.V. Rumyantcev, A.N. Artemov, E.V. Sazonova, *Koord. Khim.*, **2019**, 45(10), 584.
3. D.M. Kuzyaev, T.V. Balashova, M.E. Burin, G.K. Fukin, R. V. Rumyantcev, A.P. Pushkarev, V.A. Ilichev, I. D. Grishin, D. L. Vorozhtsov and M. N. Bochkarev, *Dalton Trans.*, **2016**, 45, 3464.

SYNTHESIS OF FUNCTIONALIZED AZO DYES AND THEIR SILOXANE DERIVATIVES TO OBTAIN COLORED POLYMER MICROSPHERES

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Nowaday, there are various methods of polymer microspheres dyeing. Such spherical particles consist of crosslinked vinyl type polymer. The colored microspheres are used for the most important areas of research, such as: studies of fluid flow, tracking of processes inside the cells, or studies of phagocytosis. Therefore, the development of new approaches for dyeing of the polymer microspheres are of great importance[1]. One of the methods for dyeing of polymer microspheres is covalent binding of dye molecules to polymer molecules in the bulk of the particles. This method has many advantages, the main of which is the absence of dye migration from the surface of a particle due to covalent binding. To implement this method of dyeing, it is necessary to develop a molecular design of a dye molecule capable of copolymerizing with the vinyl type monomers.

In this work, the synthesis of various methacryloxy-functionalized azo dyes and their copolymerization with MMA were shown.

At the first stage of this work, various phenol-type azo dyes as model compounds were obtained and characterized. It was shown, that methacrylic group, being introduced into the structure of the obtained azo dyes, can be involved in polymerization of vinyl type monomers to form colored microspheres.

Next, it was assumed, that introduction of siloxane fragments will allow to obtain stable and intensely colored polymeric microspheres. For these purposes siloxane fragments with various lengths were introduced into the structure of eugenol. For the synthesis of siloxane derivatives of azo dyes, eugenol, which is a natural, multifunctional derivative, was taken as the initial, basic substance[2]. After that, the chromophore phenylazo group was introduced into the structure of the products obtained by azo coupling reaction with aniline.

At the third stage, the obtained methacryloxy-derived azo dyes with MMA were copolymerized to form colored microspheres with siloxane fragments.

All of the intermediate compounds and resulting copolymers are characterized by NMR, UV-spectroscopy, GPC.

References

1. I.A. Gritskova, P.N. Chadayev, D.I. Shragin et al. *Chem. and Chemical Techn.*, **2011**, V. 54, iss. 9, p. 70.
2. F.V. Drozdov, G.V. Cherkaev, M.I. Buzin, A.M. Muzafarov. *J. Organomet. Chem.*, **2018**, V. 871, 135-139.

NEW RUTHENOCENE-BASED PALLADIUM AND RUTHENIUM PINCER COMPLEXES BEARING THE C5(CH3)4(CF3) LIGAND

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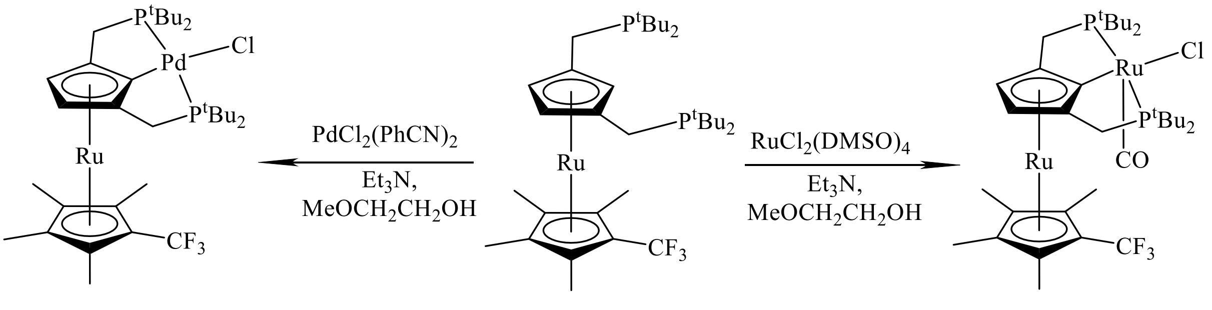
Transition metal pincer complexes are of interest due to their ability to catalyze important organic reactions. The sandwich nature of metallocene-based pincer ligands opens new possibilities for the design of organometallic compounds with the finely controlled catalytic properties by both varying the nature of the central atom of metallocene and introducing substituents of different bulkiness into the unmetallated cyclopentadienyl ring. Our interest in metallocene pincer complexes with a Cp^F ligand (Cp^F= $C_5Me_4CF_3$) arises from the fact that this ligand is very similar in its electronic properties to the Cp ligand (Cp = C_5H_5) and in its steric properties to the Cp* ligand (Cp = C_5Me_5).

The first palladium $PdCl[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Ru(Cp^F)]$ (**2**) and ruthenium[1] $RuCl(CO)[\{2,5\text{-}(Bu^t{}_2PCH_2)_2C_5H_2\}Ru(Cp^F)]$ (**3**) pincer complexes were synthesized by cyclometallation of diphosphine $\{1,3\text{-}(Bu^t{}_2PCH_2)_2C_5H_3\}Ru(Cp^F)$ (**1**) (Scheme 1).



2 **1** **3**

Scheme 1

Metallocene-based diphosphine (**1**) was obtained from 1,3-disubstituted metallocene $\{1\text{-}(CO2Et)\text{-}3\text{-}(CHO)C_5H_3\}Ru(Cp^F)$ (**1a**)[2] in a two-step synthesis. Reduction of **1a** with lithium aluminum hydride in diethyl ether afforded diol $\{1,3\text{-}(HOCH_2)_2C_5H_3\}Ru(Cp^F)$ (**1b**), whose phosphination with $HPBu^t{}_2$in hot acetic acid gave the corresponding compound **1**.

Acknowledgments

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References

1. S.V. Safronov, A.A. Koridze, *Russ. Chem. Bull. Int. Ed.,* **2018**, *67*, 1247.
2.S.V. Safronov, A.A. Pavlov, V.I. Sokolov, A.A. Koridze, *Russ. Chem. Bull. Int. Ed.,* **2018**, *67*, 255.

CONTROLLING THE FUNCTIONS OF BIOMOLECULES IN SOLUTION USING [2+2] PHOTOCYCLOADDITION

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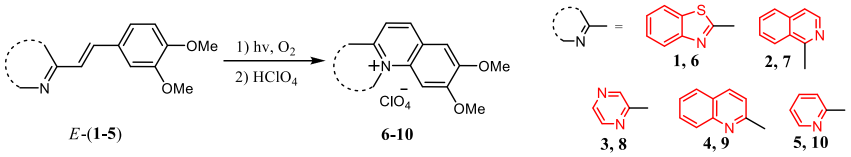
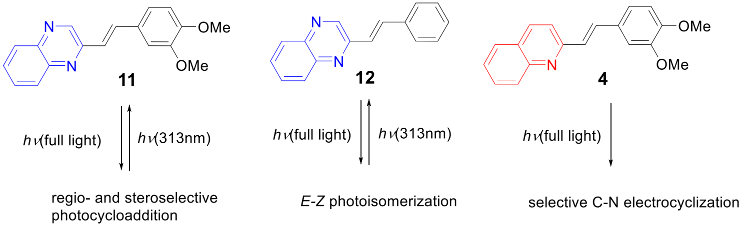
Although the photochemistry of stilbenes and its derivatives has been well studied,[1] only few studies have been reported on the photolysis of stilbene derivatives with nitrogen-bearing rings.

Recently, we have demonstrated that ortho-styryl-substituted N-heterocycles comprising one and two nitrogen atoms generally undergo regioselective C–N bond formation during photocyclization, resulting in the formation of a family of (aza)benzo [c]quinolizinium derivatives (Scheme 1).[2]



Scheme 1

In our study, we present the results of the investigation of the photochemistry of the compounds **4, 11-12** (Scheme 2) showed the effect of structural changes on the path of phototransformation. Removal of the two methoxy groups in the (E)-2-(3,4-dimethoxystyryl)quinoxaline (**11**) structure produces compound **12**, which is able to participate only in the photoisomerization reaction. The change of quixoline residue in **11** to quinoline results in the compound **4**, which demonstrates the regioselective oxidation electrocyclic transformation through the formation of novel C–N bond.



Scheme 2

To the best of our knowledge, the described reaction of the photolysis of ***E*-11** is the first example of the regioselective and stereospecific formation of cyclobutane derivative without applying any method for preorganization of the molecules in dilute solution.

Acknowledgments

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References

1. Likhtenshtein G. Stilbenes: Applications in Chemistry, Life Sciences and Materials Science. WILEY-VCH Verlag GmbH, 2010.
2. Aliyeu T. M., Berdnikova D. V., Fedorova O. A., Gulakova E. N., Stremmel C. and Ihmels H., J. Org. Chem., 2016, 81, 9075.

STABLE ALKYL- AND CATIONIC ALKYL COMPLEXES OF LN (II, III) AS EFFECTIVE CATALYSTS FOR FUNCTIONALIZATION OF SIX-MEMBERED N-CONTAINING HETEROCYCLES

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Six-membered nitrogen-containing heterocycles are the most important structural units of most natural compounds, functional materials, and drugs. However, often, the design of such systems using standard methods of organic synthesis is complicated by the formation of by-products and harsh reaction conditions. In this regard, the development of new highly efficient and atom-economical processes of direct introduction of substituents into the heterocycle attracts close attention. Due to the presence of highly reactive Ln-C bonds, the lanthanide alkyl complexes are considered as promising catalysts for the direct alkylation of the pyridine CH bonds. New alkyl and alkyl-cationic complexes Ln(II, III) with tert-butyl substituted benzhydryl ligands, which demonstrated high thermal stability, were synthesized as objects of study. Alkyl complexes of Ln (II) and alkyl-cationic complexes of Ln(III) proved to be highly effective catalysts in direct alkylation reactions of C_{sp2}-H and C_{sp3}-H bonds of pyridine and 2,6-dimethylpyridine heterocycles with various olefins and dienes, respectively. It was found that the complexes are tolerant to the presence of halogens in the olefin component in the process of catalysis and make it possible to obtain addition products with high yields.Moreover, for the first time demonstrated the possibility of dual sequential addition of norbornadiene to 2-metyl(2-ethyl) pyridine first CH_{Sp2} followed by CH_{Sp3} methyl group to form a twice alkylated product, the process has exceptional chemoselectivity.

The process of catalytic reduction of pyridine heterocycles, accompanied by de-aromatization, is an extremely important method for creating valuable building blocks for organic synthesis. The method of restoring C=N bonds by homogeneous catalytic hydrosilylation of heterocyclic substrates has proven itself well on d-transition metal complexes, however, no example has been given of performing such reactions on lanthanide complexes. We have demonstrated the possibility of reducing pyridine, as well as quinoline, pyrazine, and phenazine with various substituted silanes on Ln(III) trisalkyl and their cationic complexes. The reduction of quinoline and pyridine with phenyl and phenylmethylsilanes proceeds with a quantitative conversion at room temperature and leads to the formation of products of 1,2-addition of silanes with 100% regioselectivity.

Acknowledgments

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References

1. A. N. Selikhov, T. V. Mahrova, A. V. Cherkasov, G. K. Fukin, L. Maron and A. A. Trifonov, *Chem. Eur. J.*, **2017**, *23*, 1436.
2. A. N. Selikhov, G. S. Plankin, A. V. Cherkasov, A. S. Shavyrin, E. Louyriac, L. Maron, and A. A. Trifonov, *Inorg. Chem*. **2019**, *5*8, 5325.

SYNTHESIS OF N-(SILYLMETHYL) BENZENESULFONAMIDES

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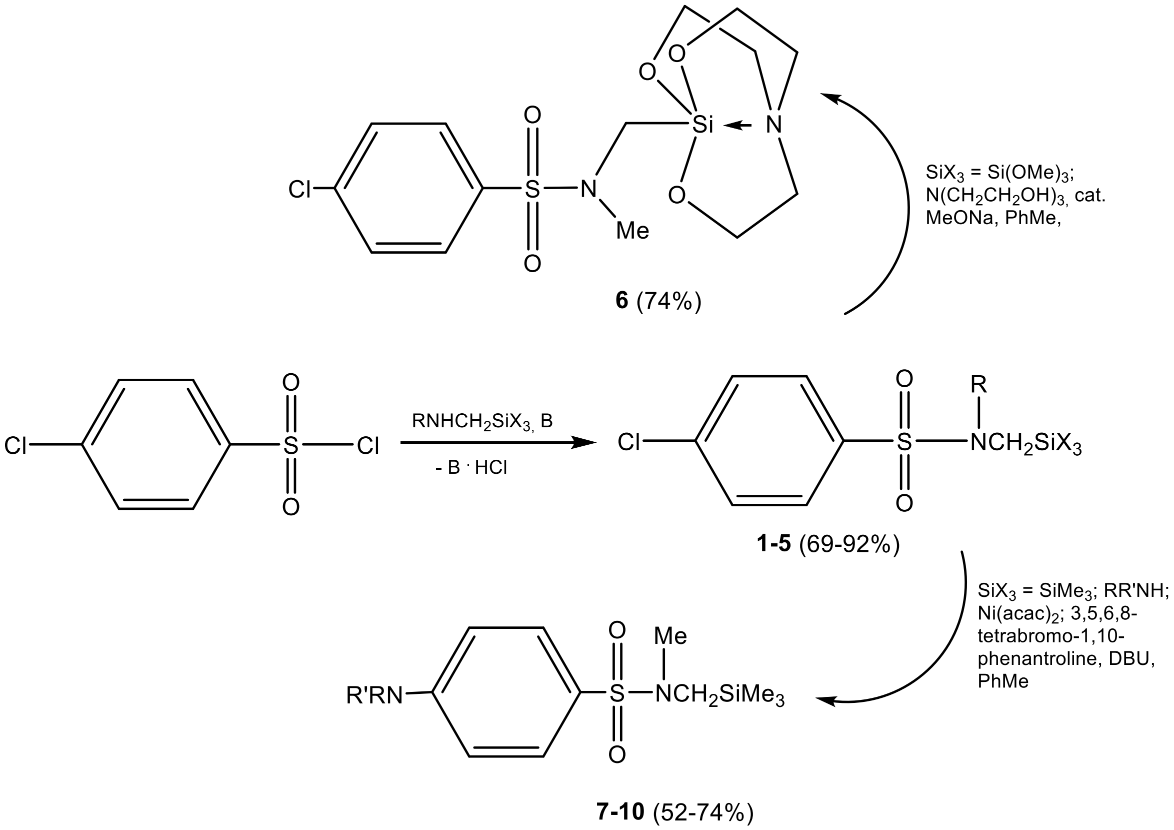
N-(Silylmethyl)-4-chlorobenzenesulfonamides **1-5** were obtained by interaction of 4-chlorobenzenesulfonic acid chloride with N-(silylmethyl)amines (Fig. 1). The reaction proceeds in benzene solution at room temperature with using an excess of triethylamine as an acceptor of hydrogen chloride. N-(Silatranylmethyl)-4-chlorobenzenesulfonamide **6** was prepared as result of the treatment of N-[(trimethoxysilyl)methyl]-4-chlorobenzenesulfonamide by tris(2-hydroxyethyl)amines. The interaction of N-methyl-N-(trimethylsilylmethyl)amide of 4-chlorobenzenesulfonic acid with amines lead to form the corresponding N-methyl-N-(trimethylsilylmethyl)amides of 4-aminobenzenesulfonic acids **7-10**. The structure of the synthesized compounds was confirmed by NMR and IR spectroscopy.



R = Me, Ph;
RR'N = Et_2N, *i*-PrNH, $MeNCH_2Si(OMe)_3$, $PhNCH_2SiMe(OEt)_2$;
$SiX_3 = SiMe_n(OMe)_{3-n}$ (n = 0-3), $SiMe(OEt)_2$

Figure 1. Synthesis of N-(silylmethyl)benzenesulfonamides

Acknowledgments

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ONE-POT CYCLOHEXYL CYCLOHEXANECARBOXYLATE SYNTHESIS FROM CYCLOHEXANOL AND CO AT CATALYSIS BY $Pd(PPh_3)_2Cl_2$ / PPh_3 / p-TOLUENESULFONIC ACID SYSTEM

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Alkenes hydrocarbalkoxylation catalyzed palladium-phosphine systems allows to obtain the esters in the mild conditions. However, not all alkenes are accessible. The most simple method of alkenes receipt is the reversible acid-catalytic dehydration of appropriate alcohols at heating. For the first time in this work two processes were conducted in one reactor. The first of them is cyclohexanol dehydration catalyzed by p-toluenesulfonic acid ($TsOH \cdot H_2O$) with cyclohexene formation and the second of them is cyclohexene hydrocarbalkoxylation by CO and cyclohexanol catalyzed by $Pd(PPh_3)_2Cl_2$ – PPh_3 – $TsOH \cdot H_2O$ system. It is known that TsOH is a strong acid which is used as co-catalyst in hydrocarbalkoxylation usually. Obtaining product – cyclohexyl cyclohexanecarboxylate – is interesting as a potential addition to different types of fuel.

The offered one-pot process is complicated by water presence in the system. Water is entered to the reaction mass in composition of $TsOH \cdot H_2O$ and formed as by-product of dehydration. Water accumulation in the reaction mass leads to dehydration equilibrium displacement to alcohol. A little quantities of water increase the hydrocarbalkoxylation rate. However, its high concentrations lead to decrease in hydrocarboxylation rate. Sodium tosylate (TsONa) is capable to bonding of water with formation of additional TsOH quantities. Therefore TsONa was used to operate the concentrations of water and TsOH.

The kinetic experiments were conducted in the periodic reactor in toluene medium. The procedure of experiments were described earlier.[1] Analysis of the reaction mass was carried out using gas chromatography.

For the first time with optimization methods using the optimal conditions of dehydration and hydrocarbalkoxylation realization in the one reactor were determined with the system parameters variety in following ranges: T=378-403 K, P_{CO}=1.5-2.5 MPa, $C(Pd(PPh_3)_2Cl_2)=(0.2\text{-}2.1)\cdot10^{-2}$ M, $C(PPh_3)=(0.8\text{-}3.2)\cdot10^{-2}$ M, $C(TsOH \cdot H_2O)$=0.04-0.23 M and C(TsONa)=0-0.22 M. In the absence of TsONa addition the most yield of the target product of 86.8 % in 320 min was obtained in the conditions: T=383 K, P_{CO}=2.1 MPa, $C(Pd(PPh_3)_2Cl_2)=2\cdot10^{-3}$ M, $C(PPh_3)= 8\cdot10^{-3}$ M and $C(TsOH \cdot H_2O)$=0.2 M. When TsONa (0.12 mol/L) was added into the reaction mass the target product yield reached 99.7 % in 320 min at the same temperature, CO pressure, $Pd(PPh_3)_2Cl_2$ and PPh_3 concentrations and $C(TsOH \cdot H_2O)$=0.23 M.

The explanation to obtained results was given in the limits of exhibitions about the dehydration equilibrium displacement, hydride mechanism of hydrocarbalkoxylation and ligand exchange reactions between palladium complexes.

References

1. V.A. Aer'yanov, N.T. Sevost'yanova, S.A. Batashev, S.A. Nesolenaya, *Petroleum Chemistry* **2006**, 46, 405.

SYNTHESIS OF BIOLOGICALLY ACTIVE METAL COMPLEXES BASED ON 3-FORMILCHROMONE DERIVATIVES

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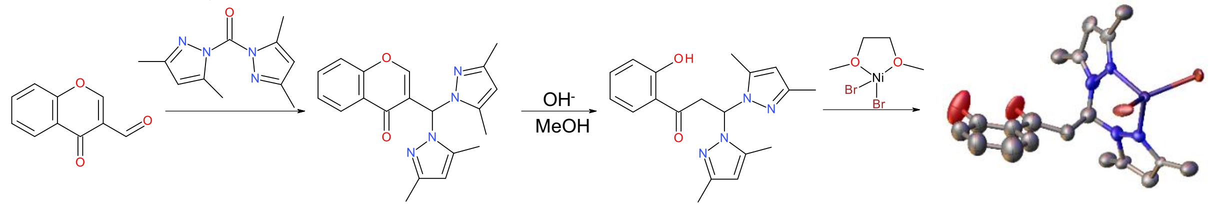
The widespread use of cisplatin in clinical practice explains the interest of researchers in medical chemistry to coordination chemistry[1]. At the same time, the high toxicity of platinum drugs explains the active search for drugs with alternative mechanism of action, including the path of metal replacement.

From this point of view, of particular interest are Ni^{2+} ions, which are a cofactor of several enzymes and according to a number of experimental studies exhibit greater anticancer activity compared to ions of other transition metals[2].

Numerous studies have established that the predominant pharmacological effect depends not only on the nature of the metal, but also on the structure of the ligand. Chromone derivatives are one of the most promising classes of organic compounds due to the wide spectrum of pharmacological activity of its derivatives and their low toxicity[3].

To study the pharmacological activity of metal complexes, we obtained compound **1** containing a fragment of bis(pyrazol-1-yl)methane capable of coordinating transition metals[4]. To create additional coordination centers by opening the pyrone cycle, compound **2** and its complex with Ni^{2+} **3** were obtained (Fig. 1). The structure of the target complex was confirmed using ^1H NMR spectroscopy and X-ray diffraction analysis.



1 **2** **3**

Figure 1. Synthesis of an acyclic derivative of 3-formylchromone and a metal complex based on it

Acknowledgments

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References

1. C. Santini, M. Pellei, V. Gandin, M. Porchia, F. Tisato, C. Marzano. *Chem. Rev.* **2014**, 114, 815−862
2. Bao-dui Wang, Zheng-Yin Yang, Ming-hua Lu, Jun Hai, Qin Wang, Zhong-Ning Chen. Synthesis, characterization, cytotoxic activity and DNA binding Ni(II) complex with the 6-hydroxy chromone-3-carbaldehyde thiosemicarbazone. *Journal of Organometallic Chemistry,* 694, **2009**, 4069–4075
3. J. Reis, A. Gaspar, N. Milhazes, and F. Borges. Chromone as a Privileged Scaffold in Drug Discovery: Recent Advances. *J. Med. Chem.* **2017**, 60, 7941−7957.
4. Higgs T.C., Carrano C.J. A New Class of Biomimetically Relevant "Scorpionate" Ligands. 1. The (2-Hydroxyphenyl)bis(pyrazolyl)methanes: Synthesis and Structural Characterization of Some Cobalt(II) Complexes. *Inorg. Chem.* ***1997***, 36, 3, 291–297.

CONDENSATION OF ORGANOYTTRIUMOXANALUMOXANES WITH CHROMIUM ACETYLACETONATE

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The process of organoyttriumoxanealumoxanes co-condensation with chromium acetylacetonate has been studied, as a result chromium-containing organoyttriumoxanealumoxanes were obtained, which are ceramic-forming oligomers and may have fiber-forming properties. Their thermo transformation leads to the production of high-purity, heat-resistant, multicomponent ceramics based on aluminum, yttrium and chromium oxides, in particular, chromium modified yttrium-aluminum garnet $Y_3Al_5O_{12}$ (YAG) is produced. It is known[1] that small amounts of Cr_2O_3 additives improve creep and strength due to the formation of solid $Y_3(Al_{1-x}Cr_x)_5O_{12}$ solutions.

The co-condensation of organoyttriumoxanealumoxanes with chromium acetylacetonate is carried out at 50 - 100 °C in organic solvents (ethyl alcohol, toluene) according to the scheme shown in Figure 1.

The synthesized organochromiumoxane yttriumoxanealumoxane oligomers were studied by ^1H, ^{13}C, ^{27}Al NMR, IR spectroscopy, SEM with EDS and mapping by element distribution, TGA and elemental analysis.

Fiber forming properties of the synthesized oligomers depending on Al:Y and Al:Cr molar ratio were investigated and polymer fibers were produced based on fiber-forming oligomers (Fig. 2).

$$(Al_m)(Y_n)\{(OR)_a(OR^*)_b(OR^{**})_x(OH)_gO_d\}_{(m+n)} + k(R^*O)_3Cr \xrightarrow[-(a-p)ROH]{} (Cr_k)(Al_m)(Y_n)[(OR)_p(OR^*)_s(OR^{**})_x(OH)_zO_y]_{(k+m+n)}$$

$a + b + x + g + 2d = 3; \quad p + s + x + z + 2y = 3$

$R = C_2H_5$, $i\text{-}C_4H_9$;

$R^* = C(CH_3){=}CHC(O)CH_3$;

$R^{**} = C(CH_3){=}CHC(O)OC_2H_5$.

Figure 1. Scheme of organoyttriumoxanealumoxanes co-condensation with $(acac)_3Cr$

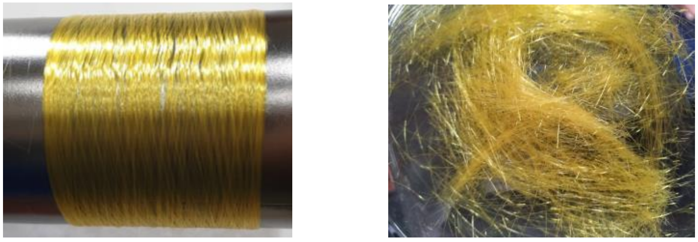

Figure 2. Polymer fibers of garnet composition

Acknowledgments

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References

1. Z. Shen, A. Ekstrand, M. Nygren, J. Eur. Ceram. Soc. **2000**, *20,* 625.

THE SYNTHESIS OF NEW COMPOUNDS WITH POTENCIAL BIOLOGIC ACTIVITY BASED ON FULLERENE C_{60} AND A DERIVATIVE OF VITAMIN B_{12}

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Approaches of preparing of biologically active substances based on transition metal complexes with biological substrates participation in closed to physiological conditions were developed for a number of years in INEOS RAS. Under academician M. E. Vol'pin's idea, catalytic sources of active oxygen species (AOS) which are capable selectively accumulate in tumor, can be active in suppressing of tumor tissue grows. The native macrocyclic cobalt complexes — vitamin B_{12} and its derivatives (cobalamins, in particular, *e*-carbonic acid of B_{12}: *e*-COOH-Cbl-CN (I) introduce the most interest.

Our results, in particular, the investigation of catalytic activity of these complexes in oxidation of natural substrates, producing active oxygen species (AOS) in these reactions, oxidative cleavage of nucleic acids in the presence of these metal complexes and medico-biological examinations confirmed, that catalytic system, capable to generated AOS, can be highly effective as antitumor and related agents.[2] Also, firstly in INEOS RAS was elaborated the method of synthesis of aminoacids and peptides fullerene derivatives.[2] It turned out to be that there is no toxicity of these substances and they have a wide spectra of biological activity. A complex of studies has shown that the most effective derivatives with antitumor activity are those compounds that contain nitrogroups or carnosine derivatives.[3]

We assumed that the introduction of a pharmacophoric fullerene derivative of the active form of vitamin B_{12} into the molecule will significantly improve the efficiency of the antitumor action of the complexes. First of all it was necessary to show the fundamental possibility of the synthesis of such compounds. On the first stage of the work the addition to carboxylic group of derivative of cobalamin *e*-COOH-Cbl-CN (I) the fullerene frame of fullerene C_{60} derivative —$HC_{60}NH(CH_2)_5COOCH_3$ (II) result in the new type of mixed biologically targeted cobalamin-fullerene complexes CN-Cbl-$C(O)$-$C_{60}NH(CH_2)_5COOCH_3$ (III). The next derivative (IV) is obtained directly by the addition of (I) to (II), but after the additional introduction of a spacer — an ethylene bridge with the formation of the following structure: CN-Cbl-B_{12}-$C(O)OCH_2CH_2$-$C_{60}NH(CH_2)_5COOCH_3$ (IV). The structure of obtained substances (III) and (IV) was established by UV, IR, CD spectroscopy and elemental analysis.

Acknowledgements

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References

1. M. E. Volpin, N. Yu. Krainova, I. Ya. Levitin, Z. Ya. Mityaeva, G. N. Novodarova, V. K. Oganezov, A. A. Pankratov, V. I. Chissov, R. I. Yakubovskaya, *Russ. Chem. J.,* **1998,** *116.*
2. RF patent № 2462473, **2007.**
3. I. I. Fayngold, R. A. Kotelnikova, N. P. Konovalova, G. N. Bogdanov, V. S. Romanova, *Yearbook Instit. Problems of Chem. Phys., Russian Academy of Sciences*, **2011**, *8*, 145.
4. V. S. Romanova, N. Yu Shepeta, A. G. Buyanovskaya, R. U.Takazova, *Processes of Petrochemistry and Oil-refining*, **2019**, *20*, № 1, 14.

SYDNONE IMINES – PLANT GROWTH REGULATORS

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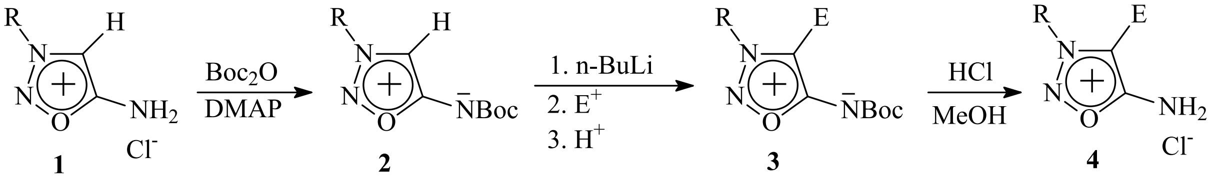
Sydnone imines are mesoionic heterocyclic compounds with a wide spectrum of biological activity. Recently, some sydnone imines derivatives have been shown to exhibit plant growth stimulating properties.[1,2] Therefore, a development of new methods for the functionalization of sydnone imines is needed for a search for novel plant growth regulating compounds.

So, we elaborated a method for modification of 3-substituted sydnone imine hydrochlorides **1** *via* their N_6-Boc derivatives **2**. Compounds **2** were deprotonated with *n*-BuLi followed by reactions with a variety of electrophiles affording the 4-substituted derivatives **3**. The final withdrawing of the Boc-group resulted in sydnone imine derivatives **4** in high yields.



Some compounds of types **3** and **4** were found to exhibit a statistically significant plant growth stimulating effect on corn seeds (Krasnodarsky 291 AMV cultivar) at doses of 0.5 or 1 g per ton increasing a weight of the seedlings up to 45%. In addition, some compounds shown sulfonylurea herbicide antidote properties significantly reducing the effect of the herbicide.

Acknowledgments

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References

1. I. A. Cherepanov et al., Agrokhimia (Russ.) **2018**, *9*, 50-55.
2. Patent RU 2656212 (2018).

1-AMINOPHOSPHONIC ACID DERIVATIVES OF P-TERT-BUTYLTHIACALIX[4]ARENE FOR CONSTRUCTION OF BIOCOMPATIBLE HYBRID NANOMATERIAL FOR BONE IMPLANTANTS: SYNTHESIS AND SUPRAMOLECULAR PROPERTIES

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Replacing and regenerating damaged bone tissue is a serious problem in orthopedic surgery[1]. The wide range of natural (allogeneic and xenogenic) transplants used in medicine has a number of disadvantages, including a limited supply, the incidence of donor sites (autografts), low availability, the probability of transmission of the disease and the risk of rejection (allografts). The limitations of these two approaches can be overcome by using synthetic bone substitutes, one of the main disadvantages of which is their low biocompatibility. Thus, the problem of creating new affordable approaches to producing synthetic bone implants, combining all the necessary requirements, including biocompatibility, is very relevant.

One of the attractive ways to solve this problem is the use of the principles of supramolecular chemistry for the assembly of nanostructured porous biocompatible materials based on three main components: nanohydroxyapatite, supramolecular receptors and proteins. Nanohydroxyapatite has a positive effect on bone remodeling[2], has excellent bone tissue repair properties[3] and is non-toxic[4]. Supramolecular receptors capable of binding to both hydroxyapatite nanoparticles and proteins due to the self-assembly process will allow the formation of a biocompatible hybrid nanomaterial to create bone implants.

In this work, derivatives of *p-tert*-butylthiacalix[4]arene containing fragments of 1-aminophosphonic acids and their salts on the lower rim of the macrocycle were synthesized. As is known, (amino)phosphonic acids have a high affinity for bone tissue hydroxyapatite crystals, and the macrocyclic platform of*p-tert*-butylthiacalix[4]arene allows to arrange functional groups in space in a certain way, and as a result increase the binding efficiency and selectivity to substrates. For the obtained macrocycles, the ability to form self-associates, as well as to form associates with hydroxyapatite nanoparticles and model proteins (BSA, lysozyme, hemoglobin), was studied by DLS.

Acknowledgments

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References

1. P. V. Giannoudis, H. Dinopoulos, E. Tsiridis, *Injury* **2005**, *36*, *20*.
2. L. Lin, K. L. Chow, Y. Leng, *J. Biomed. Mater. Res*. A **2009**, *89*, *326*.
3. D. Apelt, F. Theiss, A. O. El-Warrak, K. Zlinszky, R. Bettschart-Wolfisberger, M. Bohner,S. Matter, J. A. Auera, B. von Rechenberg, *Biomaterials* **2004**,*25*, *1439*.
4. P. Sepulveda, J. G. P. Binner, S. O. Rogero, O. Z. Higa, J. C. *J. Biomed. Mater. Res*. A **2000**, *50*, *27*.

2,2'-DIHYDROXYAZOBENZENE AS (ONO')TRIDENTATE LIGAND: SYNTHESIS AND STRUCTURE OF PENTACOORDINATE SILICON COMPLEXES

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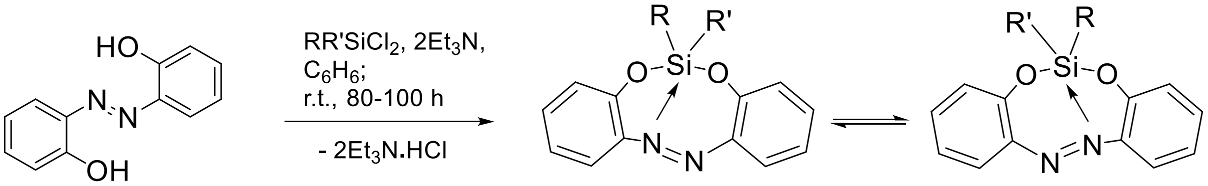
The pentacoordinate silicon compounds attract interest among chemists due their unusual physicochemical properties, reactivity and biological activity.The various kinds of chelating ligands are applied to the formation of such compounds. In particular the compounds possessing beneficial properties were obtained with the use of the tridentate ONO' type ligands. Azobenzene derivatives are widely used as photosensitive materials, in biochemical and medical research, in the field of materials science and polymers.[1] There is currently enhanced interest in use of 2,2'-dihydroxyazobenzene and related compounds as excellent tridentate ONO' type ligands[2] for synthesis of the metal complexeshaving a intriguing properties. There are only few the complexes of group 14 elements with 2,2'-dihydroxyazoarenes.[3,4] 6,6-Diorganylbenzo[*d,h*][1,3,6,7,2]dioxadiazasilonines **1-4** were obtained by the interaction of 2,2'-dihydroxyazobenzene with RR'SiCl_2 (Scheme) and their structure was studied by NMR, IR and UV spectroscopy. The structure of compound **1** and **2** was proved by X-ray diffraction (**Fig. 1**). The values of length of N→Si dative bond are 2.171(2) Å and 2.079(2) Å for compound **1** and **2**, respectively.



1, R = Me, R' = Ph (74%); **2**, R = Me, R' = ClCH_2(69%); **3**, R = R' = Ph (76%); **4**, R = Me, R' = CH_2=CH (57%)

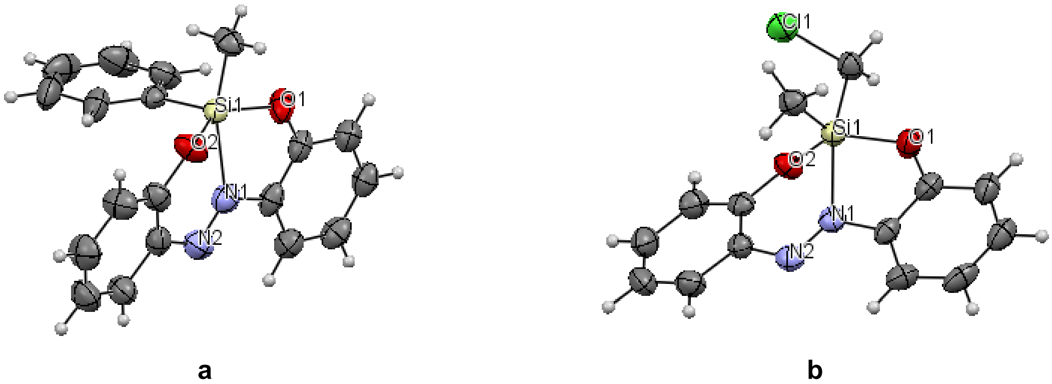


Fig. 1. Molecular structures of compound **1** (a) and **2** (b) (ORTEP, 30% thermal ellipsoid plots).

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References

1. E. Merino, *Chem. Soc. Rev.,* **2011**, *40*, 3835.
2. E. Evangelio, J. Saiz-Poseu, D. Maspoch, K. Wurst, F. Busque, D. Ruiz-Molina, *Eur. J. Inorg. Chem.,* ***2008*,** 2278.
3. U. Böhme, S. Jähnigen,*ActaCryst.* **2008**, *C 64*, 364.
4. K. E. Besslera, J. A. dos Santosa, V. M. Deflona, S. de Souza Lemosa, E. Niquet Z. *Anorg. Allg. Chem.* **2004**, 630, 742.

FEATURES OF THE ELECTRONIC STRUCTURE OF NEUTRAL COMPLEXES OF FE (III) WITH SALICYLALDEHYDE THIOSEMICARBAZONE LIGAND

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Molecular structure of ligand has an important influence on spin-crossover (SCO) behavior of the anionic complexes of Fe(III) with salicylaldehydethiosemicarbazone (thsa) ligand. Earlier we investigated the influence of coordination environment on SCO transition in the neutral complexes of Fe(III) with salicylaldehydethio-, seleno- andsemicarbazone ligands.[1] The present study is focused on the influence of end-group $-NH_2$ in thsa ligand on the SCO energetic characteristics for neutral complexes of Fe(III) by quantum chemistry methods. All calculations were carried out using the Gaussian 09 computational package with a B3LYP* hybrid functional with 6-311++G(d,p) basis set.

We carried out DFT calculations for two Fe(III) neutral complexes: [Fe(H-5Cl-thsa)(5Cl-thsa)] (**1**) и [Fe(H-5Cl-thsa-Me)(5Cl-thsa-Me)] (**2**) (Fig. 1). Structures and magnetic properties of these complexes were studied earlier[2, 3]. The electronic energy difference between HS and LS states is E_{el}(HS-LS)=13.48 kJ/mol for (**1**) and E_{el}(HS-LS)=15.60 kJ/mol for (**2**). The value of E_{el}(HS-LS) for the complex (**2**) is 2.12 kJ/mol higher compared to complex (**1**). The results are corroborated by experimental data: $T(SCO)_{1/2}$(**2**)>$T(SCO)_{1/2}$(**1**).[2,3]

The comparison of MO diagrams for HS complexes (**1**) and (**2**) displays greater energetic destabilization of iron e^*_g-like orbitals of complex (**2**) in contrast to complex (**1**). This fact indicates that the σ-bonding in complex (**2**) is stronger than in complex (**1**). The analysis of iron t^*_{2g}-like orbitals demonstrates greater energetic destabilization of these orbitals for complex (**1**) compared to complex (**2**). This fact indicates that the π-bonding in complex (**1**) is stronger than in complex (**2**), which is confirmed by the values of natural charges on Fe (III) HS: 0.773 *e* for (**1**) и 0.784 *e* for (**2**). It should be noted that the electronic effect of the acceptor substituent (5Cl-) in the benzene ring is energetically close to the considered effect of the ligand $-NH-CH_3$ end-group: 1.86 kJ/mol, if compared to the unsubstituted [Fe(H-thsa)(thsa)] analogue.[2]

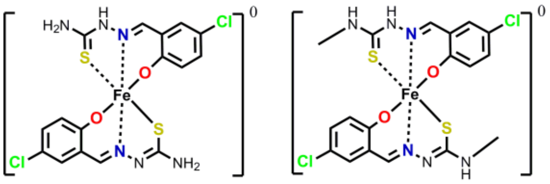

Figure 1.Scheme of complexes (**1**) and (**2**).

Acknowledgments

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References

1. N. G. Spitsyna, M.A. Blagov, V. A. Lazarenko*, et al.*, *Dalton Trans.* **2019**, *48*, 9328.
2. E. W. T. Yemeli, G. R. Blake, A. P. Douvalis,*et al.*,*Chem. – Eur. J.*, **2010**, DOI: 10.1002/chem.201002100.
3.Z.-Y. Li, J.-W. Dai, K. J. Gagnon,*et al.*, *Dalton Trans*. **2013**, *42*, 14685.

OXAPHOSPHOLENES AND PHOSPHACOUMARINS IN SYNTHESIS OF FUNCTIONALY SUBSTITUTED PHOSPHONIUM SALTS AND PHOSPHINE OXIDES WITH ANTIMICROBIAL ACTIVITY AND ANTITUMOR ACTIVITY

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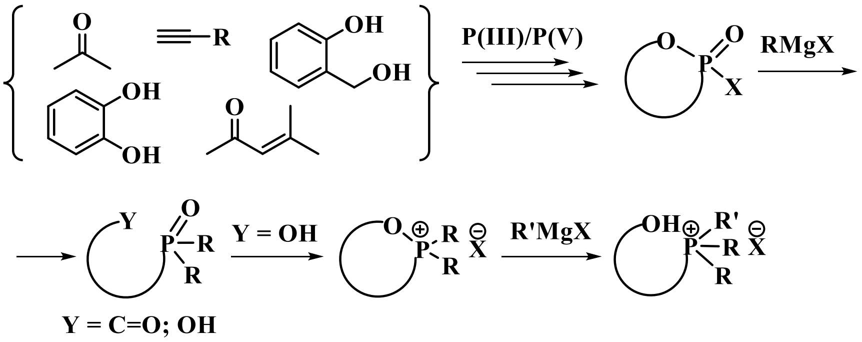
Quaternary phosphonium salts (QPS) are an object of the growing interest of biomedical sciences due to their antimicrobial,[1,2] antitumor action[4] and ability to penetrate mitochondria and regulate many vital processes in a living cell.[4] Here we report a synthesis of new 2-hydroxyarylsubstituted phosphonium salts with alkyl and aryl substituents at phosphorus atom using the two-step approach including obtaining cyclic quasiphosphonium salts from phosphine oxides and their subsequent reaction with organomagnesium compounds.[5]

All synthesized compounds were evaluated for in vitro antimicrobial activity against both Gram-positive and Gram-negative bacterial strains and fungi. Some of the synthesized compounds show submicromolar activity towards Gram-positive bacteria and fungi. The most active compounds are non-toxic to human erythrocytes and human embryonic lung cells. Moreover, some of the synthesized salts show antitumor activity up to 2μM with good selectivity.



Scheme 1. Synthetic approach to 2-hydroxyarylsubstituted phosphonium salts

References

1. Cuthbert, T. J.; Hisey, B.; Harrison, T. D.; Trant, J. F.; Gillies, E. R.; Ragogna, P. J.; *Angew. Chemie Int. Ed.*, **2018**, 57*(39)*, 12707.
2. Brunel, F.; Lautard, C.; Di Giorgio, C.; Garzino, F.; Raimundo, J. M.; Bolla, J. M.; Camplo, M. *Bioorganic Med. Chem. Lett.*, **2018**, 28*(5)*, 926.
3. Cheng, G.; Lopez, M.; Zielonka, J.; Hauser, A. D.; Joseph, J.; McAllister, D.; Rowe, J. J.; Sugg, S. L.; Williams, C. L.; Kalyanaraman, B. *Cancer Biol. Ther.* **2011**, 12*(8)*, 707.
4. Zielonka, J.; Joseph, J.; Sikora, A.; Hardy, M.; Ouari, O.; Vasquez-Vivar, J.; Cheng, G.; Lopez, M.; Kalyanaraman, B. *Chem. Rev.* **2017**, 117*(15)*, 10043.
5. Tatarinov, D. A.; Kuznetsov, D. M.; Voloshina, A. D.; Lyubina, A. P.; Strobykina, A. S.; Mukhitova, F. K.; Polyancev F. M.; Mironov, V. F. *Tetrahedron*, **2016**, 72*(51)*, 8493–8501.

CHEMOSELECTIVE OXIDATIVE PHOSPHORYLATION OF AMINOTHIOPHENOLS WITH THE SECONDARY PHOSPHINE SELENIDE/CCL_4/ET_3N SYSTEM

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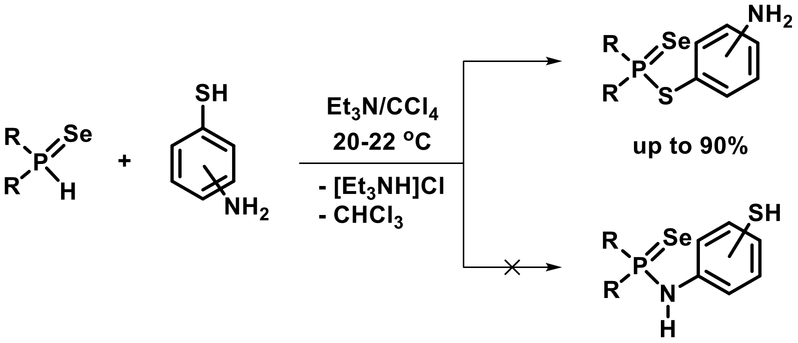
Using available secondary phosphine selenides (obtained from elemental phosphorus and arylethenes by the Trofimov-Gusarova reaction[1]), we have implemented for the first time the process of oxidative phosphorylation of aminothiophenols with secondary phosphine selenides in the CCl_4/Et_3N system and obtained original data on the direction of the studied interaction.

It turned out that under the conditions studied (20–22 °C, molar ratio of secondary phosphine selenide : aminothiophenol = 1:1, CCl_4/Et_3N system), the oxidative cross-coupling of the starting reagents proceeds chemoselectively only with the participation of the aminothiophenol SH-function and leads to the corresponding aminophenylthioesters of diorganylselenophosphinic acids in a yield of up to 90% (Scheme 1).

The high chemoselectivity of this reaction persists when using a double excess of secondary phosphine selenide with respect to aminothiophenol (*ceteris paribus*): the formation of oxidative cross-coupling products at the amino group, as well as disubstitution products (*N,S*-derivatives of selenophosphinic acid) is not observed.

Thus, fundamental information on the chemoselectivity of the oxidative phosphorylation of aminothiophenols with the secondary phosphine selenide/CCl_4/Et_3N system was obtained and a new family of functional aminophenyl thioesters of diorganylselenophosphinic acids, promising drug precursors, building blocks for organoelement synthesis, and ligands for design of important metal complexes, was synthesized.



Scheme 1

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grant no. 18-33-00120 mol_a).

References

1. B. A. Trofimov, N. K. Gusarova, *Mendeleev Commun.* **2009**, *19(6)*, 295.

OXAPHOSPHOLE 2-OXIDES ON A BASIS OF 2-HYDROXY-α,α-DIMETHYLARYLMETHANOL IN REACTIONS WITH ORGANOMAGNESIUM COMPOUNDS

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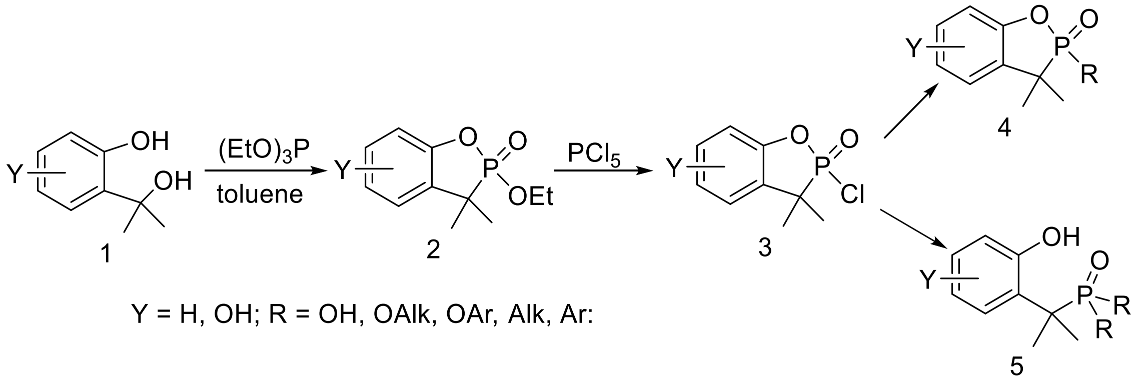
Oxaphospholenes are interesting class of organophosphorus compounds due to both, their biological activity, in particular the fact that oxaphospholenes can serve as carbohydrates mimetic, and chemical properties such as an ability to be transformed into various organophosphorus compounds.

In this work we obtained oxaphosphole 2-oxides2 on a basis of 2-hydroxy-α,α-dimethylarylmethanols 1 via interaction of corresponding alcohols with triethylphosphite.[1] Such oxaphosphole 2-oxides2 can be easily transformed to P-Cl derivatives 3 that are source to a number of chemical transformations in reactions with different nucleophiles and especially Grignard reagents to form P-C bonds[2] (Scheme 1).



Scheme 1.

Acknowledgments

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References

1. Pérez-Prieto J et al. *Org Lett*. **2005**, 7, 3869.
2. Tatarinov D.A. et al. *Russ J Gen Chem*. **2016**, 86, 530.

TETRA-4-(4-BUTYL/BUTOXYPHENOXY) PHTHALOCYANINES OF COBALT AND COPPER

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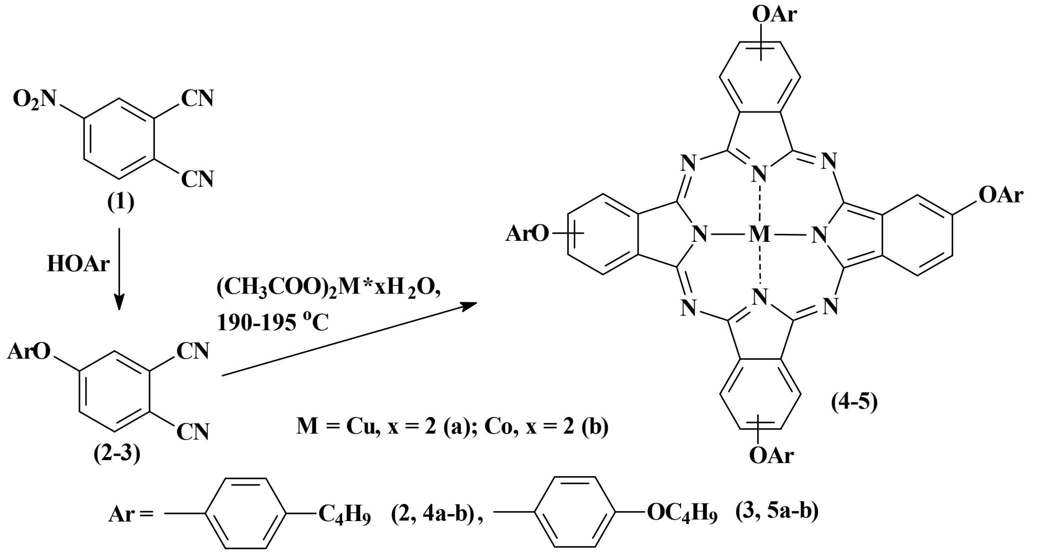
Present communication is devoted to the synthesis and study of physicochemical properties, including the catalytic activity of tetra-[4-(butyl/butoxyphenoxy)] phthalocyanines of cobalt and copper.

The most effective method for producing phthalocyanines is nitrile; therefore, the corresponding phthalonitriles were obtained by nucleophilic substitution of the nitro- group in 4-nitrophthalonitrile with 4-butylphenoxy or 4-butoxyphenoxy groups. At the next stage, by heating the phthalonitriles obtained with copper or cobalt acetates at 190-200 °C, the corresponding metal complexes were synthesized (**Scheme 1**). Purification of the target compounds was carried out by column chromatography on silica gel M60.

The structure of the compounds obtained was confirmed by elemental analysis, MALDI-TOF spectrometry, ^{1}H NMR, IR and electronic absorption spectroscopy.

The spectroscopic properties of the complexes synthesized in organic media were studied. The influence of the nature of the substituent and the metal cation in the macrocycle on the nature of the electronic spectra and the position of the Q band is determined. The catalytic activity of the synthesized complexes in the DTC oxidation reactions was studied. The thermo-oxidative stability of the synthesized compounds in air was studied.



Scheme 1. General approach of butyl/butoxy- substituted phthalocyanine complexes

Acknowledgments

The work was supported by Russian Science Foundation grant, project №19-73-10107.

SINGLE MOLECULE MAGNETS BASED ON DY3+ COMPLEXES SUPPORTED BY DIAZABUTADIENE AND ALKOXIDE LIGANDS

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Lanthanide-based materials continue to fascinate the scientific community owing to their tremendous optical and magnetic properties.[1] In particular, the ability of lanthanide coordination complex to exhibit slow relaxation of their magnetization, possibly associated with magnetic bistability of molecular origin, opens stimulating perspectives in data storage, spintronics or quantum computing.[2]

The overall approach to the design of new dysprosium SMM is to create highly symmetrical axial environments around the Dy^{3+} ion and stabilize thereby the 4f electronic density. In this aim, a series of heteroleptic half-sandwich[3], chloride and homoleptic Dy^{3+} complexes containing diazabutadiene ligands in [DAD^{2-}] as well as [$DAD^{\cdot-}$] forms and also alcoholate-based dysprosium complex [$Dy(OCPh_3)_2(THF)_4$][BPh_4] was synthesized.

All obtained homo- and heteroleptic Dy^{3+} complexes exhibit distinct slow relaxation of the magnetization dynamics and geniune Single-Molecule Magnet(SMM) behaviour.

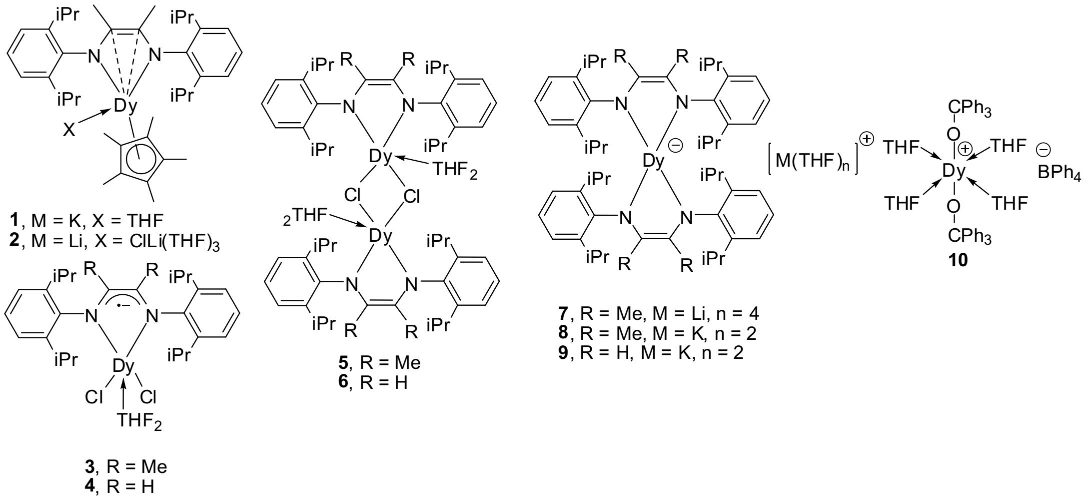

Figure 1. Caption

Acknowledgments

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References

1. S. Cotton, *Lanthanide and actinide chemistry*, John Wiley & Sons, **2013**.
2. D. N. Woodruff, R. E. P. Winpenny, R. A. Layfield, *Chem. Rev.* **2013**, *113*, 5110-5148.
3. J. Long, A. O. Tolpygin, A. V. Cherkasov, K. A. Lyssenko, Y. Guari, J. Larionova, A. A. Trifonov, *Organometallics*, **2019**, *38 (4)*, 748.

MESOIONIC DERIVATIVES OF SILOXANES

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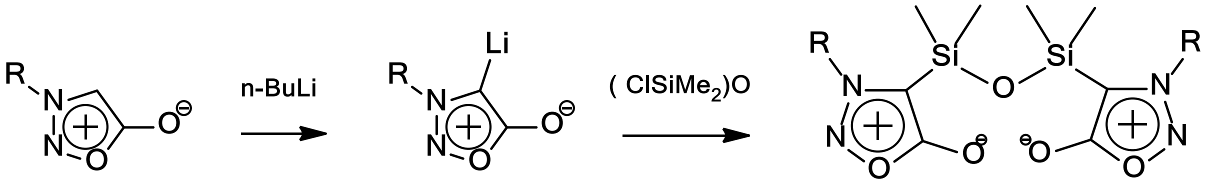
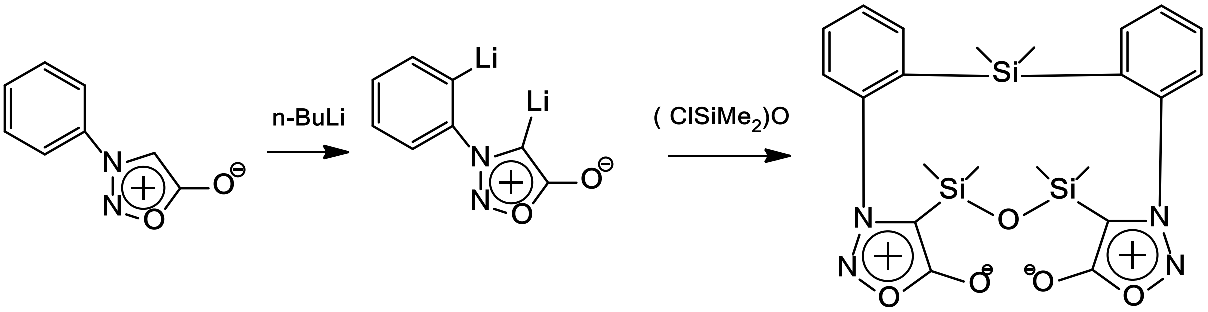
Recently, considerable attention has been paid to the synthesis of polyorganosiloxanes (POS), containing in its composition heterocyclic substituents, giving the POS unique characteristics. Sydnons belonging to the class of mesoionic heterocyclic compounds have a wide spectrum of biological activity, a unique electronic structure and unusual physicochemical properties. These characteristics make them attractive for incorporation into a polyorganosiloxane matrix.

In this work, we studied the interaction of lithium derivatives of sydnones with dichlorotetramethyldisiloxane. In the reaction of 4-lithium derivatives of sydnones, siloxanes containing sydnonyl substituents at the silicon atom were first synthesized (Scheme 1). In the interaction of the di-lithium derivative of 3-phenylsydnone with dichlorosiloxane (Scheme 2), a macrocycle containing both siloxane and silyl bridges was unexpectedly obtained.



R= Me, Ph, 4-MeO-C_6H_4.

Scheme 1.



Scheme 2.

The resulting disiloxanes are promising monomers for the creation of new POS. The structure of the obtained compounds is confirmed by NMR-spectroscopy (^{1}H, ^{13}C, ^{29}Si) and X-ray.

This work was supported by RFBR (№19-03-00333).

REDUCTIVE AMIDATION WITHOUT EXTERNAL HYDROGEN SOURCE

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Amides are irreplaceable components of life, and therefore there is always need for the development of new pathways for amide synthesis. Classical routes involve usage of stoichiometric additives which result in formation of stoichiometric amounts of wastes. For the last two decades there is great interest in the development of non-classical more atom-efficient approaches to amide synthesis. Among them reductive amidation represents very powerful approach for amide synthesis from primary amides and carbonyl compounds. Hydrogen or silanes are usually used as reducing agent for such transformation. Since both reducing systems have a hydride source, they can have low tolerance to other potentially reducible functional groups.

Recently we demonstrated the unique potential of carbon monoxide as reducing agent in reductive amination and alkylation of carbonyl compounds.[1] The developed methodologies are notable for favourable environmentally profiles and tolerance to different functional groups which can be reduced by hydrogen or hydride-containing reducing agents.[2] Herein we developed new protocol for reductive amidation (Figure 1). Reaction can be effectively catalyzed by rhodium or ruthenium complexes.[3,4] Moreover, heterogeneous rhodium catalysts were also explored and rhodium on carbon matrix demonstrated high activity in this transformation. Wide range of aliphatic and aromatic amides and aldehydes can be used.

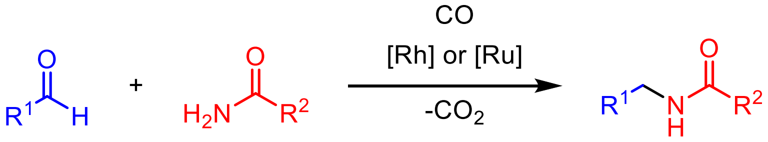

Figure 1.

Acknowledgments

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References

1. Chusov, D.; List, B. *Angew. Chemie Int. Ed.* **2014**, *53*, 5199.
2. Tsygankov, A. A.; Makarova, M.; Chusov, D. *Mendeleev Commun.* **2018**, *28*, 113.
3. Kolesnikov, P. N.; Usanov, D. L.; Muratov, K. M.; Chusov, D. *Org. Lett.* **2017**, *19*, 5657.
4. Yagafarov, N. Z.; Muratov, K.; Biriukov, K.; Usanov, D.; Chusova, O.; Perekalin, D. S.; Chusov, D. *European J. Org. Chem.* **2018**, *2018*, 557.

COMPLEXATION OF THE PERFLUORINATED THREE-MERCURY ANTICROWN (o-$C_6F_4Hg)_3$ WITH MONOHALOBENZENES

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Z.S. Klemenkova, M.Kh. Minacheva, I.A. Tikhonova, V.B. Shur

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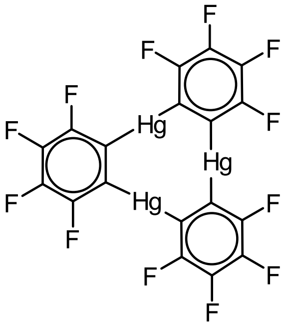
The first complexes of the perfluorinated three-mercury anticrown (*o*-$C_6F_4Hg)_3$ (**1**)[1] with monohalobenzenes have been synthesized and structurally characterized. In the case of fluorobenzene, two 1 : 1 complexes **2** and **3**, differing in their structures, were isolated. Complex **2** forms in the crystal extended binary stacks in which the molecules of **1** alternate with the halobenzene species, whereas complex **3** consists of the cofacial dimers formed from the corresponding monomeric units {[(*o*-$C_6F_4Hg)_3$](C_6H_5F)}. Each fluorobenzene molecule in both complexes is coordinated with **1** by its phenyl ring through secondary π-Hg–C interactions, whereas the fluorine atom is bonded to one of the Hg sites of **1**.


(**1**)

Analogous types of bonding are observed in the chlorobenzene and bromobenzene complexes, {[(*o*-$C_6F_4Hg)_3]_2(C_6H_5X)_4$}, (X = Cl, Br), containing four halobenzene molecules per two molecules of **1**. The complexes include two monomeric {[(*o*-$C_6F_4Hg)_3](C_6H_5X)_2$} fragments connected with one another by two bridging η^1 coordinated halogen atoms of the halobenzene ligands. The halogen atoms of two other halobenzene species are η^3 coordinated each with the Hg sites of the neighboring molecule of **1**. The reaction of iodobenzene with **1** affords a 3 : 1 complex, {[(*o*-$C_6F_4Hg)_3](C_6H_5I)_3$} (**4**), which is unstable and readily transformed into the corresponding 1 : 1 adduct (**5**). The both compounds form in the crystal extended stacks wherein each sandwiched iodobenzene molecule is bonded via the iodine atom to the adjacent molecule(s) of **1**. In the stacks formed by **4**, each two anticrown species are separated by three coordinated molecules of iodobenzene. According to ^{199}Hg NMR spectra, the highest stability among the synthesized halobenzene adducts is displayed by the iodobenzene complex **5**.

Acknowledgments

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References

1. P. Sartori, A. Golloch, *Chem. Ber.* **1968**, *101*, 2004.

SYNTHESIS OF NEW CAGE SYSTEMS BASED ON 1,3,5-TRIHYDROXY-1,3,5-TRIAZACYCLOHEXANES

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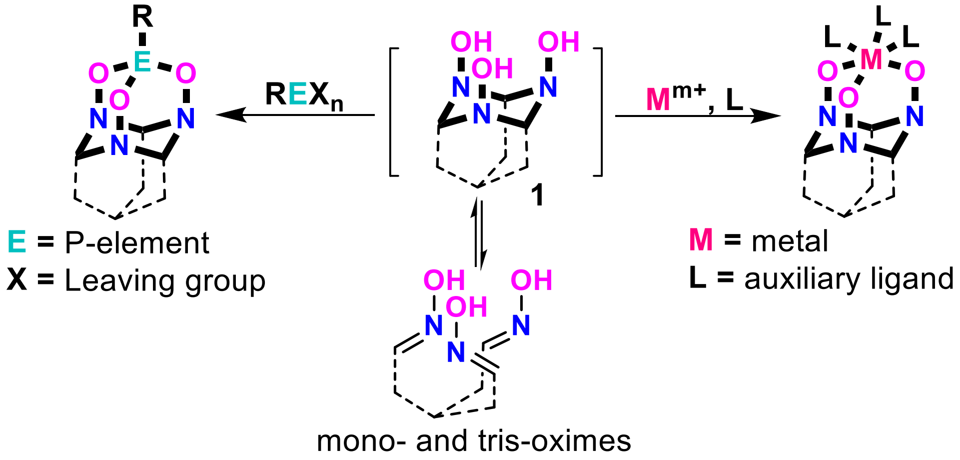
Design of new types of heterocage compounds is an actual task of both organic and organometallic chemistry. 1,3,5-Trihydroxy-1,3,5-triazacyclohexanes **1** (cyclotrimers of oximes) which have three N-OH groups are very promising organic ligands. In the present work we demonstrated that coordination of metal atom by *N*-oxy-fragments of **1** resulted in formation of unusual 3-metallo-2,4,10-trioxa-1,5,7-triazaadamantanes (Scheme). Possibility of formation of these complexes was studied for d-metals of variable valence. X-ray diffraction analyses for synthesized complexes allow us to propose that d-metals are in unusual oxidation states (Fe (+4), for instance) which are stabilized by *N*-oxy groups. We assume that such redox-active complexes may be catalysts for oxidative functionalization reactions of C-H bonds.

Furthermore we have explored complexation of some p-elements with **1**. Fortunately we managed to synthesize several examples of heteroadamantanes with B, Sb or Bi atom in cage (Scheme). Novel boron ate complexes were used for design of fluorophore-labeled natural molecules (peptides, steroids), supramolecular assemblies, modified polymers, boronic acid scavengers, solid-supported organocatalysts, and biodegradable COF-like materials.[1,2]



Scheme. New heteroadamantane complexes

Acknowledgments

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References

1. I. S. Golovanov, G. S. Mazeina, Y. V. Nelyubina, R. A. Novikov, A. S. Mazur, S. N. Britvin, V. A. Tartakovsky, S. L. Ioffe, A. Yu. Sukhorukov, *J. Org. Chem*. **2018**, *83*, 9756
2. I. S. Golovanov, A. Yu. Sukhorukov, *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. **2019**, *62,* 60.

SYNTHESIS AND STUDY OF CROWN-CONTAINING BISSTYRYL DYE COMPLEXES WITH VARIOUS METAL CATIONS BY USING FRET PROCESS

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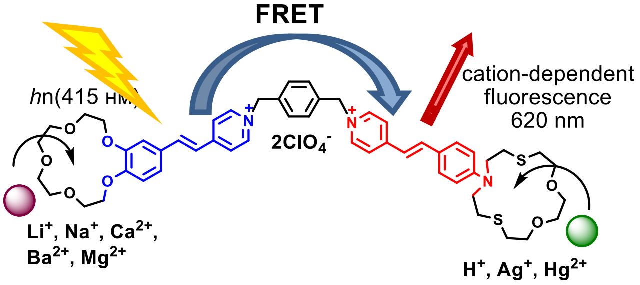
Nowadays FRET systems have been increasingly used in explaining the mechanisms occurring in biological objects.[1] This is due to the fact that FRET in the dye molecules helps to avoid errors in the fluorescence spectra associated with the effects of self-quenching and backscattering. It is known, that some metal ions play various indispensable roles for growth of all living organisms. This paper proposes novel ratiometriccation FRET system containing two binding centers of different selectivity (Scheme 1).

Asymmetric bisstyryl dye combines two fragments of styryl with different optical properties and having two centers coordination of metals was obtained and characterized.[2] The stability constants and quantum yields of fluorescence of complexes were calculated. A chemosensor based on such bisstyryl dye exhibits distinct fluorescent changes when interacting with Na^+, Li^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, H^+, Hg^{2+}, Ag^+ perchlorates. Thus, each metal cation during complexation forms an individual fluorescent response (Figure 1).[3]

From our knowledge this is the first example of the FRET ratiometric sensor possessing two different binding sites. Combination of two fluorophores and two binding sited in one system provides the information on type of bound metal ions, and helps in distinguish between the metals coordinated with the same macrocyclic center.



Scheme 1. The mechanism of appearance of cationdependent fluorescence.

Figure 1. Fluorescence changes of bisstyryl (B) after addition of 10 equivalents of different metal ions.

Acknowledgments

This work was supported by RFBR №19-03-00535, NMR studies, absorption and emission spectral characterization where performed by financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

References

1.L. D. Lavis and R. T. Raines, *ACS Chem. Biol.*, **2008**, *3*, 142–155.
2.D. V. Berdnikova, Y. V. Fedorov, O. A. Fedorova and G.Jonusauskas, *Dyes and Pigments*, **2018**, *151*, 227-232.
3. M. A. Ustimova, A. Y. Lebedeva, Y. V. Fedorov et al, *New Journal of Chemistry*, **2018**, *42*, 7908–7913.

ELECTRON-MICROSCOPIC ANALYSIS OF HYBRID MATERIALS BASED ON MULTI-WALL CARBON NANOTUBES AND WO3 AND CuO NANO-COATINGS

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Multi-wall carbon nanotubes (MWCNTs) (Fig. 1.a) are increasingly used in various fields of science. The creation of hybrid materials based on them expands the range of physical and chemical properties of nanotubes.

Hybrid materials based on MWCNTs and WO_3 and CuO nanocoatings were obtained by vapor deposition of organometallic compounds (MOCVD). Tungsten hexacarbonyl and copper formate were used as precursors respectively.

Hybrid materials were examined using a NEON 40 scanning electron microscope and a Carl Zeiss LIBRA 200MC transmission electron microscope. Analysis of the synthesized hybrid materials by these methods made it possible to establish the morphology of the studied objects and to determine the structure and the composition of materials in different parts of the samples.

It was found that the nanotubes in the composition of the hybrid material (MWCNTs / WO_3) are coated with monodispersed tungsten oxide nanoparticles (d ~ 40 nm), which tend to agglomerate and subsequently form a continuous single layer cover with an increase in the amount of precursor (Fig. 1.b).

The hybrid MWNCTs/CuO material represents carbon nanotubes decorated with copper oxide nanoparticles of various dispersions from 30 to 100 nm. With an increase of the precursor concentration, the diameters of nanoparticles also increase, however, the nanoparticles themselves retain spatial separation (Fig. 1.c).

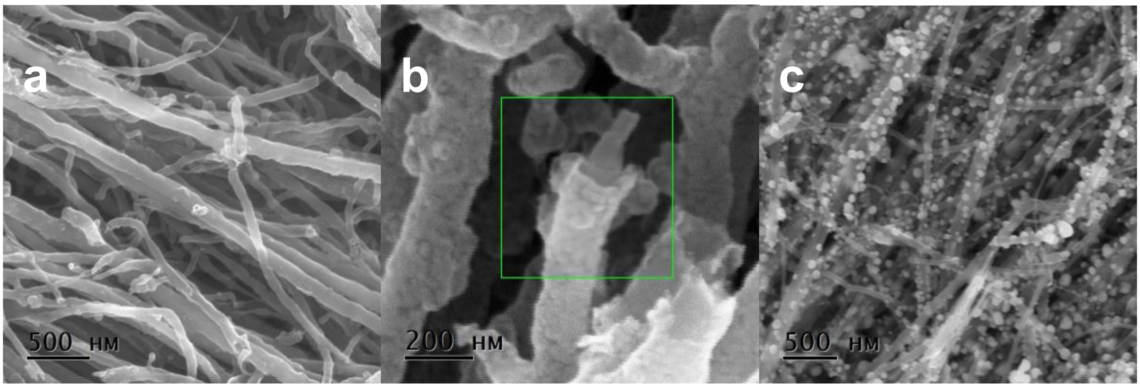

Figure 1. SEM images (a) - Initial MWCNTs, (b) - hybrid material MWNT/WO_3,
(c) - hybrid material MWNT/CuO

Acknowledgments

The reported study was funded by RFBR according to the research project № 18-33-00776.

CATALYST-FREE PHOSPHORYLATION OF PYRIDINES WITH SECONDARY PHOSPHINE CHALCOGENIDES TRIGGERED BY ACYLACETYLENES: NOVEL TYPE OF $S_N{}^HAR$ REACTION

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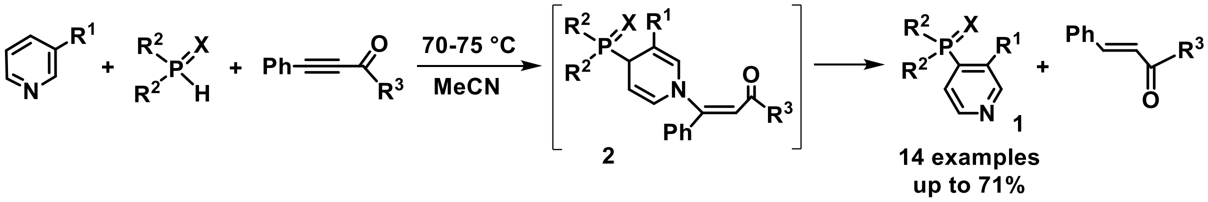
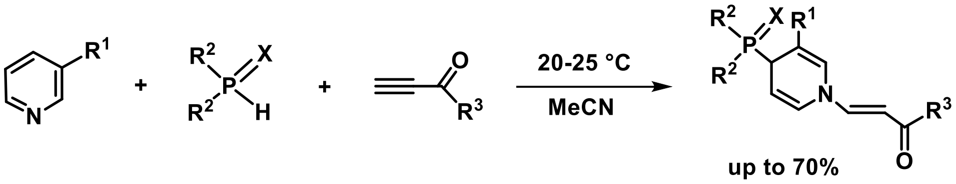
We have found that pyridines react with secondary phosphine chalcogenides (easily obtained from elemental phosphorus and arylethenes[1]) in the presence of acylphenylacetylenes without the catalyst to give 4-chalcogenophosphorylpyridines **1** in a yield of up to 71% (Scheme 1). This metal- and halogen-free cross-coupling represents a new type of nucleophilic substitution of hydrogen in heteroaromatic systems ($S_N{}^HAr$ reaction), in which electron-deficient acetylenes play the role of triggers and oxidative agents, being stereoselectively reduced to the corresponding alkenes of *E*-configuration.[2] Obviously, this interaction proceeds via the intermediate *N*-acylvinyl-4-chalcogenophosphoryldihydropyridines **2**, which readily eliminate *E*-alkenes to give aromatic chalcogenophosphorylpyridines **1**, the final products of the $S_N{}^HAr$ reaction (Scheme 1).

When using terminal acylacetylenes, functional 1,4-dihydropyridines of type **2** become practically the only products of the three-component phosphorylation/vinylation of pyridines (Scheme 2).

Thus, the developed reactions open a one-pot atom-economic access to in-demand phosphorylated pyridines, promising ligands for metal complexes, precursors of pharmacologically active compounds, and components for optoelectronics, the traditional methods for the synthesis of which are based on the use of aggressive phosphorus halides and organometallic reagents.



Scheme 1



Scheme 2

Acknowledgments

This work was supported by the Russian Scientific Foundation (grant no. 18-73-10080).

References

1.B. A. Trofimov, N. K. Gusarova, *Mendeleev Commun.* **2009**, *19(6)*, 295.
2. B. A. Trofimov, P. A. Volkov, K. O. Khrapova, A. A. Telezhkin, N. I. Ivanova, A. I. Albanov, N. K. Gusarova, O. N. Chupakhin, *Chem. Commun.* **2018**, *54*, 3371.

SYNTHESIS OF α-CF_3-α-ORNITHINE DERIVATIVES VIA COPPER (I)-CATALYZED HYDROAMINATION OF ALENNES

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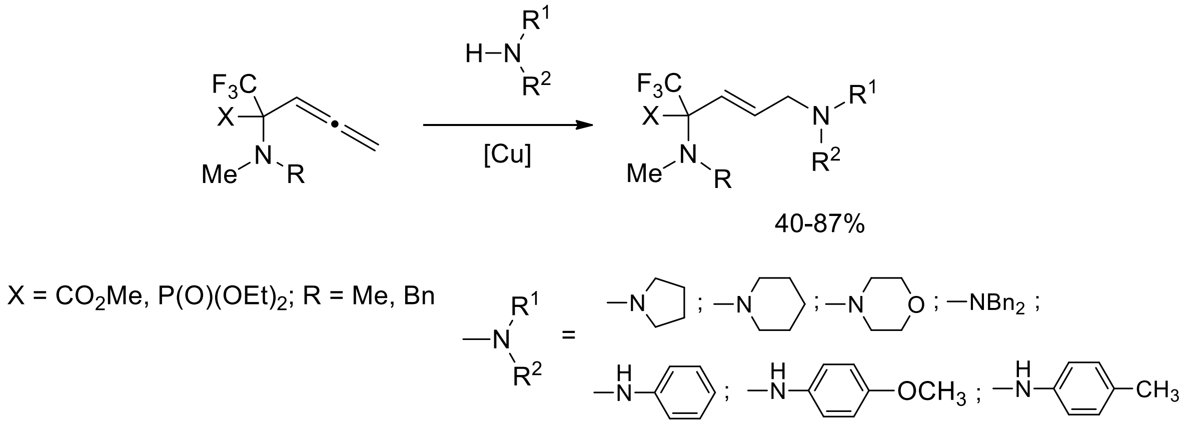
In recent times, allenes have attracted the interest of many chemists due to their unique structural and electronic features as highly valuable synthetic precursors in preparative organic chemistry. Special attention has been given to transition-metal-catalyzed hydrofunctionalizations of allenes with the view to the selective formation of the C−N bond. On the other hand, it is well known that the selective incorporation of fluorine functionalities, into specific positions of organic molecules can substantially alter their chemical and physical properties and thereby has become an essential tool in the drug discovery process. Continuing our investigations in the development of new methodologies for the synthesis of trifluoromethylated α-amino acids and their phosphorous analogues we present an efficient approach to unsaturated α-CF_3-α-ornithine derivatives and their phosphorus analogues by the copper-catalyzed interaction between CF_3-containing allene systems and different primary and secondary amines (Scheme 1).



X = CO_2Me, $P(O)(OEt)_2$; R = Me, Bn

Scheme 1.

Acknowledgments

This work was supported by Ministry of Science and Higher Education of the Russian Federation

References

1. L. Huang, M. Arndt, K. Gooßen, H. Heydt, L. Gooßen, *J. Chem. Rev.,* **2015**, *115*, 2596.
2. J. Wang, M. Sánchez-Roselló, J. L. Aceña, C. del Pozo, A. E. Sorochinsky, S. Fustero, V. A. Soloshonok, H. Liu, *Chem. Rev.*, **2014**, *114*, 2432.

SYNTHESIS OF HYDROPHOBIC, HYDROPHILIC AND AMPHIPHILIC STEREOREGULAR ORGANOCYCLOSILSESQUIOXANES

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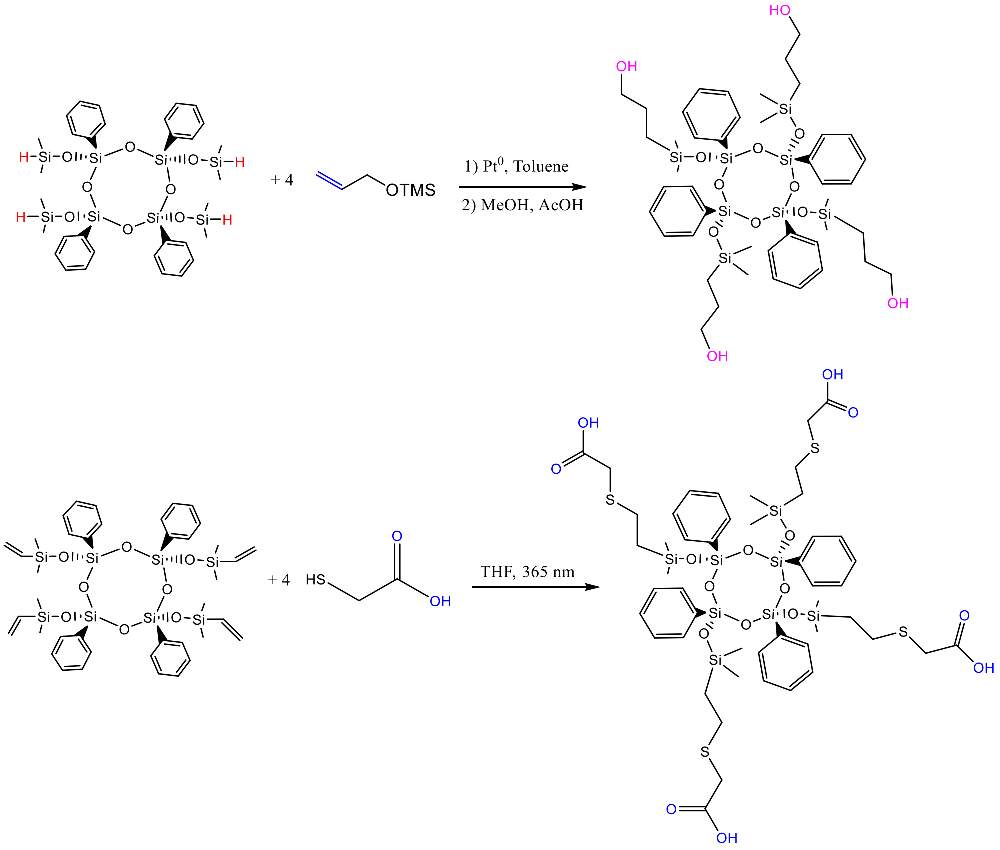
The purpose of our research is a preparation of new functional organosilicon compounds which will serve as effective components for creating complex systems such as surfactants, lubricants, orgas storage materials and etc.

General methods to prepare and to functionalize silicone compounds are usually based on hydrosilylation. We have combined in our study two approaches: hydrosilylation and thiol-ene reactionin order to obtain hydrophobic, hydrophilic or amphiphilic organocyclosilsesquioxanes. Unique cyclic organosilsesquioxanes were used as starting compounds. These compounds were obtained from polyhedral metallasiloxanes containing nickel, copper, or dysprosium and sodium ions, and having a well-defined spatial structure.

The properties of compound synthesized will be presented



Scheme 1. Synthesis of amphiphilic stereoregular organocyclosilsesquioxanes

Acknowledgments

Grant of the Ministry of Science and Higher Education of the Russian Federation No. 14.W03.31.0018.

SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF RUTHENIUM (II) COMPLEXES CONTAINING 1H-IMIDAZO[4,5-F] [1,10]PHENANTHROLINE AND BIPYRIDINE DERIVATIVES

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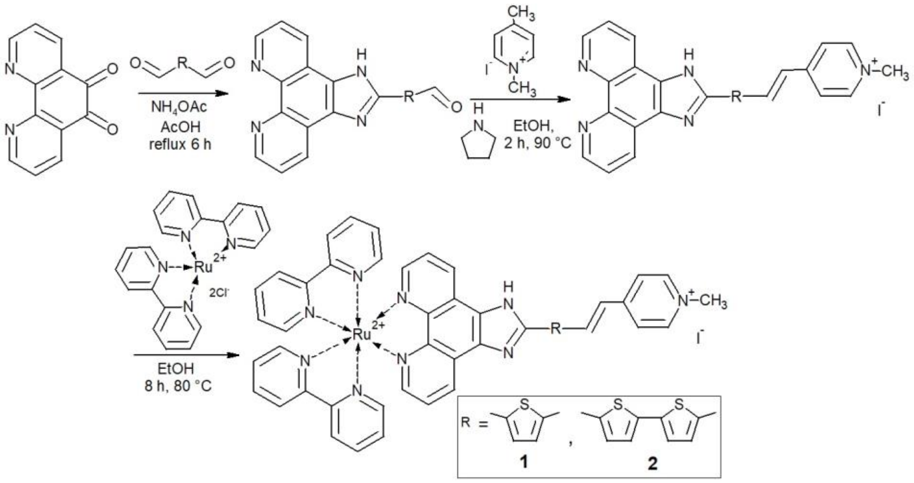
Ruthenium (II) polypyridine complexes are known for their unique photophysical properties, in particular they exhibit metal-to-ligand charge transfer (MLCT) in the visible part of the spectrum, relativechemical stability,strong luminescence emissionand long-lived triplet excited states with lifetimes in the microsecond range.[1] Studies of the compounds with general structure $Ru^{2+}(bpy)_2L$, where bpy is bipyridine and L is 1H-imidazo[4,5-f][1,10]phenanthroline ligand, demonstrate that these type of complexes are capable of photoinduced electron transfer to the conduction band of In_2O_3 and SnO_2semiconductors.[2]

In present work we synthesized new complexes **1** and**2**, containing 1H-imidazo[4,5-f][1,10]phenanthroline ligand with large conjugated system, their structural features are thiophene and methylpyridinium fragments. Synthetic route for **1,2** is shown on scheme 1. Luminescent properties of **1**,**2** were investigated by steady state and time-resolved fluorescence spectroscopy at 293 K and 77 K. According to the obtained data lifetimes of excited states and quantum yields were determined. Investigation at 77 K demonstrates triplet excited states with lifetimes over millisecond not characteristic for ruthenium (II) bipyridine complexes.[1]

Scheme 1.Synthetic route for complexes**1**,**2**



Acknowledgments

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References

1.S. Campagna, F. Puntoriero, F. Nastasi, G. Bergamini, V. Balzani, *Top Curr. Chem.* **2007**, *280, 117-214*.
2. M. Rumyantseva, A. Nasriddinov, S. Vladimirova, S. Tokarev, O. Fedorova, I. Krylov, K. Drozdov, A. Baranchikov, A. Gaskov, *Nanomaterials* **2018**, *8, 671*.

NOVEL HYBRID MATERIALS BASED ON MULTI-WALLED CARBON NANOTUBES AND NANOSCALE COATINGS OF COPPER OXIDE OR TUNGSTEN OXIDE

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Hybrid materials based on multi-walled carbon nanotubes (MWCNTs), which surface is decorated with metals and metal oxides or carbides nanoparticles have a promising properties for use as components of catalytic systems, as reinforcing components of alloys, as strengthening components of adhesive compositions and as components of abrasive or antifriction materials. In particular, the composites MWCNTs modified with copper nanoparticles is used as a catalyst in a germanium tetrachloride reduction process.[1] Modifying the MWCNTs surface will increase their affinity for the matrix material of the composite when MWCNTs are used as reinforcing fillers in composites or will allow creating a large number of active catalytic centers on the MWCNTs surface when using them as catalyst carriers.

This work proposed a method for the synthesis of novel hybrid materials based on (MWNTs) and nanoscale coatings of Cu_2O/Cu or WO_3.The MWCNTs synthesized by the metal-organic chemical vapor deposition (MOCVD) method during the pyrolysis of a mixture of toluene and ferrocene were used as the basis for such materials.[2] The Cu_2O/Cu/MWCNTs composite were prepared by pyrolysis of copper formate deposited on the MWCNTs surface from a aqueous solution. The deposition of tungsten-containing particles on the MWCNTs surface occurred during the pyrolysis of tungsten carbonyl $W(CO)_6$. The pyrolysis was carried out in vacuum. Then, the hybrid materials synthesized were further subjected to oxidation under atmospheric air to obtain copper oxide or tungsten oxide particles on the MWCNTs surface. The pristine MWCNTs and novel hybrid materials were investigated by X-Ray diffraction (XRD), scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) techniques.

Acknowledgments

This work was supported by RFBR (Project 18-33-00776).

References

1. A.V. Kadomtseva, A.V. Vorotyntsev, V.M. Vorotyntsev, A.M. Ob´edkov, K.V. Kremlev, B.S. Kaverin, *Russian Journal of Applied Chemistry* **2015**, 88, 595.
2. A.M. Ob´edkov, B.S. Kaverin, V.A. Egorov, N.M. Semenov, C.Yu. Ketkov, G.A. Domrachev, K.V. Kremlev, S.A. Gusev, V.N. Perevezentsev, A.N. Moskvichev, A.A. Moskvichev, A.S Rodionov, Pis´ma Mater., **2012**, 2,152.

EFFICIENT ACCESS TO THE CARBORANE TRIAZOLE PORPHYRINS VIA COPPER-CATALYZED 1,3-DIPOLAR CYCLOADDITION REACTION AND THEIR PHOTOPHYSICAL AND BIOLOGICAL PROPERTIES

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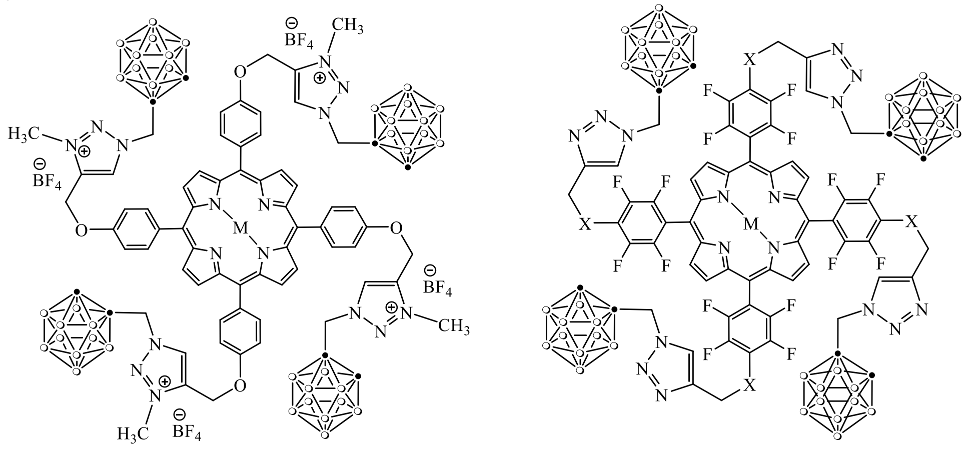
In this work the preparation of porphyrins functionalized with carborane polyhedra and 1,2,3-triazole heterocycles based on the propargylic derivatives of the commercially available 5,10,15,20-tetrakis(4-hydroxyphenyl)porphyrin (**1**), 5,10,15,20-tetrakis (pentafluorophenyl)porphyrin (**2**) and their Zn and Pd complexes is presented. Reactions of porphyrin propargyl derivatives of porphyrins **1**, **2** with 1-azidomethyl-*o*-carborane under “click-chemistry” conditions (copper acetate(II) - sodium ascorbate) proceeded smoothly and chemoselectively affording boronated porphyrin-triazole conjugates in 72-79 % yields. Alkylation of nitrogen atoms in triazole heterocycles with $(CH_3)_3OBF_4$ gives water-soluble tetracationic porphyrins (Fig.1) in quantitative yields.

The efficiency of delivery of synthesized porphyrins to cells correlates with high constants of complexation of porphyrins with albumin and low density lipoproteins. The spectral-kinetic characteristics of the triplet states of porphyrins were obtained by flash photolysis, and the quantum efficiency of the formation of singlet oxygen as a result of quenching of the triplet by molecular oxygen was measured. Biological experiments by treating HCT116 human colon carcinoma cell line with each of these compounds (up to 50 μM) for 72 h followed by an MTT-test have shown that the prepared porphyrins have low dark toxicity good cell permeability and a potent phototoxicity.



1 M = Zn, 2H

2 M = Zn, Pd, 2H; X = O, NH

Figure 1. Structures of synthesized compounds

CONJUGATES OF NAPHTHALIMIDE DYES AND BACTERIOCHLORIN DERIVATIVE AS THERANOSTIC AGENTS FOR PHOTODYNAMIC THERAPY

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Photodynamic therapy (PDT) is known to be one of the most perspective and progressing methods of treatment of cancer tumors. It is a relatively gentle approach, based on using a drug known as a photosensitizer, light and oxygen to destroy tumors and their surrounding vasculature. In lines of advance of the effectiveness of PDT, the design of theranostic agent for both photodynamic therapy and fluorescent tumor imaging seems to be a challenging task.

The aim of this work is the synthesis and photophysical study of conjugates which combine two covalently bonded functional fragments: photosensitizer (bacteriochlorin) and fluorophore (Figure 1). Conjugate excitation by the light with wavelength corresponding to the Q-band of bacteriochlorin would lead to formation of singlet oxygen responsible for cancer cell damage. Further excitation of fluorophore unit by the other light wavelength is expected to produce the strong emission signal, which could be used to monitor tumor responses to treatment.

In this work we propose a synthesis of conjugates by the click-reaction of azide-naphthalimide derivatives and bacteriochlorin-e containing a propargyl group as well as their luminescent properties studying. Photophysical studies revealed that the emission from the naphthalimide chromophore in conjugates was quenched due to Förster resonance energy transfer (FRET) between the photoactive components. The effectiveness of FRET-process was evaluated by steady-state and time-resolved fluorescent spectroscopy, also we esteemed an influence of spacer nature on FRET.

Studying the efficiency of singlet oxygen generation, as well as biological tests conducted on human adenocarcinoma cells, and then *in vivo* in mice, showed that the resulting conjugates based on bacteriochlorin and naphthalimide are promising therapeutic agents for PDT, since they demonstrate high quantum yields of singlet oxygen, antitumor efficacy and allow to obtain contrast images of cells.

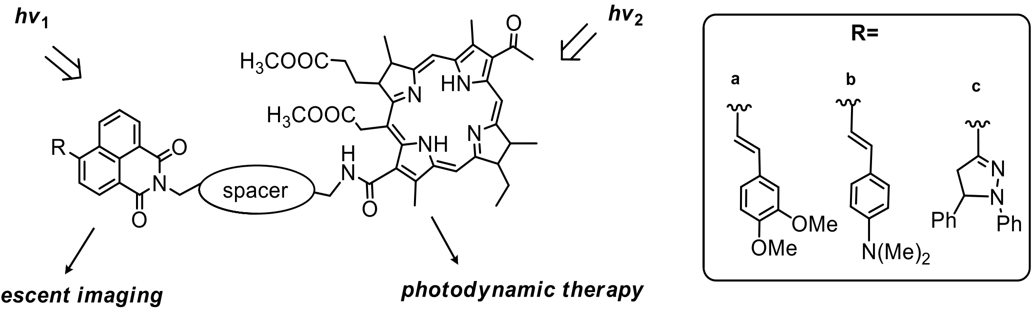

Figure 1. Prinsiple of theranostic action of conjugates

Acknowledgments

We thank the Russian Foundation for Basic Research 18-33-20111.

COMPARISON OF COMPLEXING PROPERTIES OF AMIDE-TYPE BENZO- AND PYRIDINE-AZACROWN COMPOUNDS

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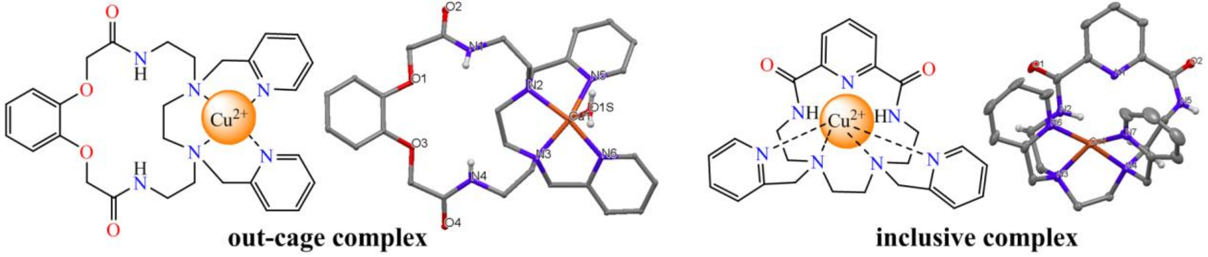
The inclusion properties of macrocyclic compounds are a very interesting subject of study – the search for selectively complexing receptors is significant in chemistry and biology as well as in medicine.[1,2] A design of macrocyclic receptors is governed by a number of factors, and the combination of these factors affect the specificity in host-guest recognition. Although amides often serve as anchoring groups in natural and synthetic receptors, the structure – affinity relationship studies of amide based macrocyclic receptors are still very limited. Therefore, we decided to investigate the influence of the size of the macrocycle, type and number of the chelating group on the strength and selectivity of ion heavy metal binding by amide-based receptors.

This work presents the synthesis of a novel bisamide azacrown compounds and their derivatives comprising carboxylic, pyridine and picolinate pendant arms. The potentiometric, NMR, ESI-MS and X-ray analysis were carried to study the binding properties towards heavy metal ions. The chelators demonstrated high stability constant of their complexes in aqueous solutions. The study of the structure of the obtained macrocycles showed that they have an open cavity due to the presence of rigid fragments that provides fast kinetics of complex formation. A fundamental difference was found between types of metal binding in complexes of benzo- and pyridinecrown compounds – they form out-cage and inclusive complexes, respectively (Figure 1).[3,4]



out-cage complex

inclusive complex

Figure 1. Different type of metal complexes of benzo- and pyridine-azacrown compounds

Acknowledgments
This work was supported by Russian Science Foundation (grant №16-13-10226).

References

1. E.V. Matazova, B.V. Egorova, E.A. Konopkina, *MedChemComm* **2019**, *10*, 1641.
2. B.Egorova, E.Matazova, A.Mitrofanov,*Nucl. Med. Biol.* **2018**, *60*, 1.
3. Fedorov Y., Fedorova O., Kalmykov S. *Polyhedron* **2017**, *124*, 229.
4. A. Zubenko, B. Egorova, S. Kalmykov, *Tetrahedron* **2019**, *75*, 2848.

3. POSTER PRESENTATIONS

Polymers

THE USE OF MICROWAVE RADIATION FOR SYNTHESIS OF WATER-SOLUBLE PORPHYRIN POLYMERS

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Interest in the various hybrid organic compounds has not passed for several decades because such substances not only combine the useful properties of the starting components, but also mutually reinforce them. As a rule, the syntheses for obtaining such supramolecular systems are multistage, and the yields are quite small. The usage of microwave radiation (MWR) allows to reduce synthesis time and increase the yield of the target products of the reaction.

The applying different in nature traditional monomers and porphyrin comonomers containing various amount of vinyl groups at the periphery of the macrocycle makes it possible to synthesize porphyrin polymers (PP) that differ in composition and characteristics.

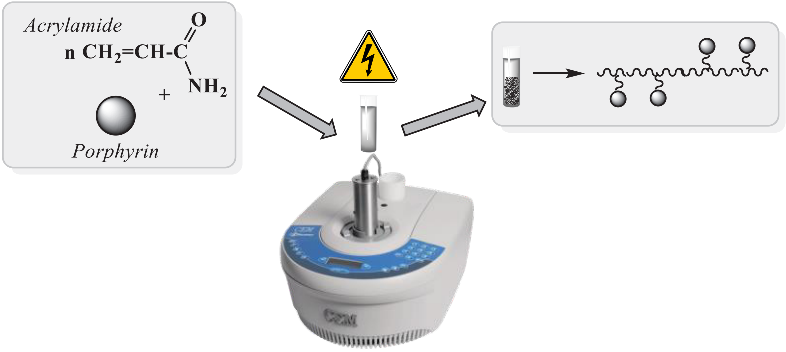

Figure 1. The obtaining of water-soluble PP under MWR conditions

Under the conditions of MWR, water-soluble PP based on acrylamide and vinylphenyl-substituted porphyrins of various functionality were obtained.

The radical copolymerization reaction was carried out in 1,4-dioxane, dinitrileazobisisobutyric acid was used as an initiator. Conducting of the reaction under MWR conditions reduced the reaction time compared with the thermal heating and gave good yields of water-soluble porphyrin polymers with various ratio of the initial components. During the study the regularities of the synthesized water-soluble PP under MWR conditions were established, the advantages of this method for the synthesis of such hybrid organic compounds are shown.

A comparison of the characteristics of the water-soluble PP prepared both under thermal heating and under MWR conditions was also performed.

Acknowledgments

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THERMAL DEPENDENCE OF LUMINESCENT CHARACTERISTICS OF LASER INDUCED LUMINESCENT STRUCTURES FORMED IN POLYBENZIMIDAZOLE FILMS

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There is a need to develop competitive polymer materials that would have a combination of several physical and chemical properties, such as flexibility, plasticity, mechanical strength, and at the same time, could maintain their structure at temperatures over 500 ° C. Most promising in this regard are nitrogen-containing heterocain polymers based on polybenzimidazoles (PBI). Taking into account the known intrinsic luminescent properties of such materials in the visible and infrared spectral regions, the possibilities of creating sensor devices based on some types of PBI are considered [1]. In 2015, the results on the production of optical fibers based on PBI [2] were presented, where the influence of orientation and packaging of polymer chains on the luminescent characteristics of these products was considered.

The purpose of this work was to create laser-induced structures with increased luminescence in PBI films and to assess the effect of temperature on the luminescent characteristics of the intrinsic and induced luminescence. The structures in the films were created by continuous and pulsed laser radiation with wavelengths of 405 and 512 nm, respectively. Comparison of the luminescence intensity was carried out using a fluorescent microscope on green and blue filters. It has been shown that luminescence in structures increases in comparison with its own luminescence by an order of magnitude. The influence of multiple annealing followed by cooling of the films on the luminescent characteristics of the material was determined. The growth of intrinsic and induced luminescence in the first annealing-cooling cycle was visualized, followed by a decrease in luminescence in laser-induced structures in the following annealing-cooling cycles. This effect is associated with changes in the morphology of laser-induced structures under the influence of temperature annealing. Visualization of the morphology before and after annealing is presented using atomic force microscopy (individual microbubbles) and profilometry (surface area up to several cm). The work was performed under grant 18-33-00645 mol_a.

References

1. Yang N. C., Lee S. M. Polymer Bulletin. 2003. 49. 5. 371-377.
2. Park J., Jeong Y. G. Macromolecules. 2015.

DETERMINATION OF THE STRUCTURE OF THE SUBSTANCE SYNTHESIZED BASED ON POLYCARBONATE AND ALIPHATIC POLYAMINE

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Polycarbonate is widely used in the modern world, especially in industries such as electronics, medicine and construction. However, there are lots of ways of an alternative application of this plastic.

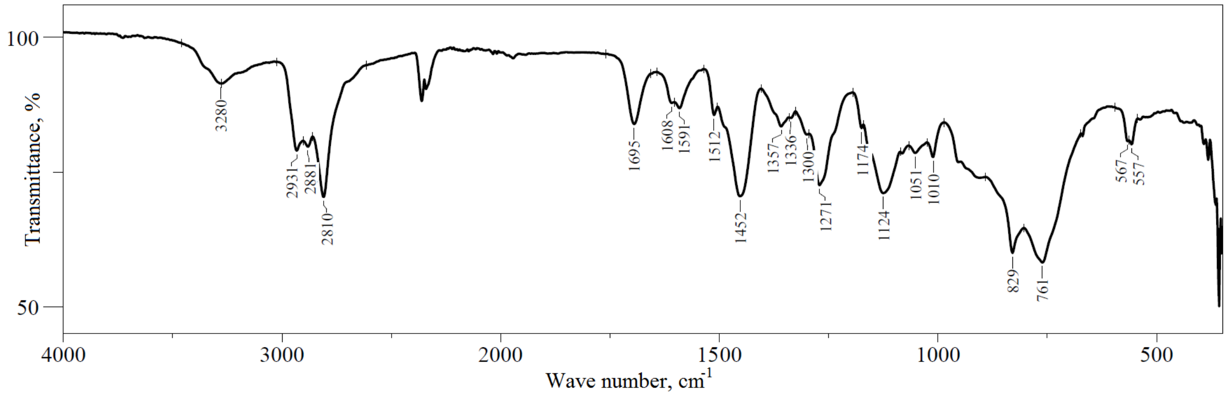
The Department of Chemical Technology of Polymers of St. Petersburg State Institute of Technology conducts research in the application of polycarbonate destruction product as modifying component of structural foams based on epoxy resins.

The purpose of this research is to determine the structure of the synthesized substance on the basis of polycarbonate and aliphatic polyamine. Our studies showed that during the reaction of an aliphatic polyamine with a polycarbonate flakes an aminolysis process occurs.

The Fourier method of IR spectrometry was used to record the IR spectrum for the synthesized polyamide in the spectral range of 400-4000 cm^{-1}. The measured results are presented in the figure.

Analyzing the obtained data shows that the emission band at 1695 cm^{-1} corresponds to stretching vibrations of the C = O group in Ar – O – C (O) –O – Ar carbonates and has a weak intensity, which indicates the destruction of ester bonds in polycarbonate. But the emission band at 1271 cm^{-1} is more remarkable, which corresponds the deformation vibrations of the C = O group in the tertiary amide. Based on this data, the obtained product is a polyamide.

Figure. IR Fourier spectrum of synthesized polyamide



THE USE OF NATURAL POLYMERS TO SEPARATE CARBON DIOXIDE FROM PHYSICAL ABSORBENTS

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One of the most urgent tasks is the extraction of acid gases, primarily carbon dioxide, from gas streams: flue gases, natural gas, etc. In recent years, in order to implement this process, CO_2 absorption is combined with a membrane separation method [1]. For the absorption of gas mixtures at elevated pressures, the most promising is the use of “physical” absorbents because of the ease of their regeneration, since the selective dissolution of acidic components proceeds without chemical reactions. This system is a gas-liquid membrane contactor in which selective mass transfer of components between two phases separated by a membrane takes place. The selectivity of the separation process is determined by the difference in the solubility of gases in the absorption liquid. In order to isolate CO_2 from physical absorbents, the membrane used in gas-liquid contactors must have chemical stability, be impermeable to organic media and have high permeability to the released gases. Promising for these tasks may be a natural biodegradable polymer, cellulose. This polymer is one of the most common renewable, inexpensive and biodegradable organic materials and can be considered as an almost inexhaustible source of raw materials with increasing demand for environmentally friendly and biologically compatible products. Cellulose-based membranes are widely used for gas filtration, pervaporation and separation processes [2]. Gas separation membranes for cellulose show high permeabilities for individual gases and high selectivities for a pair of CO_2 and CH_4, which also makes it promising for use as a membrane material in gas-liquid contactors. The existing limited number of systems of direct cellulose solvents: DMAA / LiCl, NMP / LiCl, DMSO / paraformaldehyde, N-methylmorpholine-N-oxide (MMO) makes it difficult to create cellulose-based membranes. In recent years, the method of dissolving cellulose in ionic liquids (IL), which is considered more environmentally friendly, has attracted more and more attention. Co-solvents are also added to the IL to reduce time, temperature and dissolution cost. Thus, the aim of this work is to obtain cellulose membranes from a mixture of ionic liquid 1-ethyl-3-methylimidazolium acetate [Emim]Ac with DMSO for gas-liquid contactors.

Acknowledgments

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References

1. Klaassen R, Feron P H M, Jansen A E, Chem. Eng. Res. **2005**, 83, 234.
2. Anokhina T S, Pleshivtseva T S, Ignatenko V Ya, Antonov S V, Volkov A V, *J. Inorg. Chem.* **2015**, *117*, 987.

CARBOSILANE DENDRIMERS WITH FUNCTIONAL SHELL TO CREATE NEW SUPRAMOLECULAR STRUCTURES

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Dendrimers are characterized by its extensively branched 3D structure that provides a high degree of surface functionality. Tomalia et al. obtained megamers, specifically supramolecular core-chell dendrimers assemblies [1].

In this work we obtained a number of dendrimers with different functional shell, as amine, thiol, acid group (fig 1). In the sequel we want to form new megamers out of our dendrimers.

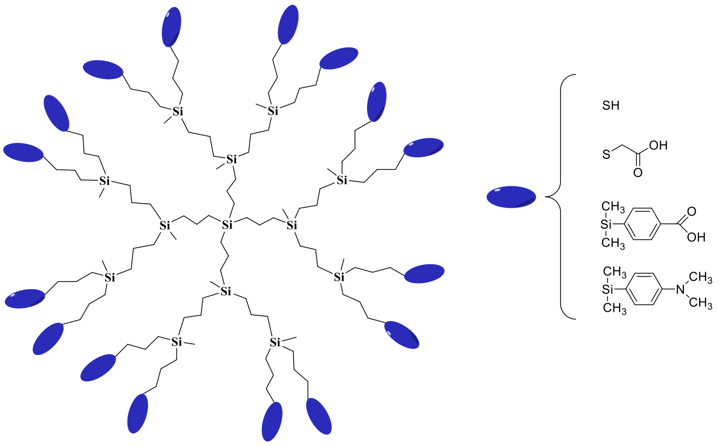

Figure 1. Carbosilane dendrimers with different functional groups

Acknowledgments

This work was supported by RFBR, research project No. 18-29-04037 мк

References

1. Uppuluri, S., Piehler, L. T., Li, J., Swanson, D. R., Hagnauer, G. L. & Tomalia, D. A., Core–Shell Tecto(dendrimers): I. Synthesis and Characterization of Saturated Shell Models, (2000) Adv. Mater. 12, 796–800

NEW HYDROPHOBIC COATINGS ON NATURAL MATERIALS

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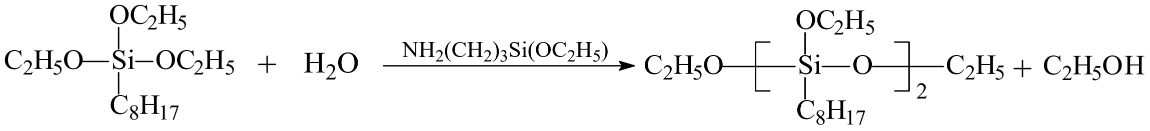
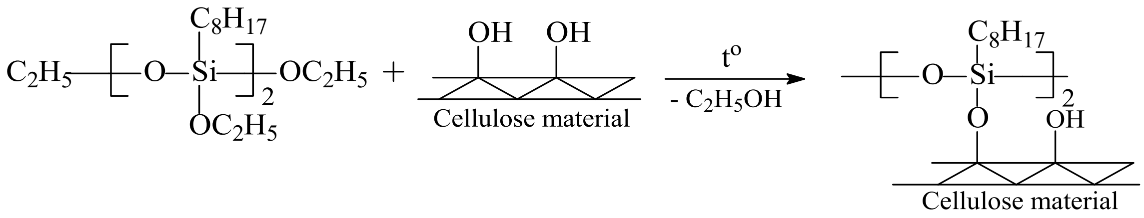
New hydrophobizator – tetra(etyoxy)di(octyl)disiloxane was synthesized and characterized (scheme 1). On the basis of this compound new hydrophobic coatings on the natural materials (cellulosetextyle of different composition) were obtained (scheme 2). The optimal conditions for obtaining coatings with maximal hydrophobicy (the value of the contact angle is 135˚) were determined. The properties of the modified cellulose materials were studied. It was shown the efficiency of the use tetra(etyoxy)di(octyl)disiloxane as a hidriphobizator when the content up to 1% and a relatively small thickness of the coating. It was found that the modified materials retain their properties of moisture absorption for a long time (more than three months).



Scheme 1



Scheme 2

Acknowledgments

This work was performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

MAIN CHARACTERISTCHARACTERISTICS OF APPLE, BEET AND NEEDLE PECTIN

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Pectins are biologically active polymers that are widely used in medicine, food processing and agriculture. They are considered to bevaluable gelling agents anduniversal, effective andsafe sorbents[1,2,3]. The ability of pectins to adsorband remove toxic substances, radionuclides, heavy metals from body is due to the presence of acid residues of polygalacturonic acid.

The aim of the work was to develop convenient methods for the hydrolysis pectin from plants of different nature (apples, sugar beets, needles), to obtain a set of data on the molecular weight characteristics (MWC) and the sorption capacity of pectin from different substrates. We were the first who extracted pectin from conifers, compared them with appleand beet pectin. Obtainingwas carried out by acid hydrolysis. MWC was measured by GPC in slightly acidic aqueous solutions, complexing ability was calculated by binding of copper ions by pectin in an aqueous solution. Our research has shown that the yield of the final product depends on the nature of the acid, the duration of the process and its temperature. The optimal parameters for substrates of different nature are choosen.

The bulk of pectin (more than 90%) has a low molecular weight and polydispersity coefficient close to one.

Sorption capacity was inversely proportional to the degree of esterification. For example, heavy metal ions were bound to pectin by 50.1 - 70.5%. Complexation depended on the species of the plant and its edparts, but did not depend on the obtaining medium. For example, in the nucleoli of apples the sorption capacity was observed to be about 15% higher than in the peel or bagasse.

Thus, we obtained new data on the pectin substance, compared pectins from different sources ofisolation and revealed the trends in the properties development of the obtained samples.

Acknowledgments

The work was carried out using the equipment of the Central Public Institution “New Materials and Resource-Saving Technologies” Research Institute of Chemistry State University in Nizhny Novgorod.

References

1. R. G. Ovodova, V. V. Golovchenko, S. V. Popov, Yu. S. Ovodov, Komi NC UrO RAS **2010**, 3, 25-30.
2. L. A. Mikheeva, M. A. Fevraleva, G. T. brynskikh, A.V., Ulyanovsk journal of biomedical **2017**, 2, 111-116.
3. J. Harholt, A. Suttangkakul, H. V., Plant Physiol **2010**, 153, 384-395.

THE SYNTHESIS OF NEW ORGANOSILICON MONOMERS AND POLYMERS WITH SEVERAL TYPES OF FUNCTIONAL GROUPS IN THE MOLECULE

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Recently, due to the rapid development of high-tech nanobiomedicine and biotechnology, as well as surface engineering, membrane technologies and environmentally friendly production, the interest in obtaining various polyfunctional polymer materials, in particular based on polydimethylsiloxanes, which have unique properties, such as: wide temperature range of application, resistance to atmospheric and ozone impact, resistance to aging, good electrical insulation properties and biocompatibility, and also the ability to easy functionalization, which not only determines their properties, but also extends the scope of their application [1-5].

In this work, it is planned to develop a universal method for the preparation of PDMS with different functional groups, capable of independently entering into chemical interaction with the corresponding functional groups and easily modifiable, differing in the structure and mutual arrangement of functional groups, as well as having different molecular mass characteristics.

We studied the process of obtaining polydimethylsiloxanes with azidopropyl functional groups using the classical method of catalytic opening of the siloxane cycle by cationic and anionic mechanism using monomers with an azide functional group. We also investigated the reactions of the azide-alkine cycloaddition by the example of siloxane polymers containing azidopropyl functional group. The structures of the products obtained were confirmed by ^{1}H NMR spectroscopy and gel-permeation chromatography. We also investigate their solubility.

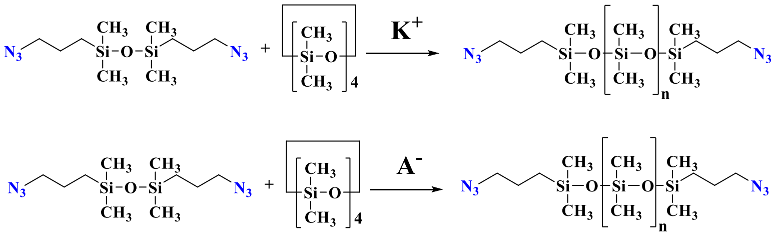

Figure 1. Obtaining polydimethylsiloxanes with azidopropyl functional groups

References

1. J. Chojnowski and M. Cypryk, in Silicon-Containing Polymers, Springer, Berlin, Heidelberg, Germany, 2000, 3 – 41S.
2. Feng, J. Zhang, M. Li and Q. Zhu, Organosilicon polymers and application, Chemical Industry Press, Beijing, 2010, 1-4
3. Z. Ren and S. Yan, Prog Mater Sci, 2016, 83, 383-416
4. F. Abbasi, H. Mirzadeh and A. Katbab, PolymInt, 2001, 50, 1279-1287
5. Q. Zhou, S. Yan, C. C. Han, P. Xie and R. Zhang, Adv Mater, 2008, 20, 2970-2976

BIOCOMPARTABLE SOLUBLE POLYELECTROLYTE COMPLEXES AND METAL-CONTAINING NANOCOMPOSITES

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Targeted drug delivery is the most perspective trend in modern pharmacology. Immobilization of pharmaceuticals into nanosized drug-delivery systems (DDS) provides a better bioavailability and selectivity due to solubilization or chemical conjugation of lipophilic pharmaceuticals, an enhanced ability to overcome biological barriers, reduction of side effects, and an increase in the time of pharmaceuticals action. Interpolyelectrolyte complex (IPEC) microparticles based on biocompartable and bioactive polysaccharide chitosan are perspective for usage as DDS and gene delivery vectors. Enhanced muco-adhesiveness of chitosan is an advantage for oral drug delivery.

To improve the chitosan solubility and its bioactivity in alkaline physiological media without lossing of biocompatibility, we carried out a partial quaternization of chitosan and oligochitosan with betain. Non-cytotoxic chitosan derivatives with an improved solubility and high antibacterial activity in alkali physiological media were prepared[1].These derivatives were used for preparation of interpolyelectrolyte complexes with a weak biocompartable polyacid – regular copolymer of maleic acid. We found that soluble nonstoichiometric IPEC could be prepared by titration both in weakly acidic and weakly alkaline media. The solubility limits of both negatively charged and positively charged complexes are determined depending on the ratio of polyions. The structural characteristics of soluble IPEC particles have been determined using static and dynamic light scattering. The results of this study show that partially betainated chitosan and oligochitosan are promising for creating physiologically active biocompartable and biodegradable complexes.

Synthesis of nanohybrid systems for cancer diagnostics and therapy is one of the rapidly developing areas. Much attention is also paid to creation of catalytic nanocomposite systems. For this purpose, soluble IPECs with embedded metal nanoparticles can be used.

In our work, we prepared nanocomposites containing silver nanoparticles (NPs) embedded in a shell of IPEC consisting of chitosan-maleic acid copolymer. Silver NPs coated with a polymer shell were synthesized by reduction of silver ions bound to the maleic acid copolymer in the form of a coordination-ion complex[2]. Titration of polyacids containing silver NPs with oligochitosan solution in a slightly acidic medium yielded the soluble IPECs in the form of microparticles (with a radius of about 100 nm) containing embedded silver nanoparticles with a radius of 1-3 nm. The prepared sols possessed a plasmon resonance spectrum characteristic of corresponding silver nanoparticles.

References

1. I.V. Blagodatskikh, O.V. Vyshivannaya, A.V. Alexandrova, E.A. Bezrodnykh, P.V. Zelenikhin, S.N. Kulikov, V.E. Tikhonov., *Microbiology* **2018**,*87*, 610.
2. N.A.Samoilova, I.V.Blagodatskikh, E.A.Kurskaya, M.A.Krayukhina, O.V.Vyshivannaya, S.S.A bramchuk, A.A.Askadskii , I.A.Yamskov, *Colloid Journal* **2013,** *75*, 409.

FUNCTIONAL MATERIALS BASED ON NANOPARTICLE MODIFIED POLYPROPYLENE FIBERS

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Polypropylene fibrous materials are widely used in filter systems for cleaning from mechanical impurities, as sorbents for ions of heavy metals, oil and oil products. However, their use as carriers in catalytic and bactericidal systems is practically unknown. The relevance of the study is due to the development of manufacturing technology for the composite active layer “polymer - inorganic nanoparticles” on the surface of polypropylene fibers to create new photocatalytic and bactericidal materials. The metal nanoparticles introduced into the structure of polypropylene microfiber will allow the creation of advanced successful catalytic and bactericidal system. They do not require the use of special equipment with mixing devices, which is necessary for the formation of a suspended reaction medium. New materials also do not require the introduction into the process of the stages of filtration release from the nanoparticles of the cleaned media.

Polypropylene materials (PPM) was obtained by the method of pneumatic spraying of a polypropylene melt jet[1]. Then, PPM with nanoparticles deposited on their surface was obtained using the sol – gel method and photoreduction. Subsequent microwave processing[2] formed stable nanostructures of metal and metal oxide particles in the surface layer of PPM. PPM have a unique combination of properties of polymeric fibrous materials (mechanical strength, developed surface, resistance to aggressive environments, small hydraulic Resistance[3,4]) with photocatalytic[5] and bactericidal[6] properties. In the work, the characteristics of the interaction of the components of a gas-polymer system in the process of spraying are established computer simulation methods. The dependence of the properties of PPM on the structure has been experimentally established. An optimal model of the dependence of the PPM properties on the conditions of the spraying process is constructed and factors of the dominant influence are identified. The photocatalytic activity of the obtained nanocomposites was studied in a photoreactor[7] for the utilization of persistent toxic substances from water.

Acknowledgments

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References

1. I. A. Lysak, T. D. Malinovskaya,G. V. Lysak, et al. *Russian Physics Journal* **2017**, 59, 10.
2. I. A. Lysak, G. V. Lysak, T. D. Malinovskaya, et al. *Advanced Materials Research* **2014**, 880, 19.
3. O. N. Chaikovskaya, A. Yu. Petrova, T. D. Malinovskaya, V. R. Artjyshin, *Optics and Spectroscopy* **2013**,144, 78.
4. I. A. Lysak, G. V. Lysak, T. D. Malinovskaya, *Key Engineering Materials* **2016**, 683, 377.
5. O. N. Tchaikovskaya, V. S. Kraukhina, V. R. Artjyshin, A. Yu. Petrova, *Luminescence* **2019**, 34, 553.
6. I. A. Lysak, T. D. Malinovskaya, O. N. Tchaikovskaya, G. V. Lysak, V. R. Artyushin, *Advanced Materials Research* **2015**,1085, 107.
7. O. N. Chaikovskaya, I. V. Sokolova, G. V. Maier, V.R. Artyushin, E. A. Sosnin, *Instruments and Experimental Techniques* **2011**, 54, 841.

STRUCTURE, PHASE COMPOSITION, SURFACE ANALYSIS AND SOME FUNCTIONAL PROPERTIES OF CHITOSAN-BASED COMPOSITE MATERIALS CONTAINING SILVER OR GOLD NANOPARTICLES

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In this work, chitosan-based powder and film composites incorporated with gold or silver nanoparticles were prepared. Metal vapor synthesis method was used for nanoparticles formation.[1] The nanoparticles were then deposited onto pristine chitosan flakes. Metal concentration in the obtained composites was varied. For film formation, solution-casting technique was used as described previously.[2]

The structure, phase composition, surface and morphology analysis of the prepared composite materials in both forms as powder and films was performed with spectroscopic and microscopic methods. XRPD analysis revealed the presence of metallic phase proving that nanoparticles were successfully incorporated into the biopolymer matrix. The particles size in the composite materials was estimated using the peaks broadening of the XRPD patterns and TEM analysis. The examination of film morphology by means of SEM and AFM showed that films are built from globular-like units aggregated to fibrils tightly packed in parallel way. Structure and possible stabilization mechanisms of metal nanoparticles in polymer matrix were studied by comparing FT-IR and XPS analyses of pristine and modified chitosan. The changes in the concentration of nitrogen-containing groups on the surface of chitosan-based materials as well as pronounced changes in absorbance intensity in mid-infrared region of FT-IR spectra were detected. The observed differences indicate that the nanoparticles are attached to functional groups of chitosan.

Some functional properties, such as mechanical, thermomechanical and swelling behavior as well as structure-properties relationship for chitosan-based films containing metal nanoparticles were studied. The effect of metal concentration on these functional properties as well as structure-properties relationship dependency for composite materials were established.

Acknowledgments

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References

1. M.S. Rubina, E. E. Said-Galiev, A.V. Naumkin, A.V. Shulenina, O.A. Belyakova, A. Yu. Vasil'kov. *Polymer Engineering and Science* **2019** (https://doi.org/10.1002/pen.25122).
2. M.S. Rubina, A.V. Naumkin, A.Yu. Vasil'kov, *Journal of International Scientific Publications: Materials, Methods and Technologies* **2018**, *12*, 100.

MACROMOLECULE WITH AMPHIPHILIC MONOMER UNITS IN A BINARY SOLVENT: DISSIPATIVE PARTICLE DYNAMICS SIMULATION

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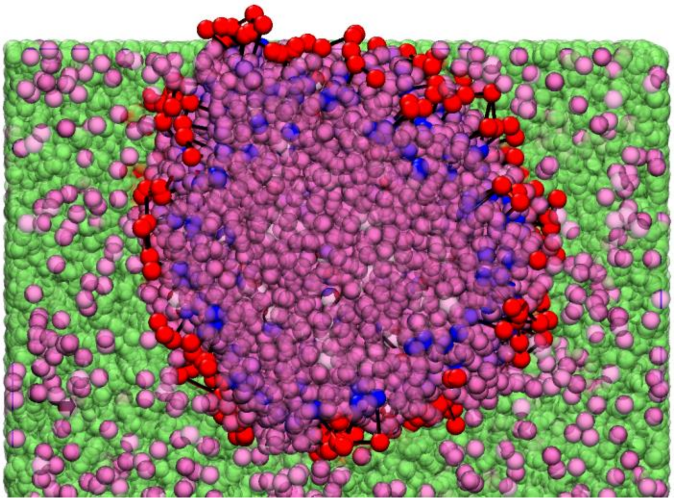
Amphiphilic macromolecules are of interest, since they are capable of self-assembling and, thus, can provide simultaneously interfacial tension decreasing while water viscosity increasing for the chemical enhanced oil recovery. Moreover, they can used as drug-delivery vectors, protein sensing devices nanoreactors and so on[1].

In the present work, conformational behavior of the amphiphilic macromolecule at the level of monomer units in a mixture of two solvents was studied in the dissipative particle dynamics (DPD) framework[2]. Using a simple model in which each monomer is represented as two DPD units, structural transitions of a macromolecule with a gradual change in the concentration ratio of two solvents were detected. Also, the dependences of the types of structure on the chain length and on the miscibility of solvents was investigated. With the right choice of parameters, cononsolvency effect can also be observed within this model.

Figure 1



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Acknowledgments

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References

1. V. V. Vasilevskaya, E. N. Govorun, *Polymer Reviews* **2019**, *26*, 1558-3724.
2. R. D. Groot, P. B. Warrenm, J. Chem. Phys. **1997**, 107, 4423,.

PREPARATION AND STUDY OF STRUCTURAL FEATURES OF SULFONATED POLYPHENYLQUINOXALINES WITH SULFACTANTS

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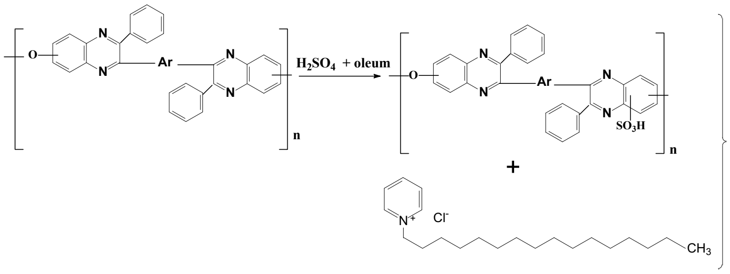
The interaction of sulfonated polyphenylquinoxalines (SPPQ) with surfactants is a possible way to modify the structure and properties of these polymers. The main task is to elucidate the most important factors affecting the solubility, mechanical, thermal, rheological and other characteristics of SPPQ with surfactants in order to develop methods for controlling the properties of these systems. The conditions of polymer-analogous transformations of SPPQ with cetylpyridinium chloride (CPC) as a cationic surfactant were studied.



It was established that the formation of complexes occurs in chloroform at 20°C. Data of IR spectroscopy and fundamental changes of solubility are the evidence of complex formation. The complex SPPQ with CPC to assumes the solubility in chloroform, which fully missing for the original SPFC. A bimodal particle size distribution for complex SPPQ-4%S with CPC in MP was determined by dynamic light scattering.

Concentration of polymer %	*D_h*, nm	Relative content, %	*D_h*, nm	Relative content, %
	Large mode		Small mode	
0.0025	279.9±90.4	72.8±9.8	43.3±17.3	27.2±9.3
0.01	266.6±32.4	72.9±3.6	24.6±4.0	27.1±3.6

These complexes form solid brown-colored homogeneous films that are completely free of hard-to-remove high-boiling solvents. The temperature of onset of decomposition exceeds 500° C according to TGA data. The films, which placed into 80 % phosphoric acid at room temperature for a long time to retain their size and the shape. This fact is allows to hope that these polymers can be used as proton-conducting membranes.

NEW HYBRID MATERIALS BASED ON METAL-CONTAINING BACTERIAL CELLULOSE OBTAINED BY METAL VAPOR SYNTHESIS

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New materials based on Au, Ag and Cu nanoparticles stabilized in a matrix of bacterial cellulose (BC) were prepared for medical applications. Au, Ag and Cu nanoparticles were synthesized by metal vapor synthesis (MVS) and incorporated into BC using metal-containing organosol[1,2]. Bacterial cellulose films were synthesized by *Gluconacetobacter hansenii* producer strain.

The materials were characterized by transmission and scanning electron microscopy (TEM, SEM) and X-ray photoelectron spectroscopy (XPS). XPS results showed that for metal-containing composites one Au $4f_{7/2}$-Au $4f_{5/2}$ spin-orbit doublet at 83.87 and 87.52 eV and Ag $3d_{5/2}$ - Ag $3d_{3/2}$ spin-orbit doublet at 368.22 - 374.22 eV with a splitting of 6.0 eV are observed, which indicates the state of $Au^0$and Ag^0 respectively. TEM data showed BC stabilized metal particles nanoformations having “a grape bunch” structure, in which smaller metal particles are combined.

The antibacterial activity against some Gram-positive and Gram-negative microorganisms (Escherichia coli, Bacillus coagulans and Staphylococcus Aureus) and the antitumor effect of the new metal-containing nanocomposites have been determined. .

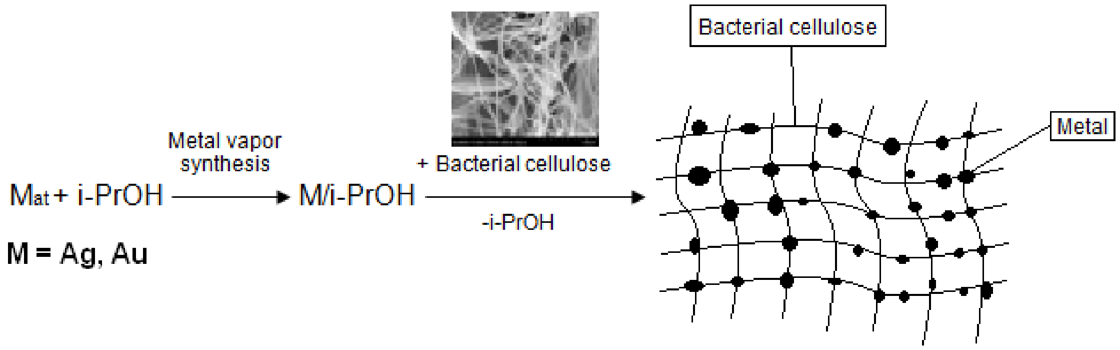

Figure 1: Scheme the preparation of metal-containing bacterial cellulose

Acknowledgments

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References

1. K.A. Abd-Elsalam, A.Yu. Vasil’kov, E.E. Said-Galiev, M.S. Rubina, A.R. Khokhlov, A.V. Naumkin , E.V. Shtykova, M.A. Alghuthaymi, *Eur. J. Plant Pathol.* **2017**, 1 DOI: 10.1007/s10658-017-1349-8
2. A.Yu.Vasil’kov, R.I.Dovnar, S.M. Smotryn, N.N. Iaskevich, A.V. Naumkin, *Antibiotics* **2018**, *7(80)*. DOI:10.3390/antibiotics7030080.

A STUDY OF CHLORO-P-XYLYLENES POLYMERIZATION KINETICS USING HIGH-VACUUM IN-SITU DIFFERENTIAL SCANNING CALORIMETRY

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Poly(*p*-xylylenes), also known by their trade name as Parylenes, are a class of polymers traditionally synthesized by vapor deposition polymerization technique enabling preparation of thin pinhole-free conformal coatings of controlled thickness without solvents or catalysts. Although over twenty types of Parylenes have been developed, only a few of them are commonly available, i.e. Parylenes N, C, D (unsubstituted poly(*p*-xylylene), poly(chloro-*p*-xylylene), and poly(dichloro-*p*-xylylene), correspondingly), as well as recently commercialized Parylene HT (a fluorinated version of the polymer), as well as Parylenes A and AM, having amino groups attached to the benzene rings.

The high reactivity of *p*-xylylenes and low polymerization temperatures make a study of the polymerization mechanism a nontrivial problem. In this work the polymerization kinetics of *p*-xylylene (PXN), chloro-*p*-xylylene (PXC) and dichloro-*p*-xylylene (PXD) in condensed state was studied by in-situ non-isothermal DSC measurements, using a custom-made heat-flux calorimeter integrated into a vacuum vapor deposition polymerization reactor. The total exothermal effect of polymerization reactions (86 ± 8 kJ/mol for PXN, 71 ± 9 kJ/mol for PXC, and 57 ± 6 kJ/mol for PXD) and its temperature range (–110 to –75 °C for PXN, –140 to –80 °C for PXC, and -150 to –80 °C for PXD) were determined. The differential isoconversional method by Friedman was applied for the kinetics analysis. The variation of the effective activation energy with conversion degree reveals a transition from reaction-controlled to diffusion-controlled regime of the polymerization reaction. The reaction model was evaluated using a model-free method based on the use of the compensation effect. The calculated reaction model values were independent on the heating rate and correspond to the Avrami-Erofeev A2 model for PXN polymerization in the conversion degrees interval α of 20 – 80 %, the second-order reaction model for PXC polymerization for α = 30 – 90 %, and a linear combination of the first-order and the second-order reaction models for PXD polymerization for α > 20%. One can suggest that this discrepancy can be related to heterogeneous kinetics of the *p*-xylylenes polymerization reaction in solid state, and difference in nucleation and growth kinetics.

Acknowledgments

The work was supported by the Russian Foundation for Basic Research (grant nos. 18-03-00916, 18-03-00662).

FEATURES OF HYDROLYSIS OF MARINE COLLAGEN AND FIBRINOGEN PROTEINS BY THROMBIN

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Nowadays there is a high demand for tissue engineering products, especially scaffold technology products. One of the most popular biopolymer materials for the formation of hydrogel scaffolds are fibrinogen/fibrin and collagen[1]. However, it remains unclear how collagen interacts with fibrin in the formation of composite scaffolds under conditions of enzymatic hydrolysis. During our previous work it was obtained that in case of isolated from the skin of different animals native high-molecular collagen (type I) hydrolysis by Pancreatin has significantly high rate under standard conditions[2].

Due to the fact that both proteins - collagen and fibrinogen are structure-forming parts in fibrin – collagen scaffolds[3], the purpose of this work is to analyze the rate of hydrolysis of high-molecular cod collagen (CC) and fibrinogen (Fn) by thrombin (used in the formation of scaffolds[1,3]). Fn is isolated from blood plasma. The hydrolysis rate was analyzed by comparing the molecular-mass parameters of proteins.

Collagen was isolated according to the author's method[4]. Enzymatic hydrolysis by thrombin was performed under standard conditions at the ratio protein: thrombin $=10^3:1$. Molecular-mass characteristics of CC and Fn hydrolysates were determined by GPC.

Thrombin is known to hydrolyze the bonds between arginine and lysine (Figure1). It was found that the hydrolysis of fibrinogen and collagen by thrombin under the same conditions occurs at different rates: fibrinogen decays slower than collagen.

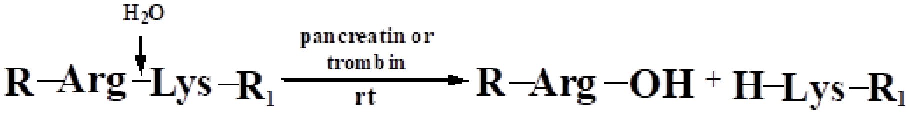

Figure 1.Scheme of Arg-Lys bond hydrolysis by thombin

Acknowledgments

The study was performed with equipment at the Center for Continuing Education “New Materials and Resource-Saving Technologies” (Scientific Research Institute of Chemistry of N.I. Lobachevsky State University of Nizhny Novgorod)

References

1. De la Puente P., D. Ludeña, *Exp. Cell Res. Elsevier*, **2014**, *322(1)*, 1.
2. L. L. Semenycheva, [et.al], *PolymerScience. Series D.*, **2019**, *4*, 27.
3. Patent RU 2653434 C1; Bul. invetion. №13, 2018
4. Patent RU 2567171 C1; Bul. invetion. №31, 2014.

A COPOLYMER OF BUTYL ACRYLATE WITH VINYL BUTYL ETHER, SYNTHESIZED BY THE TRIETHYLBORON-OXYGEN SYSTEM IN A COMPENSATORY WAY AS A MACROINITIATOR

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In the work[1] the copolymerization of butyl acrylate (BA) and vinyl butyl ether (VBE) with large excess and boiling of VBE in the presence of triethylborane (TEB) and oxygen as initiating system was carried out. It was found out that the part of macromolecules of alternating copolymer are formed by the reversible inhibition mechanism due to the participation of boroxyl radical which is formed during the oxidation of TEB together with alkoxyl and alkyl radicals[2] .

The aim of this work is to determine the coefficient of microheterogeneity (Km) of the copolymer of butyl acrylate with vinyl butyl ether synthesized under the conditions given in the work[1] and to obtain a block copolymer using it as a macroinitiator.

Km was calculated from ^{13}C NMR spectra of the copolymer[3,4]. In order to carry out post-copolymerization the copolymer BA-VBE was dissolved in excess of VBE and brought to the boil, then new portion of BA was added. The reaction mass was thermostated at boiling temperature of VBE. The post-copolymer was isolated from the solution. Its composition was analyzed by IR spectroscopy wherein molecular weight parameters – by gel penetrating chromatography.

Km for BA copolymer with VBE synthesized under the conditions given in the work[1] has a value of 1.8, the average block lengths of 1.03 for BA and 1.24 for VBE. These parameters confirm the close to alternating microstructure of the copolymer chain.

The increase in the average molecular weight and the displacement of the molecular mass distribution curves, as well as the increase in the total mass of the product isolated from the reaction mass, indicate the formation of a post-copolymer BA with VBE, whose composition according to IR spectroscopy is close to equimolar.

Acknowledgments

The work was carried out using the equipment of the CCP "New materials and resource-savingntechnologies" The Research Institute for Chemistry UNN

References

1. Semenycheva L. L., et al. *Russian Chemical Bulletin,* **2017**, 9, 1660-1664 *[Proceedings of the Academy of Science. Ser. Chemistry*, **2017**, 9, 1660-1664].
2. Zaremsky M.Yu. et al. *Russian Chemical Bulletin,* **2013**, 55, 5, 601–624 *[High Molecular Weight Compounds. Ser. B,* **2013**, 55, 5, 601–624].
3. Vasnev V. A., Kuchanov S. I. *Advances in chemistry,* **1973,** 42, 2194.
4. Mingaleev V. Z. et al. *Russian Chemical Bulletin,* **2011**, 440, 4, 488-490 *[Reports of the Academy of Sciences,* **2011**, 440, 4, 488-490].

INFLUENCE OF PLASTICIZERS ON PROCESSIBILITY OF POLYACRYLAMIDE COMPOSITIONS

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Polyacrylamide (PAM) is a high molecular weight polar amorphous polymer, commonly used in the form of a powder or aqueous solutions as a flocculant in water and wastewater processing, and as a viscosity modifier in enhanced oil recovery. The use of PAM-based compositions as materials for processing into end-products is hampered by high glass-transition temperature (T_g = 190 ℃), moreover, the transition of the polymer in a high-elastic state is accompanied by reactions of intermolecular and intramolecular imidization resulting in crosslinking.

Thus, effective way to achieve easier processability of the polymer-based compositions is its plasticization. In this procedure additives injected into composition diminish interaction of polar functional groups and consequently reduce glass-transition temperature.

In this paper the following substances were selected as potential plasticizers of PAM: Erythritol, Xylitol, Sorbitol and Isomalt having melting points 122 ℃, 92 ℃,95 ℃, 145 ℃ respectively. The choice is mainly due to the presence of polar hydroxyl groups in the molecules of the substances and also thermal stability and low cost.

As method of analysis reflecting the effect of plasticizer on processability of the polymer was selected thermo-mechanical method (TMA). Samples for research were prepared by pressing at a temperature of 130 ℃ for 70 min. The T_g of samples consisting of PAM and one of the plasticizers in an amount of from 10 to 50 mass parts by weight of the polymer were determined. The results are listed in Table 1.

The presented results confirm the possibility of using Isomaltite, Erythritol, Sorbitol and Xylitol as plasticizers of PAM for the subsequent processing of the obtained compositions into end-products.

Table 1. The effect of the type and amount of plasticizer on glass transition temperature of PAM

Plasticizer	The glass transition temperature of the samples (Tg, ℃) with the content of the modifier, mass. p. per 100 mass. p. PAA					
	5	10	15	20	30	50
Isomalt	163	132	110	104	99	97
Erythritol	160	141	136	132	120	111
Sorbitol	163	149	114	108	107	104
Xylitol	161	128	119	112	106	97

SYNTHESIS, PROPERTIES AND APPLICATIONS OF COPOLYIMIDES WITH DIMETHYLSILOXANE FRAGMENTS OF VARIOUS LENGTHS

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Nowadays, optical fibers are widely used in various high performance polymers applications including aerospace, power, oil and gas industries, and medicine. Polyimides proved themselves to be high heat resistant optical fiber coatings. However, common method of PI coatings formation is based on the application of poly(amicacid)s (PAA) and has essential disadvantages: PAA instability, incomplete cyclization of PAA to PI during the coating formulation, insolubility in organic solvents, and, as a rule, high rigidity of coatings. It is assumed that more flexible and high thermostable coatings can be made from polyimides bearing siloxane fragments.

In this study we've demonstrated one- and two-step synthesis of (co)polyimides containing dimethylsiloxane fragments of different lengths in the main polymer chains (Fig. 1):

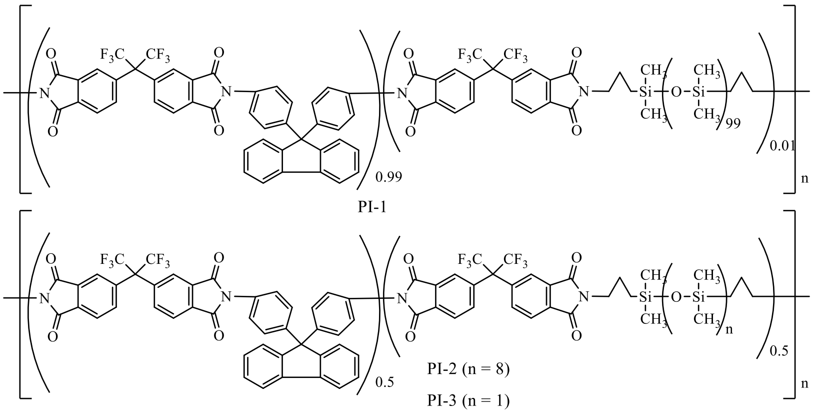

Figure 1. The structures of the synthesized (co)polyimides.

The synthesized high molecular weight copolymers (η_{inh} = 0.2 ÷ 0.6 dL/g) have high thermal characteristics: 240°C $<T_g<$355°C; 440°C $<T_{10\%}<$545°C (in air). The films there from have tensile strength from 55 up to 95 MPa, the tensile modulus - 1340÷2550 MPa and the elongation 6÷8%.

It was found that the fiber coating formation from 30 wt. % solutions of PI's in NMP leads to the defective coatings. This short coming was successfully overcome using coupling agent such as γ-aminopropyltriethoxysilane, which facilitates the production of smooth uniform coatings.

The resulting polyimide coatings have high thermal stability. In particular PI-3 coated fiber can with stand 72 hours at 300°C without any strength loss.

Acknowledgments
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EFFECT OF THE SYNTHETIC STRATEGY ON THE PROPERTIES OF LIQUID CRYSTALLINE OLIGOESTERS

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Herein, we consider a class of high-molecular compounds, so-called liquid crystalline polymers (LCP) that address the requirements for the high-performance polymeric materials, such as withstanding the high temperature (over 160 °C), mechanical stress, aggressive chemical medium, and radiation. Presence in the structure of these polymers of rigid mesogenic units is key to existing of mesomorphic phase that exhibits anisotropic properties of solids together with fluids rheological behavior.

The liquid crystalline oligoesters were derived from terephthalic acid (TA), 4-hydroxybenzoic acid(HBA) and bisphenol A (BA). The yield of the obtained compounds synthesized via the various synthetic routes varied considerably. Hence, the direct copolymerization of TA, HBA, and BA has resulted in the lowest amount of oligoesters owing to the decarboxylation of TA and HBA at the elevated temperatures. Introduction of protective groups, such as methyl- and phenyl ester groups, in the structure of monomers, led to enhancing of polycondensation process.

The FTIR spectra of the investigated polymers were almost identical. We observed the shifting of the band at 1670 cm^{-1} assigned to C=O stretching vibrations in 4-HBA towards higher wave number (1732 cm^{-1}) that indicates the formation of the ester bond. The absence of the band at 3200 cm^{-1} confirmed the complete esterification of -OH groups of bisphenol A. Alongside with this, since the spectra of oligoester synthesized via the direct polycondensation has shown the appearance of a shoulder at 1695 cm^{-1} attributed to the terminal –COOH groups, this sample was characterized by lower molecular weight than other ones.

The 10% mass loss temperatures for the samples were found to be 223 ºC, 302 ºC, and 360 ºC (for the polymers based on neat carboxylic acids, methyl esters, and phenyl esters, respectively). Results of the thermal decomposition analysis have revealed that the activation energy of thermal decomposition for those oligoesters turned out to be 152 kJ / mol, 194 kJ / mol, and 253 kJ / mol, respectively. The samples with a higher degree of polymerization were more thermally resistant. Thus, the synthetic approach involving the synthesis of phenyl esters of carboxylic acids leads to forming of the most thermally stable product with higher yield and molecular weight.

References

1. A. I. Akhmetshina, E. K. Ignat'eva, T. R. Deberdeev, L. K. Karimova, Yu. N. Yuminova, A. A. Berlin, R. Ya. Deberdeev, *Polymer Science, Series D* **2019**, *120*, 427.

MORPHOLOGY EVOLUTION DURING SUBMONOLAYER GROWTH OF POLY(CHLORO-P-XYLYLENE) FILMS FORMED BY VAPOR DEPOSITION POLYMERIZATION

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Thin poly(chloro-*p*-xylylene) (C-PPX) films are promising material for microelectronic applications as low-k interlayer dielectric and encapsulation coatings. Vapor deposition polymerization (VDP) method allows to prepare uniform pinhole-free C-PPX coatings of desired thickness in the absence of solvents and catalysts.[1] Properties of thin films strongly depend on initial stages of their formation, therefore understanding the details of the growth process is a topic of current interest.

Island films of C-PPX were formed in a custom built VDP reactor using the Gorham process.[2] Cyclic dimer of chloro-*p*-xylylene (i.e. dichloro-[2,2]*p*-cyclophane) was sublimated at 50, 60 and 70 °C and then cleaved into two monomer molecules in the pyrolysis furnace at 650 °C. Subsequently the monomer was condensed on a Si wafer placed in the deposition chamber followed by its polymerization. The substrate temperature was maintained at 25 °C, while the surface coverage was controlled by varying the deposition time.

The surface morphology of the C-PPX island films was studied by AFM with a Multimode 8 microscope and a Nanoscope V controller (Bruker-Nano Inc., USA) in tapping mode under ambient conditions. The RTESPA silicon cantilevers (supplier specs.: 20–80 N/m, 200–400 kHz) were used as AFM probes.

The dependences of surface coverage, island density, effective island film thickness as well as island mean size and island size distribution on deposition time were analyzed and compared with the results reported in our previous work for unsubstituted poly(*p*-xylylene).[3]

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (grant number 18-33-00600).

References

1. W. F. Beach, *Xylylene Polymers. Encyclopedia of Polymer Science and Technology (New York: JohnWiley & Sons)* **2004**
2. W. F. Gorham, *J. Polymer Sci.* **1966,** *A1, 4*, 12
3. A. S. Mitko, D. R. Streltsov, P.V. Dmitryakov, A.A. Nesmelov, A.I. Buzin, S.N. Chvalun, *Polymer Science Series A,* **2019**, *61(5), 555*

RHODIUM AND IRIDIUM CATALYSTS ALLOW TO OBTAIN SILICONE RUBBERS WITH ENHANCED PROPERTIES

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Silicone rubber is abundant in both home applications and industry. Due to outstanding electrical insulation, thermal resistance and weather stability it is good alternative to rubbers based on carbon-chain polymers. One of the systems used to obtain rubber from linear polysiloxanes include vinylcontaining polysiloxanes, hydride-containing (poly)siloxane crosslinker and hydrosilylation catalyst. In industry platinum(0) complex – Karstedt's catalyst – is often used, however it has tendency to form platinum colloids and needs inhibitor to cross-link silicones effectively at heating. New catalysts based on platinum group metal complexes are perspective solutions for these problems.

Our work makes use of acetylacetonate rhodium(I) and cyclometalated iridium(III) complexes as hydrosilylation catalysts for reaction of vinyl-terminated polydimethylsiloxane and poly(dimethylsiloxane-co-methylhydrosiloxane) which results in silicone rubber. Compared to Karstedt's catalyst, these complexes allow to obtain silicone rubber without inhibitors. Acetylacetonate rhodium(I) complexes crosslink polysiloxanes at RT and improved their elastic properties (elongation at break increased by ca. 100%)[1]. Cyclometalated iridium(III) complexes did not need inhibitors to store reaction mixture at RT at least for a year without visible changes and catalyzed crosslinking only at temperatures above 80 °C; rubbers obtained with iridium(III) complexes are luminescent and decompose at higher temperatures (by ca. 90°C)[2].

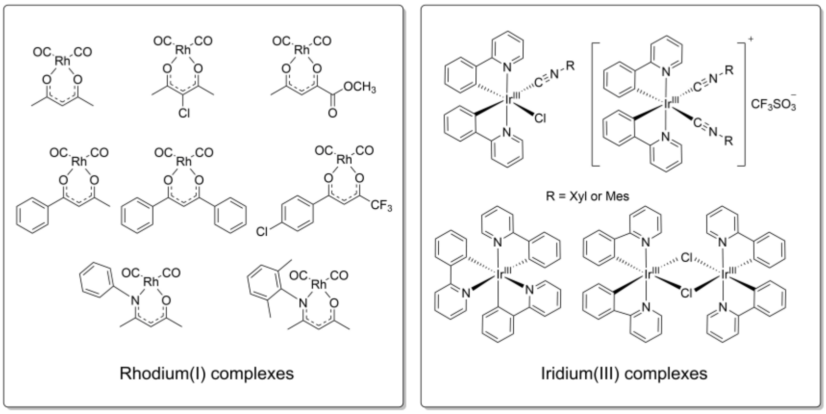

Figure 1. Platinum group metal complexes used as catalysts.

Acknowledgments

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References

1. M.V. Dobrynin, C. Pretorius, D.V. Kama, A. Roodt, V.P. Boyarskiy, R.M. Islamova, *J. Catal*. **2019**, *372*, 193.
2. R.M. Islamova, M.V. Dobrynin, A.V. Vlasov, A.A. Eremina, M.A. Kinzhalov, I.E. Kolesnikov, A.A. Zolotarev, E.A. Masloborodova, K.V. Luzyanin, *Catal. Sci. Technol.* **2019**, *7*, 5843.

NEW MAGNETIC NANOMATERIALS BASED ON SOLUBLE FERROCENE-CONTAINING POLYMERS

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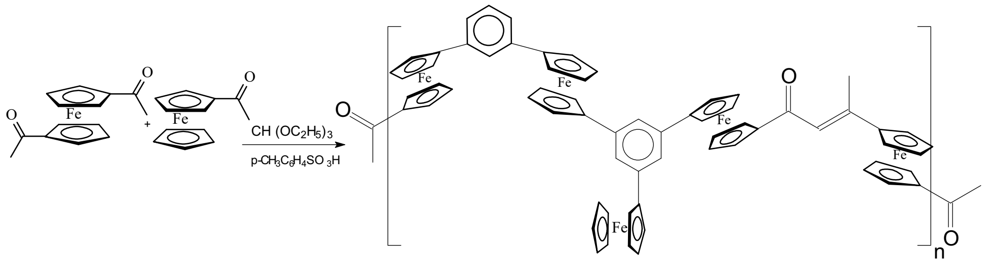
New magnetic nanomaterials based on soluble ferrocene-containing polyphenylenes (FP) were obtained. The reaction of copolycyclocondensation of 1,1´-di- and 1-acetylferrocene in presence of triethylorthoformate and *p*-toluenesulfonic acid within 20-80ºC under common conditions and under ultrasonic irradiation was carried out to give FP as precursors of magnetic nanomaterials[1,2] in accordance with the scheme :



The heating of the FP in the range of 200-750 ºC resulted in the crosslinking of macromolecules and formation of crystalline iron-containing magnetic nanoparticles (figure 1) in a carbonized polymer matrix. The magnetization of these nanomaterials, containing magnetite nanoparticls was 14-23 G·cm^3/g in magnetic field of 2.5 kOe. According to transmission (TEM) and scanning electron (SEM) microscopy results, the average size of magnetic nanoparticles was 12-42 nm.

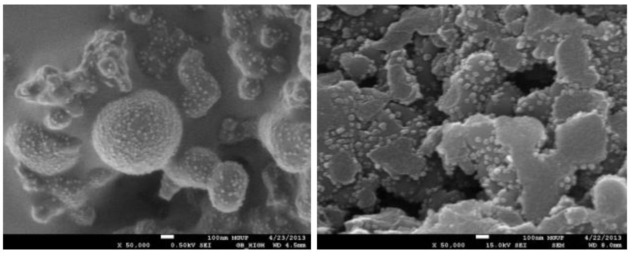


Figure 1.SEM PFs, after heating at 400ºC

Acknowledgments

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References

1. R. A. Dvorikova, Yu.V. Korshak, L.N. Nikitin et. al, *Engineering of Polymers and Chemical Complexity,* Apple Academic Press, Toronto, New Jersey, **2014**,*2*, 145.
2.R.A. Dvorikova et.al, *Russian Chemical Bulletin*, **2019**, 7, 1445.

STUDY OF THE PHYSICOCHEMICAL PROPERTIES OF NEW FERROCENE-CONTAINING FLUORINATED MONOMERS

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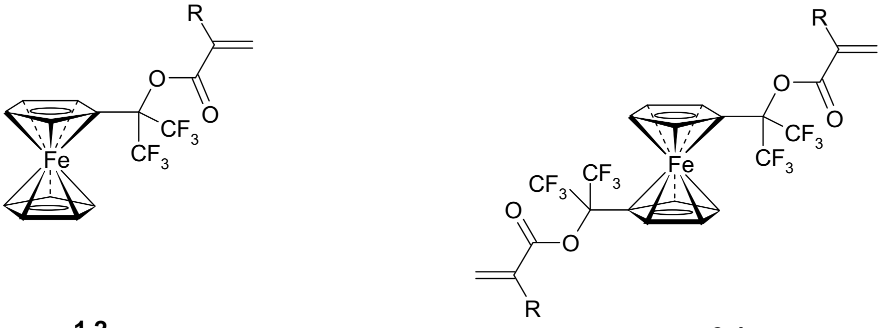
We synthesized new organoelement monomers — fluorine-containing (meth) acrylates 1-4 (Fig. 1) bearing a ferrocenyl substituent in the alcohol part of the molecule[1,2]. Based on them, “side-chain” (co) polymers were obtained which became the starting materials for the preparation of pyrocarbon materials containing nanovalent iron nanoparticles[3]. The antioxidant properties of these methacrylates were studied. It was established that insignificant (1-3%) introduction of 1,2 into the polymer chain of polymethylmethacrylate increases the temperature of its thermal destruction by 50-55 °C[2].



1,2

3,4

R = H, Me

Figure 1. Ferrocene-containing (meth)acrylates

The study of solubility in supercritical carbon dioxide (sc-CO_2) has been started in order to identify the possibility of applying an ultrathin coating of fluorine-containing organoelement polymers to a substrate. It turned out that, the synthesized ferrocene-containing polymethacrylate is relatively soluble in the sc-CO_2 media unlike the vast majority of polymers. Apparently, the solubility of the polymer is possible due to the presence of fluorine atoms in the composition of this polymer, as well as to the absence of NH and OH groups capable of forming hydrogen bonds between the polymer chains.

The prospects of their use in biomedical applications, in particular, as antioxidants are discussed.

References

1. Dyachenko V.I., Nikitin L.N., Mel'nik O.A., Peregudova S.M. ,. Peregudov A.S., Igumnov S.M., Khokhlov A.R., Fluorine notes, **2011**, 79, 7.
2. Dyachenko V.I.,. Mel'nik O.A., Nikitin L.N., Igumnov S.M., Fluorine notes, **2018,** 117, 5.
3.Dyachenko V.I., Mel'nik O.A, Bushmarinov I.S., Igumnov S.M., Nikitin L.N. Doklady Chemistry, **2016**, 467, 665.

METAL-CONTAINING CHITOSAN-BASED FILMS: MORPHOLOGY STUDY

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Certain intrinsic biological properties, such as biocompatibility, biodegradability and antimicrobial activity, makes chitosan a promising candidate for the use in biomedical applications. Silver nanoparticles can be introduced into this biopolymer to further extend the antimicrobial activity.[1] Metal vapor synthesis is an effective method to prepare metal organosols that can be further used to modify substrates of various chemical nature, including biopolymers.[2]

In the present work authors studied the morphology of chitosan and silver-containing chitosan-based films by means of scanning electron microscopy and atomic force microscopy (AFM). The latter was chosen for the non-distractive nature of AFM studies, which is especially important for biopolymers that can readily degrade in contact with electron beam.

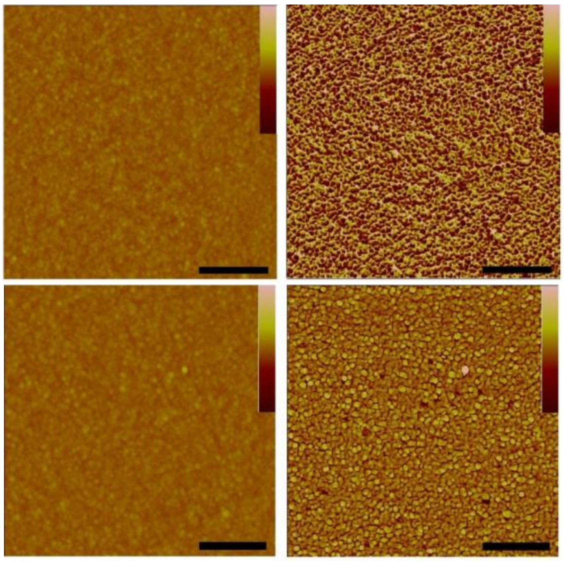

Figure 1. Typical AFM images of chitosan films. Upper row: pristine chitosan, bottom row: silver-containing chitosan. Scale bar: 500 nm, height scale: 30 nm.

Typical AFM images of chitosan-based films studied in this work are presented in Figure 1. Globular-like structures with rather monodispersed size distributions can be observed. The work demonstrates that the structure and size distribution features are typical for all the studied films. Silver content and solvent concentration were varied, the results were analyzed and compared to the relative scientific literature.

Acknowledgments

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References

1. T.A. Ahmed, B.M. Aljaeid, *Drug Des. Devel. Ther.* **2016**, *10*, 483–507.
2. M.S. Rubina, A.Y. Vasil'kov, A. V. Naumkin, E. V. Shtykova, S.S. Abramchuk, M.A. Alghuthaymi, K.A. Abd-Elsalam, *J. Nanostructure Chem.* **2017**, *7*, 249–258.

METAL POLYMERIC NANOCOMPOSITES AG BASED ON HYDROPHILIC NITROGEN AND SULFUR CONTAINING POLYMER

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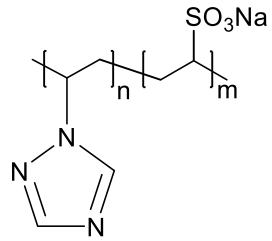
Obtaining organo-inorganic nanocomposites based on polyfunctional polymer compounds is a promising direction. The functionalization of the initial polymer matrix by introducing into the polymer chain highly reactive groups capable of stabilizing metal nanoparticles in nanocomposites opens up new ways of using target nanocomposites.

The stabilizing polymer matrix plays a significant role in the formation of nanocomposites, providing stabilization according to one of the types: electrostatic or steric stabilization, as well as their combination.



Previously, we discussed data on the copolymerization of 1-vinyl-1,2,4-triazole with the sodium salt of vinyl sulfonic acid[1].

This paper presents the results of the synthesis and study of the properties of new silver-containing nanocomposites based on copolymers of 1-vinyl-1,2,4-triazole with the sodium salt of vinyl sulfonic acid.

To obtain nanocomposites, a chemical method for the reduction of silver ions from silver nitrate with sodium borohydride in an aqueous medium in the presence of a polymer matrix was used. A hydrophilic non-toxic copolymer of 1-vinyl-1,2,4-triazole with a sodium salt of vinyl sulfonic acid of various compositions was used as a matrix.

The resulting polymer nanocomposites are brown powders, soluble in water. According to atomic absorption spectroscopy, the silver content in nanocomposites is 4.3–5.0%.

According to transmission electron microscopy synthesized nanocomposites consist of silver nanoparticles predominantly spherical shape. The method of dynamic light scattering was used to measure the hydrodynamic radius of the macrocoils of the synthesized nanocomposites. Studies of synthesized nanocomposites by electrophoretic light scattering with phase analysis show that with an increase part of sulfonate units in the stabilizing polymer matrix, the zeta potential (ζ) changes from –35.0 to –74.8 mV, which indicates an increase in the stability of the colloidal system.

Acknowledgments

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References

1. A. S. Pozdnyakov, E. A. Sekretarev, A. I. Emel’yanov, G. F. Prozorova, *Russ. Chem. Bull. (Int. Ed.),* **2017**, 66 (12), 2293.

WATER INSOLUBLE ORGANOSILICON SURFACTANTS AS STABILIZERS OF POLYMER SUSPENSIONS

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A study of the polymerization kinetic laws of styrene, methyl methacrylate, butyl methacrylate and vinyl acetate in the presence of organosilicon surfactants of various structures made it possible to identify common characteristics inherent in all monomers studied that substantially distinguish these processes from those known in the presence of water-soluble surfactants.

The main property characteristic only of these processes is the formation of particles of the dispersed phase according to one mechanism – from microdrops of monomer when radicals get into them. The resulting polymer-monomer particles do not change sizes during polymerization until the monomer is completely converted and maintain a narrow particle size distribution.

Another characteristic feature of these processes is an increase in the particle diameters of polymer suspensions with increasing surfactant concentration, which is explained by the effect of surfactants on dispersion.

An increase in monomer concentration (a change in the monomer/aqueous phase volume ratio) leads to an increase in particle diameter, and in some cases, to a decrease in the stability of the reaction system. It was shown that the concentration of organosilicon surfactants, equal to 0.15-1.0 wt.% of the monomer mass, is sufficient to obtain a stable reaction system.

All of the above polymer suspensions synthesis features make it possible to distinguish this process as an independent section of heterophase polymerization.

The reported study was funded by RFBR according to the research project № 18-33-01193

COMB-LIKE POLYELECTROLYTES FOR ALKALINE HYDROLYSIS OF ESTERS

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Comb-like polyelectrolyte, combining the properties of surface-active substances and polyelectrolytes, as well as the ability to self-organize in solution and in a condensed state, can be used in various fields [1,2]. In this work these compounds were used as micellar catalysts for the reaction of alkaline hydrolysis of p-nitro-phenyl esters of aliphatic acids. The main objects of research in this work are cationic polyelectrolytes obtained from acrylic and methacrylic monomers of 11-bromundecanol with various sources of quaternary nitrogen (trimethylammonium, triethylammonium, pyridinium group were used in the work).

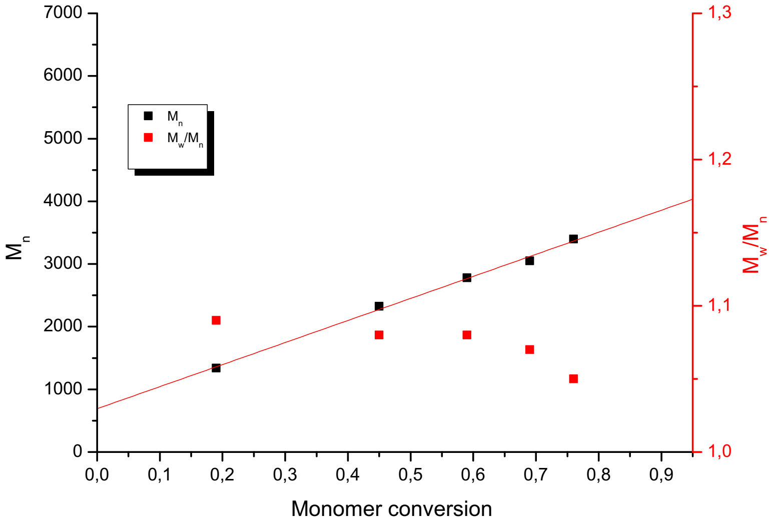

Figure 1. The dependence of molecular weight characteristics of poly-11-bromoundecilacrylate from monomer conversion

Microemulsion polymerization of the corresponding monomers and RAFT polymerization of 11-bromoundecylacrylate (methacrylate) followed by the transformation of the polymers into cationic polyelectrolytes by reaction with selected amines were used for the synthesis of selected polyelectrolytes. The influences of the molecular weight of the catalyst and the type of ammonium group on the rate of hydrolysis reaction are discussed in the work.

Acknowledgments

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The authors are grateful Center for magnetic resonance, Interdisciplinary Resource Centre for Nanotechnology, Centre for Diagnostics of Functional Materials for Medicine, Pharmacology and Nanoelectronics of Saint Petersburg State University.

References

1. P.A.Fetin, I.M.Zorin, *European Polymer Journal* **2019**,*116*, 562-569.
2. I.M. Zorin, T.M. Scherbinina, *Talanta* **2014**, *130, №1*. 177-181.

THE DIFFUSION ROLE IN THE KINETICS OF THE INTERFACE POLYADDITION REACTION

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A theoretical study of polyaddition and diffusion processes in the system initially consisting of two separated oligomers containing reactive end groups is presented. During the reaction, A and B oligomers are combined in AB dimers, ABA and BAB trimers and two kinds of tetramers. This model can describe the film formation process at the boundary of two phases, such as two drops.

We study the film formation kinetics dependently on various input parameters, such as the initial length of oligomers, their mobility and polymer mobility, the reaction rates, the Flory-Huggins parameter. Moreover, to investigate the thermodynamic stability of the system, the spinodal equation was derived and analyzed, the critical value of the Flory-Huggins parameter was deduced. A fast diffusion model was used to calculate the kinetic coefficients. The system of equations for simultaneous diffusion and reaction processes was further solved by numerical methods.

As part of the study, the changes in the oligomer and polymer volume fractions over time, the reaction zone width, and the average reaction rate were calculated. In particular, it was found that in case of oligomers of different sizes, the maximum of the reaction product concentration and the reaction zone were shifted towards the initial position of longer oligomers.

COARSE-GRAINED SIMULATION OF MOLECULAR ORDERING IN POLYLACTIC BLENDS UNDER UNIAXIAL STRAIN

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Studying mechanical properties of polymer systems by aids of computer experiments requires simulations on large time and spatial scales. In many cases, such simulations can be made feasible only by switching to coarse-grained molecular dynamics. The earlier developed coarse-grained model of polylactic acid (PLA)[1] was used to estimate the mechanical properties and ordering of pure PLA caused by uniaxial straining above the glass transition temperature, as well as the effect of oligolactic acid (OLA) content in the mixtures of PLA and OLA.

It was shown that the values of the elastic modulus observed in the coarse-grained simulations are in the same range as those observed experimentally. The coarse-grained model qualitatively reproduces the dependence of the elastic modulus on the strain rate and content of OLA molecules.

The coarse-grained model also reproduces the high degree of orientation of the macromolecules and its dependence on strain rate. In the mixtures with the OLA content of 40%, the segregation between PLA and OLA chains was observed at certain strain rates.

The coarse-grained samples can be converted to all-atom representation using the reverse mapping algorithm[2]. The coarse-grained approach provides an efficient way to speed-up molecular dynamics simulations without compromising the validity of the results.

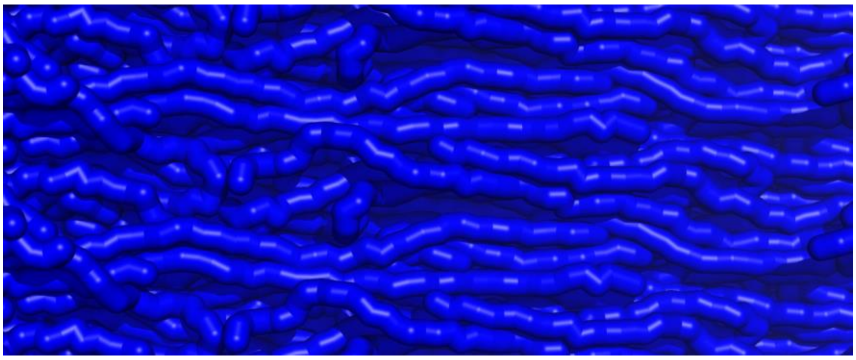

Figure 1. Backbones of PLA chains in neat PLA sample at 500% strain.

Acknowledgments

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References

1. M. Glagolev, A. Glova, D. Mezhenskaia, S. Falkovich, S. Larin, V. Vasilevskaya, S. Lyulin , *Science Journal of Polymer Science, Part B: Polymer Physics* **2018**, *56*, 604.
2. M. Glagolev, V. Vasilevskaya, *Supercomputing Frontiers and Innovations* **2018**, *5*, 103.

HOLLOW MORPHOLOGIES FORMED BY INTERPOLYELECTROLYTE COMPLEXES: COMPUTER SIMULATION

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In the present work, the inner structure of the polyelectrolyte complexes, formed by two oppositely charged flexible macromolecules of similar length and similar degree of ionization, is studied by means of computer simulation. The nonionic groups of the investigated polyions have different affinity to the solvent, i.e. the solvent is good for the groups of one chain and poor for the groups of the other chain.[1]

When the solvent is good for both chains, the charged and non-charged groups of the both macromolecules are distributed homogeneously within the complex. Upon the solvent worsening for one of the chains, the resulting morphologies acquire the outer shell consisting of the groups of solvophilic chain. Depending on the solvent quality, three morphology types are distinguished in poor solvent: particles with solvophilic shell and relatively loosely packed monomer units in the core (Fig. 1a); hollow “vesicle-like” particles (Fig. 1b); dense particles with strongly segregated chains (Fig. 1c).[2]

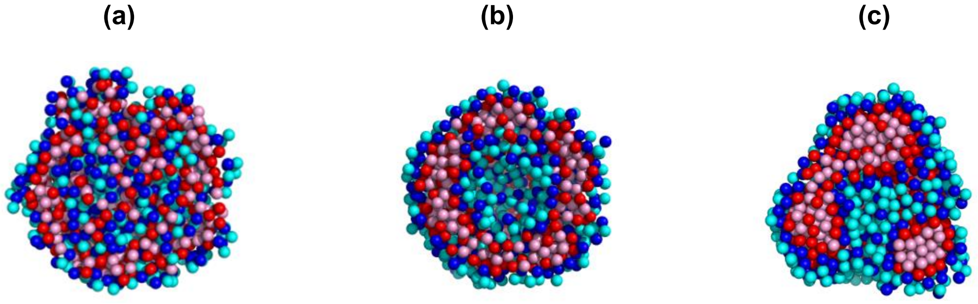

Figure 1. Snapshots of the typical morphologies of the studied complexes (cross-sections). Red and pink groups are charged and non-charged groups, respectively, of the chain being in poor solvent; blue and cyan groups are charged and non-charged groups of solvophilic chain.

Acknowledgments

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References

1. V. V. Vasilevskaya, L. Leclercq, M. Boustta, M. Vert, A. R. Khokhlov. *Macromolecules* **2007**, 40, 5934.
2. A. A. Glagoleva, V. V. Vasilevskaya, *Polymer Science, Series A* **2019**, 61, no. 6 (in press).

AGGREGATION OF ASSOCIATING POLYELECTROLYTES

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The aggregation of associating polyelectrolytes with a high degree of charge units in dilute aqueous solutions has been investigated in this work. Intramolecular and intermolecular hydrophobic domains are formed via hydrophobic side groups. Such polymers are paid attention because they are widely used in healthcare, biotechnology, and membrane technology[1].

Aqueous solutions of hydrophobically modified polyacrylate (GM PA) at different concentrations in the presence of NaCl salt were investigated.

Using the method of dynamic light scattering in dilute aqueous solutions of GM PA, slow and fast modes were found corresponding to the diffusion motion of individual macromolecules and their aggregates.

The characteristic sizes of objects and their dependence on the concentration of polymer and salt are determined. A model of the resulting aggregates is proposed. Using the cryo-TEM approach, images of objects in the system were revealed. In addition to individual macromolecules and aggregates, aggregate clusters consisting of two or three spherical aggregates that are about 90 nm in size were also detected. The formation of aggregate clusters is explained by a high degree of hydrophobicity of polymers, which leads to the existence of hydrophobic groups that are not included in hydrophobic domains and are able to combine aggregates into clusters[2].

The aggregates and aggregate clusters discovered in the work, due to the size of less than 200 nm, can be promising for use as nanocontainers for the delivery of drugs or biologically active substances.

References

1. L. Bromberg, *Ind. Eng. Chem. Res.* **1998**, *37,* 4267-4274
2. G.Bai, L. Santos, M. Nichifor, A. Lopes, M. Bastos, *J. Phys. Chem. B* **2004,** 108, 405-413

KINETIC AND STRUCTURAL FEATURES OF 2,2,3,3-TETRAFLUOROPROPYL METHACRYLATE RAFT-POLYMERIZATION

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In recent years, control radical polymerization methods have been widely used to synthesize (co)polymers with a given architecture. Reversible addition-fragmentation chain transfer (RAFT) polymerization can be applied to a wide range of monomers unlike the rest of techniques; therefore, it is a more versatile technique for the synthesis of amphiphilic copolymers.[1] Fluorinated (co)polymers draw the attention of scientists due to some of their properties such as thermic and chemical resistance, atmospheric sustainability and low surface energy.[2] Controlled (co)polymerization of fluorine (meth)acrylates has not received proper attention in literature yet.

This work dwells on the issues of controlled synthesis of polymers based on 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA).

Polymerization of 2,2,3,3-tetrafluoropropyl methacrylate (TFPMA) was carried out. Initially, the effectiveness of different chain transfer agents was investigated (AIBN was used as initiator, benzene was used as solvent). It was estimated through analyzing the curves of the molecular mass distribution of polymers at different conversions. It turned out that 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) and 4-cyano-4-[(dodecylsulfanyl-thiocarbonyl)sulfanyl]pentanoic acid (CDTPA) are more effective in RAFT polymerization of TFPMA which is confirmed by the linear increase of MW and the decrease of polydispersity with the rise of conversion. The chain transfer constants (Ctr) of CPDT and CDTPA were estimated by GPC measurement. End-groups of PTFPMA were defined by MALDI-TOF MS/MS. Further, polymerization of TFPMA in the presence of polymeric chain transfer agent PTFPMA was carried out. Then, amphiphilic block-copolymers were obtained using acrylic and methacrylic acid, and glycidyl methacrylate.

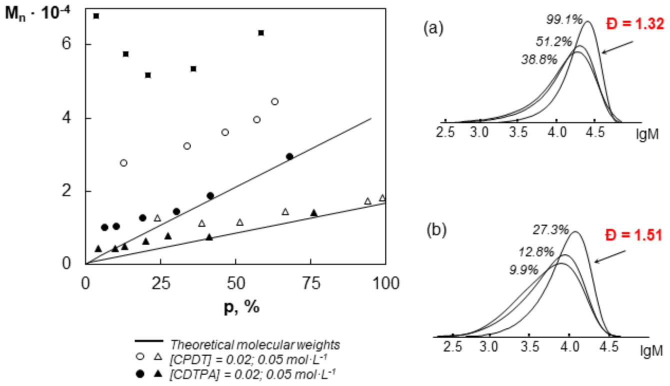

Figure 1.. Molecular-weight characteristics of PTFPMA obtained in the presence of (a) [CPDA] = 0.05 mol·L^{-1} (b) [CDTPA] = 0.05 mol·L^{-1}. [AIBN] = 0.001 mol·L^{-1}, T = 70°C

Acknowledgments

This work was supported by the Russian Science Foundation (project No 19-03-00843).

References

1. Moad G., Rizzardo E., Thang S. H., *Aust. J. Chem* **2006**. V. 59. P. 669–692.
2. Bruno A, *Macromolecules* **2010**. V. 4. P. 10163–10184.

SATURATION OF BACTERIAL CELLULOSE WITH LIPID NANOPARTICLES WITH SILYMARIN FLAVOLIGNANS AND STUDY OF ITS HEMOLYTIC AND ANTIMICROBIAL ACTIVITY

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Bacterial cellulose (BC) produced by the *Gluconacetobacter hansenii* strain GH-1/2008 is an elastic, biocompatible nanoporous material, the medical applications of which are currently being actively studied [1]. To create perspective coating materials for medical purposes, liposome nanoparticles with silymarin (LF-SM) were obtained and the kinetics of saturation / release (BC) of these particles was studied. The hemolytic and antimicrobial activity of BC films saturated with LF-SM was also studied.

Silymarin (CM) from *Silybum marianum* (L.) is the sum of flavolignans (silibinin, silikristin, silidianin and isosilibinin) that exhibit a wide range of biological activity and have anti-inflammatory, antitumor, hepatoprotective, immunomodulatory effects. Using a modified emulsion method with evaporation of the solvent, lipid nanoparticles with silymarin (LNCh-SM) were obtained, the size of which was 257 ± 6 nm, the zeta potential was –20.8 ± 1.6 mV. The efficiency of inclusion of SM in VLF-SM was 89.8%, the degree of loading was 5.4%. A study of the dynamics of the release of SM from the composition of the obtained VLFs showed that the maximum release was achieved after 48 hours and amounted to 68.3 ± 5.4%.

A study of the saturation / release kinetics of VLF-SM in bacterial cellulose (BC) films produced by *Gluconacetobacter hansenii* showed that after 24 hours of incubation, the maximum saturation of the CM BC film reached 0.745 ± 0.038 mg / cm2, and the maximum release was 0.520 ± 0.041 mg / cm2. It was demonstrated that both LNC-SM sols and BC samples saturated with LNC-SM showed extremely low hemolytic activity, which indicates the potential biosafety of these drugs. The LNCH-SM preparation, in contrast to free SM, showed a fungistatic effect against fungi A. niger and C. albicans. Both free SM and the LPS-SM preparation inhibited the growth of gram-positive bacteria, however, the effect of the LPS-SM preparation was significantly more effective. The LPC-SM of the preparation for B. subtillus and B. coagulans was 105 µg / ml and 210 µg / ml, respectively.

The data presented indicate the possibility of developing biocompatible coating materials for medical purposes based on BC saturated with LF-SM.

1. T. I. Gromovykh, V. S. Sadykova, S. V. Lutsenko, A. S. Dmitrenok, N. B.Feldman, T. N. Danilchuk, V. V. Kashirin. // Applied Biochemistry and Microbiology. 2017.Vol. 53 (1). S. 69-75. doi: 10.7868 / S0555109917010093

THE STRUCTURE
OF ROSINTERPENOMALEIC ADDUCTS

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The development of epoxy resin hardeners is a promising area of scientific research. Hardeners based on wood chemical raw materials are developed in our Institute. Terpenoid nomaleic adducts are a technical mixture of resin acids and terpene hydrocarbons, which is chemically modified with maleic anhydride. Adducts have film-forming properties. The chemical composition of rosinterpenomaleic adducts was studied in article[1].

The search for rosin substitutes has led to the creation of secondary products based on the styrene co-oligomer and maleic anhydride[2], which are used in adhesives[3], in paint and varnish[4], rubber and oil[5] industries. The resulting copolymer - styromal - has high physicochemical properties: softening point $T \geq 150.0$ °C and acid number AN = 500.0 mg KOH/g.

Currently known and widespread methods for producing styromal in an environment of aromatic and non-aromatic high boiling solvents. This is a significant drawback. In this regard, the search and research of new technologies is relevant. For the first time in the world practice of forest chemistry, a new rosinterpenostyrenemaleic adduct was proposed[6]. The essence of the method: turpentine is used as a solvent, and the final product is a multicomponent alloy of maleopimaric acid, adducts of terpene hydrocarbons with maleic anhydride, styromal and resin acids, not reacting with maleic anhydride. The proposed product is synthesized based on affordable and fairly cheap raw materials. The technology doesn’t require additional capital investments. The rosinterpenostyrenemaleic adduct is a hard glassy substance of light yellow color, dissolves in alcohols, ethers and acetone.

Previously, the structure of the components of rosinterpenostyrenemaleic adduct hasn’t been studied. The purpose of this research work is to establish and confirm the formation of styromal in the target product. To achieve this target, the method of NMR spectroscopy was used. The ^{1}H and ^{13}C NMR-spectra were recorded on an AVANCE-500 spectrometer (Germany) (500 MHz for ^{1}H nuclei and 126 MHz for ^{13}C nuclei).

After analyzing the data obtained by NMR-spectroscopy, the presence of styromal in the technical mixture was established and proved. Further work is under way to establish the final structure of the adduct.

References

1. I. A. Latyshevich, A. I. Hapankova, A. Yu. Klyuev, N. G. Kozlov, A. V. Baranovsky, T. V. Bezjazychnaya, *Proceedings of the St. Petersburg forestry Academy*. **2017**, 221, 294–308.
2. E. G. Poluiko, V. V. Afanasyeva, L.G. Beloborodova, I.I. Kolesova, A*uthor's certificate* SU 730709, **1980**.
3. Yu.A. Krylatov, V.A. Volkov, M.I. Likhtman, *Author's certificate* SU 502995, **1976**.
4. V.Ya. Paderin, N.A. Dyudkova, N.L. Vinogradova, *Hydrolysis and wood chemical industry*. **1991**, 6, 18–19.
5. D.Kh. Akchurina, Yu.I. Puzin, G.G. Yagafarova, A.Kh. Safarov, Yu.A. Fedorova, D.I. Yagafarova, *Bashkir chemical journal*. **2014**, 21, No. 3, 124–128.
6. A.Yu. Klyuev, V.E. Agabekov, N.V. Puchkova, N.R. Prokopchuk, V.V. Mulyarchik, V.N. Danishevsky, *Patent* BY 10641, **2007**.

DISTRIBUTION OF PAH BETWEEN SOLID AND LIQUID PHASES DURING DEASPHTHALTING OF PYROLYSIS OIL OF TIRES

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Pyrolysis oils obtained from waste tires contain significant amounts of polycyclic aromatic hydrocarbons (PAHs) in the form of complex mixtures [1].

PAHs are toxic and carcinogenic chemical compounds, the degree of toxicity of which depends on the structure of the substance. The most dangerous of these substances are benz(a)pyrene and benz(a)anthracene. However, many PAH derivatives with various functional groups have carcinogenic activity. The investigation of methods for the PAHs extraction from pyrolysis oils is necessary to develop an approach for their separation and isolation, contributing to additional purification of pyrolysis extracts.

The main methods for the analysis of pyrolysis oils are GC-MS, elemental analysis, NMR and IR spectroscopy. Deasphalting of pyrolysis oils with low molecular weight alkane (*n*-hexane or *n*-heptane) is widely used for the precipitation of resinous substances and asphaltenes, as well as extending the life of expensive equipment (for example, GC-MS). Currently, the question of the extraction of PAHs from pyrolysis oil during deasphalting has not been studied. It is likely that heavy multi-core aromatic hydrocarbons precipitate with asphaltenes and resinous substances.

The aim of the work is to study the distribution of PAHs between solid and liquid phases in the process of deasphalting of pyrolysis oil.

It was found that pyrolysis oil contains about 6% of resinous substances and asphaltenes. The process of deasphalting of pyrolysis oils by diluting it with *n*-hexane was studied. In terms of pyrolysis oil, about 1.8% of PAHs are precipitated together with asphaltenes and resinous substances from pyrolysis oil in the deasphalting stage.

It was found that the majority of multi-core aromatic hydrocarbons are selectively precipitated into the solid phaseduring deasphalting. The degree of PAHs extraction from pyrolysis oil for benzo(a)anthracene, benzo(b)fluorantene, benzo(k)fluorantene, benzo(a)pyrene, dibenz(a,h)anthracene and indeno(1,2,3-c,d)pyrene exceeds 99%. Thus, the larger the aromatic compound molecule, the greater its degree of co-precipitation from the liquid phase to the solid.

References

1. Themistoklis Sfetsas, Chrys aMichailof, Angelos Lappas, Qualitative and quantitative analysis of pyrolysis oil by gas chromatography with flame ionization detection and comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry Journal of Chromatography A **2011**, 1218, 3317.

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RADICAL-INDUCED CURING OF THE VINYL-CONTAINING POLYDIMETHYLSILOXANES USING CYCLIC ORGANOSILICON TRIPEROXIDES

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Peroxide curing is one of the most known methods in industry to obtain a silicone rubbers. It is appropriate to search for new curing agents, which are close in nature to PDMS. Organosilicon peroxides satisfy these requirements. The use of silicon-containing peroxides is made possible by the development of methods for their synthesis from inexpensive and widespread reagents. In this work, we report that cyclic organosilicon triperoxides (Figure 1) allow curing liquid linear PDMSs (mixtures of trivinyl-terminated PDMS and polymethylhydrosiloxane) leading to high-quality silicone rubbers. Thus, cyclic organosilicon triperoxides are found to be vinyl-selective initiators for free radical-induced curing at 100–180 °C of vinyl-containing PDMS and allow obtaining homogeneous transparent silicone rubbers. Thermal curing was monitored by curing time measurement, IR spectroscopy and the DSC method. The peroxide with the Me–Si–Me moiety is a much more active curing agent than other cyclic organosilicon triperoxides.The optimal concentrations of peroxides are around 0.09–0.22 mol/L.[1]

As a result, prepared silicone rubbers have improved mechanical properties: organosilicon triperoxides provide more than 200% elongation, and less than 1% compression sets. The obtained silicone rubbers showed pronounced antibacterial activity. This curing approach can be used to obtain silicone materials, in particular, for the food processing industry and medicine.[1]

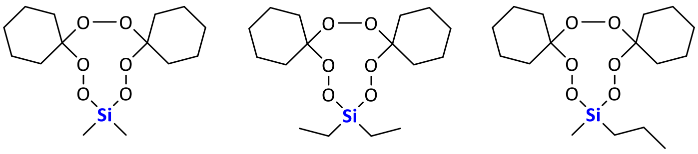

Figure 1. Cyclic organosilicon triperoxides.

Acknowledgments

Preparation of silicone compositions and assessment of their properties were supported by the Russian Foundation for Basic Research according to the research project no. 18-33-00769 mol_a. Measurements were performed at the Center for Magnetic Resonance, the Center for Chemical Analysis and Materials Research, the Center of Thermal Analysis, Calorimetry and the Chemistry Educational Centre and the Centre for Culture Collection of Microorganisms (all in Saint Petersburg State University).

References

1. K. V. Deriabin, I. A.Yaremenko, M. V.Chislov, F. Fleury, A. O. Terent’ev, R.M. Islamova, *New J. Chem.*, **2018**, *42*, 15006–15013.

SYNTHESIS OF POLYPORPHINE FILMS CONTAINING TRANSITION METAL ION BY ELECTROCHEMICAL METHOD

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Recent synthesis of Mg(II) porphine (MgP) based polymer films[1,2] has paved the route towards other representatives of this new electroactive polymer family, via the replacement of coordinated Mg(II) ions. Such transition-metal containing polyporphine materials might be prospective as catalysts of various processes, in particular for the oxygen reduction, owing to the presence of MeN_4 active centers. Polyporphines possess an important advantage, compared to other porphyrin-based polymers, as having the maximal possible content of this macrocycle due to the absence of polymer chains of a different nature or linking/substituent groups. Besides, polyporphines may be obtained in the "type II" form composed of polymer chains having a condensed structure owing to three single bonds between neighboring monomer units.

Conventional treatment of the free base polyporphine with a metal ion salt had allowed us to prepare for the first time polyporphines of cobalt and zinc[2]. However, this method suffers from potential contamination of the polymer by salt hydrolysis products, as well as from poor adhesion and poor stability of the electroactive layer, extended duration of the procedure and high temperature (requiring a sufficiently high thermal stability of the polymer and the support).

The goal of this work has been to develop an original alternative method of the metalation of polyporphine films, by replacing the thermal treatment with electrochemical polarization of the film in solution of the corresponding salt (salt of Co(II) or Mn(II) in this study).

First, films of Mg(II) polyporphine of type I, pMgP-I, have been prepared. Then, they were demetalated by ion exchange of Mg(II) by protons from CF3COOH solution, according to the method described in Ref.[2]. Subsequent metalation step has been performed via electrochemical treatment in acetonitrile solution of corresponding metal (II) perchlorate. Resulting films were characterized by means of electrochemical and spectral techniques.

Oxidative transformation of these metalated polyporphine films of type I, pMP-I (M = Co or Mn), results in condensed structure materials (metalated polyporphines of type II, pMP-II), characterized by combination of electrochemical and spectroscopic methods.

References

1. M.A. Vorotyntsev, D.V. Konev, C.H. Devillers et al, *Electrochim. Acta* **2010**, *55*, 6703.
2. D.V. Konev, C.H. Devillers, K.V. Lizgina et al, *Electrochim. Acta* **2014**, *122*, 3.

SILATRAN-CONTAINING BRANCHED POLYMERS AND THEIR EFFECT ON CROP GROWTH

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Silatranes are intra-complex organosilicon ethers of tris (2-hydroxyalkyl) amines, which are known for their unique biological properties[1]. These low-molecular compounds have attracted the attention of researchers in recent years; silatrans of various structures were produced, and the most important parameters influencing their physiological activity have been established[2]. Unfortunately, the vast majority of publications devoted to low molecular weight silatrans and studies of silane-containing polymers are practically absent.

In this work a number of branched polymers containing silatrane groups bonded to the polymer framework with an amide bond have been synthesized and investigated. Branched silatran-containing polymers are represented by structures based on polyethers and polyesters. The structure of the obtained silatrans-containing polymers was confirmed by NMR spectroscopy and gel permeation chromatography. The effect of silatran-containing polymers on plant growth was studied in the by a number of physiological parameters - germination, germination energy and seed growth force. When biotesting on examples of important crops, such as wheat (*Triticum aestivum L., var. "Spring Kharkov 46"*), rye (*Secale cereale L., var. "Winter Orlovskaya 9"*) and barley (*Hordeum vulgare, var. "Heather"*) It was shown that most of the samples studied silatran-containing polymers had a positive effect, consisting in an increase in seed germination rates compared to the control. It has been established that the structure of silatran-containing polymers has a significant effect on seed germination. An increase in the number of silatrane fragments in the polymer contributes to a significant increase in the effect exerted by it and leads to an increase in the germination rate, energy, and seed growth force. The size of the molecular weight and the topology of the branched polymer block of the macromolecule also influence the germination of seeds. It was found that with an increase in the molecular weight of the polymer, seed germination decreases, while their growth rate increases, however, no exact correlation was found between the detailed structure of the branched macromolecular block of silatrans-containing polymers and their effect on the physiological parameters of seed germination. The results presented in the study convincingly show for all of the studied agricultural crops a noticeable increase in the germination rate and growth rate observed in the presence of silatran-containing polymers.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (grant Nr 17-03-01089)

References

1. Voronkov M.G. Biological Activity of Silatranes// Topics in Current Chemistry. 1979. v. 84. p. 77-137.
2. Puri J.K., Singh R., Chahal V.K. Silatranes: a review on their synthesis, structure, reactivity and applications //Chem. Soc. Rev. 2011. v.40. p.1791–1840

SILATRANE-CONTAINING BIODEGRADABLE POLYMERIC NETWORKS

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The synthesis of silatranes initiated by M.G. Voronkov, is one of the important directions of modern chemistry of organoelement compounds. These intra-organosilicon esters have unique antiviral, anti-inflammatory, antitumor, antibacterial and antifungal properties, which implies the use of these substances in medicine, cosmetology and agriculture. The biological activity of these low molecular weight substances is well described in the literature. As in the case of most low molecular weight drugs, use of a silatrane-containing polymer system, which provides a slow release of silatran, can significantly increase its effectiveness. Aliphatic polyesters based on hydroxyacids - lactic, glycolic, etc., are one of the widely used biodegradable synthetic polymer for prolonged release formulations because of their high biocompatibility and the ability to decompose into non-toxic and easily excreted compounds.

In the present work, silatrane-containing polymer networks were synthesized by reaction of branched biodegradable polyesters with the polyacrylate polymers bearing anhydride moieties; Silatrane molecules were introduced chemically or physically into the polymer network. For synthesized polymers were performed kinetic studies of polymer hydrolysis and release of silatranes; It was found that these parameters depended mainly on the molecular weight of the branched polyester polymer, and ratio of polyerster to acrylic polymer. It was shown that synthesized silatrane-containing polymeric networks are suitable for creation of biomedical polymer systems with preset silatrane release profile.

Acknowledgments

This work was supported by Russian Foundation for Basic Research (grant Nr 17-03-01089)

SPECTRAL AND STRUCTURAL PROPERTIES MODIFICATION OF POLY(p-XYLYLENE)−CADMIUM SULPHIDE NANOCOMPOSITES ON DEPENDENCE OF FILLER CONTENT AND FILM THICKNESS

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Effect of filler concentration ($C \approx 0$ -100 vol.%) and film thickness ($d \approx 0.02$, 0.2, 0.5 and 1.0 µm) on spectral (optical and IR absorption spectra) properties and surface morphology of thin nanocomposite films, based on poly(*p*-xylylene) and cadmium sulphide (PPX - CdS), was studied. The PPX-CdS films were prepared by low-temperature vapor deposition polimerization on quartz and silicon substrates. Non-monotonic dependence of the absorption spectrum red shift on the filler concentration was revealed. The red shift of the spectrum reaches maximum at some critical C_0 filler concentration. It was observed that C_0 critical concentration increases with the film thickness and equals $C_0 \approx 11$, 30, 50 vol.% for $d \sim 0.02$, 0.5, 1 µm, correspondingly. The average size of nanoparticles was evaluated by analysis of the absorption spectra (via estimation of exciton peak wavelength). It was found the shift of the absorption spectra is determined by nanoparticles' size. IR-spectra (500 - 4000 cm^{-1}) variations were studied for the PPX-CdS films ($d \sim 0.5$ and 1 µm). As filler concentration increases the low-frequency shifts of C-H out-of-plane deformation vibrations of aromatic ring and the intensity change of PPX characteristic bands were observed. The additional IR-bands were revealed in the ranges of 1000-1800 cm^{-1} and 3100-3600 cm^{-1}. These bands caused by formation of complex compounds with sulpho (SO_4), hydroxyl (OH) and carboxylate (COO^-) groups and structure modification of aromatic ring in the PPX-CdS films. Atomic force microscopy reveals effect of the filler content on surface morphology and their surface roughness of the polymer matrix in the nanocomposite films. The size distribution of the polymeric grains was evaluated. The most significant changes in the absorption spectra and surface morpology of the composites with variation of filler content were observed in the range of 0 - C_0. The absorption spectra are similar for the films with filler concentration above C_0, which can be attributed to almost equal nanopartiles' size in these nanocomposites. The correlation between changes of the matrix morphology and filler optical properties was established.

NEW OLIGO(DIMETHYL)SILANES WITH 1,7-BIS(METHYL)-M-CARBORANE UNITS

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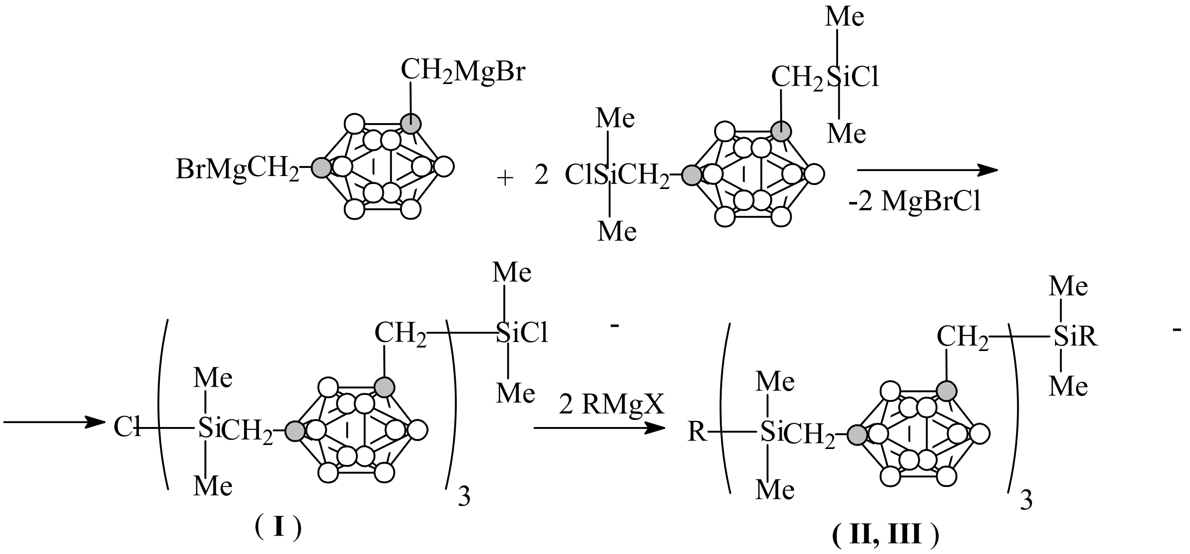
A new type of carboranesiliconeorganooligomers – oligo(dimethyl)silanes with 1,7-bis(methyl)-m-carborane units, that do not contain oxygen atoms in the macromolecular chain, was obtained by the exchange reaction between 1,7-bis(bromomagnesiummethyl)-m-carborane and an excess of 1,7-bis[chloro(dimethyl)silylmethyl]-m-carborane in the ether medium at the boiling point of the solvent (scheme)



(I)

(II, III)

where R=CH_2Ph (**II**), $CH_2CB_{10}H_{10}CH$ (**III**); X = Cl, Br

The composition and properties of oligomer (**I**) are established by elemental analysis, IR and NMR spectroscopy. The oligomer (I) is a highly viscous substance with a molecular weight of 815, soluble in ether, benzene, toluene, chloroform. In the reaction of the oligomer (**I**) with benzylmagnesium chloride and bromomagnesiummethyl-m-carborane under the same synthesis conditions, oligomers with bensyl(dimethyl)silyl- and m-carboranylmethyl(dimethyl)silyl terminal groups were obtained (scheme). Oligomers (**II**) and (**III**) are liquid highly viscous products with molecular weights of 930 and 1070, respectively, soluble in most organic solvents. They are highly heat-resistant substances with a temperature of the intense weight loss in inert atmosphere -above 500^0C and in air above 400^0C in both cases

Acknowledgments

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CONFORMATION AND FLEXIBILITY OF POLY (4-VINYLPYRIDINE) AT THE HYDROPHOBIC CORE – HYDROPHILIC CORONA INTERFACE

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The present contribution is devoted to the study of impact of the volume of localization of polymer poly(4-vinylpyridine) (P4VP) on its conformation and flexibility by small-angle neutron scattering (SANS) and nuclear magnetic resonance (^{1}H NMR).

Two different states of polymer were investigated: polymer injected into the wormlike micelles of anionic surfactant potassium oleate and its diluted solution in dimethyl sulfoxide (DMSO), known to be good solvent for P4VP.

To obtain SANS curves from P4VP injected into the wormlike micelles separately from molecules of potassium oleate mixture of water and deuterium oxide (D_2O) was used to match the scattering from the surfactant. Deuterated dimethyl sulfoxide (dDMSO) was used instead of DMSO to increase the scattering intensity from P4VP in its diluted solution.

For the polymer inside the micelleslog-log scattering curves in the low-Q region demonstrate the slope close to -2, which is typical for macromolecules under θ-conditions suggesting that macromolecules of P4VPin this state have the conformation of a Gaussian coil. The same slope for the polymer solubilized in dDMSO was close to -1.6, that indicates the good solvent conditions for P4VP. Dependence log(IQ) on Q^2(Kratky plot) was used to obtain the values of persistent length of polymer in both cases. It was shown, that persistence length of polymer embedded into wormlike micelles at least 4 times larger than of polymer in dDMSO.

To receive the information about the area of localization of P4VP inside the micelles was ^{1}H NMR applied. From comparison of ^{1}H NMR spectra of potassium oleate in the polymer-free and polymer-loaded micelles followed, that peaks most affected by addition of polymer belong to two methylene groups closest to the surfactant head (16th and 17th), indicating that the polymer is located inside the thin layer at the interface between the hydrophobic core and hydrophilic corona of the micelles.

Thus, it was demonstrated that injection of P4VP into the reduced volume at the core-corona interface of wormlike micelles of the anionic surfactant potassium oleate leads to collapse of polymeric chain and loss of the flexibility.

Acknowledgments

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INVESTIGATION OF IMPACT OF NANOSIZED SiO_2 ON ABRASION RESISTANCE OF TRANSPARENT SILICONE COATINGS

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One trend of the modern world is that nanotechnologies are being introduced in the wider fields of science and production. In particular, nanotechnologies have their place in the paint industry, the essence of which is the introduction of nanoobjects into the composition of the polymer matrix as additives to impart the necessary properties to coatings.[1,2]

The aim of the work was to study the effect of nanoscale silica on abrasion resistance of transparent silicone resin lacquer coatings. Optimal ratio of used substances is determined, at which improvement of abrasion resistance of coatings without change of their optical characteristics is achieved.

For testing, the coating was applied by pneumatic spraying to glass plates. Abrasion resistance of the coatings was determined using a Taber 5155 abrasive tester and analytical weights. The light transmission coefficient of the coatings was determined using a Proscan MC122 spectrophotometer.

The results of the tests showed an increase in abrasion resistance of organosilicon coatings when silicon dioxide nanoparticles are added to their composition up to 3% content and its decrease when this value is exceeded. The transparency of the coatings remains virtually unchanged up to 8% concentration of nanoparticles.

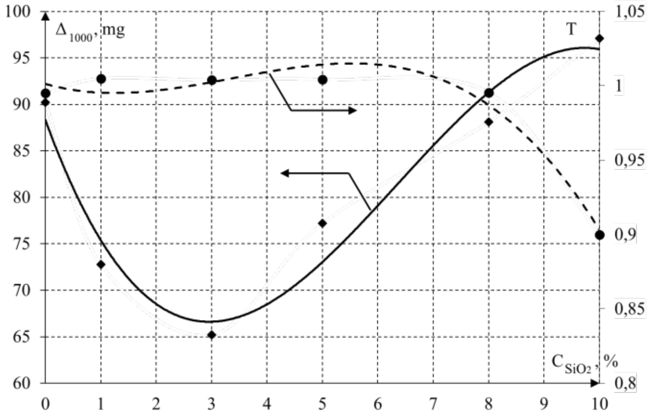

Figure 1. Weight loss after 1000 revolutions (Δ1000, mg) and light transmission coefficient (T) of silicone coatings depending on the content of silicon dioxide nanoparticles

References

1. T.R. Vakhitov, et al., *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* 473.2199 (**2017**): 20160827
2. O.N. Gadomsky, *Journal of Experimental and Theoretical Physics.* 127.6 (**2018**): 994-1002.

LUMINESCENCE OF IMPREGNATED LASER-INDUCED STRUCTURES IN POLYBENZIMIDAZOLE FILMS

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Polymeric materials with embedded metal complex compounds (MCC) of trivalent rare-earth ions (REI) are of great interest for use in optoelectronics, photovoltaics, biomedical research and sensors.[1,2] In our previous work,[3] the possibility of the formation of a structure of Ag nanoparticles on the surface of poly-2,2'-*p*-oxydiphenylene-5,5'-bis-benzimidazole (OPBI) films under exposition of continuous laser radiation with a wavelength 405 nm. In the case of an OPBI-based material, the creation of laser-induced foam-like structures with their subsequent functionalization with luminescent compounds to enhance the initial luminescent characteristics opens up possibilities for their use not only in the sensors, but also in the field of polymer optoelectronics, in the creation of protective markings for various products, etc.

The aim of this work is to develop approaches to the creation of new photoluminescent materials and to study the spectral properties of highly porous polymer structures obtained on the basis of OPBI matrices with organometallic complexes of trivalent europium impregnated into their bulk. The enhancement of luminescent properties is confirmed by X-ray microanalysis and photoluminescent spectra before and after impregnation of the initial and structured polymer films.

Acknowledgments

The reported study was funded by RFBR according to the research project No 18-33-00645 mol_a

References

1. Q.G. Meng, L.S. Fu, S.B. Wang, H.J. Zhang, H.R. Li, X.H. Chuai, Y.H. Li, S.Y. Zh, *Thin Solid Films* **2001**, *388*, 87.
2. A.G. Mirochnik, N.V. Petrochenkova, A.S. Shishov, B.V. Bukvetskii, T.B. Emelina, A.A. Sergeev, S.S. Voznesenskii, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2016**, *155*, 111.
3. A.A. Akovantseva, N.A. Aksenova, T.S. Zarkhina, L.I. Krotova, N.V. Minaev, A.O. Rybaltovskii, B.C. Kholkhoev, I.A. Farion, V.I. Yusupov, V.F. Burdukovskii, V.N. Bagratashvili, P.S. Timashev, Russ. J. Appl. Chem **2017**, *90*, 84.

POLYPHENYLENE AND POLYAZOMETHYNE BASED ON 1,2-BIS-(4'-ACETYLBENZYL)-O-CARBORANE

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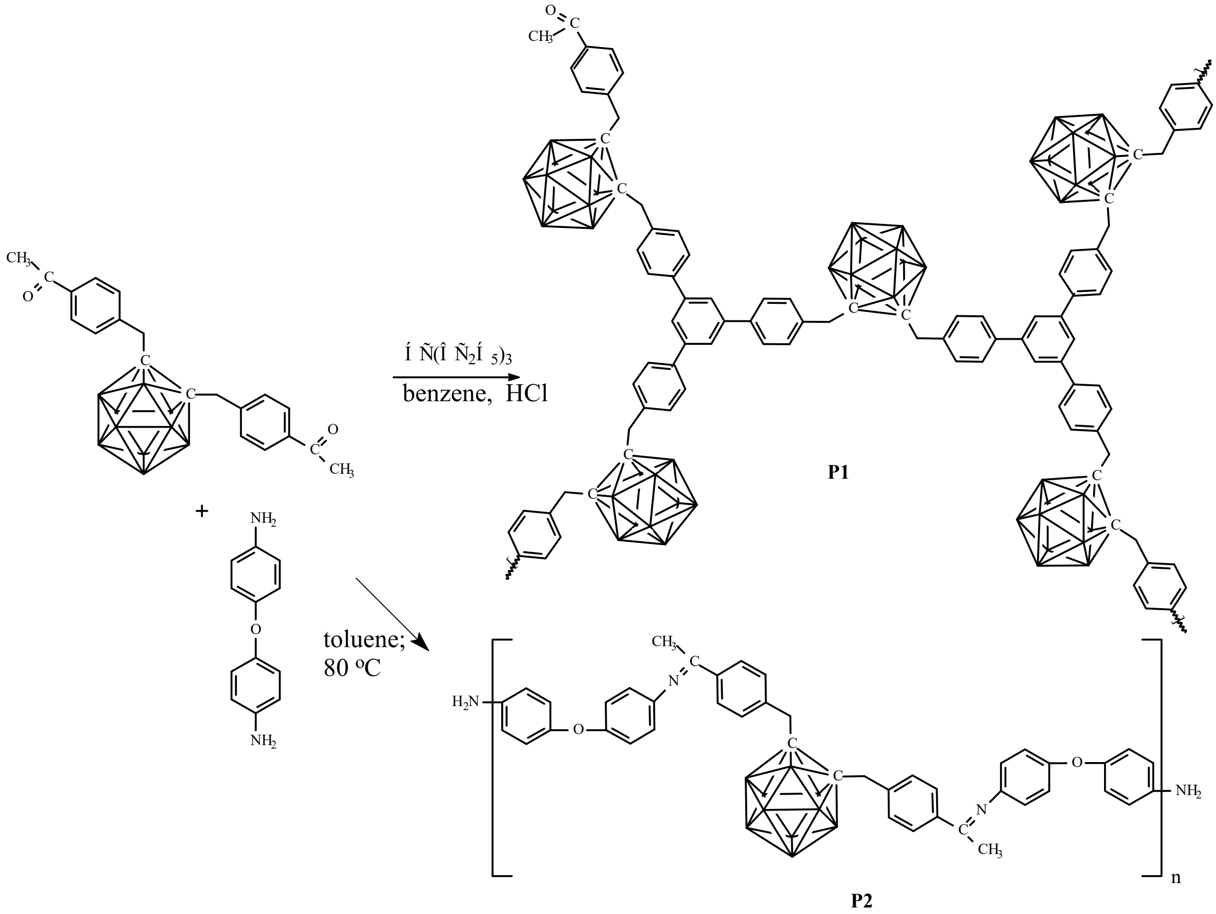
Luminescent materials consisting of boron clusters have recently been of great interest [1-3]. In these studies, luminescent organo-inorganic conjugated systems based on electron-withdrawing o-carboranes associated with electron-donating π-conjugated groups were developed as new optoelectronic materials. Based on 1,2-bis-(4'-acetylbenzyl)-o-carborane, polymers — polyphenylene (P1) and polyazamethine (P2) were synthesized (Scheme 1).



Scheme 1.

A dynamic thermogravimetric analysis (TGA) of polymers with o-carborane fragments in the chain was performed in air. For polyphenylene, an increase in weight after 400°C is observed due to the oxidation of the carborate core.

References

1. J. Mei, Y. Hong, J. W. Y. Lam, A. Qin, Y. Tang, B. Z. Tang, Adv. Mater. **2014**, 26, 5429.
2. K. Kokado, Y. Chujo. J. Org. Chem. **2011**, 76, 316.
3. R. Furue, T. Nishimoto, I. S. Park, J. Lee, T.Yasuda, Angew. Chem. Int. Ed. **2016**, 55, 7171.

SYNTHESIS OF POLY(VINYLIDENE FLUORIDE-CO-CHLOROTRIFLUOROETHYLENE)-GRAFTED-POLY(ACRYLONITRILE) POLYMERS FOR FERROELECTRIC ORGANIC FIELD-EFFECT TRANSISTORS

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Ferroelectric polymers have been the subject of intensive research during past fifty years [1-6]. It has been shown that the most perspective ferroelectric polymer applied for wide range of applications was poly(vinylidene fluoride) (PVDF) [3-6].

In fact, PVDF is typically crystalline polymer having five crystal polymorphs named α, β, γ, δ, ε, where the β phase is more significant due to it's piezo- and ferroelectric properties [2]. It is well known that the technique of obtaining PVDF films from solution or melt leads to producing a polymer with α phase. The polar crystalline phase β can be obtained by post treatment of the films using straining, stretching or quenching techniques, which is quite complicated. In order to reverse the difficulties of phase β production - copolymers based on PVDF can be applied.

In this work, polyacrylonitrile (PAN) was grafted onto the side chain of vinylidene fluoride-co-chlorotrifluoroethylene copolymers through atom transfer radical polymerization (ATRP). The content of PAN was determined by the method of NMR spectroscopy. The influence of various synthetic parameters on properties of polymers obtained such as solubility and content of incorporated PAN segments was studied.

Acknowledgments

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References

1. B. Ameduri, Chem. Rev., 2009, 109, 6632-6686.
2. B. Stadlober, M. Zirkl, M. Irimia-Vladu, Chem. Soc. Rev., 2019, 48, 1787-1825.
3. X. Zhang, Ch. Zhang, Yu. Lin, P. Hu, Ya. Shen, K. Wang, S. Meng, Yu. Chai, X. Dai, X. Liu, Yu. Liu, X. Mo, C. Cao, S. Li, X. Deng, L. Chen, ACS Nano, 2016, 10, 7279-7286.
4. X. Han, X. Chen, X. Tang, Yu. Chen, J. Liu, Q. Shen, Adv. Funct. Mat., 2016 26, 3640-3648.
5. X. Chen, X. Liu, S. Lui, Yu. Cui, X. Chen, H. Ge, Q. Shen, Appl. Phys. Letters, 2013, 102, 063103-1-063103-4.
6. Z. Zhang, T. C. M. Chung, Macromolecules, 2007, 40, 783-785.

COPOLYMERS BASED ON UNDECENOIC ACID DIAMIDES AND POLYDIMETHYLSILOXANE

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Siloxane polymers are of great importance, due to which they have unique characteristics, namely a very low glass transition temperature (Tg), an order of 120 ° C, good thermal and oxidative stability, high gas permeability, excellent dielectric properties and physiological inertness or biocompatibility, as well easy modification of these polymers by various privileged groups.

PA are widely used due to their excellent properties such as high Young's modulus, mechanical strength, relatively high melting points and heat resistance, oxidative stability, abrasion resistance, as well as chemical inertness, outstanding resistance to destruction by high-energy particles, γ-radiation and atmospheric corrosion [1].

The obtained by us copolymers based on amide and siloxane fragments of a linear structure demonstrate interesting morphological, thermal, and mechanical properties, which is apparently associated with strong hydrogen interactions between rigid amide segments and a significant difference between the solubility parameters of PDMS and the amide group.

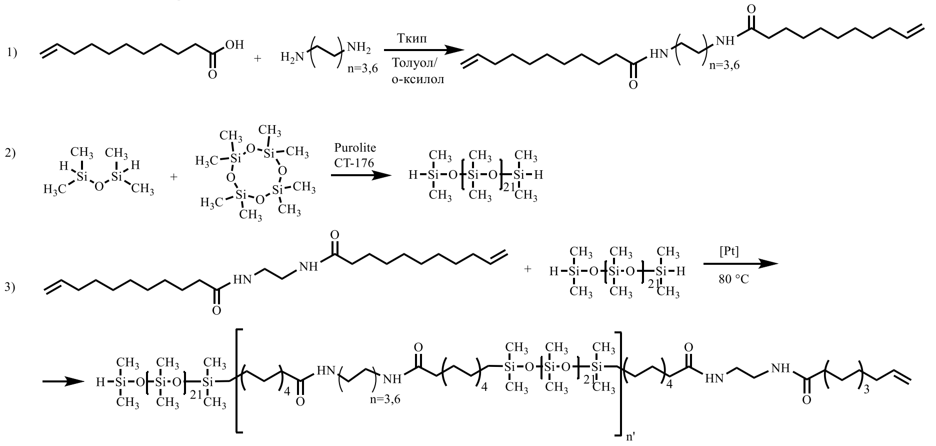

Figure 1. Synthesis of copolymers of N, N’-hexamethylenediundecenamide,

N, N’-dodecamethylenedienedecenamide and α, ω-dihydropolydimethylsiloxane

References

1. Zhang, Q.; Liu, H.; Chen, X.; Zhan, X.; Chen, F. Inc. J. Appl. Polym. Sci. 2015, 132, 41725

METAL-FREE PHOTOCONTROLLED POLYMERIZATION OF VINYL MONOMERS USING PHENOXAZINE DERIVATIVE SYSTEMS

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The synthesis of high molecular weight compounds by Atom Transfer Radical Polymerization (ATRP) is the actual direction of modern synthetic polymer chemistry. This method is based on the use of transition metal complexes in the polymerization stages. Despite the significant advantages of this technique, its drawback is the presence of metal residues in the polymer structure, which limits the use of the obtaining materials in electronics and medicine. The method of photocontrolled polymerization, based on the use of organic catalysts (Metal - Free ATRP), allows overcoming the challenge of metal contamination in traditional ATRP systems.[1]

One of the classes of organic compounds proposed for the Metal - Free ATRP process is phenoxazines. This research is devoted to the study of polymerization of vinyl monomers under Metal - Free ATRP conditions using phenoxazine derivatives as organic catalysts.[2]The 10-aryl derivatives were prepared by heating phenoxazine and an aryl iodide with palladium compounds as catalysts according to Figure 1.The process was carried out in a degassed ampoule with heating to 120 °C and stirring for 8 hours.

The polymerization was carried out in degassed ampoules at room temperature. N,N-dimethylformamide and N,N-dimethylacetamide were selected as solvents. Ethyl-2-bromoisobutyrate (EBiB) was used as an initiator. The molar ratio of reagents for all experiments was kept constant – monomer : EBiB : catalyst = 100 : 1 : 0.1. Irradiation with UV light was carried out using radiation sources with wavelengths of 360 and 400 nm. Our research has shown the possibility of the polymerization process of a wide range of monomers in these conditions. The polymerization is accompanied by an increase in molecular weight in accordance with the Metal-Free ATRP mechanism. The influence of the radiation wavelength and solvent on the polymerization rate and polydispersity of the samples is investigated.

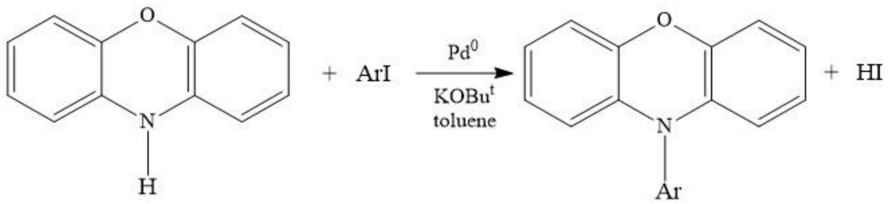

Figure 1. Synthesis of N-aryl phenoxazine catalysts

Acknowledgments

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References

1. N. J. Treat, H. Sprafke, J. W. Kramer, P. G. Clark, B. E. Barton, J. Read de Alaniz, B. P. Fors, C. J. Hawker, *J. Am. Chem. Soc.* **2014**, *136*, 16096.
2. R.M. Pearson, C.H. Lim, B.G. McCarthy, C.B. Musgrave, G.M. Miyake, *J. Am. Chem. Soc.* **2016**, *138*, 11399.

INFLUENCE OFAMINO ACIDS OF THE H2N(CH2) nCOOH SERIES ON THE FORMATION AND PROPERTIES OF POLY(VINYL ALCOHOL) CRYOGELS

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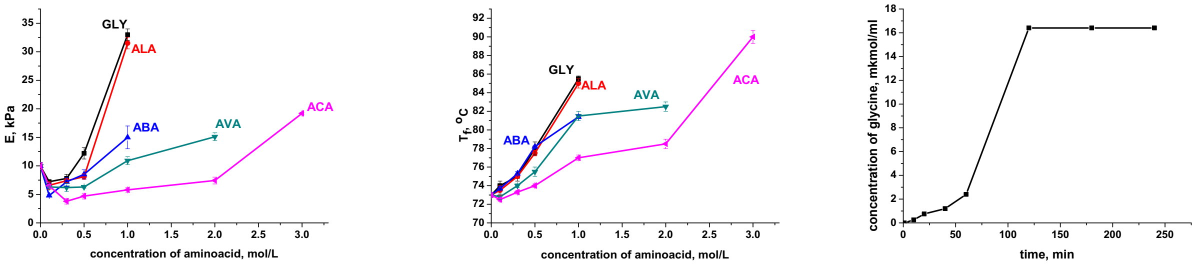
Poly(vinyl alcohol) cryogels are the noncovalent macroporous gels formed as a result of freeze-thaw processing of concentrated PVA solutions. PVA cryogels are widely used as biomedical materials due to their mechanical durability, biocompatibility and also viscoelastic properties similar to the soft biological tissues. PVA cryogels have been applied as functional materials in clinical application for dialysis membranes, wound dressing, artificial skin, cardiovascular devices, drug delivery systems and spine disc replacement[1].

The properties and microstructure of PVA cryogels depend on the characteristics of the gel-forming polymer itself, its concentration in the feed solution, presence or absence of soluble and insoluble (fillers) additives, as well as on the conditions of cryogenic processing[2]. In this regard, diverse chaotropic and kosmotropic additives exert rather pronounced influence, deteriorative or enhancing, respectively, on the properties of PVA cryogels. Therefore, such solutes can be used for adjusting the matrices' characteristics to the desired level.

In this study the PVA cryogels have been prepared from the aqueous solutions of the polymer that also contained the additives of one of the series of amino acids that are differed by the amount of methylene units between the amino- and carboxylic groups. Rheological and thermal properties of the resultant cryogels have been measured and compared (Figs. ***a*** and ***b***). It was found out that the length of the oligomethylene chain affected the mechanical and thermal properties in the following way: the longer the chain was, the weaker cryogels were formed. In turn, it was also demonstrated that similar gel matrices can perform as the efficient depot-forms of the above-indicated solutes (Fig. ***c***), i.e. the spatial polymeric network of the carrier did not interfere the diffusion of the amino acids from such "model drug release system".



(***a***) (***b***) (***c***)

Influence of the added amino acid concentration on the elastic modulus (***a***) and fusion temperature (***b***) of the PVA cryogels formed in the presence of the following solutes: glycine (GLY), β-alanine (ALA), γ-aminobutiric acid (ABA), aminovaleric acid (AVA), aminocaproic acid (ACA), as well as the dynamic of glycine release from the respective cryogel (***c***).

References

1. V.I. Lozinsky, *Russ. Chem. Revs.***1998**, 67, 573.
2. W. Wan., A.D. Bannerman, L. Yang, H. Mak, *Adv. Polym. Sci*. **2014**, 263, 283.

ATOM TRANSFER COUPLING REACTIONS PERFORMED WITH RADICAL TRAPS OF VARIOUS STRUCTURE

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Atom transfer radical polymerization (ATRP) has been widely implemented to synthesize a myriad of polymers with predictable molecular weights, low dispersity (Đ), precise functionality, and complex architecture. Typically, atom transfer reactions rely on a redox-active, ligand-bound transition metal catalyst, typically Cu(I) to transfer the halogen species from the alkyl halide chain end to itself, allowing for propagation to occur (ATRP) or termination (ATRC). Most promising areas in this case are radical trap-assisted Atom Transfer Radical Coupling (RTA-ATRC reactions) [1, 2].

Monobrominated polystyrene (PSBr) was prepared by ATRP in the presence of the CuBr catalyst and the initiator (1-bromethyl)benzene for polystyrene. The resulting polymer was characterized by a low molecular weight (MW) – 2300 Da and Đ=1.3. Based on the obtained polymer with low molecular weight, we carried out the coupling reactions of polymer chains by the ATRC and RTA-ATRC methods in the presence of mononitrones (C-phenyl-N-tert-butylnitrone, C,N-diphenylnitrone, 2-(benzylideneamino)-2-methyl-1-phenylpropanol-1-N-oxide), nitroso compounds (2-methyl-2-nitrosopropane, nitrosodurene, 2,4,6-tribromonitrosobenzene) and dinitrones (N,N-dimethylglyoxal dinitrone (MDN), N,N-ditert.-butylglyoxal dinitrone (BDN) and N,N-diphenylglyoxal dinitrone (PDN)).

The results obtained via gel permeation chromatography have clearly shown, that the addition of the aromatic nitroso compounds in high concentrations does not result in a doubling of molecular weight. The nature of the radical trap plays a role in halting the reaction at the end-capped nitroxide polymer, rather than undergoing dimerization via atom transfer radical coupling-type pathways.

The performed studies demonstrate that the proposed mono- and dinitrones, exhibit high efficiency in combination reactions regardless of the structure, while the degree of combination is significantly higher in contrast to the ATRC process. The degree of combination depending on structure nitrones can reach a value from 0.5 to 0.96.

It is shown that the activity of dinitrones in the combination reactions is proportional to the steric hindrance created by the substitutes at the dinitron group. So the activity in the reactions of the combination dinitrones can be arranged in the following series: MDN>BDN>PDN, because exactly in this order the degree of combination is reduced. Thus, the developed RTA-ATRC technology allows obtaining polymers with various molecular weights and is promising for the implementation in macromolecular design.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project No. 17-03-00498).

References

1. K.E. Heiler, C.W. Pan, A. J. Heiler, J. P. Wu, E. S. Tillman, *Macromol. Chem. Phys.* **2018**, *219*, 1800171.
2. K. Xia, A. J. Rubaie, B. P. Johnson, S. A. Parker, E.S. Tillman, J*. Polym. Science, Part A: Polym. Chem.* **2019**, (accepted for print)

THERMOGRAVIMETRIC ANALYSIS OF THERMAL STABILITY OF POLYMERS SYNTHESIZED IN THE PRESENCE OF NON-TRANSITION AND TRANSITION METALS COMPLEXES WITH REDOX-ACTIVE LIGANDS

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Nowadays, production, processing, and modification of polymers are important branches of the chemical industry. The area of polymer application is very extensive. Polymers are used in electronics, medicine, transport, construction, aviation, in production of textiles, glue, tapes, paints, etc.

In last decades a wide range of metallocomplexes was offered for polymerization processes, allowing for the facile synthesis of specific macromolecular architectures with excellent control over the chemical and physical properties. In this paper the different complexes of non-transition (Sn) and transition (Co) metals with redox-active ligands (Fig. 1, 2) in the radical polymerization of methyl methacrylate (MMA), styrene (St) and their block copolymers were investigated. The aim of our work was to study the influence of polymerization conditions on polymethyl methacrylate (PMMA) and polystyrene (PS) thermal stability.

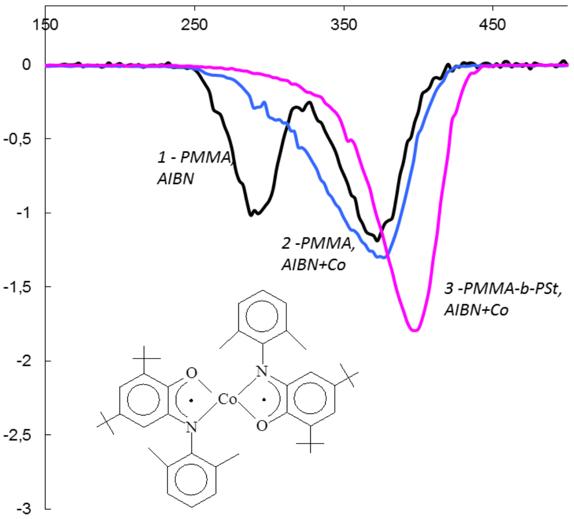

Figure 1. DTG curves of PMMA and block copolymer

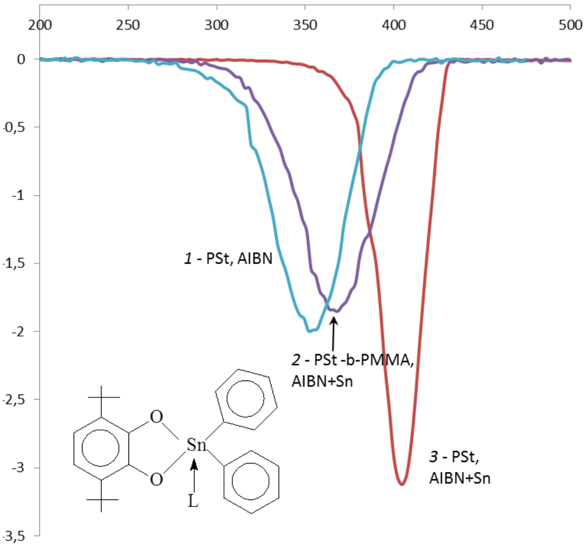

Figure 2. DTG curves of PSt and block copolymer

The polymer degradation characteristics were determined by thermogravimetry (TG) using a Thermal Analysis TG209F1 (Netzsch Geratebau, Germany) instrument. Measurements were carried out under argon atmosphere, in the temperature range from 25 to 550 C, at a heating rate of 10 C× min^{-1}.DTG curves are shown in Fig. 1 and 2. It was worth noticing that decomposition of samples was completed at 450 C. The increase of polymers thermal stability in the presence of metals complexes can be explained by controlled mechanism of polymerization in their presence and absence of unsaturated vinyl ends in the polymer chains.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project No. 17-03-00498).

NOVEL CONJUGATED POLYMERS BASED ON DITHIENOPHTALIMIDE DERIVATIVES FOR APPLICATION IN NON-FULLERENE SOLAR CELLS

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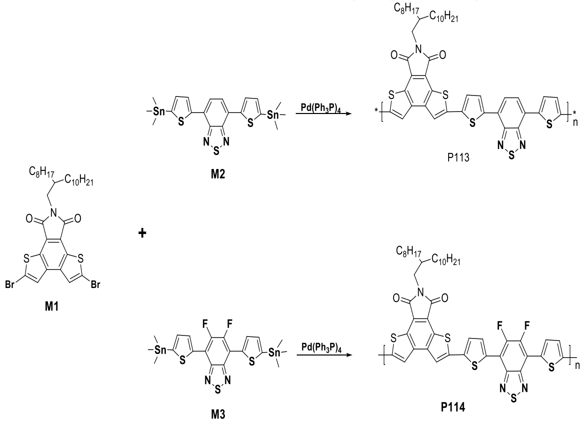
The fast evolution of the narrow bandgap non-fullerene acceptors requires the new conjugated wide bandgap polymers for the use of non-fullerene polymer solar cells. In this work, we have designed two new wide bandgap D-A conjugated polymers with same donor unit i.e. Dithienophtalimide (DTP) and different acceptor units i.e. benzodiathiadiazole (BT) and fluorinated benzothiadiazole (f-BT) denoted as P113 and P114 (Scheme 1) to investigate the effect of fluorination on photovoltaic properties of non-fullerene polymer solar cells. We found that with the incorporation of fluorine atom into the benzothiadizole acceptor unit increases the absorption coefficients and the relative dielectric constant. The increase in the photoluminescence quenching, reduction in charge recombination loss and improvement in the charge carrier life are observed for the P114. These all factors resulted in dramatically improved the power conversion efficiency of P114:ITIC-m based polymer solar cell to 10.69 %with small energy loss of 0.56 eV as compared to P113 counterpart (8.74 % with energy loss of 0.69 eV) under identical conditions. The low energy loss is beneficial to overcome the trade-off between open circuit voltage and short circuit current (Figure 1).



Scheme 1. Synthetic routes of the copolymers.

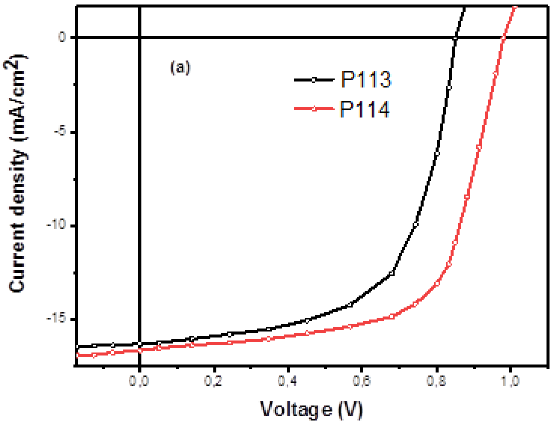


Figure 1. Current-voltage characteristics

Acknowledgments

This work was supported by RFBR (№18-53-80066, №18-53-45028, №18-29-23004, №18-53-53031) and RAS Project P14. NMR studies, elemental analysis were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

FORMATION OF 3D-STRUCTURES BASED ON AROMATIC HETEROCHAIN POLYMERS BY LASER STEREOLITHOGRAPHY

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At present, additive technologies are perspective ones from the point of view of a design of wares of complex shape. One of types of these technologies is laser stereolithography, which permits forming complex shape wares by means of the direct impact of a focused laser radiation of high intensity on photocurable polymers or oligomers. The problem of the search of new photopolymerizable systems, which are able to form non-fused and insoluble products with a valuable set of properties during a crossliking process, is actual one.

The purpose of the presented work is a solution of the fundamental problem of the development of new reactive systems, which are able to form three-dimensional network structure with high thermal, heat, abrasion, chemical and radiation resistance under the action of laser radiation.

Based on the results obtained in the study of model compounds, various oligomeric benzotriazolilmaleimids capable to form insoluble cross-linked three-dimensional structures as the result of the thermal or photopolymerization across the terminal double bonds were synthesized. Along with bis-maleimide oligomers, the synthesis of series of aromatic oligoamides and oligoimides with terminal (meth)acrylamide groups was carried out. The structure and composition of the oligomers were confirmed by IR, NMR spectroscopy, and elemental analysis. The resulting oligomers are readily soluble in various organic solvents, including active unsaturated solvents (N-vinyl pyrrolidone and N,N-dimethylacrylamide), forming a high concentration solution (up to 50%). Obtained oligomers were used for fabrication of photosensitive systems for obtaining of 3D-structures on stereolithography installation. Approaches to control modifying of parameters of cross-linked matrix by changing the intensity and frequency of the laser pulses were worked out. Using thermal methods of analysis, it has been shown that the decomposition temperature of the obtained structures is 400-450°C, which indicates their high thermal stability. Thus, it has been shown that the proposed synthetic approaches to the preparation of heat-resistant oligomers allow their further use for fabrication complex products, which could be used in critical areas of industry, by methods of laser additive technology.

Acknowledgments

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STATE DIAGRAM OF DENSELY GRAFTED AMPHIPHILIC HOMOPOLYMER BRUSHES: GRAFTING DENSITY VS SOLVENT QUALITY

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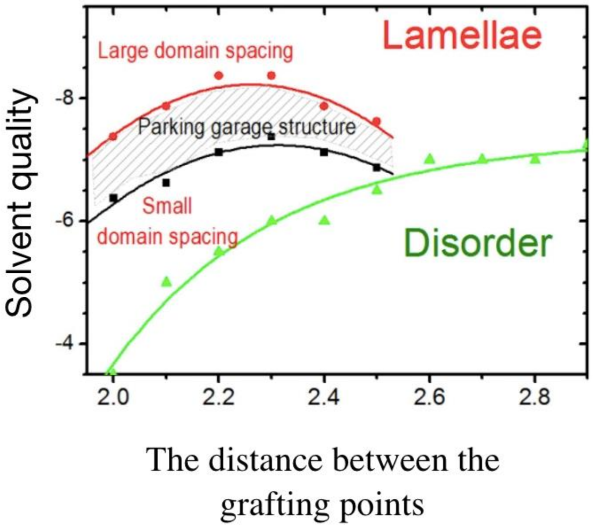
The report presents the research of polymer layers of amphiphilic homopolymers densely grafted to a flat surface at the nodes of a square lattice. Monomer units of these homopolymers containing groups with different affinities. It was demonstrated that in a selective solvent such layers form lamellas with different period depending on the grafting density and the solvent quality.

The results are summarized as a state diagram in the variables “the distance between grafting points” and “the solvent quality”. There are several regions on the diagram: disorder, region of stability of lamellae, lamellae with significantly different periods and a transitional area with a parking garage structure. The diagram is built by calculating the layer-by-layer structure factor and the angle of inclination of the lamellae in the layer. The calculations were executed for commensurate cell sizes, determined by a special procedure for each grafting density.



Acknowledgments

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References

1. A. A. Lazutin, A.N. Kosmachev and V. V. Vasilevskaya, J. Chem. Phys. **2019** *(accepted)*

NEW HYBRID MATERIALS BASED ON FISH COLLAGEN WITH THE INCLUSION OF POLY BUTYL ACRYLATE

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In addition, much attention is now paid to the creation of materials with fish collagen[1], which has a number of advantages over the analog of animal origin. For example, it has a greater structural similarity with human collagen, providing a higher level of biocompatibility.[2]

The aim of the scientific work was to synthesize of a stable under normal conditions grafted collagen copolymer with butyl acrylate (BA) using such initiators as azoisobutyric acid dinitrile (AAD) and triethylboran (TEB) – oxygen complex.

Copolymers were based on a fish collagen, which was extracted like a colloidal solution of fish collagen in 3% acetic acid using the method, developed in our laboratory[3], and then was characterized by a number of parameters. The synthesis was carried out at 50 ° C in an argon atmosphere with vigorous stirring of a mixture of collagen with BA with initiator for a certain time. After stirring, the reaction mixture exfoliated.BA homopolymer in the organic phase was determined by the method of IR-spectroscopy.

Using the methods of the gravimetric analysis, IR-spectroscopy and gel permeation chromatography it was shown that collagen-butyl acrylate copolymers were located in aqueous solution (fig.1).

The research was conducted using equipment in Collective use center “New materials and resource-saving technologies” Research Institute of chemistry UNN.

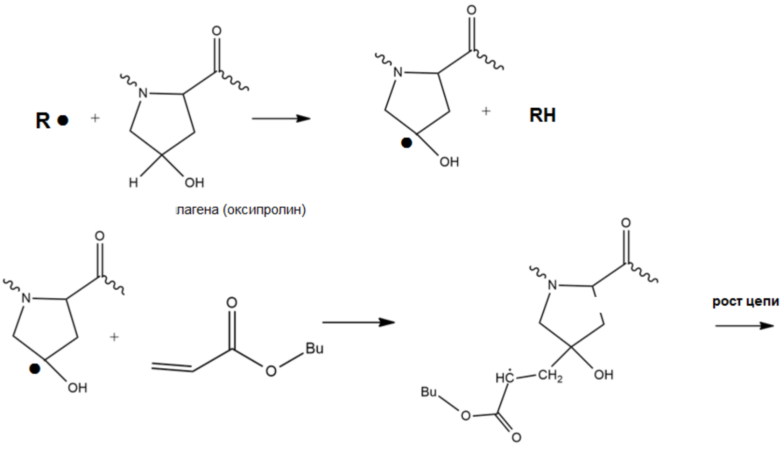

Figure. 1. A scheme of the synthesis

References

1. L.L. Semenycheva, N.B. Valetova, Y.O. Chasova. Molecular mass parameters of collagen from different raw materials and the dynamics of their change during enzymatic hydrolysis of pancreatin. // N.N.: UNN, 2018, 169p.
2. DelaPuenteP., LudeñaD. Cell culture in autologous fibrin scaffolds for applications in tissue engineering // Experimental Cell Research. 2014. V. 322. N 1. P.1–11.
3. patent 2567171 Russian Federation, IPC C14C1 / 08, C07K14 / 78, C08H1 / 06. A method of obtaining a vinegar dispersion of high molecular weight fish collagen. / Semenicheva L.L., Kuznetsova Yu.L. Geraskina E.V. Astanina M.V .; patent holder of LLC “Quality of Life Systems”. - No. 2014140300; declared 10/06/2014; publ. 10/15/15. - 16 p.

WETTING PROPERTIES OF FLUORINATED POLYSILOXANES COATINGS BASED ON DIMER OF HEXAFLUOROPROPYLENE

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Polysiloxanes containing perfluorinated side groups are of great interest in surface hydrophobization due to their low surface energy: they show high wetting angles with water, high heat resistance, chemical inertness and insolubility in most organic solvents. However, perfluorinated polysiloxanes can be obtained in different conditions, which affect their wetting properties.

The goal of this work was to investigate wetting properties of perfluorinated di- and trifunctional polysiloxanes obtained in different conditions. Conditions varied in reagents used, active media composition, and acid-monomer ratio.

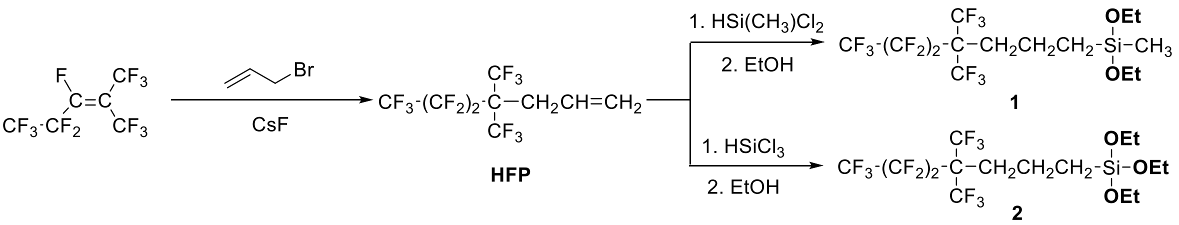

Figure 1. Synthesis of two- and trifunctional alkoxysilanes, containing branched perfluorohexyl substituent

Further, based on them, linear and branched polysiloxane polymers were synthesized under the active medium conditions or in the presence of trifluoroacetic acid. It is shown, that the ratio of acid-monomer, reaction time, and the presence of various additives, can significantly change both the molecular weights of polymers and the ratio of linear and cyclic products. These properties affect the hydrophobicity of polysiloxanes films on different surfaces, such as aluminium, titanium and glass.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Grant 17-03-01037)

VDP SYNTHESIS AND STUDY OF SURFACE STRUCTURE OF POLY(p-XYLYLENE) FILMS CONTAINING PbSe AND PbTe NANOPARTICLES

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The development of new thin-film semiconductor coatings is an actual task for the creation and optimization of various electronic devices. The aim of the work is to synthesize and study the effect of concentration on the formation of nanostructured films on different substrates, to study their morphology and surface structure. Thin-film polymeric nanocomposites (by thickness ≈ 0.5 μm) based on the poly(*p*-xylylene) matrix (PPX) and nanoparticles of lead selenide (PbSe) and lead telluride (PbTe) have been obtained by vapor deposition polymerization (VDP method) on the substrates from silicon and sitall. Optimal synthesis conditions of PPX–PbSe ($C_{PbSe} \approx$ 10, 15, 20, 30, 50 and 100 vol. %) and PPX–PbTe ($C_{PbTe} \approx$ 30, 50, 70 and 100 vol. %) nanostructured polymeric films have been defined. The morphology and surface characterictics of synthesized nanocomposites have been studied by scanning atomic force microscopy (Fig.1). The peculiarities of morphological and structural changes of the film surfaces have been revealed at various concentrations of PbSe and PbTe nanoparticles and substrate material. These changes indicate the reorganization of the polymeric matrix. Globules of different shapes and sizes were observed on the surface of composite PPX–PbTe films, which were uniformly distributed all over the study area. It should be noted that ordering of surface structure with the formation of a periodic surface relief in the form of dendritic formations (for silicon substrate) and in the form of layered pointed pyramids (for sitall substrate) was observed at a concentration of PbSe nanoparticles approximately equal to 15 vol. %. The values of root-mean-square roughness (Rq) and the size distribution of the matrix globules have been evoluated. The mechanism of the formation of the nanostructured PPX-PbSe and PPX–PbTe films is discussed. The obtained results are of interest for purposeful modification of the surface of thin-film nanocomposites PPX–PbSe and PPX–PbTe by VDP method and further investigation of their structural and optical properties.

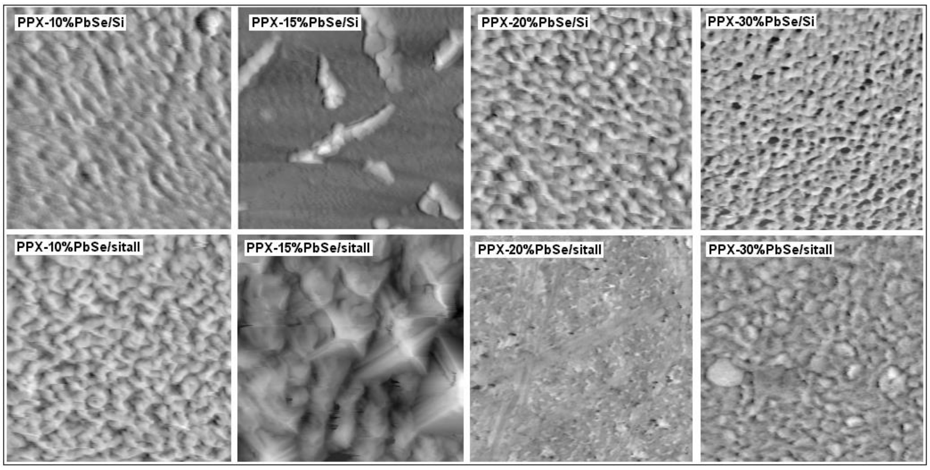

Figure 1. AFM images of the surface nanocomposite PPX–PbSe films ($C_{PbSe} \approx$ 10, 15, 20 and 30 vol. %) obtained by VDP. Substrate material – silicon and sitall glass. The size of images is 5 × 5 μm.

NOVEL ANTIBACTERIAL CHITOSAN DERIVATIVES

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We developed the procedure of ultrasound-assisted phenol-yne addition of *p*-hydroxybenzaldehyde and propargylic ester of betaine hydrochloride resulting selectively in 2-((3-(4-formylphenoxy)allyl)oxy)-*N*,*N*,*N*-trimethyl-2-oxoethan-1-aminium chloride in aqueous solution 100 kHz 300 W. The ultrasound-mediated phenol-yne addition was introduced into carbohydrate polymers chemistry. The phenolic chitosan derivatives were synthesized by interaction of chitosan with *o*-, *m*- or *p*-hydroxybenzaldehyde followed by reduction of the resulted Schiff bases by sodium borohydride. The phenolic chitosan derivatives (as a phenolic component) were involved in ultrasound-assisted phenol-yne addition with propargylic ester of betaine hydrochloride (as an yne component). This ultrasound-mediated interaction resulted in betaine chitosan derivatives in different degree of substitution. The phenolic and betaine derivatives were tested as antibacterial agents against E. coli in comparison with reference antibiotics ampicillin and gentamicin. Betaine derivatives showed high antibacterial activity. The most effective polymer was p-isomer of high substituted betaine derivative and its activity was more than 2 times higher than the activity of Tetracycline. The nanoparticles based on this polymer were obtained by ionic gelation method. They had 2Rh 126 nm, ξ-potential 20 mV and were effective than the corresponding chitosan derivative [1]. Moreover, we tested also transfection activity of the betaine derivatives of chitosan. We revealed that low substituted and moderate substituted betaine derivatives differ little in their transfection activity, but are much more active than highly substituted analogues.

Acknowledgments

This work was supported by RFBR (projects 19-016-00077 and 19-33-60039) and «RUDN University Program 5-100»

References

1. A.S. Kritchenkov, A.R. Egorov et al., International Journal of Biological Macromolecules, 2019, 139, 103.

SYNTHESIS OF COPOLYMERS OF BUTHYLMETHACRYLATE AND VINYLBENZOTRIAZOLE AND ITS FILMS CONDUCTIVITY

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In recent years the properties of well known compounds as azoles are investigated actively to create perspective materials on its base[1]. Polymers of vinylazoles are at the center of attention now for the creation of ion-selective membranes, sorbents, hydrogen fuel elements etc[2].

The aim of this work was the synthesis of buthylmetacrylate (BMA) and vinyl benzotriazole (VBTA), preparing of films on the base of copolymerization products and study of its conductivity.

Copolymers of BMA and VBTA have been synthesized by radical polymerization mechanism at different relations of monomers. Accordingly the size-exclusive chromatography and UV-spectroscopy analysis the products of copolymerization were the mixtures of two polymers - PBMA and copolymer of BMA and VBTA – in relation of 1:1,5. Both components demonstrated high molecular homogeneity while molecular mass (MM) of PBMA was at the range of 43-50 kDa, MM of copolymers – 20-28 kDa. At the base of IR-absorption intensity of 1730 sm^{-1} the composition of copolymers and reactivity constants were calculated by means of Kelen-Tyudosh method. These results indicate on the tendency of links alternation in copolymers.

Films on the base of PBMA and products of copolymerization were prepared and exposed in phosphonic acid during 30 days. Conductive properties of obtained films were studied at 25 ^{0}C by impedance spectroscopy method at the range from 10 Hz to 2 MHz.

It has been shown that films conductivity is conditioned by VBTA links in copolymers and it raises with the increasing of copolymers MM. More than for real dielectrics values of ε' (real permittivity) and ε'' (dielectric loss factor) were marked. It corresponds to ion-migration type of sample polarization. The shape of plots of ε''-vs-log(f/Hz) indicates the availability of two parts of conductivity: reach-through and relaxation.

Referances

1. V. N. Kizhnyaev, G. V. Ratovski, D. N. Bazhenov, F. A. Pokatilov, *Polymer Science*. *Series A*. **2005***, 47*, 1072.

2. A. B. Yaroslavtzev, Yu. A. Dobrovolsky, L.A. Frolova, E. V. Gerasimova, E. A. Sanginov, N. S. Shaglayeva, *Russ. Chem. Rev.* **2012**, *81,*191.

OLYMER SUPPORTED PD PLACED ON MAGNETIC SILICA AS EFFECTIVE CATALYST IN SUZUKI REACTION

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The nature of the ligand used for stabilization of catalytic nanoparticles is known to have a significant impact on the properties of the final catalytic composite. Ease of processable branched structure with numerous cavities makes hyperbranched polymers promising candidates for this purpose. However, the reusing and separation of the catalyst are still actually problem. The attaching polymeric ligands to the solid support can solve it. The catalysts on solid supports made of magnetic materials can be removed very simply by using an external magnet.

Here, we report the synthesis of novel Pd-containing catalyst using magnetic silica gel (Fe_3O_4-SiO_2) as solid support and hyperbranched pyridylphenylene polymer (HPP) as a ligand for the stabilization of Pd^{2+} species. First the synthesis of iron oxide nanoparticles (NPs) in the silica pores was carried out according to a procedure described elsewhere[1]. Then Fe_3O_4-SiO_2 NPs were modified with HPP (Fe_3O_4–SiO_2–HPP). In our earlier publication[2] the synthesis of HPPs based on first generation dendrimer via Diels-Alder polycondensation was reported. It was determined that the formation of crosslinked HPP can be controlled by reaction parameters such as concentration of monomers, molar ratio of monomers, reaction time, etc. Based on that results in the present work the magnetic silica gel was coated by HPP synthesized in situ by Diels-Alder polycondensation of two monomers: A6 (pyridylphenylene dendrimer first generation with ethynyl periphery groups) and B2 (tetraphenyl substituted biscyclopentadienone with oxygen bridge - 3,3'-(oxydi-1,4-phenylene)bis(2,4,5-triphenylcyclopenta-2,4-dien-1-one)) in the presence of magnetic silica gel. The availability of a polymer layer on the surface of magnetic silica was determined by transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). In the next step, the composite Fe_3O_4-SiO_2-HPP was employed to coordinate palladium ions due to pyridyl functional groups in the polymer layer. The Fe_3O_4-SiO_2-HBP-Pd demonstrated high catalytic activity as a recyclable nanocatalyst in Suzuki cross-coupling reactions of phenylboronic acid with aryl halides and revealed negligible activity loss after second reuse.

Acknowledgments

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References

1. T. Oracko, R. Jaquish, Y.B. Losovyj, D.G. Morgan, M. Pink, B.D. Stein, V.Y. Doluda, O.P. Tkachenko, Z.B. Shifrina, M.E. Grigoriev, A.I. Sidorov, E.M. Sulman, L.M. Bronstein*, ACS Appl. Mater. Interfaces* **2017,** *9*, 34005

2. N. V. Kuchkina, M. S. Zinatullina, E. S. Serkova, P.S. Vlasov, A.S. Peregudov, Z.B. Shifrina *RSC advances*. **2015**, *5,* 99510.

HYBRID MAGNETIC NANOCOMPOSITES BASED ON NIPAM-PAA AND IRON(III)-CONTAINING NANOPARTICLES FOR DOXORUBICIN LOADING AND ANTICANCER THERAPY

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Currently, effective control of various diseases requires targeted delivery of drugs, as many of them are harmful to the body, so it is necessary to reduce the harmful effects of the drug on other organs and tissues.[1] Also, a lot of drugs are not water-soluble; moreover, the drug "dissipates" until it reaches the desired organ, so targeted delivery helps to reduce the dose of the drug and increase the therapeutic effect.

To sovle this problem a water-soluble magnetosensitive composite was obtained. Nanogel based on polyacrylic acid, N-isopropylacrylamide was used as a matrix.[2] Iron(III)-containing nanoparticles were synthesized on the matrix using the original technique.[3]

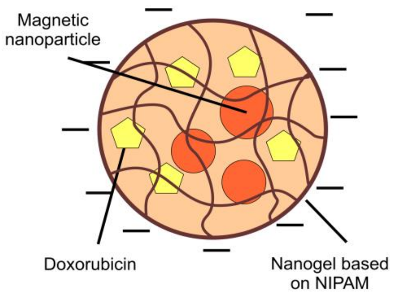
The iron content in the nanocomposite was determined spectrophotometrically.

The size of magnetic nanoparticles in the composite was determined in a range from 8 to 22 nm using TEM.

The ferromagnetic properties of the inorganic phase were established.

It was shown that a magnetically sensitive nanogel is able to bind doxorubicin. The anticancer properties of magnetic nanogel loaded by doxorubicin were studied. It was found that the immobilization of doxorubicin by nanogel does not reduce its anticancer activity. It has also been shown that the initial magneto-sensitive nanogel has no toxicity.

Figure 1. Schematic representation of the magnetosensitive composite filled with doxorubicin



Acknowledgments

This work was supported by RFBR Project № 18-03-01024 A

References

1. C. Alexiou, R.J. Schmid, Eur. Biophys. J. **2006**, *35(5)*, 446.
2. S. Ito, K. Ogawa, Langmuir, **1999**, *15(12)*, 4289.
3. V. V. Spiridonov, I. G. Panova, Carbohydr. Polym., **2017**, *177*, 269.

ULTRASONIC SYNTHESIS OF WATER-SOLUBLE POLYMER-METAL(OXIDE) MAGNETIC NANOCOMPOSITE BASED ON CROSS-LINKED CALCIUM/SODIUM ALGINATE AND MAGHEMITE NANOPARTICLES

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Synthesis of metal/organic materials containing magnetic nanoparticles is one of the actual tasks. Being combined with biological objects, magnetic nanoparticles can be used for such medical problems as controlled drug delivery, and magnetic-induced cancer therapy.[1,2] Maghemite (γ-Fe_2O_3) represents an important class of magnetic transition metal oxide materials. To reduce the possible toxic effects of the magnetic phase, and to increase their physico-chemical stability, as well as create the possibility of immobilizing additional drugs, magnetic nanoparticles must be isolated. This problem can be solved by encapsulating the nanoparticles in some matrix materials.[3]

In this work, we used UltraSonication approach for the direct synthesis of hybrid non-toxic metal (oxide)–polymer magnetic nanocomposite. As a stabilizing matrix, a microgel based on Na-Alginate, preliminarily cross-linked by Ca^{2+} ions (Na/Ca-Alginate), was used. It was established that in the presence of the Na/Ca-Alginate microgel, maghemite nanoparticles stabilize into magnetically ordered structures which demonstrate the high magnetic properties. It was shown that the linear polysaccharide (Na-Alginate) cannot keep the nanoparticles from aggregation in the same conditions. The structural characterization of magnetic nanocomposite (Na/Ca-Alginate– Maghemite) were performed by X-ray diffraction (XRD) as well as Small Angle X-Rays Scattering (SAXS). Möessbauer spectroscopy was used too. The physicochemical properties of magnetic nanocomposite the were studied by techniques of Infrared spectroscopy (IR), Dynamic Light Scattering (DLS), laser microelectophoresis. The morphological analysis was performed by transmission electron microscopy (TEM). The magnetic behavior of organo-metal(oxide) magnetic nanocomposite (Na/Ca-Alginate–Maghemite) was studied by means of magnetization.

Acknowledgments

This work was supported by RFBR Project № 18-03-01024 A

References

1. Y. Huang, K. Mao, Materials Science and Engineering: C, **2017**, *70(1)*, 763.
2. M. Häring, J. Schiller, Gels, **2015**, *1(2),* 135.
3. M. Arruebo, W. Ho, Chem. Mater, **2008**, *20(2)*, 486.

STABILIZATION OF MESOGLOBULES BY A SOLUTE VIA SPECIFIC INTERACTIONS

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Amphiphilic homopolymers andpolymers in the mixtures with surfactants or chaotropic salts self-assemble into micelles, vesicles, nanoworms that are promising nanoplatforms for usage as nanoreactors, containers for targeted delivery of therapeutic agents and imagining modules in theranostic nanomedecine.[1]

Adapting theoretical models of amphiphilic homopolymers,[2,3] a theory of dense finite size aggregates in dilute solutions of macromolecules in the presence a solute that can bind to polymer via specific interactions was developed.[4] The possibility of formation of spherical mesoglobules, lamellas, nanoworms and macrophase separation were analyzed. It was assumed that molecules of a solute do not penetrate into the polymer-containing domains and can only bind to the surface of aggregates. We supposed that the main factor for diverse shapes of assemblies is the surface energy. The volume free energy term was assumed to be independent on shape, so the surface free energy was only taken into account. The two cases of polymer-solute binding were studied: molecules of a solute could bind to functional groups separated from main chain (pendant functional groups, (Fig. 1 a)) or directly to monomers (Fig.1 b). In the former case we predict formation of lamellas (possibly vesicles), nanoworms, and spherical mesoglobules. In the latter case it was found that solubilization of individual macromolecules occurs and polymer chains form a necklace-like structure. The shape diagrams were constructed.

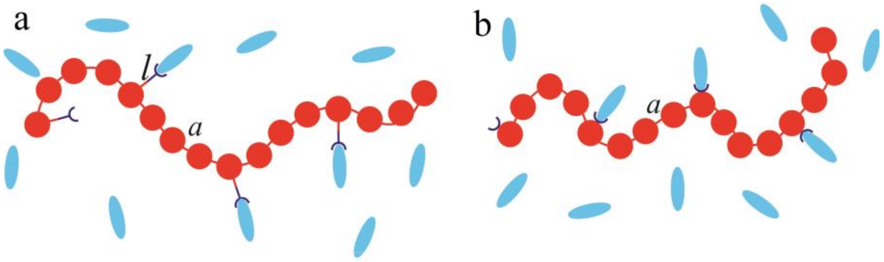

Figure 1. Schematic representation of two types of macromolecules studied.

Acknowledgments

The research was supported financially by Russian Foundation for Basic Research (Project No. 18-33-01249).

References

1. F.Wang, J.Xiao, S.Chen,H. Sun, X.Zhou, J.Du, *Adv. Mater.* **2018**, *30*, 1705674.
2. E.A.Maresov, A.N.Semenov, *Macromolecules* **2008**, *41*, 9439.
3. D.E. Larin, A.A. Glagoleva, E.N. Govorun, V.V. Vasilevskaya, Polymer **2018**, *146*, 230.
4. D.E. Larin, E.N. Govorun,*Polym. Sci., Ser. A* **2019**, *61*, 710.

CATALYTIC CROSS-LINKING OF SI–H-CONTAINING SILICONE COPOLYMERS

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Platinum (0) and (II) complexes, notably *cis*-[$PtCl_2(BnCN)_2$] and Karstedt's catalyst, are used for cross-linking of the Si–H-containing silicones, in particular, ferrocenyl-containing polymethylhydrosiloxanes, by the reactions between Si–H groups. Karstedt's catalyst leads to Si–O–Si and Si–Si bond formation, but *cis*-[$PtCl_2(BnCN)_2$] generates predominantly Si–O–Si cross-links and allows creating high-quality silicone rubbers without visible mechanical defects (cracks and bubbles) in comparison with hyperactive Karstedt's catalyst. Swelling measurements and SSNMR indicated that *cis*-[$PtCl_2(BnCN)_2$] forms silicone rubbers with a 1.5–2 times lower cross-linking degree than in the case of Karstedt's catalyst. This cross-linking approach can be used to obtain new Si–H- and ferrocenyl-containing silicone rubbers, in particular, for creation heterogeneous reducing agents and electroactive materials for electronic devices.[1]

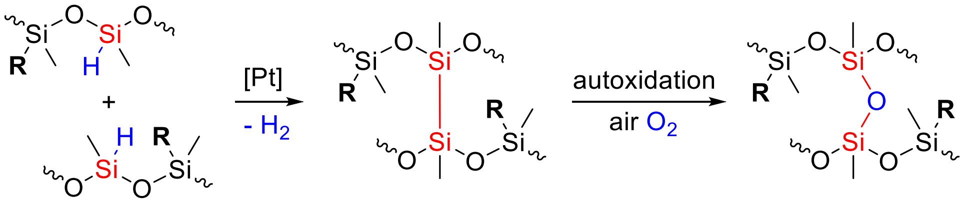

Figure 1. Cross-linking of Si–H-containing polysiloxanes (R: -H, $-CH_3$, $-CH_2CH_2Fc$).

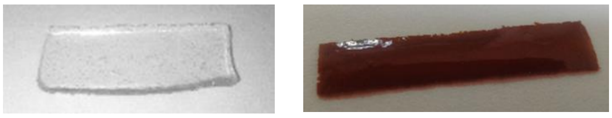

Figure 2. Silicone rubbers: **a**–cross-linked polymethylhydrosiloxane; **b**–cross-linked ferrocenyl-containing polymethylhydrosiloxane.

Acknowledgments

This work was supported by the Russian Foundation for Basic Research (project № 18-33-20062_mol_a_ved). NMR measurements were performed at the Centre for Magnetic Resonance (in Saint Petersburg State University).

References

1. K.V. Deriabin, E.K. Lobanovskaia, A.S. Novikov, R.M. Islamova,*Org. Biomol. Chem.* **2019**, *17*, 5545–5549.

REACTION OF PROPIOLIC ACID WITH 1,3-BIS(3-AZIDOPROPYL)-1,1,3,3-TETRAMETHYLDISILOXANE

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Organosilicon compounds and materials based on them (silicone or siloxanes) are one of the most important products, which find the applications in many braches of modern science, technology and medicine. It relates with unique physical and chemical properties of the siloxanes: low glass transition temperature and high thermal stability, high hydrophobicity, gas permeation, biocompatibility, radioactive stability, low dielectric constant, etc.

A serious drawback of organosilicon macromolecules is their low mechanical strength, which substantially organizes the practical use of these polymers.

The introduction of a “polar” function in organosilicon compounds will open up possibilities for the production of new hybrid materials, in particular, unique copolymers, MOFs, HOFs, etc. [1], and will also make it possible to solve the problem of low mechanical strength and the "incompatibility" of silicones with organic polymers.

In our work, we proposed a simple method for introducing a carboxyl group into a siloxane’s structure.

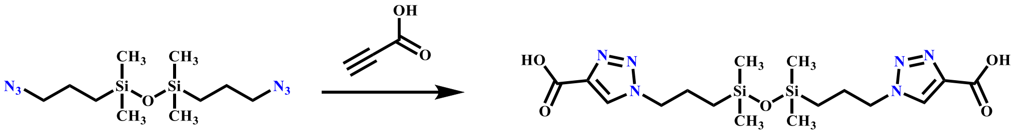

Figure 1. Reaction of Propiolic acid with 1,3-Bis(3-azidopropyl)-1,1,3,3-tetramethyldisiloxane

References

1. Zongbi Bao, Danyan Xie, Ganggang Chang, Hui Wu, Liangying Li, Wei Zhou, Hailong Wang, Zhiguo Zhang, Huabin Xing, Qiwei Yang, Michael J. Zaworotko, Qilong Ren, and Banglin Chen. J. Am. Chem. Soc., 2018, 140 (13), pp 4596–4603.
2. A. B. Author, C.D. Coauthor, *J. Inorg. Chem.* **2015**, *117*, 987.

POLYMER NANOPARTICALS FROM SELF-ORGANIZED MONOMERS

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Polymerization of self-assembled amphiphilic monomers in polar media lead to obtain well-organized macromolecular nanoobjects (polymerized micelles or «polysoaps»). Present work describe preparation such micelle-forming polymers by free-radical polymerization of sodium N-acryloylaminoundecanoate under different reaction conditions (concentration, ionic strength).

Copolymerization of the monomeric surfactant with bifunctional comonomer solubilized in the micelle core open the way to preparation more complicated nanoparticles with less volatile shape and size in various solvents.

Molecular weight characteristics, forms and behavior features of obtained objects not only in aqueous media, but also in organic solvents were investigated by varied methods, among them viscosimetry, dynamic light scattering, atomic force microscopy and GPC.

The use of anthracene derivatives as a comonomers allows one to study features of copolymerization, and control the composition of the macromolecular nanoobject by spectro-photometric and spectro-fluometric methods.

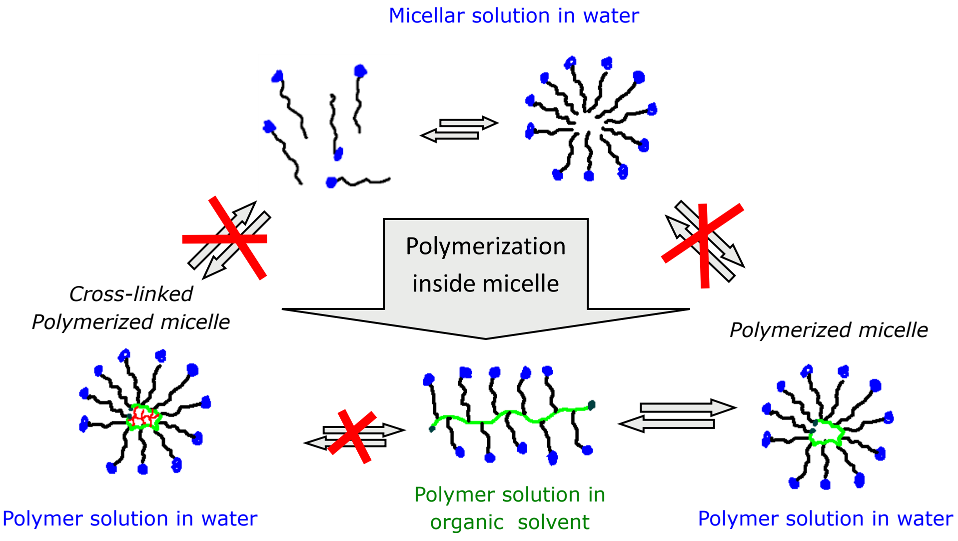

Figure 1. Fixation structure of polymer nanoparticles.

Acknowledgments

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CATALYTIC OXIDATION OF BENZENE ON THE METAL POLYMER CATALYST

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N.A. Zeynalov

Institute of Catalysis and Inorganic Chemistry named after academician M.Nagiyev of ANAS
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Oxidation of organic compounds such as benzene in the liquid phase is an industrially important reaction since the product such as maleic anhydride is very valuable intermediates. Maleic anhydride (MAN) is toxilic anhydride and maleic acid anhydride. This multifunctional chemical inter- mediate finds applications in almost any field of industrial chemistry. The principal use of MAN is in the manufacture of alkyd and unsaturated polyester (UPE) resins, surface coatings, plasticizers, lubricating oil additives, agricultural chemicals, textile chemicals, paper reinforcement, food additives and pharmaceuticals. Furthermore, due to its double bond and a hydride function, MAN is a versatile intermediate for the production of copolymers of MAN and, for example, ethylene glycol and vinyl monomer. Recently, potential new uses of MAN have been found in its conversion to 1,4-butanediol and the manufacturing of tetrahydrofuran (THF) [1, 2]. MAN is produced industrially by oxidation of suitable hydrocarbons in the gas phase.

But carrying out the process of liquid-phase oxidation of benzene with atmospheric oxygen, improving technological conditions was one of challenge for the laboratory study. Studies in that field have shown that silver-containing catalysts are highly efficient in oxidizing arenes.

Taking into consideration the above mentioned, present work is devoted to investigation of the process of benzene oxidation on a modified polymer catalyst Ag-polyvinylpyrrolidone in the temperature range 25-110°C, in the molar ratio of reagents are benzene:oxygen:nitrogen=1:0.48:1.78, and under conditions providing of the reaction progress in the kinetic-area.

The obtained data have been identified on an Agilent 7890B gas chromatograph with an HP-5 column, with a gas carrier velocity (H2 and N2) of 1.2 ml / min. and with a pressure of 5.41 psi (pound-force per square inch).

It has been found that, in the process of benzene oxidation except the main product maleic anhydride were formed side products of the full oxidation, such as formic, acetic and acrylic acids. The yield of the reaction products has been from 0.5 to 27.8%.

References

1. Kirk-Othmer, Encyclopedia of Chemical Process and Design Vol.14, Marcel Dekker, New York 1977.
2. http://www.vanadium.com.au/ScienceStuff/Chemistry/MaleicAnhydride.htm.
3. N.K. Kala Raj, V.G. Puranik, C. Gopinathan, A.V. Ramaswamy, App. Cat., A 2003, 256, 265.
4. F. C. Jentoft et al., App. Cat., A 2003, 256, 291.
5. J.C. Dillon, J.H. Holles, M.E. Davis, J.A. Labinger, Cat.To-day 2003, 81 (2), 189.

SYNTHESIS AND LUMINESCENT PROPERTIES OF COMPOSITES OF POLY(ALPHA-FLUOROACRYLATES) DOPED WITH TB(III) COMPLEX

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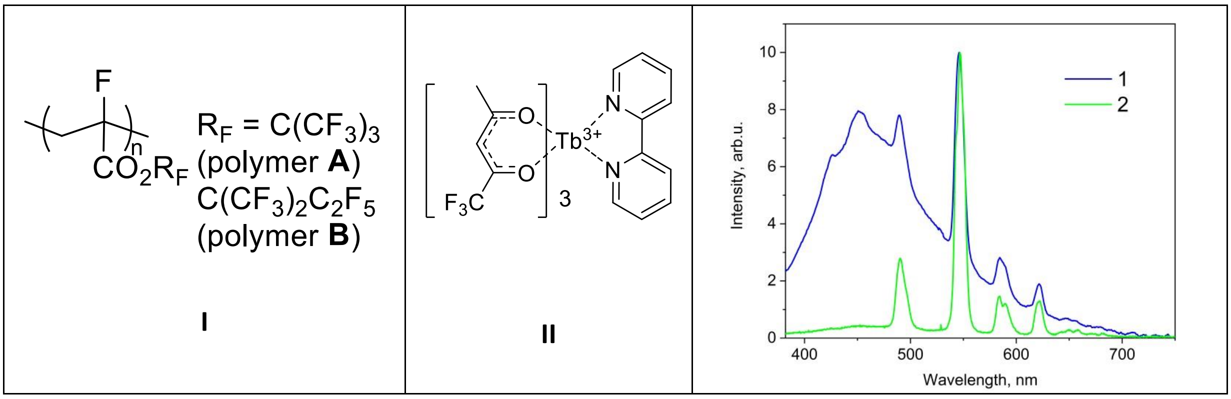
The polymers based on fluoroaliphatic esters of acrylic acid are more stable to optically induced degradation and have better optical properties when compared to conventional aliphatic acrylates. Composite materials based on the fluorinated polyacrylates doped with Eu(III) complex were demonstrated to be prospective for electrooptical application.[1]

In this work we used optically transparent poly(б-fluoroacrylates) as polymer matrices. Hybrid materials were prepared by free-radical polymerization of monomers doped with 0.05-0.1 wt % of tris(1,1,1-trifluoropentane-2,4-dionato)(2,2'-bipyridine)terbium(III). Polymer blocks are optically transparent and colorless under daylight, but demonstrated bright green luminescence under UV irradiation (365 nm). The emission spectrum of material based on monomer **B** was typical for the emission of Tb^{3+} ion, while for polymer **A** broad emission of polymer matrix was also observed. The lifetimes of exited state of Tb^{3+} ion in both polymers are about 1.1 ms, which indicates excellent compatibility of polymers and dopant. These materials are promising candidates for fabrication of UV-radiation converters for organic light emitting diodes.



I

II

Figure 1. The chemical composition of polymers **A** and **B** (**I**), structure of Tb complex (**II**) and emission spectra for hybrid materials based on polymer **A** (line1) and polymer **B** (line2) under UV-excitation (365 nm).

Acknowledgments

I. Taydakov and V. Korshunov are grateful to the Russian Science Foundation for the financial support of their work (project №19-13-00272).

References

1. I.V.Taydakov, et al., *J. Rus. Laser Res.* **2016**, 37, 192.

THIAZOLE-BASED (MIX)MOFS: SYNTHESIS, CHARACTERIZATION AND APPLICATIONS IN GAS ADSORPTION AND CATALYSIS

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Metal-Organic Frameworks (MOFs) are a class of nanoporous materials that, in recent years, have gained great attention for their widespread application in several field of materials science (catalysis, luminescence or gas storage and separation).[1] Typical MOFs ligands belong to the classes of aliphatic or aromatic polycarboxylic acids and polydentate N-heterocyclic bases. However, there are few examples of MOFs built with more than one heteroatom type in the heterocyclic core. In thiazoles, the simultaneous presence of polarized C-N or C-S bonds and of multiple basic sites of both hard (N) and soft (S) nature favour the coordination to both hard and soft metal ions, making the related ligand more versatile for MOF design. Given the experience of our group in the preparation of thiazole-containing linkers and MOFs (Figure 1),[2] we present selected results about the synthesis of a library of thiazole-based (MIX)MOFs for applications in CO$_2$ storage (Carbon Capture and Sequestration, CCS) and its conversion into added value chemicals (Carbon Capture and Utilization, CCU).[3]

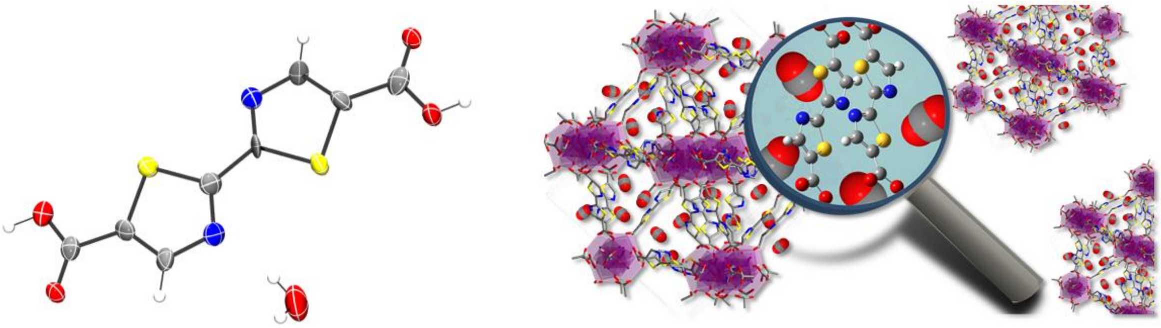

Figure 1. XRD structures of [2,2'-bithiazole]-5,5'-dicarboxylic acid (H_2TzTz) and its“UiO-67 analogue” $[Zr_6O_4(OH)_4(TzTz)_6]_n$.

Acknowledgments

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References

1. A. Rossin, G. Giambastiani, *CrystEngComm* **2015**, *17*, 218-228.
2. (a) A. Rossin, G. Tuci, G. Giambastiani, M. Peruzzini, *ChemPlusChem* **2014**, *79*, 406-412. (b) S. Staderini, G. Tuci, M. D'Angelantonio, F. Manoli, I. Manet, G. Giambastiani, M. Peruzzini, A. Rossin, *ChemistrySelect***2016**, *6*, 1123-1131. (c) S. Staderini, G. Tuci, L. Luconi, P. Müller, S. Kaskel, A. Eychmüller, F. Eichler, G. Giambastiani, A. Rossin, *Eur. J. Inorg. Chem.* **2017**, 4909-4918.
3. P. Müller, B. Bucior, G. Tuci, L. Luconi, J. Getzschmann, S. Kaskel, R. Q. Snurr, G. Giambastiani, A. Rossin, *Mol. Syst. Des. Eng.* **2019**, DOI: 10.1039/C9ME00062C.

NEW MONOSODIUMOXYORGANOALKOXYSILANES FOR PRODUCTION OF FUNCTIONAL POLYALKYL(ARYL) TRIAZOLEALKOXYSILOXANES WITH CONTROLLED MOLECULAR ARCHITECTURE

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A number of new sodiumoxyorganoalkoxysilanes (a.k.a. Rebrov Salts)[1] have been synthesized and characterized.

New monomers with independent functional groups were used to obtainpolyalkyl(aryl)triazole polyorganoalkoxysiloxanes - functional organosilicon polymer objects with controlled molecular architecture - promising matrices for development of new functional materials.

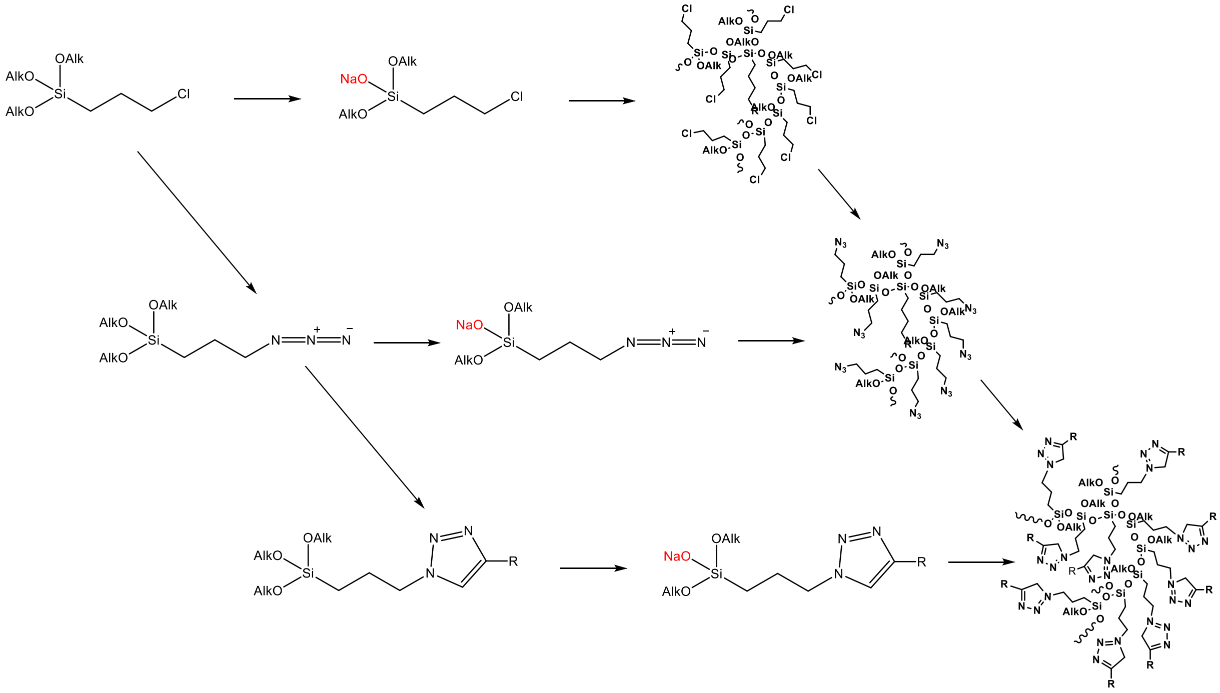

Figure 1. General synthetic scheme

Acknowledgments

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References

1. E. A. Rebrov, A. M. Muzafarov, *Heteroatom Chemistry* **2006**, 17, 514.

CARBORANCARBOSILANE DENDRIMERS: SYNTHESIS AND PROPERTIES

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Dendrimers are globular, hyperbranched and mono-dispersed macromolecules with clear three-dimensional structure and consisted of a core and several layers of repeating branched links. Due to their unique physical and chemical properties and potential applications in different fields of science, in recent years, interest in hyperbranched polymers is growing rapidly. Much interest has been developed in a group of carborane-containing dendrimers. They have attracted attention due to the unique properties of the icosahedral boron-rich carborane clusters. As a result of their high thermodynamic stability, these compounds have been postulated as potential flame-retardant materials. Also, compounds of this class are used as protective coatings from radiation and are promising materials for use in medicine.

Modification of dendrimers with boron-substituted carboranes allows us to study the effect of the carboranyl shell on the properties of the target products, as well as to suggest the possibility of further functionalization of the obtained macromolecules, due to the presence of –CH groups in the carborane structure.

This research work describes the synthesis of new boron-substituted carborancarbosilane dendrimers of different generations (zero G_0, first G_1, third G_3, fifth G_5) using the hydrotiolation reaction of allyl groups of carbosilane dendrimers with 9-thio-*m*-carborane initiated by DMPA and UV radiation (figure 1).

The structure and purity of the compounds obtained were determined by a complex of physicochemical analysis methods: ^{1}H, ^{29}Si, ^{13}C, ^{11}B NMR, IR spectroscopy, GPC and elemental microanalysis, DSC and TGA.

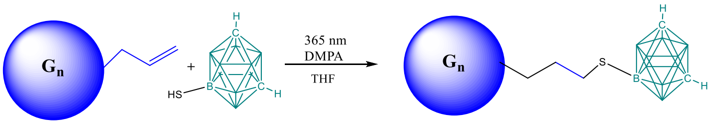

Figure 1. General scheme for the synthesis of carborancarbosilane dendrimers using the hydrothiolation reaction

Acknowledgments

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NEW MULTIBLOCK COPOLYMERS CONTAINING NORBORNENES AND CARBOSILANE/ CARBOSILOXANE BLOCKS

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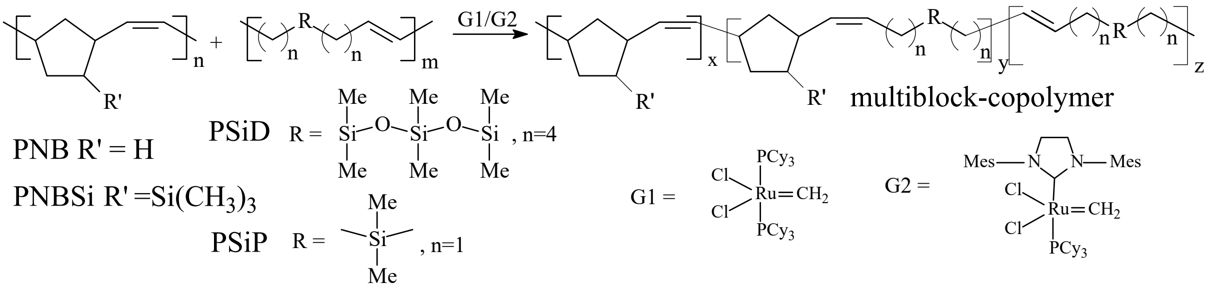
Multiblock copolymers (MBCs) attract growing interest as a tool to combine properties of two polymers in one macromolecule. Recently we have developed a new method for their synthesis via the interchain macromolecular cross-metathesis reaction (MCM) involving polynorbornenes [1]. This study aimed at the synthesis of new MBCs containing rather rigid norbornene glassy blocks and flexible carbosilane or carbosiloxane rubbery blocks. This kind of copolymers may be interesting for applications as gas separation membranes [2].

Initial polynorbornene (PNB), poly(5-trimethylsilylnorbornene) (PNBSi) and poly(dimethylsilapentene) (PSiP) were prepared by ring-opening metathesis polymerization (ROMP) of corresponding monomers: norbornene (NB), 5-trimethylsilylnorbornene (NBSi) and 1,1-dimethylsilacyclopentene-3 (SiP) in the presence of 1st (G1) and 2nd (G2) generations Grubbs' catalysts. Poly(1,1,3,3,5,5-hexamethyltrisiloxanyl-5-decenylene) (PSiD) was obtained by ADMET of 1,5-bis(hexenyl-5)-1,1,3,3,5,5-hexamethyltrisiloxane (SiD) mediated by G1 and G2 catalysts. MCM between PNB/PNBSi and PSiD/PSiP was carried out in $CHCl_3$ solution using different molar ratios of the initial reagents in the presence of the same catalysts (Scheme 1). New NB-SiD and NB-SiP MBC with different average blocks lengths were obtained. All the copolymers were characterized by 1H, 13C, 29Si NMR, GPC, and DSC. It was shown that the block lengths depended on the molar ratio of the initial reagents, catalyst activity and reaction conditions. By adjusting the average block lengths one can regulate Tg of copolymers. The obtained copolymers exhibited promising gas permeation properties.



Scheme 1. Macromolecular cross metathesis (MCM) between PNBs and PSiD or PSiP

Acknowledgments

The work was supported by the Russian Foundation for Basic Research, project № 18-33-00961

References

1. M. Gringolts, Yu. Denisova, E. Finkelshtein, Y. Kudryavtsev, et al. *RSC Adv*., **2015**, *5*, 316;
M. Gringolts, Yu. Denisova, E. Finkelshtein, Y. Kudryavtsev Beilstein *J. Org. Chem*. **2019**, *15*, 218.
2. Yu. Yampolskii and E. Finkelshtein (Eds). Membrane Materials for Gas and Vapor Separation. Synthesis and Application of Silicon-Containing Polymers.: *John Wiley & Sons, Inc*., United Kingdom. **2017**, 399.

TUNING THE WETTING ANGLE OF THE FLUORINATED POLYMER BY MEANS OF MODIFIED NANODIAMONDS

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Fluorine-containing materials are often used to inhibit surface biofouling by increasing the wetting angle[1]. An additional important property is the resistance to singlet oxygen, due to which fluorinated polymers are used in optical sensors of molecular oxygen using the phenomenon of phosphorescence. However, sometimes tasks arise, such as creating biosensors, when good or controlled wettability of the material is important[2]. This work is devoted to the development of technology for fine tuning the characteristics of an optical sensor by means of incorporation of modified nanodiamonds with various functional groups onto the surface.

The technique for creating optical sensory material was developed and optimized by us earlier[3]. It consists of nanostructured SiO_2 microparticles with adsorbed dye (PtTFPP), which are distributed in a fluorine-containing polymer (fluoroplast 42), which protects the dye from leaching and prevents the adhesion of biomaterial. In the present work, a suspension of detonation synthesis nanodiamonds (brand UDA-GO-SP) of three modifications was additionally applied to the surface: aminated (DNA_{amin}), chlorinated (DNA_{chl}), and mixed treatment ($DNA_{amin+chl}$). The samples were annealed in an argon atmosphere at the temperature close to the polymer melting point (150–160 °C) for 12 h.

The fouling results (Fig. 1) show that the highest wettability is observed for samples with $DNA_{amin+chl}$, while for DNA_{amin}, on the contrary, inhibition of bacterial growth is observed.

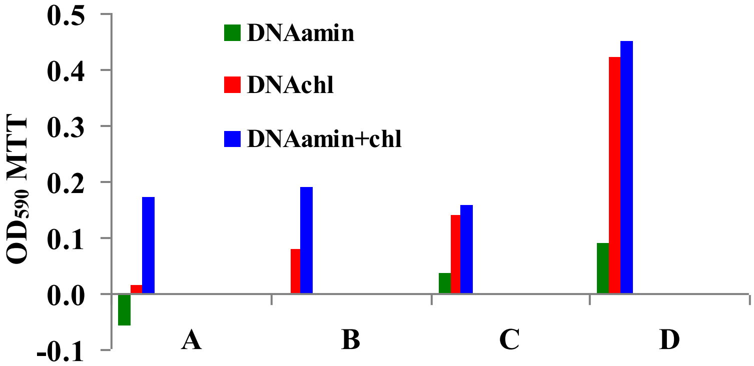

Figure 1. Microbial fouling of samples (OD590 MTT relative to the control) with the content of nanodiamonds 2.3 (A), 3.1 (B), 3.8 (C) and 4.6 (D) •10^{-4} g/cm^2 after aging for 7 days in a microbiological environment with bacteria *Pseudomonas putida strain k12*

Acknowledgments

This study was supported by a grant from the Russian Science Foundation (project no. 17-79-10439)

References

1. P. Zhu, W. Meng, Y. Huang, *RSC Adv.* **2017**, *7*, 3179-3189.
2. J.M. Bolivar, S. Schelch, T. Mayr, B. Nidetzky, *ACS Catal*. **2015**, *5* (10), 5984−5993.
3. P.V. Melnikov, A.O. Naumova, A.Yu. Alexandrovskaya, N.K. Zaitsev, *Nanotechnologies in Russia* **2018**, *13 (11-12)*, 602–608.

COMPOSITE CHITOSAN GELS WITH METAL NANOPARTICLES IN CARBONIC ACID SOLUTIONS UNDER HIGH PRESSURE

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Modification of polymers and formation of corresponding polymer-based functional composites in solutions containing pressurized CO_2 at hundred bars pressure is extremely promising for many possible applications. Solutions of CO_2 in water, i.e. carbonic acid solutions formed under high pressure of CO_2 saturating the aqueous phase, are both antimicrobial and biocompatible after decompression. Moreover, they are pronouncedly acidic (pH is below 3) when pressurized and can dissolve polycations, chitosan in particular, but they are also self-neutralizing at atmospheric pressure. Furthermore, they are environmentally safe, and also have a number of other technological advantages (providing one-stage process, sterility of the obtained material, no necessity to get rid of any unwanted solvent traces in the modified product*, etc.*).

We proposed a new method of formation of chitosan composite gels with metal nanoparticles (NPs) in the solutions of carbonic acid that opens up a promising way to create antimicrobial composite products that can be used in biomedical applications: for example, during subsequent preparation by freeze-drying of hemostatic chitosan sponges with additional antimicrobial activity provided by Ag NPs. Another example is a composite gel of chitosan with polymer-stabilized Pt NPs where chitosan will play the role of an antimicrobial agent and Pt NPs will protect against skin inflammation and allergies caused by UV radiation.

Themorphology of metal-containing chitosan gels, obtained in the solutions of carbonic acid under high pressure was examined by SEM, the size and distribution of NPs were studied by TEM, the mechanics was investigated by rheology measurments, the kinetics of reduction of nanoparticles was explored by UV-vis, IR and X-ray photoelectron spectroscopy and X-ray diffraction analysis.

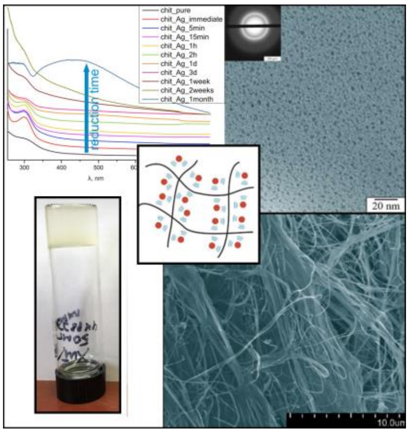

Figure 1.The illustration of chitosan-metal composite, its inner structure, the NPs distribution and the kinetics of Ag NPs reduction by chitosan, dissolved in carbonic acid under high pressure.

Acknowledgments

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HETEROPHASE RAFT-POLYMERIZATION IN THE PRESENCE ZINC OXIDE NANOPARTICLES

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Synthesis of hybrid nanocomposites filled with inorganic nanoparticles has been one of the actual directions of polymer chemistry for many years. Such objects are widely used in various fields depending on the nature of the polymer matrix and filler. Increasingly, there are publications where dispersions of amphiphilic block copolymers obtained by heterophase reversible addition-fragmentation chain-transfer polymerization (RAFT-polymerization) are used as a polymer matrix[1]. This method is based on the use of a polymer precursor that acts as a RAFT-agent and stabilizer of the resulting particles, avoiding the use of traditional emulsifiers and stabilizators[2]. The introduction of inorganic nanoparticles in the monomer or dispersion phase will allow the nanoparticles to immobilize in the polymer matrix on the surface or in the volume, depending on the nature of the nanoparticles and the monomer.

In the present work the role of the polymer matrix will act triblock copolymer (polyacrylic acid-block-polybutyl acrylate-block-polyacrylic acid) (C1)[3] and pentablock copolymer (polyacrylic acid-block-polybutyl acrylate-block-polystyrene-block-polybutyl acrylate-block-polyacrylic acid) (C2), and the role of a filler of nanoparticles of zinc oxide (ZnO) (average diameter – 10 nm)[4]. Preparation of composite particles will be conducted in 3 stages: obtaining a stable dispersion of ZnO stabilized polyacrylic acid with trithiocarbonate group (PAA-TTC) in a mixture of methanol and water, the synthesis of the copolymer C1 (average diameter 60 nm) in ZnO dispersion, seed polymerization obtaining a copolymer C2, where the seed particles is used as the copolymer C1.

First was the sample C2 in the absence of ZnO that was used for the seed dispersion polymerization of styrene (St): volume ratio of methanol/water = 4/1, mass ratio of S1/St = 1/1, the concentration of AIBN – 5 x 10-3 mol/l), the curing temperature is 65 °C. Particles with an average diameter of 120-130 nm were synthesized. Stable dispersions of ZnO were obtained in a mixture of methanol and water (volume ratio methanol/water = 4/1) in the presence of PAA-TTC (2% wt.). Further, in the resulting dispersion, the synthesis of C1 and C2 in the presence of nanoparticles will be carried out.

Acknowledgments

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References

1. A.C.C. Esteves *J. Polym. Sci., Part A: Polym. Chem.* **2009**, 47, 5367.
2. M.J. Derry, L.A. Fielding, S.P. Armes, *Prog. Polymer Sci.* **2016**, 52, 1.
3. E.V. Chernikova, A.V. Plutalova, K.O. Mineeva, I.R. Nasimova, E.Yu Kozhunova and coauthors *Polymer Science, Series B,* **2015**, 57, 547.
4. S. Dazhi, W. Minhao, S. Luyi, L. Yuntao, M. Nobuo, S. Hung-Jue *J. Sol-Gel Technol.* **2007**, 43, 237

A STUDY OF THE SORBTION CAPACITY, PHYSICO-CHEMICAL CHARACTERISTICS AND STRUCTURE OF UREAFORMALDEHYDE OLIGOMERS FOR DECORATION OF THE CERAMIC SURFACES

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Decoration of ceramic surfaces, including porous pottery surfaces, is the last operation of production. It.s necessary the requires for ceramic surfaces and vanish-paint composition. Changing aggregative steadiness of various CF-oligomers and different meanings of adsorbtion on the pottery surfaces causes the change for the worse of the quality of vanish paint coatings on the ceramics[1].

The object of this researching is to study the correlation of physico-chemical characteristics and structure of CF-oligomers in the paint composition on coating properties for correct choice of CF-oligomers of definite chemical structure and characteristics. The following tasks have been achieved thereby: preparation of paint pasts for material MCh-578(with adding of polyvinyl alcohol and without it), apply the paint compositions and to research physico-chemical properties of coatings on the ceramic surfaces[2]. It.s necessary for creating of new vanish-paint material on water base with CF-oligomers for decorating ceramic surfaces.

References

1. E.W. Washburn. Phys. Rev. **1921,** 17, 273;
2. P.V. Nartzisova, E.P. Golovin, J. Glass and ceramics**. 2008**, 8, 21

REVERSIBLE INHIBITION IN THE FORMATION OF (CO) POLYMERS BASED ON ALKYL(METH)ACRYLATES WITH VINYLALKYL ETHERS UNDER COMPENSATION OF THE ACTIVE MONOMER DEPENDING ON THEIR NATURE WHEN INITIATED BY THE TRIETHYLBORANE-OXYGEN SYSTEM

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Previously[1], the analysis of monomer conversion in the copolymerization of butyl acrylate (BA) with vinyl butyl ether (VBE) with a large excess, and boil latter for initiating system triethylborane (TEB)-oxygen, and the product properties to identify signs of the formation of macromolecules of alternating copolymer on the mechanism of reversible inhibition (Figure 1), with the participation boroxyl radical formed during the oxidation of TEB along with alkyl and alkoxyl radicals[2].

The aim of this work is to conduct similar studies for a number of alkyl(meth)acrylates (AMA) and to identify features associated with the structure of AMA.

AMA and vinylalkyl ether (VAE) copolymers were obtained by the gradual introduction of the AMA together with the methacrylic acid in comparable with the concentration of initiator amount to highlight the TEB of complex hexamethylendiamine (HMDA) to the boiling solution of the complex 2ТЭБ•HMDA in VBA and subsequent temperature control of the reaction mass. For samples of all copolymers isolated from the solution, the composition was analyzed by IR and NMR spectroscopy, molecular weight parameters - by gel permeation chromatography. The obtained data show the formation of parts of macromolecules of copolymers AMA-VBE close to alternating the structure on the mechanism of reversible inhibition in the above scheme, along with the formation of the copolymer according to the usual scheme bimolecular break. The features characteristic for each studied acrylic monomer are revealed. Copolymers of methyl methacrylate (MMA) with VBA used as macroinitiator to obtain block copolymers of MMA-MBA-BA.

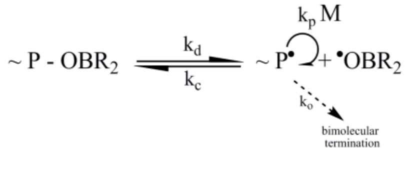

Figure 1. The mechanism of reversible inhibition

Acknowledgments

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References

1. Semenycheva L. L., et al. *Russian Chemical Bulletin.* **2017**, 9, 1660-1664 *[Proceedings of the Academy of Science. Ser. Chemistry*, **2017**, 9, 1660-1664].
2. Zaremsky M.Yu. et al. *Russian Chemical Bulletin* **2013**, 55, 5, 601–624 *[High Molecular Weight Compounds. Ser. B,* **2013**, 55, 5, 601–624].

HYDROPHOBIC COATINGS BASED ON FLUORINATED AND NON-FLUORATED COPOLYMERS OBTAINED VIA SUPERCRITICAL CARBON DIOXIDE DEPOSTION

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Lyophobic modification is universally used to impart water-repellent properties to fiber materials which may be obtained by different methods. In present work we use supercritical carbon dioxide (SC-CO_2) as solution medium since it has low surface tension which allows to decrease coating roughness and reduce residual solvent amount compared to common organic solvents.

In our work we used new fluorinated water repellent compounds based on N-[3-(triethoxysilyl)propyl]-3-(polyfluoroheptyloxy) propane-1-sulfonamides[1], as well as non-fluorinated hydrophobic compounds based on vinyl laurate and vinyltriethoxysilane copolymers. Coatings based on these compounds were obtained under supercritical conditions via deposition onto polyester and polycotton fabric samples directly from SC-CO_2 medium.

It was found that obtained coatings possess high water-repellent properties with a contact angle >140°, as well as high resistance to washing and wearing tests. For certain types of water repellent compounds, certain post-processing conditions were found to increase contact angle up to 145°.

The proposed and implemented approach allows to significantly increase the hydrophobicity of fabric surfaces and impart them with strong hydrophobic properties. Obtained results allow to conclude that it is possible to use these copolymers as water repellents for fabrics and other materials.

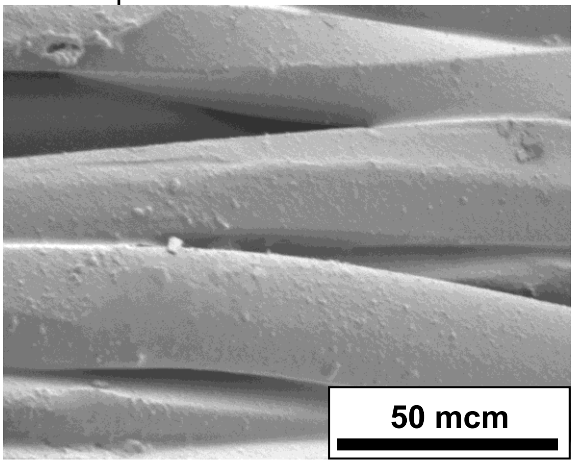

Figure 1. SEM micrograph of the fabric surface coated with hydrophobic compound.

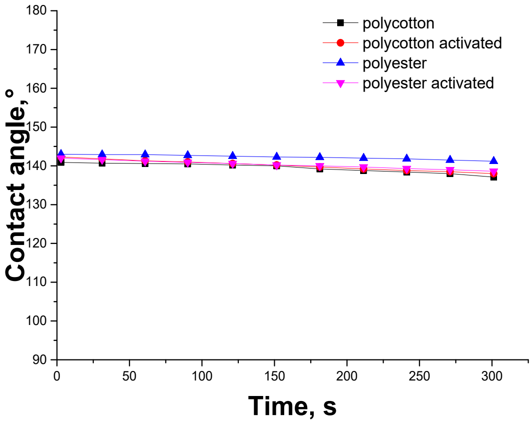

Figure 2. Contact angle of different fabrics coated with hydrophobic compound

Acknowledgments

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References

1. V.I. Dyachenko, L.N. Nikitin, S.M. Igumnov,*Dokl Chem* **2018**, *481,* 139.

PROTON CONDUCTION OF SULPHONATED POLYPHENYLQUINOXALINES

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The synthesis of new polymer proton-conducting electrolytes, which are one of the main components of fuel cells, has attracted considerable attention of researchers [1]. Particularly intensive work is underway to create proton-conducting electrolytes based on sulfonated aromatic condensation polymers [2].

Among the aromatic condensation polymers used to obtain polymeric proton-conducting membranes, there are few works devoted to sulfonated polyphenylquinoxaline, despite the fact that polyphenylquinoxaline meet such important requirements as high thermo- and oxidative stability, high glass transition temperature, good film-forming properties due to solubility in organic solvents and ease of polymer-like conversion. In published works devoted to the electrochemical characteristics of membranes based on sulfonated polyphenylquinoxaline, there are no systematic studies of the dependence of the proton conductivity of these membranes on the degree of sulfonation, temperature, and humidity.

The synthesis of polyphenylquinoxaline was carried out on the basis of 3,3´,4,4´-tetraaminodiphenyl oxide and 1,4-bis (phenylglyoxalyl)benzene, sulfonation of polymer resulted with a mixture of concentrated H_2SO_4 with oleum and obtained sulfonated polyphenylquinoxaline films for research. According to thermal analysis, the films dried at the humidity of 20 rel. % contain 5–10 mass % water and are stable up to 300°C; the initial polyphenylquinoxaline does not decompose up to 300° C.

The conductivity of the initial polyphenylquinoxaline in the form of powder and film does not exceed 10^{-8} S/cm even at the humidity of 95 rel. %. The study of the influence of environmental humidity on the conductivity in tablet form from powders of the initial sulfonated polyphenylquinoxaline showed that the proton conductivity with increasing humidity increases to 10^{-4} S/cm for sulfonated polyphenylquinoxaline with 5.5 mass % sulfur. Activation energy of conductivity at humidity 42 rel. % is 0.4 eV and decreases down to 0.2 eV at 95 rel. %. It is shown that the proton conductivity of sulfonated polyphenylquinoxaline at an ambient humidity of 98 rel. % reaches values of 10^{-6}–10^{-3} S/cm, depending on the degree of sulfonation. Long-term measurements were made on film samples (over 7 years) of the proton conductivity of sulfonated polyphenylquinoxaline with varying degrees of sulfonation. So the proton conductivity of sulfonated polyphenylquinoxaline (9 mass % sulfur) after long-term storage reaches $6*10^{-4}$ S/cm at 98 rel. %

Acknowledgments

This work was performed in accordance with the state task, state registration No AAAA-A19-119061890019-5. The work has been performed using the equipment of the Multi-User Analytical Center of IPCP RAS.

References

1. A.L. Rusanov, N.M. Belomoina E.G. Bulycheva N.A. Yanul, D.Yu. Likhatchev, Yu.A. Dobrovolskii, C. Iojoiu, J.Y. Sanchez, V.Yu. Voytekunas, M.J.M. Abadie *High Performance Polymers*. **2008**, *20*, 627. DOI: 10.1177/0954008307082446
2. N.M. Belomoina, A.L. Rusanov, N.A. Yanul, Y.E. Kirsh *Vysokomol. Soed. Ser. B.* **1996**, *38*, 355.

PROPERTIES AND MICROSTRUCTURE OF POLY(VINYL ALCOHOL) CRYOGELS CONTAINING DIFFERENT FORMS OF CHITOSAN

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Macroporous physical cryogels of poly(vinyl alcohol) (PVA) are generated as a result of cryogenic processing (freezing, further storing frozen and subsequent thawing) of the concentrated solutions of the polymer. PVA cryogels (PVACGs) have wide applied potential in such fields as medicine, biotechnology, food industry, ecology, construction, etc. Variation of the freezing-thawing conditions, as well as the use of soluble and insoluble additives of various nature, are among the factors capable of influencing significantly on the physico-chemical characteristics and microstructure of PVACGs.

In this study, properties and macroporous morphology of complex and composite (filled) PVACGs that contained various forms of polyaminosaccharide, chitosan, have been explored. These types of chitosan additives were as follows: (i) water-soluble chitosan hydrochloride (ChHCl), (ii) water-insoluble coagulate of chitosan-base (ChB) and (iii) dried chitosan powder (ChP). The additives of ChHCl and ChP were introduced in the initial PVA solutions prior to their cryogenic processing, while ChB was formed quite inside the already prepared matrix of PVA/ChHCl complex cryogel by the ChHCl transformation to ChB via the alkaline treatment. Both the above indicated complex (PVA/ChHCl) and composite (PVA/ChP and PVA/ChB) cryogels had elevated rigidity and heat endurance in comparison with the additive-free PVACGs of identical PVA concentration. In the case of filled cryogels, higher elastic modulus was inherent in the samples that contained entrapped disperse particles of powdered chitosan, whereas gel fusion temperature turned out to be higher for the composites that contained entrapped particles of coagulated chitosan, i.e. ChB. Most likely, the latter effect was because of the larger surface of interfacial contact between discrete and continuous phases inside the PVA/ChB-cryogels.

The microstructural features of the above-indicated complex and composite PVACGs have been studied with optical microscopy of thin sections for the respective gel matrices. It was found that macroporous morphology of such cryogels, as well as size and shape of the discrete particles are dependent on the thermal conditions of the cryotropic gel-formation, type and amount of the introduced soluble (ChHCl) or insoluble (ChP, ChB) additives. The characteristic feature of the PVA/ChB-composites is a rather uniform distribution of the filler within the gel bulk.

Owing to the chitosan presence such composite PVACGs can be used as the so-called “smart” absorbents for the heavy metal ions. It was demonstrated that the sorbents that contain the amorphous form of chitosan (i.e. ChB) possess the binding capacity with respect of Cu^{2+}-ions close to the theoretic value, whereas the capacity of the composite cryogel which contains powdered chitosan (i.e. ChP) is lower notably because of the dense high-crystallinity structure of this filler matter.

The study was supported by the grant No. 18-33-00324 of the Russian Foundation for Basic Research.

THE INFLUENCE OF THE DURATION OF THE SYNTHESIS ON THE PROPERTIES OF THE OBTAINED OLIGOMER

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Polyethylene terephthalate (PET) has found it's application in many industries from the manufacture of fibers, filtering and absorbing elements till PET bottles and sound insulation materials. However, mechanical processing is not the only way for usage of recycled PET, the alternative chemical conversion is presented in this paper.

Department of chemical technology of polymers of SPbSTI(TU) conducts researches in getting products of PET aminolysis, which can then be used the modifier component for foamed materials. As everyone knows, the duration of the synthesis can significantly affect on the product properties. The aim of this research is to consider the effect of the duration of the synthesis of oligomers based on aliphatic polyamines and secondary PET on its properties.

The object of the study is the product of reaction of PET aminolysis at a temperature of 190-210 °C. During the four-hour synthesis, we had been taking samples of the synthesized oligomer every 30 minutes and later measured their viscosities and "amine numbers", the results are shown in the table.

All obtained values are within the margin of error, so we can assume that the destruction and formation of functional groups does not occur. Conducted Fourier-IR studies also confirm this conclusion, so we can say that the duration of synthesis does not affect the quality of the resulting product.

Table. The Dynamic Viscosities of the Hardener Samples and the Amine Number

Sample №	Dynamic viscosity, Pa·s	Amine Number, mg KOH/g
1	21,9	874
2	19,4	871
3	19,9	873
4	20,6	875
5	19	870
6	18,1	871
7	19,8	874
8	19,1	871

FERROCENE- AND THIOPHENE-CONTAINING POLYMERS AS PRECURSORS OF MAGNETIC MATERIALS

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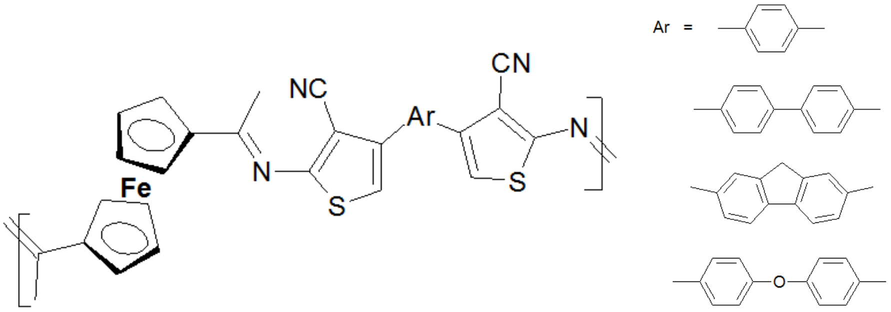
Organometallic moieties such as ferrocene involved in conjugated systems like thiophene are of large interest as a foundation for the synthesis of organometallic polymers with the aim, among others, to obtain models for electron transfer models[1].

It is known that ferrocenyl-containing compounds upon appropriate treatment produce magnetic nanoparticles[2], while polythiophene exhibits hole conduction, which is used to design optoelectronic and magnetic materials for various data storage devices, magnetic sensors, and magnetic elastomers[3].

The aim of this work is to synthesis a new thiophene- and ferrocene-containing precursor for preparing ordered organohybrid assemblies to design new materials showing unique mechanical, electrical, optoelectronic, and paramagnetic properties.



Polymers when heated at 573-673 K show magnetic properties.

Acknowledgments

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References

1. B. Jin, F. Tao, P. Liu *J. Electroanalyt. Chem.* **2008**, 624, 179.
2.M. Saleem, H. Yu, L. Wang, Z. Abdin, H.Khalid, M. Akram, N.M. Abbasi, J. Huang *Anal. Chim. Acta*. **2015**, 876, 9.
3. H. Muraoka, S. Ogawa *Pure Appl. Chem.* **2013**, 85, 777.

LIQUID-CRYSTALLINE POLYMERS AS SURFACE AGENTS FOR SEMICONDUCTORS QUANTUM DOTS ACCORDING TO QUANTUM-CHEMICAL CALCULATIONS

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Due to stabilization, localization and organization of quantum dots provided by combination of semiconductor quantum dots with liquid-crystalline polymers it is possible to create efficient optical materials with varying spectral characteristics. The present study reports the results of quantum-chemical simulation of structural and photophysical properties of some liquid-crystalline polymers that are used for development of optoelectronics devices containing quantum dots. The study of interaction of studied polymers with the surface of cadmium and zinc selenide and sulfide by the density functional theory revealed the influence of functional groups of interacting liquid-crystalline polymer on the energy of the corresponding donor-acceptor bond. The difference between geometrical parameters in the bulk and on the surface of quantum dots was established, which indicates a deviation of the surface morphology from the internal structure of the substance. It has been established that liquid-crystalline polymers can form strong bonds with the surface cadmium and zinc atoms and act as passivating surface agents, that can stabilize the physicochemical properties, shape and size of quantum dots. According to the results of quantum-chemical simulation it is been established that polymers with nitrile groups are capable of forming stronger bonds with the surface atoms. Simulation of the quantum dot surface with a polymer containing carboxyl groups has shown that the symmetrical bidentate coordination of the carboxyl group of the polymer through oxygen atoms onto a single atom of cadmium or zinc on the surface is more preferable. The obtained simulation results are confirmed by experimental data. Periodic plane-wave density functional theory calculations were carried out with PBE implementation of the generalized gradient approximation in conjunction with the projector-augmented wave representation of the atomic cores.

Quantum-chemical calculations were performed using the facilities of the Joint Supercomputer Center of Russian Academy of Sciences and the Supercomputing Center of Lomonosov, Moscow State University.[1]

Acknowledgments

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References

1. V.V. Voevodin, S.A. Zhumatiy, S.I. Sobolev, A.S. Antonov, P.A. Bryzgalov, D.A. Nikitenko, K.S. Stefanov, V.V. Voevodin, *Open Syst. J.* **2012**, *7*, 36.

RESEARCH OF INFLUENCE OF RECYCLED POLYETHYLENE TEREPHTHALATE PRODUCTS ON PROPERTIES OF FOAM MATERIALS

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In these days, the polymer industry is developing rapidly. So, production has reached 348 million tonnes per year. An important place among polymers is occupied by polyethylene terephthalate (PET), whose world production has reached 29 million tonnes per year. Alongside this, the waste of used polymer products increases, which involves the problem of processing products. Recycling of waste polymeric materials is becoming relevant not only from the standpoint of environmental protection, but also allows you to significantly save on primary raw materials.

In this research, the possibility of using secondary PET products as a modifier for foam materials based on phenol-formaldehyde novolac resin (PF) was considered.

To obtain a modifying additive, secondary PET were sequentially subjected to glycolysis with ethylene glycol and aminolysis with triethylenetetramine. Modified compositions of the PF with the obtained oligomeric product were obtained by fusion of the components in a sand bath at a temperature of 150-160 ° C. In the preparation of composite foams, we used phenol-formaldehyde novolac resin of the SF-0112 brand, hardener hexamethylenetetramine (HMTA), a chemical blowing agent 2,2'-azobisisobutyronitrile, and a block copolymer of oligosiloxane and oligo-etherpolyols 48 as a surfactant.

The resulting compositions were investigated for tensile stress in compression and bending. From the graphical dependencies (Figure 1), it can be seen that the introduction of the modifier practically didn't affect the strength characteristics of the material during bending. The introduction of a modifying additive in an amount of 15 mass parts leads to a significant increase in the value of the breaking stress during compression.

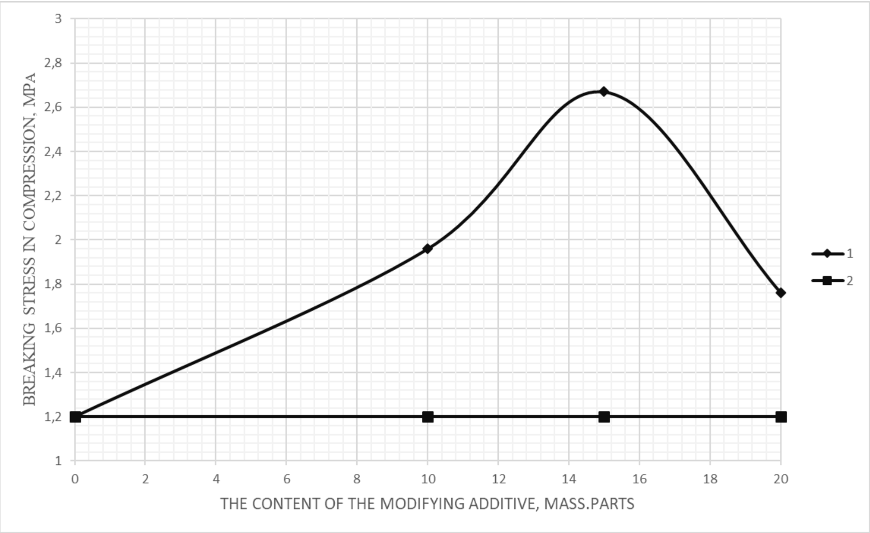

Figure 1. The dependence of the breaking stress on the content of the modifying additive: 1 - in compression, 2 - in bending

SYNTHESIS OF BIOSIDE CHITOSAN DERIVATIVES AS A DRUG CARRIER

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In the recent years researchers focus on the work done on the synthesis of biocide polymers, their targeted transport of medical drugs and their long-term effects. In this sense, the use of polymers is one of the most modern methods in the delivery of medicines to the right organs. In this case the polymers are used as matrix and contain the drug, and also promote them to be isolated from the body. Thus, the drug cannot be released from the polymer until the polymer macromolecules enter the cell they need. Taking into account the above, the present work is devoted to the generation of naturally occurring bioside polymer chitose derivatives. Due to the fact that the chitosan polymer is non-toxic and it has excellent quality materials for the transport of drugs in medicine, it provides the basis for research in this area. For this purpose we have synthesized N, N diethyl chitosan, N methyl chloride derivatives. The synthesis was carried out in two stages - redox and alkylation, and was performed according to the known method of "Schiff" reaction. For this, chitosan is suspended in a solution of acetic acid, and the acetate aldehyde is given in the form of drops. $NaBH_4$ is added to it, the pH of the medium is measured and the pH is determined to be 4-4.5, and the pH of the medium is then transmitted and extracted by alkaline (KOH) 10. After extraction the substance is dried and brought to a stable weight. Alkylation is done on the Soxlet machine. N, N is quaternized at the temperature of 35^0C in the presence of ethylene chitosan acetonitrile and mixed with methyl iodide addition in an inert nitrogen environment. As a result, N, N diethyl, N methyl chitosan iodide are obtained. The substance is diluted in NaCl solution by ion exchange for 24 hours. The sample was investigated using RFA, SEM methods, and the acquisition of N, N diethyl, N methyl chitosan chloride derivatives was confirmed. The modified chitosan is intended to continue the practice of immobilization of L-thyroxine and its use in the treatment of rheumatic diseases in medicine.

References

1. Chen Z., Mo X. He C, Wang H (2008) Carbohydrate Polymers 72: 410-418.
2. Kweon DK, Song SB, Park YY (2003) Biomaterials 24: 1595-1601.
3.Meiyan Wu, Zhu Long, Huining Xiao, Cuihua Dong (2017) Carbohydrate Polymers http://dx.doi.org/on.1016.

POLYCONDENSATION IN SUPERCRITICAL CARBON DIOXIDE: INEOS CONTRIBUTION

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The report is dedicated to current state of fluid polycondensation. The bulk of polycondensation polymers was synthesized in the last decade of the XX-th century. If a polymerization has been studied to date in detail (monomers are excellent soluble in supercritical carbon dioxide (SC CO_2)), a polycondensation has been investigated much weaker and the number of polymers synthesized does not exceed two dozen. This phenomena is related with a bad solubility of condensation monomers in supercritical carbon dioxide, high heterogeneity of the reaction system and respectively small polymers MM. The general advantages of SC CO_2 application in polymers synthesis are favourable ecology and spontaneous and complete evaporation of the fluid after the end of the experiment that eliminates “the problem of residual solvent”. A specific feature of the synthesis in SC CO_2 is the reversible plasticization of polymers (Tg reduction “in situ”) and Tmelt reduction of monomers which allows the reaction to be conducted in the melt at a reduced temperature, preventing undesirable side processes in the system. The SC CO_2 was used in the work as a solvent, extractant, plasticizer and bifunctional catalyst. Methods of heterogeneity overcoming and high MM achievement are discussed. INEOS RAS, V. V. Korshak school have made a worthy contribution to fluid polycondensation: the aromatic polyimides, copolyimides, fluorinated polyimides and polyimidosiloxanes [1], polyesters (polyarylates) [2], photoluminescent phenilated polyfluorenes [3], ferrocene-containing polyphenylenes [4], poly(phenylquinoxaline)s [5] and finally poly(naphthoylenebenzimidazole)s [6] have been firstly synthesized here in SC CO_2.

Acknowledgments

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References

1. Ernest E. Said-Galiyev, Yakov S. Vygodskii, Lev N. Nikitin, Rostislav A. Vinokur, Marat O. Gallyamov, Inna V. Pototskaya, Vyacheslav V. Kireev, Alexei R. Khokhlov, *J. Supercrit. Fluids.* **2003,** *26,147.*
2. E. E. Said-Galiev, Yu. N. Leonov, V. A. Vasnev, G. D. Markova, R. A. Vinokur, L. N. Nikitin, and A. R. Khokhlov, *Polym. Sci.* **2005,** *47,5.*
3. M. L. Keshtov, E. I. Maltsev, A. M. Lopatin, L. N. Nikitin, D. V. Marochkin, V. P. Perevalov, P. V. Petrovskii, A. R. Khokhlov, *Polym. Sci.* **2012***,54,106.*
4. Raisa Dvorikova, Lev Nikitin, Yurii Korshak, VIctor Shanditsev, Alexander Rusanov, Sergei Abramchuk, Alexei Khokhlov, *”Doklady Chemistry.* **2008**, *422, Part 1, 231.*
5. Nataliya M. Belomoina, Elena G. Bulycheva, Lev N. Nikitin, Viktor G. Vasil’ev, Igor V. Elmanovich, Maria Bruma, *J. Supercrit. Fluids.* **2016,** *113, 66.*
6. Nataliya M. Belomoina, Elena G. Bulycheva, Igor V. Elmanovich, Mikhail I. Buzin, Roman S. Begunov, Ivan S. Chaschin, Lyubov A. Wasserman, *J. Supercrit. Fluids.* **2019***, 148, 148*

SYNTHESIS OF BIOSIDE CHITOSAN DERIVATIVES AS A DRUG CARRIER

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ABSTRACT

The use of polysaccharide-containing magnetic adsorbent in which magnetite particles are tightly covered by the polysaccharide(chitin) shell for pollutant removal from water media has been described. Multi-purpose magnetic chitin combines magnetic properties of magnetite and adsorption properties of polysaccharide. This composite is easy to obtain and use. It is shown that such obtained magnetic chitin has a high adsorption capacity for a number of pollutants both inorganic ($Co^{2+}$and Cr^{6+}) and organic (2- and 4-nitrophenols (NPhs)) nature. The adsorption capacities of the magnetic chitin for cobalt and chromium cations reached 41 mg·g^{-1} and 15 mg·g^{-1}composite, respectively. The maximum adsorption value for 4-NPh were about three times higher than those for 2-NPh at the same adsorbent-adsorbate ratio, and reached 19 mg·g^{-1} composite or 56 mg·g^{-1} of chitin constituent. Synthesized adsorbent is recyclable and *environmental friendly*.

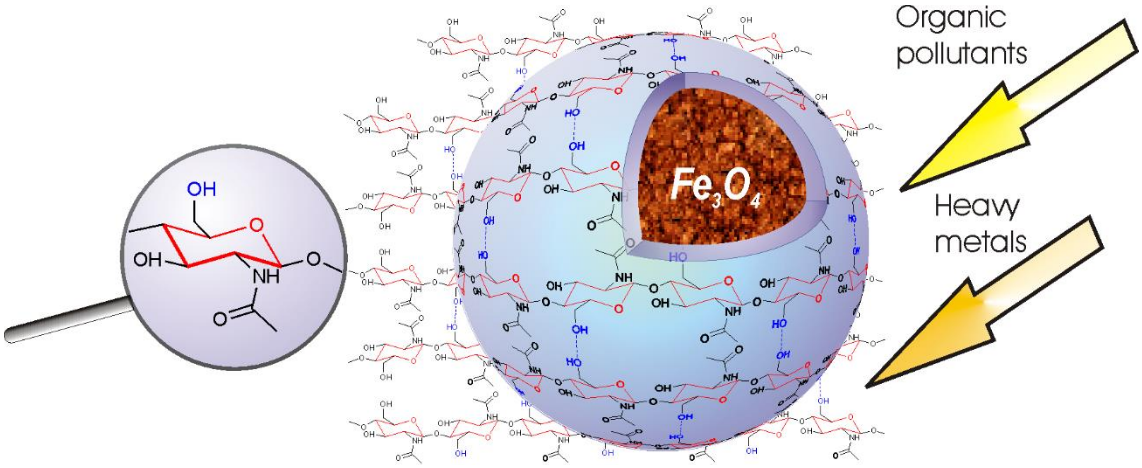

Figure 1. Schematic representation of magnetic chitin – adsorbent of pollutants

Acknowledgments

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This work was performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

PREPARATION AND EVALUATION OF GELS BASED ON POLY(TRIMETHYLENE CARBONATE) FOR REGENERATIVE MEDICINE APPLICATIONS

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In the present study we propose the use of poly(trimethylene carbonate) (pTMC) solutions with controlled degradation time intended for transport of therapeutic and other biologically-active agents for surgical purposes to manage bone tissue regeneration process and treatment of surgical site infection. One of the key features of the aliphatic polycarbonates is the ability to resorb in human body without pH change in the surrounding tissue[1], accompanied with the zero-order kinetics of degradation[2].

Oligomerization and polymerization of the trimethylene carbonate was performed in the monomer mass with stannum(II) octanoate as a catalyst using own original phosgene-free patented method – as a result, linear structure samples of oligoTMC and pTMC were obtained, with medium polymerization degree equal to 4 and 35, respectively, confirmed using IR- and NMR ^{1}H spectroscopy.

For all oligoTMC and pTMC samples were set biocompatible settings for gel formation by the selection of solvents and components concentration (with polymer concentration from 20% to 80%). To improve mechanical characteristics of TMC homopolymer it was cross-linked using next agents: ethylene glycol diglycidyl ether, diethylene glycoldiglycidyl ether, propanediol-1,3diglycidyl ether, glycerinediglycidyl ether, dimethyldimethoxysilane,and methyltrimethoxysilane– the most effective gel combination was pTMC with ethylene glycol diglycidyl ether.Gel was sterilized using X-ray radiation with dosage of 25 kGy for subsequent biocompatibility evaluation *in vitro*. To our knowledge, there are only a few published studies[3] where pTMC gels were fabricated and tested for its functional abilities.

However, a subsequent experiment for biocompatibility evaluation of produced gel*in vitro* with cell culture of human fibroblast cells during one week cultivation showed that gel requires an increase in its hydrophilic properties because of cell culture death signs after contact with the gel. This could be explained with still persist (after all treatments) high material hydrophobicity and absence of functional groups – thus, pTMC-based gel requires further more hydrophilic polymer structure and functionalization before biocompatibility evaluation.

References

1. P. Gunatillake, R. Mayadunne, R. Adhikari, *Biotechnol. Ann. Rev.*, **2006**, *12*, 301-347
2. Kluin OS, Van der Mei HC, Busscher HJ, Neut D. *Biomaterials*, **2009**, 30, 4738-42
3. Sharifi S, Blanquer SB, van Kooten TG, Grijpma DW. *Acta Biomater*. **2012**, 8(12), 4233-43. doi: 10.1016/j.actbio.2012.09.014.

HETEROPHASE RAFT-POLYMERIZATION IN THE PRESENCE COPOLYMERS OF ACRYLIC ACID AND N-ISOPROPYLACRYLAMIDE WITH TRITHIOCARBONATE GROUP

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Currently, the synthesis of dispersions of amphiphilic block copolymers is the subject of research by many scientific groups around the world. Among the huge variety of such objects, a special role is played by stimulus-sensitive block copolymers, which under the influence of various parameters (pH, temperature, etc.) can change their morphology, which is very popular in various fields of engineering and technology.[1]

One of the methods of obtaining such particles is reversible addition-fragmentation chain-transfer polymerization (RAFT-polymerization). Unlike traditional radical polymerization, a RAFT-agent is introduced into the initial system, which allows controlling the molecular weight characteristics of the product. Polymers containing the required functional group are used as such compounds in heterophase polymerization. The polymer RAFT-agent will not only control the MMD, but also act as a stabilizer of the resulting polymer-monomer particles.

In this paper, heterophase polymerization of n-butyl acrylate (n-BA) in the presence of a copolymer of acrylic acid (AA) and N-isopropylacrylamide (NIPAM) with a tritiocarbonate group inside the chain will be used for the synthesis of dispersions of amphiphilic block copolymers. Links the NIPAM should give the future to the copolymer of thermosensitive properties.[2]

n-BA polymerization was performed in methanol and water (volume ratio monomer/medium = 1/7.5, methanol/water = 4/1), AIBN (2.7×10^{-3} mol/l) was used as the initiator. The agent was a copolymer of AA and NIPAM (mole ratio AA/NIPAM = 75/25, 50/50) (1.1×10^{-3} mol/l). The polymerization temperature was 65 °C.

In the presence of a copolymer with a lower NIPAM content, polymerization proceeded at a higher rate to high limit values of monomer conversion. Polymerization with a copolymer AA/NIPAM with a molar ratio of 50/50 was almost completely inhibited, the conversion did not exceed 15 %.

Further studies will be conducted with the copolymer AA/NIPAM with a molar ratio of 75/25.

Acknowledgments

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References

1. S. Sugihara, A. Blanazs, S.P. Armes, A.J. Ryan, A.L. Lewis *J. Am. Chem. Soc.* **2011**,*133*, 15707.
2. X.L. Lang, A.D. Patrick, B. Hammouda, M.J.A. Hore, *Polymer* **2018**, 145, 137.

THE INFLUENCE OF THE PLASTICIZERS ON ELASTICITY OF THE POLYMER COMPOSITION

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Widespread polyethylene terephthalate (PET) has lots of various ways of its processing and disposal. Nowadays there are many ways to process PET, but intensive pace of industrial development cause further researches in this subject. And also the industry is always interested in the invention and producing new cheap structural materials with improved characteristics.

The Department of Chemical Technology of Polymers of SPbSTI(TU) conducts the invention of an alternative method for processing PET by its aminolysis with aliphatic polyamines and using the resulting product as one of the components of the foaming composition. To increase the elasticity of the material, prevent premature cracking under mechanical loads and modify the characteristics, developed material was improved by the use of plasticizers.The purpose of this research is making the elastic material using various plasticizers in different proportions. As the plasticizing agents dibutyl phthalate (DBP) and dioctyl phthalate (DOP) were used. The test results depending on the amount of plasticizer are summarized in the table.

As can been seen the use of DBP has almost no effect on the toughness of the compositions if small amount of plasticizer is added. But at the same time unmodified samples are brittle and break with a little effort, although adding the plasticizer makes the material much more elastic. Using DOP as a plasticizing agent increases the toughness of the samples, but this reagent has no effect on the elasticity.

According to the test results, it was found that the use of plasticizers has a positive effect on the properties of the compositions, researches should be continued and tests of various fillers and other plasticizers carried out.

Table. Strength characteristics of modified samples

Plasticizer, massparts	The toughness of the 150 kg/m^{3}compositions , MPa
No plasticizer	
-	1,8
DBP	
1	1,6
2	1,7
4	1,4
6	1,1
DOP	
1	2,8
2	2,3
3	2,3
4	2,4

VISCOELASTIC PROPERTIES PH SENSITIVE SUSPENSIONS OF WORMLIKE MICELLES AND HALLOYSITE NANOTUBES

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This work is devoted to the study of viscoelastic properties of solutions of polymer-like wormlike micelles of surfactant and nanotubes of natural halloysite clay. Wormlike micelles, also called living polymers, intertwine like linear polymers and form a dynamic network of entanglements at the certain concentrations, therefore they impact aqueous solutions viscoelastic properties. The properties of such solutions depend on various parameters such as surfactant concentration and pH. It has been shown in the literate that the properties of such a system can be modified by addition of nanoparticles or nanotubes, because wormlike micelles can be crosslinked by nanoparticles into stronger networks at the certain conditions [1]. Moreover nanocomposite systems acquire new functional properties due to the introduction of nanoobjects. In our work, we study viscoelastic suspensions of wormlike micelles and nanotubes of halloysite clay.

We used a zwitterionic surfactant: oleylamidopropyl betaine, which contains a small admixture of oleylamodopropyl dimethylamine (OA). In the weakly alkaline and acidic environment OA acts as a cationic co-surfactant due to the transition from a neutral to a cationic form, therefore the system is pH sensitive. Natural nanotubes of halloysite were used as nanofiller. It's a non-toxic, safe and easily accessible material, which charge also depends on the pH of the system.

We study the concentrations of the components and the pH range at which stable homogeneous suspensions were obtained. An increase in the viscoelastic properties of the system up the introduction of nanotubes was observed, which can be explained by the incorporation of halloysite into the network of wormlike micelles. The elastic response of the system increased with an increase in the concentration of nanoparticles due to the binding of components. The rheological properties of the system were also studied in a wide pH range in two cases: in the presence and absence of nanotubes.

Thus, pH sensitive stable viscoelastic suspensions of wormlike micelles and halloysite nanotubes were obtained. Such objects are promising for targeted delivery of substances, because nanotubes can act as nanocontainers, and wormlike micelles create a matrix for their stabilization in an aqueous medium.

Acknowledgments

This work was supported by the Russian Science Foundation (project no.17-13-01535).

References

1. O.E. Philippova and V.S. Molchanov, *Current Opinion in Colloid and Interface Science* **2019**, *43*, 52.

WORMLIKE MICELLES AND OPPOSITELY CHARGED HALLOYSITE NANOTUBES NETWORKS

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Surfactants are known to form spherical micelles in water medium. By adding a salt, they can transform to long cylindrical flexible micelles – co-called wormlike micelles, which lead to the formation of spatial network with the pronounced viscoelastic properties similarly to polymer semidilute solutions.

Halloysite nanotubes are in interest for our work because it is a readily available and nontoxic material with the different inner and external surfaces and therefore different properties on them.

To create wormlike micelles, we used the cationic surfactant having long hydrophobic tail containing 22 carbon atoms in the presence of potassium chloride salt. The halloysite has a negative charge on the wide range of pH. Amount of adsorbed surfactant correlates to electrostatic attraction between them. Moreover, it is believed nanotubes can link wormlike micelles. An interaction between wormlike micelles and halloysite nanotubes leads to the change of viscoelasticity of system. The nanotubes are assumed to be embedded in the micelles' network do it more tenacious.

We have observed changes in the rheological properties system varying the different parameters: pH, the concentration of surfactant and the halloysite concentration. Studying of all these dependences gives the opportunities to study nanotube and wormlike micelles interaction because rheological parameters are quite sensitive to network structure. Nanoclay nanotube filled wormlike micelles networks have desirable properties for practical application.

Acknowledgments

This work was supported by the Russian Science Foundation (project no.17-13-01535).

SMALL ANGLE X-RAY SCATTERING EXAMINATION OF CHITOSAN-BASED POWDERS, FILMS, AND AEROGELS WITH SILVER OR GOLD NANOPARTICLES PREPARED USING METAL VAPOR SYNTHESIS

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Small angle X-ray scattering (SAXS) technique using synchrotron radiation is very suitable and unique tool for characterization of the supramolecular structure of biopolymer materials in different forms.[1]

In this work we studied the structure of chitosan-based composite materials in the powder, aerogel and film form by means of SAXS. The composite materials were prepared using metal vapor synthesis technique as described previously.[2] Various polymer matrices either containing metal nanoparticles (gold or silver) or not were evaluated.

To study dimensional characteristics of the composites the model-fitting analysis for SAXS results using simulation programs from ATSAS software was used.[3] When modeling the SAXS calculated curves, the scattering models based on the microscopy results were postulated. As a result, the dimensional characteristics of chitosan units (fibrils in case of aerogel and globule-like structures in case of films) were determined.

For metal nanoparticles (gold or silver) in different polymer matrices (powder, film, and aerogel) the volume size distribution function was calculated from difference curves, representing the scattering only from metal particles. During the modeling process, metal nanoparticle was represented as single rigid sphere with a characteristic diameter that did not interact with others. The modeling results showed an asymmetric size distribution function for all scattering objects (such as chitosan units and metal nanoparticles) containing several fractions with characteristic sizes.

SAXS analysis revealed that nanoparticles in chitosan powder are agglomerated into metastable aggregates from few to several thousand individual particles. During the films and aerogels formation from chitosan-based powder composites redispersion of aggregated metal nanoparticles occurred.

Acknowledgments

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References

1. D. I. Svergun, E. V. Shtykova, V. V. Volkov, L. A. Feigin, *Crystallography Reports* **2011**, *56*, 725.
2. E. E. Said-Galiev, M. S. Rubina, A. Yu Vasil'kov, A. V. Naumkin, A. R. Khokhlov, and K. A. Abd-Elsalam, *Conference Proceedings* **2018**, *1981*, 1.
3. D. I. Svergun, Journal of Applied Crystallography **1992**, 25, 495.

HYBRID METAL(OXIDE)-POLYMER NANOCOMPOSITES BASED ON CARBOXYMETHYLCELLULOSE CROSS-LINKED BY IN-SITU FORMED COPPER (I) OXIDE NANOPARTICLES FOR PHOTOCATALYTIC APPLICATIONS

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Semiconductor nanoparticles have been explored extensively for catalytic decomposition of organic contaminants in water[1]. Photochemical decomposition catalyzed by nanoparticles of semiconductor metal oxides is a competitive method for removing dyes due to its simplicity, high efficacy and economic feasibility[2]. To increase their physical-chemical stability and photo-catalytic activity semiconductor nanoparticles must be isolated. This problem can be solved by encapsulating of the photo-catalytic nanoparticles in polymer matrix.

Here, we describe a simple on-air one-stage synthesis of hybrid metal(oxide)–polymer composites based on semiconducting Cu_2O nanoparticles distributed within a carboxymethylcellulose (CMC) matrix. The structural characterization of hybrid metal(oxide)–polymer nanocomposites Cu_2O–CMC were performed by X-ray diffraction (XRD) and Infra-Red (IR) spectroscopy. The morphological analysis was made by Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM). For determination of inorganic phase content in a Cu_2O–CMC hybrid nanocomposites ultraviolet (UV) spectrophotometry technique was used. A high efficacy of the obtained metal(oxide)–polymer nanocomposite for photo-catalytic decomposition of azo-dye Methyl Orange (MO) both in air oxidation by oxygen and in the presence of hydrogen peroxide was demonstrated.

Acknowledgments

This work was supported by RFBR Project № 18-03-01024 A

References

1. X. Qu, P. J. J. Alvarez, Water Research, **2013**, *47(12)*, 3931.
2. I. Arabatzis, Journal of Catalysis, **2003**, *220(1)*, 127.

CONTROLLED SYNTHESIS OF POLYMERS BASED ON ACRYLONITRILE CATALYZED BY COPPER COMPLEXES WITH NITROGEN-CONTAINING LIGANDS

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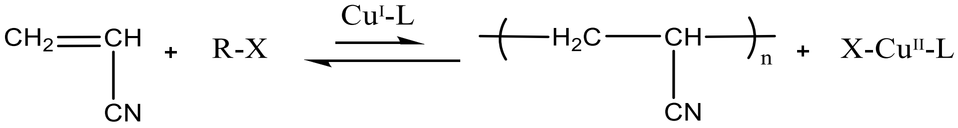
Lobachevsky State University of Nizhny Novgorod, Russia grishin_i@ichem.unn.ru

Atom Transfer Radical Polymerization (ATRP) has been successfully used for the production of a wide range of modern materials with the desired mechanical and strength properties. Interest in the synthesis of polymers based on acrylonitrile with desired molecular weight characteristics and composition is due to its usage as precursors for high-quality carbon fibers.

The key component of the polymerization system is a metal complex catalyst. Catalytic systems based on copper halides and nitrogen-containing ligands are one of the most studied ones. Meanwhile, despite the large number of proposed systems, there are no universal systems to produce polymers based on a wide range of monomers, but the problems of finding the most efficient catalyst and conditions for polymerization are important and relevant.

In this work the process of synthesis acrylonitrile polymers was carried out in the presence of various copper-based catalytic systems for evaluation of their influence on the dynamic of the process and characteristics of the obtained samples. Copper bromide (I) based systems were used as a metal complex catalysts. The compounds of different activity such as tris(2-pyridylmethyl)amine (TPMA), tris[2-(dimethylamino)ethyl]amine (Me_6TREN) and 2,2'-bipyridyl (bpy) were used as ligands. The process was carried out at a temperature of 60 ^oC in dimethylsulfoxide media. It was shown that the use of these compounds as ligands allows carrying out the polymerization in accordance with the atom transfer radical polymerization mechanism. The controlled nature of the process is evidenced by an increase of molecular weight throughout the reaction in common with sufficiently low polydispersity coefficient of the synthesized samples (1.3-1.9). The obtained values of molecular weights are in a good agreement with the theoretically calculated ones. It was demonstrated that increase of the initial molar amount leads to a decline of polymerization control that indicated by the broadening of molecular weight distribution and in deviation of the obtained values of molecular weights from the theoretically ones.

The results showed that to achieve a high yield of the target product, the most appropriate is the use of a catalytic system containing TPMA and BiPy. The systems containing TPMA and Me_6TREN are attractive to achieve high yield of the product in the shortest time (9 hours).



Scheme 1. The synthesis of polyacrilonitrile by ATRP.

Acknowledgements

The work was supported by Russian Foundation for Basic Researches (Proj No 18-43-520016).

CHEMICAL STRUCTURING OF POLYORGANOSILOXANE COATINGS

Sergey Stepin, Vladislav Suchkov

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Polyorganosiloxane oligomers have found quite wide application in paint technology due to such valuable properties of coatings on their base as heat resistance and hydrophobicity. However, without chemical structuring, which requires thermal treatment at temperatures above 250 °C, polyorganosiloxane-based coatings have insufficient chemical resistance and physical and mechanical properties. The complication of the painting technology when the thermal treatment steps are included in the coating formation process, as well as the additional costs and impossibility of heating large-sized objects, makes it necessary to find hardeners providing chemical structuring of polyorganosiloxanes without heat supply.

In this work, the possibility of chemical structuring of coatings based on polyorganosiloxane lacquer by commercially available and synthesized alkoxysilane group-containing compounds has been investigated. As the film-forming base of the coatings, methylphenylsiloxane oligomer containing terminal butoxysiloxane groups in macromolecules dissolved in a mixture of xylene and butanol (silicone lacquer) was used. Following hardeners were utilized, 3-(3-trimethoxysilyl)propyl)isocyanurate, silylated polyurethane, gamma-aminopropyltriethoxysilan, and the products of its reactions with tetraethoxysilane with polyols of different nature and structure.

It was assumed that chemical structuring of the film-forming oligomer would occur when its terminal butoxyl groups will react with silanol groups of hardeners produced by hydrolysis of their alkoxysilane groups by air moisture. Tin dibutyldilaurate catalyst was used to accelerate these processes.

Lacquer-based coatings with different hardeners were applied on steel and glass plates, and the process of forming the paint film was controlled by the hardness determined on the pendulum device. The end of the process was recorded by no change in hardness. The degree of structuring of the coatings was assessed by the gel fraction content, which was determined by exhaustive extraction of the cured films with acetone in a Soxlet apparatus.

As a result of experiments, it has been shown that the introduction of additives in the coating composition leads to increase in the duration of coating formation, obviously due to the chemical reactions of hydrolysis and structuring. The degree of crosslinking of the coatings (gel fraction content in the formed coating) and their resistance to solvent action (wiping with acetone) depends on the content of alkoxysilane groups in the hardener and on how far these located from each other. Addition of tin dibutyldilaurate accelerates the structuring process and imparts a positive effect on the degree of chemical structuring of coatings.

Use of mixtures of structuring additives makes it possible to optimize physical and mechanical properties of silicone coatings. In particular, the combination of polyether polyol adducts with alkoxysilanes and products containing urethane moieties allows achieving the best ratio between hardness and elasticity of coatings.

YNTHESIS OF GRAFT-COPOLYMERS OF ACRYLAMIDE AND GELATIN IN THE PRESENCE OF TRIBUTYLBORON

Sustaeva Karina, Vavilova Anna, Kuznetsova Yulia, Markin Alexey, Mitin Alexander, Podguzkova Marina, Semenicheva Lyudmila

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Grafted polymerization of acrylamide on natural polymer gelatin molecule allows to obtain hybrid copolymer. These copolymers have a more valuable chemical and biological properties compared to their natural counterparts and are much more promising in practice.

The graft-copolymer of acrylamide and gelatin was synthesized in the presence of various concentrations of tributylboron in a water suspension at 60°C under argon flow. Grafting is carried out at the reaction centers which are formed due to the interaction of gelatin with alkylborane (Figure 1). Molecules of borylated gelatin initiate polymerization by the mechanism of reversible inhibition (Figure 2), similarly to that proposed in research[1].

The IR spectrum of the copolymers contains absorption bands related to polyacrylamide, gelatin and unreacted acrylamide. One value of the glass transition temperature was determined by differential scanning colorimetry, therefore, the high molecular weight products are copolymers. The molecular weight of the copolymer increases with increasing concentration of tributylboron.

An increase in the concentration of tributylboron promotes an increase in the proportion of polyacrylamide in the copolymer and a decrease in the amount of unreacted acrylamide. Extraction with chloroform in a Soxhlet apparatus was used as an effective method for removing residual monomer.

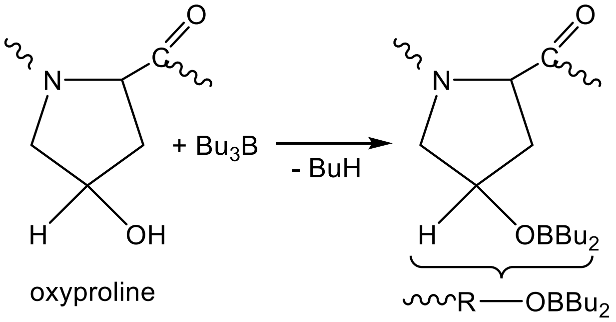

Figure 1. Interaction of gelatin with alkylborane

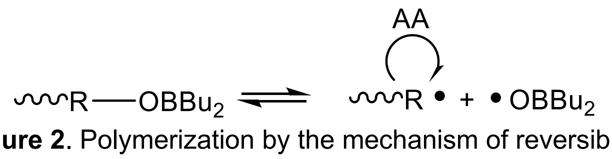

Figure 2. Polymerization by the mechanism of reversible inhibition

References

1. M.Yu. Zaremsky, E.S. Garina, M.E. Gursky, Yu.N. Bubnov,*High Molecule B* **2013**, *55*, 601-624.

SYNTHESIS AND PROPERTIES OF 128-ARM POLYDIMETHYLSILOXANES WITH DIFFERENT LENGTH OF ARMS

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This study is devoted to the study of a number of multi-arm polydimethylsiloxane systems, the branching center of which is the 6th generation carbosilane dendrimer with a bidodecyl shell, namely, the study of the behavior of these systems in bulk using a complex of methods, including rheological, to establish the dependence of various characteristics on the arm length in star polymers.

Previously it was shown that the properties of similar objects change significantly with an increase in the number of arms (f), and at f = 128 the intrinsic viscosity of the PDMS star in solution is lower more than 10 times[1] than for a linear analogue. Besides this, the formation of column type mesophase in a wide range of temperatures was discovered for multi-armed star-shaped PDMS[2]. For these reasons, it is undoubtedly of interest to further study these objects.

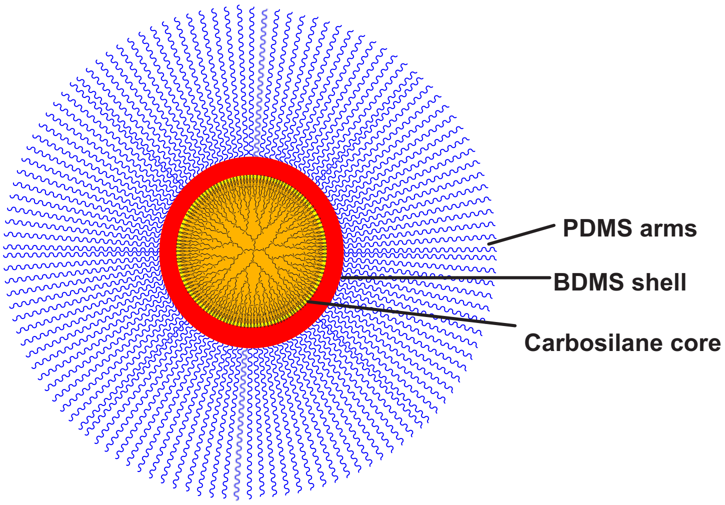

Figure 1. Schematic image of 128-arm star-shaped PDMS.

Acknowledgments

This work was financially supported by Ministry of Science and Higher Education of the Russian Federation (Grant of the Government of the Russian Federation No. 14.W03.31.0018)

References

1. O. V. Novozhilov, I. V. Pavlichenko, N. V. Demchenko, A. I. Buzin, N. G. Vasilenko, A. M. Muzafarov// *Russian Chemical Bulletin, International Edition, 2010, 59(10), 1909—1917.*

2.O. V. Novozhilov, N. G. Vasilenko, M. I. Buzin, M. A. Scherbina, S. N. Chvalun, and A. M. Muzafarov// *Russian Chemical Bulletin, International Edition, 2011, 60(5), 1019—1021.*

CATALYTIC SYSTEMS BASED ON NEW MACROMOLECULAR COMPOUNDS FOR BETULIN OXIDATION

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Catalytic nanoparticles (NP) are actively used but there is a problem of catalyst fixation without further loss, and stable operation under repeated use. Investigation of catalytic magnetically separable systems is of great interest nowadays[1-4]. Many stabilizing agents are used, basically new catalysts are expected to combine properties of heterogeneous and homogeneous substances. That is why dendrimers, which belong to a group of highly branched polymers, attract more and more attention as supports with stabilizing effect.

The purpose of the present work was to synthesize new pyridylphenylenecyclopentadienon (3,4-bis-(4-phenylethenyl)phenyl)-2,5-di(pyridine-2-yl)cyclopenta-2,4-diene-1-on) to be utilized in dendrimer and polymer production with further use in catalysis as a support. Three steps to the new catalytic system were done in this work: 1) developing the synthesis procedure for new (3,4-bis-(4-phenylethenyl)phenyl)-2,5-di(pyridine-2-yl)cyclopenta-2,4-diene-1-on), that could be serve as “building block” or monomer AB2; 2) synthesis of dendrimer and polymer; 3) synthesis of the catalysts, containing magnetic NP of Fe_3O_4 and ruthenium NP.

Structures of the new compounds were proved by NMR, GPC, elemental analysis and MALDI-ToF spectrometry.

The formation of iron oxide NP was provided by the thermal decomposition of iron acetyl acetonate in the presence of the poly(phenylenepyridyl) dendrimer and polymer. Adding ruthenium (III) acetyl acetonate and reduction step were resulted in ruthenium NP formation as confirmed by TEM analysis.

Catalysts were tested in betulin oxidation process, exhibiting 53% and 17% of conversion for dendrimer and polymer based samples, respectively. Different products with biological activity were formed.

The development of the dendrimer and polymer based systems is promising, as the catalysts based on macromolecular stable carrier can be regenerated and reused.

Acknowledgments

This work was supported by RFBR (No 18-33-00609). NMR and elemental analysis were performed with the financial support from Ministry of Science and Higher Education of the Russian Federation using the equipment of Center for molecular composition studies of INEOS RAS.

References

1.Z.B. Shifrina, V.G. Matveeva, L.M. Bronstein, *Chem. Rev.* **2019**, *in press*
2. D. Wang, D. Astruc, Chem. Soc. Rev. **2017**, 46, 816
3. Z.B. Shifrina, L.M. Bronstein, *Front. Chem.* **2018**, 6:298 2.
4. S. Shylesh, V. Schünemann, W. R. Thiel*, Angew. Chem. Int. Ed.* **2010**, 49, 3428

CONTROLLED RADICAL POLYMERIZATION OF STYRENE IN THE PRESENCE OF BLATTER RADICAL

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The polymerization of styrene in the presence of the Blatter radical was studied (Fig. 1, radical A). The induction period is present when using 0.25 and 0.4 mol.% Blatter radical, then the rate of polymerization is lower than the rate of polymerization of styrene without an inhibitor, which is not typical of traditional inhibitors of radical processes. Oligomers accumulating during the induction period act as macroinitiators of controlled radical polymerization by the stable free radical polymerization mechanism (Fig. 1). The rate of polymerization increases with increasing concentration of Blatter radical from 0.25 to 0.4 mol.% due to the formation of a larger amount of macroinitiator.

The use of 0.1 mol.% radical initiator azobisisobutyronitrile together with the Blatterradical allows to bring the polymerization of styrene without an induction period. Equimolar (0.1 mol.%) amounts of azobisisobutyronitrile and Blatter radical allow to bring the polymerization of styrene to high conversions without gel effect. There is a tendency to narrow the molecular mass distribution with a decrease in the concentration of the Blatter radical.

The incorporation of the Blatter radical into the polymer chain was confirmed by UV spectroscopy and MALDI mass spectrometry. The main part of polymer chains contains Blatter radical at the ends the share of "dead" polymer is insignificant.

Polystyrene samples obtained in the presence of the Blatter radical, as well as in combination with azobisisobutyronitrile, initiate post-polymerization and block copolymerization with methyl methacrylate.

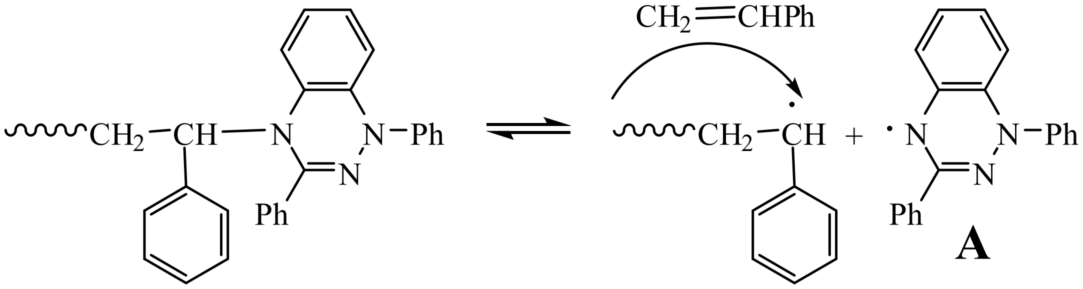

Figure 1. Controlled radical polymerization of styrene by the stable free radical polymerization mechanism.

Acknowledgments
The reported study was funded by RFBR, project number 19-33-90090.

SYNTHESIS OF VINYL DERIVATIVES FROM SUSTAINABLE SOURCE AND DEVELOPING NEW APPROACHES FOR CONTROLLED MATERIALS DESIGN

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[b] *N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences, Leninsky Prospect 47, Moscow 119991, Russia*

Vinyl ethers are valuable monomers. Manufacturing of vinyl ethers are based on common procedures: nucleophilic addition of alcohols to gaseous acetylene; exchange reaction started from vinyl acetate or another vinyl function source; elimination processes; and some special cases [1]. Using gaseous acetylene remains the only industrial method while the others can be reproduced in a laboratory only. Increased demand for vinyl monomers requires a sustainable methodology for manufacturing in ton-scale manner. A suitable raw material must be available and renewable. Calcium carbide meets all the necessary requirements [2].

Previously, an efficient route to a wide range of vinyl monomers based on calcium carbideas an acetylene source and water was developed in our laboratory [3, 4]. Then, we investigated the opportunity to isolate deuterated vinyl derivatives using heavy water instead of H_2O. A wide range of deuterated monomers were obtained as a result.The deuterated vinyl derivatives are stable substances and can be purified according to the standard procedures. Polymerization of the deuterated compounds leads to corresponding deuterated polymers. Deuterium atoms are included in the main chain instead of protium providing new and improved properties.

Currently, we study kinetics of free-radical polymerization of deuterated vs non-deuterated vinyl monomers.The possible isotope effect has a great potential as an additional tool for controlling specificity of polymerization.

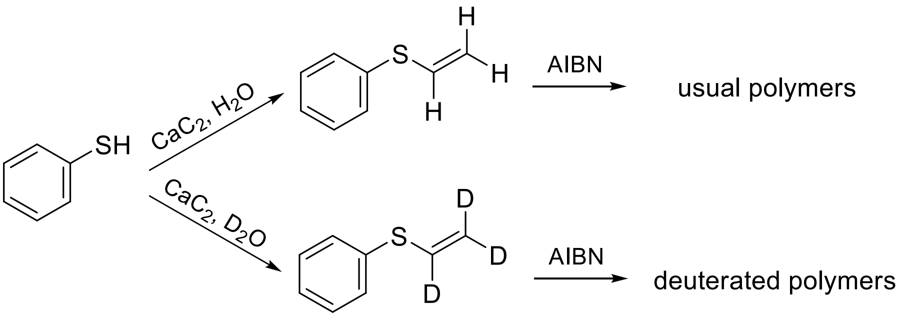

Figure 1

References

1. Ledovskaya M.S., Voronin V.V., Rodygin K.S., *Russ. Chem. Rev.* **2018**, *87*, 167.
2. Rodygin K.S., Vikenteva Y.A., Ananikov V.P., *ChemSusChem* **2019**, *12*, 1483.
3. Werner G., Rodygin K.S., Kostin A.A., Gordeev E.G., Kashin A.S., Ananikov V.P., *Green Chem.* **2017**, *19*, 3032.
4. Rodygin K.S., Werner I., Ananikov V.P., *ChemSusChem* **2018**, *11*, 292.

2,3-DIHYDRO-1,2,4-OXODIAZOLE CHITOSAN DERIVATIVES AND THEIR ANTIBACTERIAL ACTIVITY

Niyaz Yagafarov,[a] Andreii Kritchenkov,[a] Victor Khrustalev[a]

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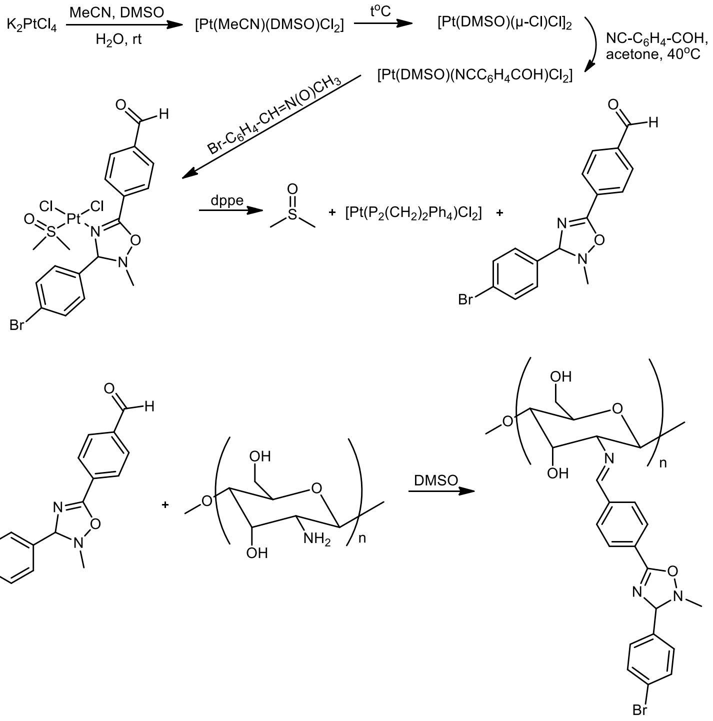
Transformation of ligands in transition metal complexes are of paramount importance in metal complex catalysis and metal-mediated synthesis, since in this report we will consider 1,3-bipolar cycle addition [1] of acyclic nitrone *p*-$BrPhC(H)=N(O)CH_3$ to the nitrile ligands in complex $[PtCl_2(NCC_6H_4COH)(DMSO)]$. The interaction of the nitrone with the nitrile NCC_6H_4COH without the metal center is not possible even in harsh conditions (90 °C, 240 h). However coordination of nitrile to Pt(II) center leads to activation of the nitrile functionality of the interaction of the nitrone with the nitrile ligands in the complex $[Pt (NCC_6H_4COH)(DMSO)Cl_2]$ via [2+3]-cycloaddition becomes feasible. The obtained 2,3-dihydro-1,2,4-oxadiazole ligands containing aldehyde functionality could be liberated from its Pt(II) complex by the treatment of the complex with 2 equiv. of dppe. The obtained free heterocycles were conjugated to chitosan primary amino groups by reductive amination to give the corresponding oxadiazoline chitosan derivatives.

The resulted chitosan derivatives are water soluble and possess pronounced in vitro antibacterial activity against E. coli and S. aureus.



Acknowledgments

This work was supported by RFBR (projects 19-33-60039 and 19-016-00077) and «RUDN University Program 5-100».

References

1. N.A. Bokach, "Cycloaddition of nitrones to metal-activated nitriles and isocyanides", Russ. Chem. Rev, **2010**, *79* (2), 89-100.

SYNTHESIS OF DISENTANGLED UHMWPE USING BINUCLEAR AND HEXANUCLEAR TI(IV) COMPLEXES SUPPORTED BY [OOOO]4–- TYPE LIGAND

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Vladislav A. Tuskaev[a,b], Svetlana Ch. Gagieva[a]

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Ultra high molecular weight polyethylene (UHMWPE) is a perspective engineering polymer[1]. The disentangled UHMWPE nascent reactor powders can be processed in solid-state below its melting temperature, leading to the high-strength and high-modulus oriented materials[2-3]. In this study mononuclear **1**, binuclear **2** and hexanuclear **3** Ti^{+4} complexes, supported by tetradentate $[OOOO]^{4-}$-type ligand, were compared for their ability to produce disentangled UHMWPE with desired properties and high activities.

Precatalysts **1-3** proved to be inactive in the presence of traditional co-catalysts (Me_3Al, iBu_3Al or MAO; ratio Al/Ti = 1:500), but the use of binary activator {$3Et_2AlCl$ + Bu_2Mg}, proposed in[4-5] resulted in highly active systems (activity up to 4100 $kg(PE)\cdot mol(Ti)^{-1}\cdot atm^{-1}$). The activity of the discussed catalytic systems decreases in the following order: **2**>**3**>**1**. Most of the polymers obtained on them are UHMWPE with $M_W > 1.50\cdot10^{-6}$ Da.

The oriented film tapes, obtained from these samples by solution-free processing below the melting point of the polymer and uniaxial drawing, are characterized by tensile strength in the range 2.4-2.5 GPa and a tensile modulus of up to 105 GPa. The samples of UHMWPE obtained on complex **3** are characterized by a bimodal distribution.

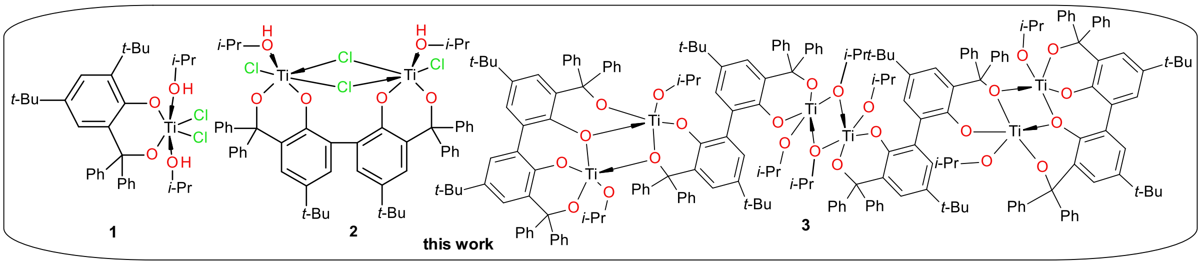

Figure 1. Structures of mono-, di- and hexanuclear Ti^{+4} complexes with saleginin ligands.

Acknowledgments

This work was supported by the Russian Science Foundation – grant № 16-13-10502.

References

1. The UHMWPE handbook: ultra-high molecular weight polyethylene in total joint replacement / Kurtz, S. M., *Elsevier Academic Press*, **2004**.
2. Rastogi, S.; Yao, Y.; Ronca, S.; Bos J.; van der Eem, J.,*Macromolecules.* **2011**, 44, 5558-5568.
3. Yao, Y.; Jiang, S.; Rastogi, S.,*Macromolecules*. **2014**, 47, 1371–1382.
4. Kissin, Y.V.; Nowlin, T.E.; Mink, R.I.; Brandolini, A.J. *Macromolecules* **2000**, *33*, 4599-4601.
5. Kissin, Y.V.; Mink, R.I.; Brandolini, A.J.; Nowlin, T.E. *J. Polym. Sci: Part A: Polym. Chem.* **2009**, *47*, 3271-3285.

PROTOLYSIS OF SEVEN-MEMBERED ZIRCONACYCLOCUMULENES

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Wolfgang Baumann,[b] Anke Spannenberg,[b] Uwe Rosenthal,[b] Torsten Beweries,[b]
Vladimir B. Shur.[a]

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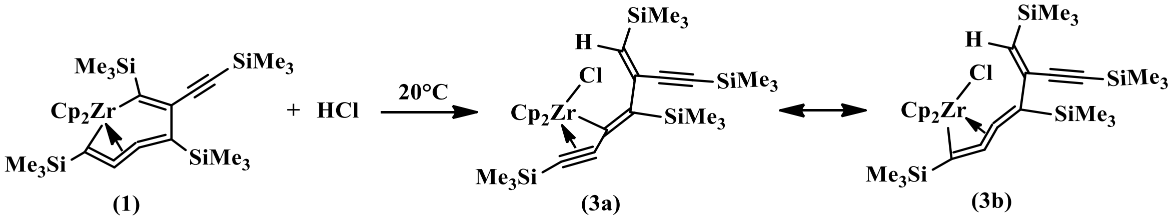
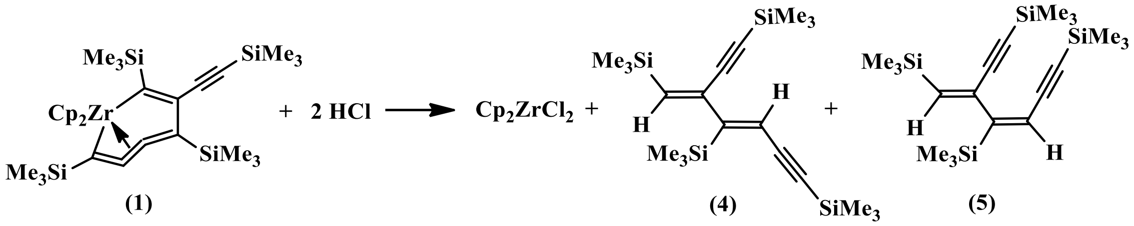
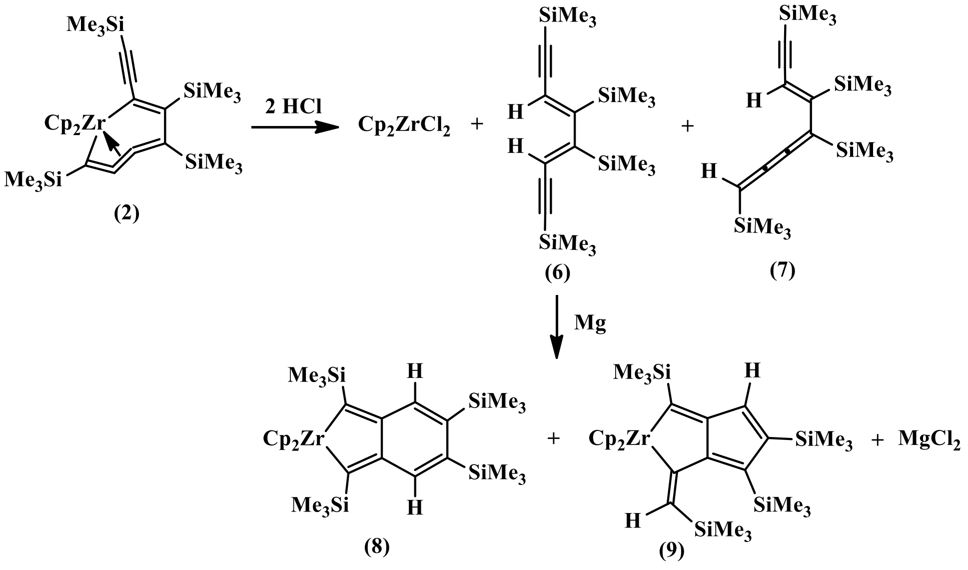
Unusual reactions of protolysis of the Buchwald seven-membered zirconacyclocumulene complex (**1**) and its isomer (**2**) are reported. It has been found that the interaction of **1** with an equimolar amount of HCl at 20°C results in the formation of a complex (**3**), whose structure can be described by two resonance forms (**3a**) and (**3b**).



Under similar condition, the reaction of **1** with an excess of HCl affords Cp_2ZrCl_2 and a mixture of two isomeric bis-enynes (**4**) and (**5**).



The protolysis of complex **2** with two equivalents of HCl gives a mixture of Cp_2ZrCl_2, bis-enyne (**6**) and [3] cumulenic enyne (**7**). The subsequent reaction of this mixture with Mg in THF yields zirconabicycles (**8**) and (**9**).



Acknowledgments

This work was supported by the Russian Foundation for Basic Research (Project code 19-03-00332).

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18 NOVEMBER (MONDAY)

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10:30	PL1 Beletskaya
11:00	PL2 Khokhlov
11:30	Coffee break
12:00	PL3 Copéret
12:30	PL4 König
13:00	Lunch
14:30	PL5 Poli
15:00	PL6 Harder
15:30	PL7 Pombeiro
16:00	Coffee break
16:30	PL8 Fedin
17:00	O1 Sporzyński
17:20	O2 Guedes da Silva
17:40	*Welcome Party*

19 NOVEMBER (TUESDAY)

10:00	PL9 Matyjaszewski	
10:30	PL10 Möller	
11:00	PL11 Sheiko	
11:30	Coffee break and Poster session (Polymers)	
12:00	PL12 Vamvakaki	
12:30	PL13 Davankov	
13:00	Lunch	
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14:50	O5 Zhu	O6 Sachkova
15:10	O7 Tikhonov V	O8 Hasche
15:30	O9 Novakovskaya	O10 Gurina
15:50	O11 Lozinsky	O12 Kharitonov
16:10	Coffee break and Poster session (Polymers)	
16:40	O13 Nikoshvili	O14 Lukin
17:00	O15 Skupov	O16 Loukova
17:20	O17 Matson	O18 Erzunov
17:40	O19 Davydova	O20 Tokarev
18:00	O21 Sheveleva	O22 Shagurin

20 NOVEMBER (WEDNESDAY)

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11:00	PL16 Nolan	
11:30	Coffee break and Poster session (Organoelement Compounds)	
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12:30	PL18 Yokozawa	
13:00	Lunch	
	Room-1	Room-2
14:50	O23 Beweries	O24 Pigaleva
15:10	O25 Nechaev	O26 Drozdov
15:30	O27 Filonenko	O28 Sorokina
15:50	O29 Kirkina	O30 Anisimov A
16:10	Coffee break and Poster session (Organoelement Compounds)	
16:40	O31 Afanasyev	O32 Pankratov
17:00	O33 Lyubov	O34 Rudnitskaya
17:20	O35 Osipova	O36 Yakovlev
17:40	O37 Bolotin	O38 Semenova
18:00	O39 Larionov	O40 Ushakova

21 NOVEMBER (THURSDAY)

10:00	PL19 Belkova	
10:30	PL20 Cui Y	
11:00	PL21 Jin	
11:30	Coffee break	
12:00	PL22 Mironov	
12:30	PL23 Cui C	
13:00	Lunch	
	Room-1	Room-2
14:30	O41 Negrebetsky	O42 Sivaev
14:50	O43 Zaitsev	O44 Grishin
15:10	O45 Kazakov	O46 Stogniy
15:30	O47 Zhigulin	O48 Snegur
15:50	O49 Grishanov	O50 Tskhovrebov
16:10	Coffee break	
16:40	O51 Reiß	O52 Timofeeva
17:00	O53 Andreev	O54 Gavrilov
17:20	O55 Titov	O56 Tikhonov A
17:40	O57 Gorbachuk	O58 Lysova
18:00	O59 Zagidullin	O60 Ivanova

22 NOVEMBER (FRIDAY)

10:00	PL24 Jonusauskas
10:30	PL25 Rakitin
11:00	O61 Nadtochenko
11:20	O62 Panchenko
11:40	Coffee break
12:00	O63 Novikov V
12:20	O64 Syzgantseva
12:40	O65 Aksenova I
13:00	Lunch
14:00	O66 Banakova
14:20	O67 Ilichev
14:40	O68 Perekalin
15:00	*Closing Remarks*