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Organic Electronics

Book of Abstracts

September, 23-29, 2019,
Novosibirsk, Russia

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Novosibirsk 2019

Compiled by Ekaterina A. Radiush and Dr. Nikolay A. Semenov

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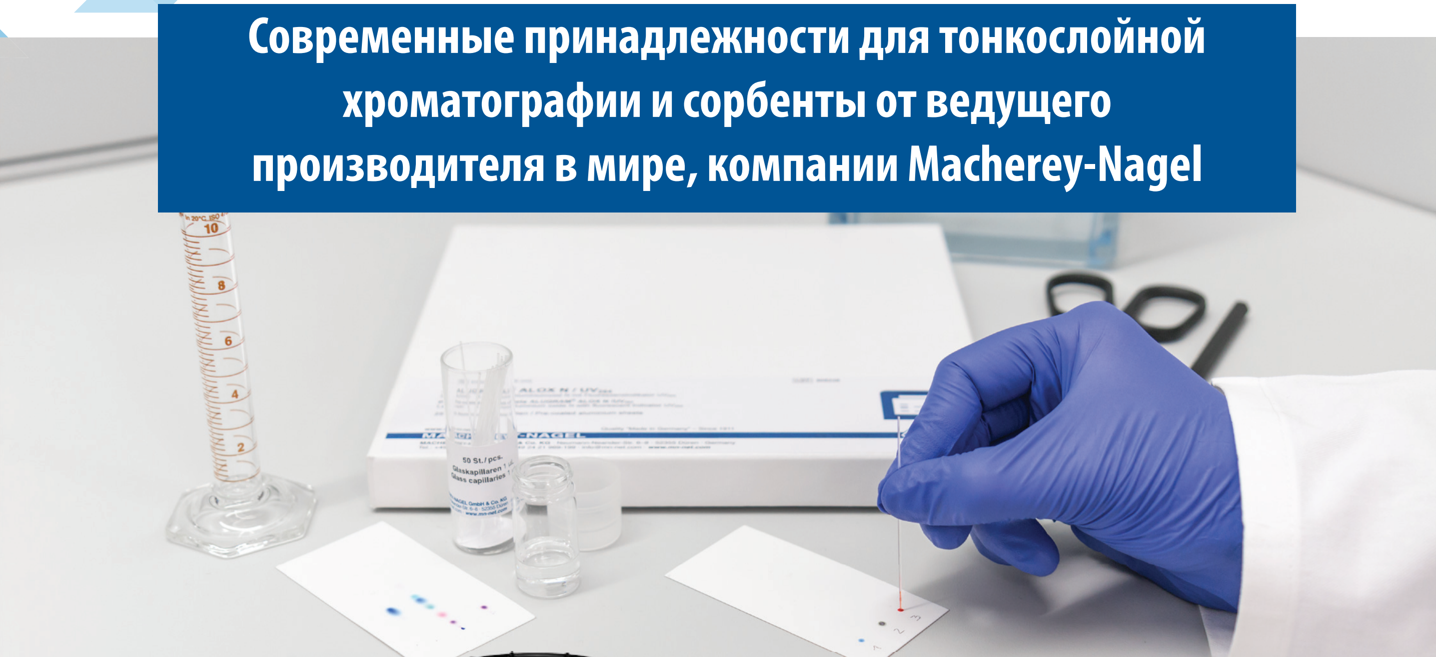

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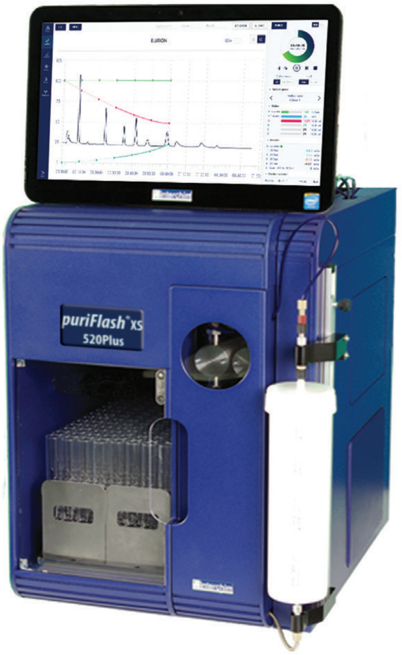

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Organic Electronics

September, 23-29, 2019, Novosibirsk, Russia

Timetable

	Monday, 23.09	Tuesday, 24.09	Wednesday, 25.09	Thursday, 26.09	Friday, 27.09	Saturday, 28.09	Sunday, 29.09
		8:30 - 9:00 Registration					
9:00 - 10:00	Arrival	9:00 - 9:20 Opening 9:20 - 10:05 S. Ponomarenko	9:00 - 9:45 M. Baumgarten 9:45 - 10:15 Y. Shuku	9:00 - 9:45 M. Fedin 9:45 - 10:15 N. Gritsan	9:00 - 9:45 A. Yakimanskiy 9:45 - 10:15 K. Takahashi	9:00 - 9:45 S. Dorovskikh 9:45 - 10:15 E. Tretiakov	Departure
10:00 - 11:00		10:05 - 10:35 R. Suizu 10:35 - 11:00 Coffee Break	10:15 - 10:35 L. Kulik 10:35 - 11:00 Coffee Break	10:15 - 10:35 E. Vasiliev 10:35 - 11:00 Coffee Break	10:15 - 10:35 D. Nevostruev 10:35 - 11:00 Coffee Break	10:15 - 10:35 E. Bagryanskaya 10:35 - 11:05 M. Fittipaldi	
11:00 - 12:00		11:00 - 11:30 M. Kazantsev 11:30 - 11:50 S. Yokokura 11:50 - 12:10 Group Foto	11:00 - 11:30 G. Selivanova 11:30 - 11:50 L. Samsonova 11:50 - 12:10 M. Uvarov	11:00 - 11:30 S. Veber 11:30 - 11:50 A. Odinokov 11:50 - 12:10 E. Vinogradova	11:00 - 11:30 S. Konchenko 11:30 - 11:50 I. Koskin 11:50 - 12:10 O. Rakitin	11:05 - 11:30 Closing ceremony Departure	
12:00 - 13:00		12:10 - 14:00 Lunch	12:10 - 14:00 Lunch	12:10 - 14:00 Lunch	12:10 - 14:00 Lunch		
13:00 - 14:00							
14:00 - 15:00		14:00 - 14:45 A. Fissyuk 14:45 - 15:15 A. Shundrin	14:00 - 14:30 T. Basova 14:30 - 15:00 V. Shelkovnikov	14:00 - 19:00 Social program/ excursion	14:00 - 14:45 P. Stuzhin 14:45 - 15:15 M. Bushuev		
15:00 - 16:00	15:00 - 18:00 Registration	15:15 - 15:35 E. Chulanova 15:35 - 16:00 Coffee Break	15:00 - 15:20 A. Kurtsevich 15:20 - 15:40 A. Zibarev 15:40 Coffee		15:15 - 15:35 N. Semenov 15:35 - 15:55 A. Makarov 15:55 Coffee		
16:00 - 17:00		16:00 - 19:00 Poster Session					
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PLENARY LECTURES

Ambipolar conjugated organic semiconductors

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After starting from benzothiadiazole (BTZ) in donor acceptor copolymers, we concluded to strengthen the acceptor part upon introducing thiadiazoloquinoxalines (TQ) leading to a lowering of the LUMO levels and more suited n-type and ambipolar character [1-3]. Upon condensation of the diamino benzothiadiazoles with benzodithiophene-dione the acceptor part could be further strengthened and open a variety of new copolymers as PBDTTQ-2 and small molecule acceptor structures [4,5].

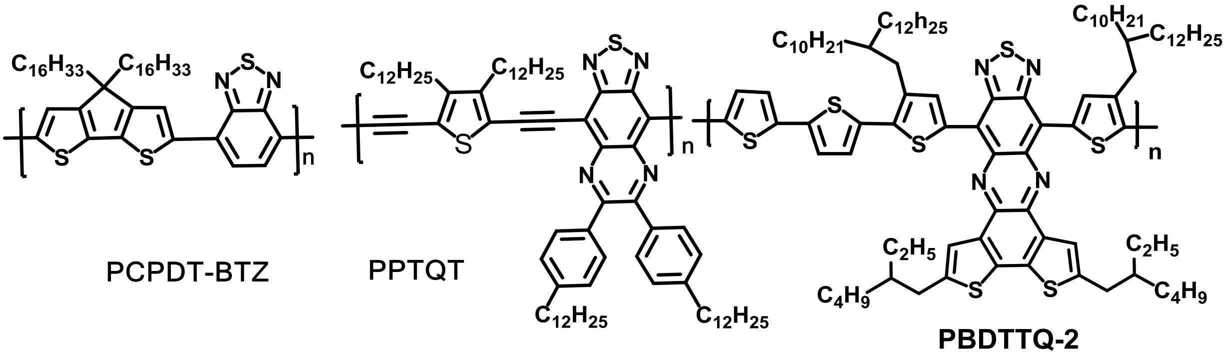

Fig. 1: Development of polymers for ambipolar transistors

We further went into devoloping extended N-heteroacene structures in linear with up to 18 rings and 2D-3D extensions, keeping the strong TQ acceptors as end cap units [6,7].

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MOCVD of noble metals: fabrication and application of film materials

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Noble metals, including ruthenium, rhodium, iridium, palladium, platinum, silver, and gold, are one of the most demanded materials for modern high-technology applications. The high chemical inertness to corrosion and acids, metal conductivity, catalytic activity, biocomotability allows to apply such materials in electronics, protective coatings, catalyst industries, manufacturing of medical equipment [1, 2].

Metalorganic chemical vapor deposition is one of the most promising techniques to fabricate nanoparticles, layers and coatings of noble metals as well as their oxides, composites, etc., in the wide temperature range from 150 to 700°C at reduced and atmospheric pressure in the presence of various gas mixtures. One of the main advantages of MOCVD is possibility to produce materials with required characteristics on non-planar substrates made of various materials (SiO_2, Al_2O_3, Si, SiC, Cu, Mo, Ti, steel, polymers and other). The success in realization of chemical deposition process depends on initial metal source – precursor, on it availability and physicochemical characteristics: evaporation behavior, vapor thermo-decomposition mechanisms. The major requirements to precursors are high volatility (vapor pressure), thermal stability in the solid and gas phases during evaporation, not high threshold of precursor vapor stability; clean vapor decomposition (decomposition of precursor vapor with formation of the film material and simple gaseous by-products only), non-toxicity, storage stability, high purity.

Different classes of inorganics, coordination and organometallic compounds are applied as precursors. The active development of the chemistry of these compounds is associated with the wide variety of properties depending on the chemical composition and structure and, as a consequence, with the possibility of their practical application.

Some classes of volatile compounds of noble metals for MOCVD technique, together with the chemical approaches to the synthesis, physico-chemical properties, thermal behavior, mechanisms of vapor thermo-decomposition and MOCVD application are presented.

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Acknowledgements

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EPR studies of switchable molecular magnets

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Switchable molecular materials are being intensively studied due to many potential applications, including spintronics and nanoelectronics. Molecular magnets represent one of the directions in this research. Among switchable molecular magnets, most attention during past decades was drawn to spin-crossover complexes able to change their spin state and magnetization under various external stimuli. Apart from spin-crossover in its original meaning, related spin-crossover-like phenomena have been found and intensively investigated in exchange-coupled clusters of copper(II) with stable nitroxide radicals.[1] These polymer chain compounds (often called “breathing crystals”) are formed by copper(II) hexafluoroacetylacetonates and various nitroxides and exhibit cooperative magnetic switching induced by temperature or light. Depending on external stimuli, they can be found in two different structural and spin states: (i) the elongated geometry of CuO_6 octahedral units with the nitroxides in axial positions, a weakly exchange-coupled spin state (WS), and (ii) the elongated geometry of CuO_6 octahedra with another long axis and nitroxides in equatorial positions, a strongly exchange-coupled spin state (SS). Typically, the WS state is observed at high temperatures, whereas the SS state is found at lower temperatures, with the transition temperature varying between ~50 and 250 K. In addition to thermal switching, the WS can also be photoinduced at low temperatures (T < 20-60 K), where the system remains trapped for hours-to-days.[2]

In this work we review our recent studies of thermal and photoswitching in breathing crystals and Fe(II) based spin-crossover compounds using Electron Paramagnetic Resonance (EPR)[1-2,5-6] and femtosecond optical spectroscopy.[3-4] We discuss the main trends and potential advantages of copper-nitroxide-based molecular magnets for the future design of ultrafast magnetic materials.

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Conjugated ensembles of five-membered aromatic heterocycles

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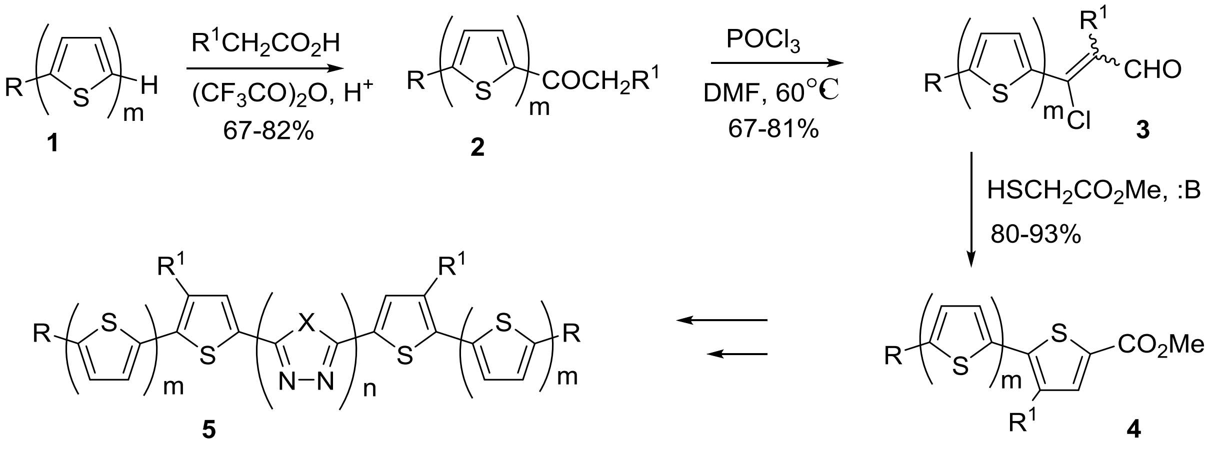
A simple and efficient approach for the synthesis of substituted 2,2′-bithiophene-5-carboxylic acid esters **4** was developed which is based on thiophene ring closure in the Fiesselmann reaction. Using this method, derivatives **4** containing a long alkyl chain with or without an end functional group or an aryl substituent can be conveniently prepared [1-2].



R = H, n-C_6H_{13}; R^1 = n-$C_{10}H_{21}$, Ar; X = O, S, NAr; n = 1-4; m = 1-3

Conjugated oligomers **5**, which contain different acceptor units, such as 4-phenyl-4H-1,2,4-triazole, 1,3,4-oxadiazole, 1,3,4-thiadiazole, bi-1,3,4-oxadiazole, bi-, ter- and quater-1,3,4-thiadiazole were obtained based on compounds **5** [3]. The prepared oligomers **5** were characterized by electrochemical methods. Their absorption and luminescence spectra were recorded. The effect of the conjugation length of the donor and acceptor parts of the molecules on the ionization potential and electron affinity, as well as on the optical properties has been established. Detailed studies of the "structure - electronic properties" relationship allowed to predict the frontier orbitals levels for the similar families of semiconductors. The obtained new organic semiconductors were used as active components of host-guests organic light emitting diodes [4].

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Ultrathin organic field effect transistors: from materials to devices

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Performance of organic field-effect transistors (OFETs) strongly depends on the organic semiconducting materials structure, their purity and morphology. On the one hand, it is well-known that charge carriers in the OFETs are induced on the interface between dielectric and organic semiconducting layers by external electric field from the gate electrode. Hence, most of the charges are passed through the first monolayer of the organic semiconductor, while the following 2-3 monolayers improves the field-effect mobility somewhat further if the first monolayer is not perfect. On the other hand, mobility in OFETs is affected by the degree of ordering of organic semiconductors, with the highest mobility reported for monocrystalline OFETs. Hence, an ideal OFET should be ultrathin and monocrystalline.

Monolayer OFETs are particularly interesting due to low consumption of organic semiconductors as well as their unique sensitivity to the environment, which allows creation of ultrasensitive gas sensors [1]. Monolayer OFETs can be prepared either by physisorption or by self-assembly. The former can be grown from solution of conjugated thiophene or thiophene-phenylene oligomers by drop or spin casting with subsequent slow solvent evaporation, leading to single-crystal monolayers of unprecedented structural order, which demonstrated excellent performance in OFETs [2]. The latter may be easily prepared from highly stable organosilicon derivatives of organic semiconductors [3], capable to self-assembly on the water-air interface, which allows fabrication of monolayer OFETs by Langmuir-Blodgett (LB) or Langmuir-Shaeffer (LS) techniques [4]. Investigation of their electrical characteristics in various gas environment suggested their application as ultrasensitive gas sensors capable to detect up to hundreds ppb of hydrogen sulfide or ammonia, which pave the way of the development of electronic nose based on this technology [5].

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Synthetic work was made in the framework of Leading Science School (grant NSh-5698.2018.3). Investigation of monocrystalline OFETs was supported by RSF (grant 18-12-00499), preparation and measurements of monolayer LS OFETs was supported by RSF (grant 19-73-30028).

Porphyrazinoides with fused electron-deficient heterocycles: New results and some application aspects

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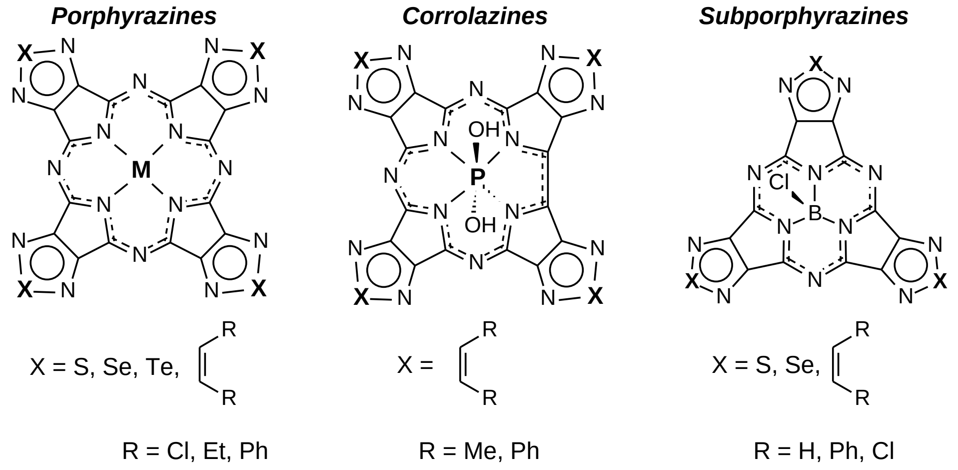
Phthalocyanines and their ring contracted analogues – subphthalocyanines and tetrabenzo-corrolazines - are widely studied as perspective materials for organic electronics. Usually they are more easily oxidized than reduced and can serve therefore as electron-donors or p-type semiconductors. Switching to the electron-acceptor materials amd n-type conducting properties usually requires introduction in benzene ring of strongly electron acceptor groups (CN, NO_2) or electronegative halogen atoms (usually chlorination or perfluorination).

Another approach to endow phthalocyanine type materials with strong electron affinity is heteroatomic substitution in benzene rings, i.e. fusion of π-deficient heterocycles s instead of benzene rings to the central porphyrazine, corrolazine or subporphyrazine core.

We present our recent results in the synthesis and study of novel porphyrazinoids bearing annulated 1,2,5-(thia/selena/tellura)diazole or pyrazine rings and their low-symmetry analogues in which these heterocycles are present in combination with benzene ring(s).



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Acknowledgements

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Water-soluble polymer brushes as carriers of luminophores for photodynamic theranostics

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Water-soluble graft-copolymers with a polyimide (PI) or cellulose (Cell) backbone and polymethacrylic acid (PMAA) (PI-g-PMAA and Cell-g-PMAA, respectively) are synthesized and characterized by NMR, FTIR, and SEC methods. A regular brush character of PI-g-PMAA copolymers is proved by the data of TEM (Fig. 1) for their Yb(III)-porphyrazine conjugates.

a b

Fig. 1. (a) TEM micrograph and (b) schematic representation of the architecture of a conjugate between PI-g-PMAA molecular brush and Yb(III)-porphyrazine complexe.

The conjugation of porphyrazines with PI-g-PMAA and Cell-g-PMAA gives water-soluble biocompatible nanoparticles, possessing a bright red emission in 630-670 nm region. In the cell culture experiments the nanoparticles were shown to be internalized and accumulated in the tumor cells on the nuclear membrane and nucleus (Fig. 2a).

a b

Fig. 2. (a) Intracellular localization of the porphyrazine photosensitizer incorporated into PI-g-PMAA nanoparticles:1 – nucleus, 2 – nuclear membrane. (b) Whole-body fluorescence imaging (left – before, right – 3 hours after injection of of PI-g-PMAA/porphyrazine conjugate aqueous solution.

The accumulation of the photosensitizer in nuclear and perinuclear regions has a very significant value in photodynamic therapy, because nuclear membranes are most vulnerable to photodamage. Cell investigations confirmed a high photodynamic activity of the nanoparticles. Whole-body fluorescent imaging experiments on mice bearing metastatic colorectal carcinoma showed the selective nanoparticle accumulation in a model tumor (Fig. 2b).

Acknowledgements

The work was supported by the Ministry of Science and Highest Education of the Russian Federation within the State Contract No. 14.W03.31.0022.

KEYNOTE LECTURES

Hybrid materials on the basis of carbon nanotubes with phthalocyanines and other polyaromatic molecules as active layers of chemical sensor

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Carbon nanomaterials, viz. carbon nanotubes (CNT), graphene and reduced graphene oxide, are widely used as promising materials both for chemiresistive sensors toward gases and vapors (e.g. NH_3, NO_2, H_2, CO, H_2S etc.) and for electrochemical sensors [1]. However, the selectivity of chemical sensors based on carbon nanomaterials usually is not good enough. One of the ways to improve their sensitivity and selectivity is covalent or non-covalent functionalization of their surface with metal phthalocyanines (MPc) and other organic molecules in order to define the chemically active sites. Variation of functional groups in the organic molecules allows to attach them to CNT surface both covalently and non-covalently as well as to use them as linking molecules to obtain 3D cross-linked carbon nanotube structures.

In this contribution, the brief overview of the results of our researches of CNT-based hybrid materials with metal phthalocyanines and other polyaromatic molecules (pyrene, coumarine, BODIPY derivatives) as active layers of chemiresistive and amperometric sensors is given [2-5]. The influence of phthalocyanines containing different central metals, symmetric or asymmetric substitution, and type of substitutes on the structural and sensor properties of SWCNT/MPc hybrids has been studied. It has been shown that the interaction of asymmetric MPcs containing one pyrene substituent with SWCNTs is more favorable than in the case of symmetric without pyrene counterpart that provided a higher sensor response toward low concentration of ammonia (10-50 ppm). The effect of covalent and non-covalent linking of the phthalocyanines to SWCNT on the electrical sensor response has also been verified.

Apart from this, the hybrid materials were used for modification of glassy carbon electrodes of amperometric sensors for the detection of eserine and glucose in water solutions and real biological samples. It has been shown that the electrode modified with 3D SWCNT-BODIPY hybrid was highly selective and sensitive to eserine with the limit of detection (LOD) of 160 nM [4], while the electrode modified with the hybrid of iron phthalocyanine with graphene nanoplatelets was used for the selective detection of glucose with LOD of 604 μM [5].

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Metal complexes with polydentate azole and azine ligands: spin crossover, luminescence, proton transfer

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The problem of controlling the processes of switching the system between the ground and excited states and understanding the mechanisms of these processes is one of the main challenges in modern chemistry and materials science. The solution of this problem is important for creating “smart” materials that demonstrate properties depending on external stimuli. In this presentation we will consider approaches to solving this problem on the example of metal complexes with azaaromatic ligands exhibiting spin crossover, luminescence and proton transfer.

To control the spin state and spin transition regime in mononuclear and polymer iron(II) complexes with N-donor azole and azine ligands, we used strategies based on (1) modification of the ligand core, (2) modification of the ligand backbone, (3) changing the size of the chelate cycle, (4) the synthesis of complexes with isomeric ligands, (5) the search and study of polymorphic modifications of complexes showing hysteretic spin transition, (6) the synthesis of mixed-ligand and heteroanion complexes. Investigations within the framework of this strategies allowed us to obtain iron(II) complexes that demonstrate spin transition with very wide thermal hysteresis loops (bistability) [1].

For the synthesis of complexes demonstrating stimuli-responsive emission, we used the strategy related to the synthesis of pyrimidine and imidazole-based compounds featuring a short intramolecular hydrogen bond O–H···N (O···N ≈ 2.6 Å) as a prerequisite for excited state intramolecular proton transfer (ESIPT). Incorporating Zn^{2+} ions into proton transfer ligands led to an intriguing interplay of the excitation-wavelength-dependent emission, ESIPT and thermally activated delayed fluorescence (TADF). TADF is favored by a narrow singlet–triplet gap, $\Delta E_{ST} \approx 10$ kJ mol^{-1}. Our experimental observations (including the excitation-wavelength-dependent emission and the dependence of the excitation spectra on the emission wavelength) point to a violation of Kasha’s rule in the zinc(II) complexes. Compounds breaking this rule use high energy excited states (n > 1) for emission or photochemical reactions. Our hypothesis is supported by the results of DFT calculations according to which Zn^{2+} ions facilitate the $S_2 \rightarrow T_2 \rightarrow T_1$ and $S_2 \rightarrow T_1$ intersystem crossing. To our knowledge, the interplay of the anti-Kasha behaviour, ESIPT and TADF is observed for the first time and opens new possibilities in the design of colour-tuneable emitters and fluorescence sensors [2].

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Spin-Electric Coupling Revealed by Electric Field Modulated EPR

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The possibility to operate on magnetic materials through the application of electric rather than magnetic fields - promising faster, more space confined and energy efficient circuits - continues to spur the investigation of magnetoelectric (ME) effects [1]. Symmetry considerations, in particular the lack of an inversion centre, characterize the ME effect. In addition, spin–orbit coupling is generally considered necessary to make a spin system sensitive to a charge distribution. However, a ME effect not relying on spin–orbit coupling is appealing for spin-based quantum technologies. We have very recently reported the detection of a ME effect that we have attributed to an electric field modulation of the magnetic exchange interaction without atomic displacement [2]. The effect is visible in electron paramagnetic resonance (EPR) absorption of molecular helices under electric field modulation (EFM-EPR) and confirmed by specific symmetry properties and spectral simulation.

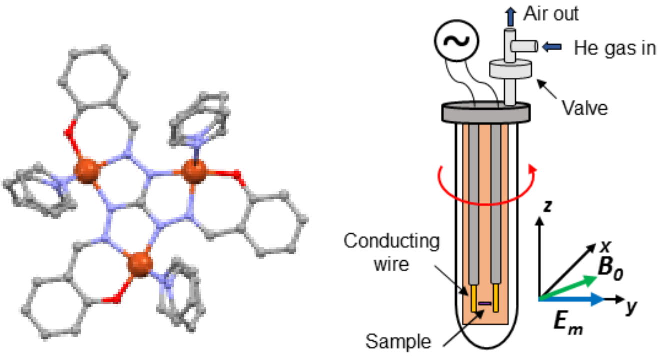

Fig. 1 Left: the molecular structure of the spin-frustrated Cu_3, with a ground state S=1/2. Right: schematic view of the modified version of the sample holder used for the EFM-EPR measurements. The orientations of the static magnetic field (B_0), and the electric field (E_m) are shown. E_m is obtained by applying an alternating voltage $V = V_0 \cos(\omega t)$, with $V_0 = 170$ V over a distance of 1.5 mm, and $\omega = 2\pi \times 30$ kHz.

After this report, an oscillating electric field ten times stronger was imparted to the sample by an improvement in the experimental setup. This made possible the observation of a ME effect in a single-crystal of a frustrated Cu_3 triangle (Fig. 1). The orientational dependence of the effect was recorded paving the way to its deep comprehension.

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Quantitative prediction of the magnetic and spectroscopic properties of lanthanide complexes

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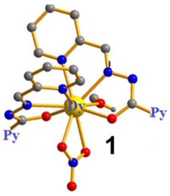
Lanthanides are the corner-stone components of molecular magnetic materials due to their large magnetic moments, large anisotropies and slow magnetic relaxation.[1] Understanding the electronic structure and properties of lanthanide complexes requires the use of both a large set of experimental techniques and comparison of their results with quantum chemical calculations. High-level quantum chemical methods are successfully used to analyze the magnetic properties of single-molecule magnets, including those based on lanthanides [1]. However, the most challenging objects for computational chemistry are the lanthanide complexes with paramagnetic and redox non-innocent ligands [2,3], which are also very promising for applications.

This report will present and discuss results of the high-level *ab initio* calculations with non-perturbative account of spin-orbit coupling at the SA-CASSCF/CASPT2/SO-RASSI level for the dysprosium complex **1** exhibiting the properties of a single molecule magnet and ytterbocene complexes **2** and **3** with non-innocent ligands [2,3]. For complex 1, the energy splitting of the ground $^6H_{15}$ multiplet, the g-tensors for Kramers doublets, their orientations in the molecular exes and temperature dependence of the molar magnetic susceptibility were evaluated using results of calculations. The matrix elements of the transversal magnetic moment for the transitions between Kramers doublets were also calculated and the most probable relaxation pathway for the reversal of magnetization was predicted.



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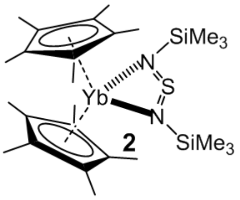

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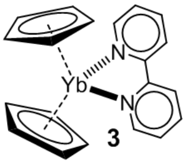

3

In agreement with experiment, calculations predict for **2** and **3** unusual temperature dependences of magnetic susceptibility with a maximum at ~300 K, which is caused by the population of the lowest energy pseudo-singlet and pseudo-triplet states. The splitting of these states is unexpectedly large and not typical of lanthanides. In the framework of the concept of spin-Hamiltonian, the splitting is determined by the isotropic and asymmetric exchange interactions between the Yb(III) and the radical anion of the ligand; their parameters were calculated to be very large (for **3**, J ~ –250 cm^{-1}, D ~ –60 cm^{-1}).

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Highly-Emissive Semiconductors Based on Furan/Phenylenes

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Materials combining high luminescence efficiency and good charge transport are in strong demand for organic optoelectronics because of their potential applications in various light-emitting devices, e.g. light-emitting diodes, transistors and lasers.[1,2] Attainment of both these functionalities simultaneously possesses a great challenge because high mobility requires close molecular packing that usually leads to very weak emission.[3] However a lucky combination of these properties were reported for a materials based on heteroaryl-containing co-oligomers which are considered to be the most promising emissive organic semiconductors. Furan incorporation was also proved to be a powerful tool for an increase of luminescence efficiency, molecular rigidity and solubility, highly favorable for industrial applications.[4]

This talk overviews our recent results on the synthesis and systematic study of a series of linear furan/phenylene co-oligomers to evaluate their luminescence and charge transport properties[4,5] as well as suggest tools[6,7] to control their crystal packing and optoelectronic performance.

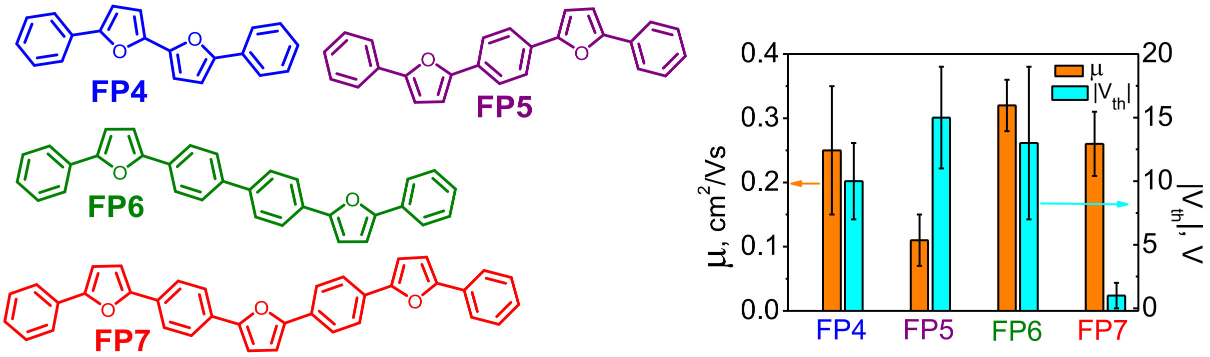

Fig. 1. Chemical structures and charge transport properties of furan/phenylene co-oligomers with an increase of conjugation length and the effect of the latter on the OFET performance of linear co-oligomers.

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Coordination chemistry of functionalized benzothiadiazoles and their analogues

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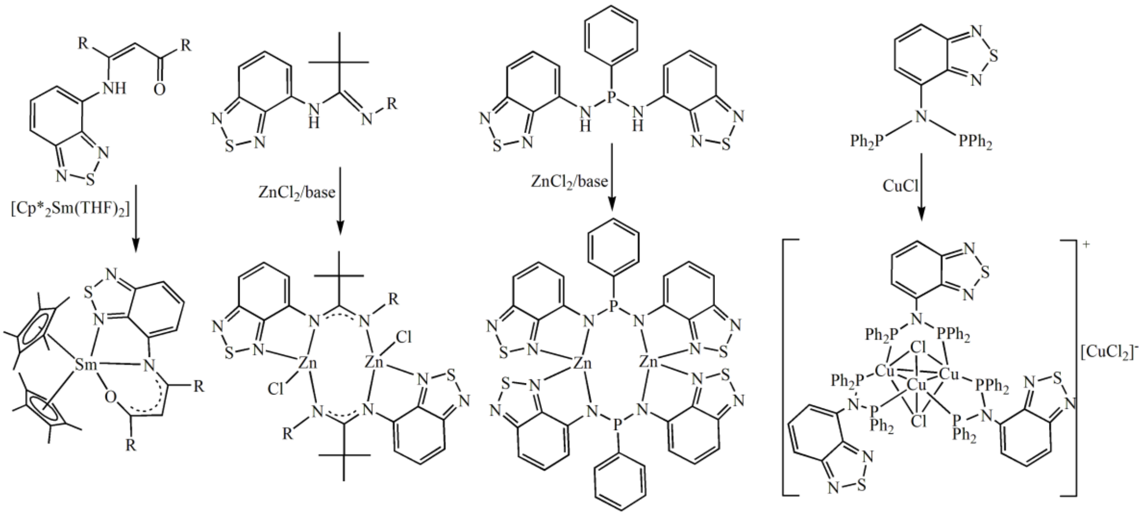
Molecular materials containing a 2.1.3-benzothiadiazole (**btd**) unit attract an attention mainly due to the intensive luminescence. That encourages synthesis of new organic derivatives of **btd**, and study of their photophysical properties. At the same time, coordination chemistry of **btd**-based ligands is still limited with few complexes, containing unsubstituted **btd** or its derivatives with such simple functional groups as -NH_2, -OH or -COOH [1-6].

This report is focused on an overview of our ongoing study devoted to the synthesis, complexation and photophysical properties of new **btd**-based ligands containing more advanced functional groups. Some representative examples of the ligands and the complexes obtained are shown in the scheme 1.



Scheme 1. Examples of some functionalized 2.1.3-benzothiadiazoles and the complexes with them.

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Azo compounds for nonlinear optics (literature data)

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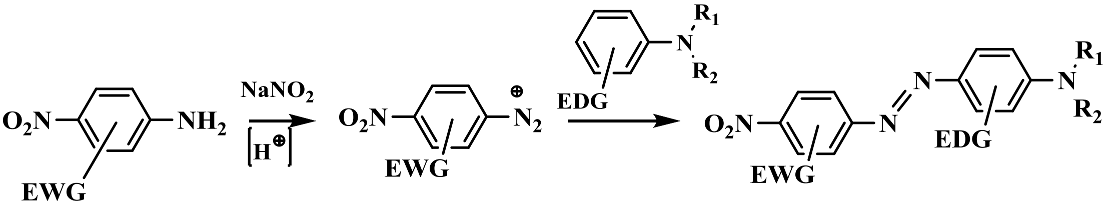
The organic chromophores are widely used in the optical communication devices, including low-voltage miniature optical switches and optical modulators. Azo compounds fully comply with the request for NLO chromophores. We reviewed the literature data (after 2000) devoted to azo chromophores, whose nonlinear optical (NLO) properties studied theoretically or experimentally.

Coupling the diazonium arene(heteroarene)amine salt, the preparation efficiency of which increases with the presence of acceptor, with the azo-component, the reactivity of which increases in the presence of donor, is the only way to form diazenyl fragment in known NLO azo chromophores.



The most of research efforts are aimed at improving the non-linearity of optical materials through the molecular properties of the chromophore. The variety of known azo chromophores is determined by the diversity of the diazo and azo components used and the possibility of modifying the substituents present in them. In terms of further modifications, azo chromophores containing the formyl group are most promising.

However, consideration of the applicability of NLO chromophore is impossible in isolation from polymer systems. A clear understanding of the possibilities of creating a “symbiotic” azo chromophore/polymer relationship is the only way to promote advanced achievements in this area.

A new strategy for the production of composite materials is the introduction of guest chromophores into azo chromophore-containing polymer matrices of a dendrimeric type, that is, the use of two chromophores of different structures in the same material at the same time.

The electronic spectra of azo chromophores contain maxima of absorption bands in the range of 400–680 nm, and the polarizability have a wide scatter from $1900 \cdot 10^{-30}$ to $5400 \cdot 10^{-48}$ esu. The nonlinear optical coefficient (d_{33}) of composite material with an azo-chromophore reaches values up to and more than ~ 100 pm$\cdot$B^{-1}.

Acknowlegements

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Synthesis and second harmonic generation stimulated by electrical field in polymer-chromophore films based on donor-acceptor dyes polyfluorotriarylpyrazoline-dicyanoisophorones

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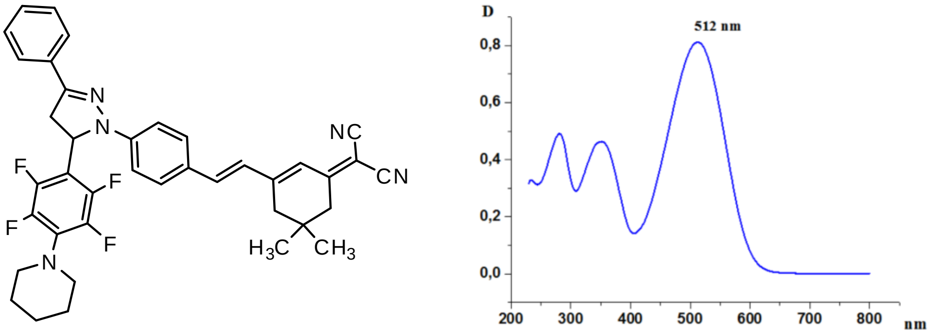
The nonlinear-optical cromophore-polymer materials attract attention last decades due to high potential of the application in photonics and electro-optics devices [1-2].

A series of donor-acceptor dyes based on polyfluoro-substituted triarylpyrazolines (as adonor block) and a dicyanoisophorone group (as an acceptor) were synthesized using the Knoevenagel condensation. The dyes have an absorption in the region of 509—514 nm and intense luminescence at 648—663 nm in chloroform with a large Stokes shift (4410 cm–1). Based on the synthesized dyes, chromophore—polymer films were obtained in a polycarbonate matrix (guest–host polyfluoro-substituted triarylpyrazoline-dicyanoisophorone - polycarbonate **PFTAP-DCI-PC**) with a chromophore content up to 27 wt.%.



PFTAP-DCI structure and absorption spectrum

Poling of chromophore—polymer films was carried out in an electric field of a corona discharge and the coefficient of nonlinear optical response *d*33 was measured by the second-harmonic generation method of the fundamental frequency of a Nd-YAG laser (1064 nm). The obtained films have a high initial thermal stability and a nonlinear optical response after poling up to 80 pm V–1.

The poling conditions for guest – host films were studied by the second-harmonic generation signal measurement simultaneously with the growth of the temperature of the polymer-chromophore film in the field of the corona discharge. The temperature dependence of the second harmonic generation intensity will be discussed.

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Honeycomb Crystal Structures Formed by Redox Active Triptycene Derivatives

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The unpaired electrons of organic radical species are attracted much attention in the field of solid state physics because of their unique magnetic, conductive and optical properties. Organic π planar molecules, in general, form strong dimers or 1D π stack columns due to its strong exchange interaction between radical species. To create multi-dimensionally π interacted crystal structures of organic radicals, we focused on polyhedrally π conjugated molecules such as triangle NDI-Δ (Fig 1a) and paddle-wheel shaped triptycene derivatives (*p*-TT and *o*-TT, Fig. 1 c and e). Notable feature of these molecules is that their π planes face toward different three directions with 3-fold symmetry that can realize highly symmetric multidimensional π-π interactions and is expected to form the isostructures of sp^2 carbon allotropes. In previous work, we have successfully obtained a unique highly isotropic 3D crystal structure, namely gyroid structure with $I4_132$ symmetry by using NDI-Δ radical anion as a building block (Fig 1b) [1,2]. In our present work, reduced specie of *p*-TT and *o*-TT were used as building blocks to form 2D honeycomb structure with their unique molecular structure and potential to strong intermolecular interaction.

The triptycene derivatives *p*-TT and *o*-TT consist of three *p*- and *o*-benzoquinone moieties, respectively. Reflecting the electron accepting skeletons, CV measurements of *p*-TT and *o*-TT in DMF show multistep reductions with the first reduction potentials of −0.71 V and −0.57 V vs Fc/Fc$^+$, respectively. Single crystals of radical anion salt of *p*-TT (Rb$_3$•*p*-TT) and transition metal complex of reduced *o*-TT (Co•*o*-TT) were prepared by electrochemical and chemical reduction. In these crystal structures, *p*-TT and *o*-TT forms honeycomb like structures with strong pancake bonds between *p*-TT radicals (Fig. 1d), and coordination bonds between *o*-TT anion and Co^{2+} (Fig. 1f). Detailed crystal structures and physical properties of these radical anion species will be discussed.

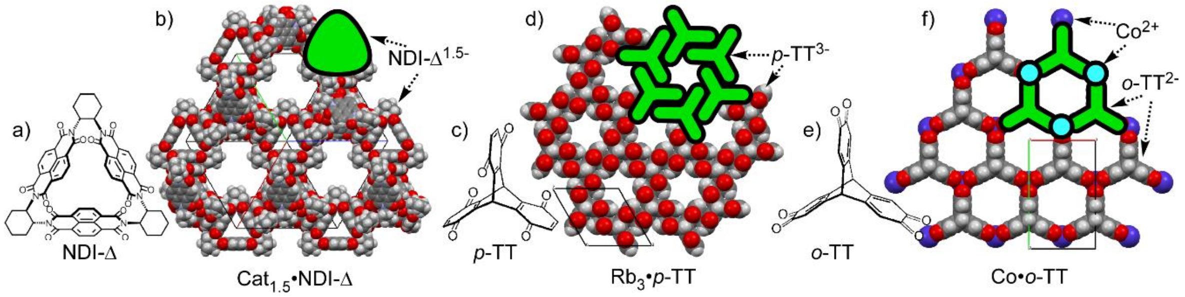

Fig. 1 Molecular structures of NDI-Δ(a), *p*-TT (c) and *o*-TT (e). The Gyroid crystal structure in radical anion salt Cat$_{1.5}$NDI-Δ (b). Honeycomb structures in radical anion salt Rb$_3$•*p*-TT (d) and transition metal complex Co•*o*-TT (f).

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Electro-active polyimides with pendant groups based on 9*H*-thioxanthene-9-one and its 10,10-dioxide: synthesis, electrochemical and electrochromic properties

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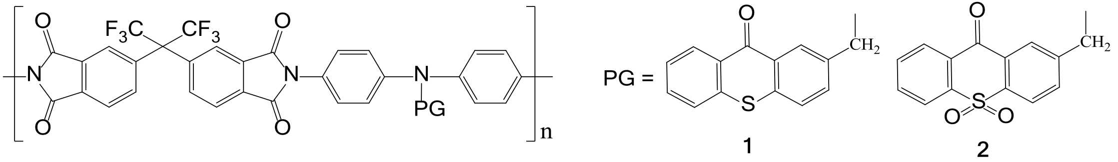
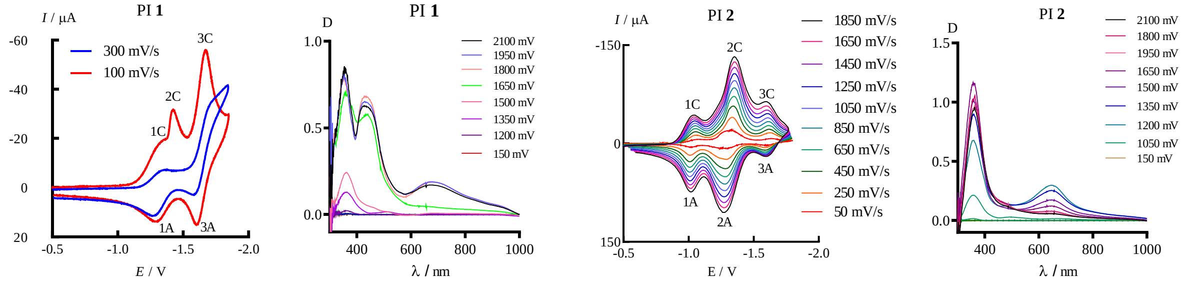
Electro-active polyimides with pendant groups (PG) based on 9*H*-thioxanthene-9-one (EP **1**) and its 10,10-dioxide derivative (EP **2**) have been synthesized by the formation of the corresponding polyamide acids with the following imidization. Synthesis and electrochemical properties of the corresponding monomers with these PGs have been described earlier in [1].



Thermogravimetric analysis showed very high thermal stability of the polyimides EP **1, 2**. Noticeable loss in mass was observed at temperatures above 390 °C only.

With solid state cyclic voltammetry (CV) of the PI's films immobilised on the surface of working electrode it was shown that PI **1** is characterized by two reversible CV-waves (1C-1A, 3C-3A), the latter one is associated with electron transfer to PG **1**. PI **2** is characterized by three reversible CV-waves (1C-1A, 2C-2A, 3C-3A), the first and the third waves are associated with electron transfer to PG **2** while the second wave corresponds with electron transfer on the main chain of the polyimide.

Electrochromic properties of the PI's films deposited on ITO-electrode surface showed three electronic transitions in UV-VIS-NIR area for PI **1**. Absorption bands at wavelenths 430 nm and 670 nm are associated with electron transfer on PG **1**. Electronic spectrum of PI **2** is characterized by two absorbtion bands (355, 644 mn) assosiated with electron transfer on PG **2**. The nature of the observed electronic transitions was proved by comparision with 3D spectroelectrochemical studies of the starting compounds (2-methyl-9*H*-thioxanthene-9-one and its 10,10-dioxide derivative) used for the synthesis of the corresponding monomers.



Electrochemical studies showed that PIs **1, 2** have low electrochemical reduction potentials, the values of which are varied in the range -1.0<E<-1.7 V. Taking into account high termal stability of the PIs **1, 2** we consider them as perspective electro-active materials for elaboration of non-volatile resistive-type memory devices with low ON/OFF switching voltage.

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Acknowledgements

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Supramolecular structure and physical properties of [Ni(dmit)2] salts with dibenzo-24-crown-8

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Molecular motions within the crystalline state have been attracting much attention because of the potential application to functional materials such as ferroelectrics. We already reported flip-flop motion of a *m*-fluoroanilinium (*m*-FAni$^+$) ferroelectric supramolecular crystal of (*m*-FAni$^+$)(DB-18-crown-6)$[Ni(dmit)_2]^-$ (where DB-18-crown-6 and dmit^{2-} are dibenzo-18-crown-6 and 1,3-dithiole-2-thione-4,5-dithiolate^{2-}, respectively), in which the ferroelectricity was originated from the inversion of dipole moment associated with flip-flop motion of *m*-FAni$^+$.[1]

In this study, we incorporated various heterocyclic cations in $[Ni(dmit)_2]^-$ crystals with dibenzo-24-crown-8 (DB-24-crown-8), which expected to capture heteroaromatic cations to form supramolecular entities due to the large ring size compared to 18-crown-6.

Black crystals of $(H\text{-}pdaz^+)_2(DB\text{-}24\text{-}crown\text{-}8)_3[Ni(dmit)_2]^-{}_2$ (1), $(H\text{-}praz^+)_2(DB\text{-}24\text{-}crown\text{-}8)_3[Ni(dmit)_2]^-{}_2(H_2O)$ (2), and $(H\text{-}bpy^+)(DB\text{-}24\text{-}crown\text{-}8)[Ni(dmit)_2]^-$ (3a and 3b, which were polymorphs) were obtained by slow evaporation of acetone solution of BF_4 salt of H-pdaz$^+$, H-praz$^+$ or H-bpy$^+$, DB[24]crown-8, and (tetrabutylammonium)$[Ni(dmit)_2]^-$.

In crystals 1 and 2, a one-dimensional (1D) columnar structure along the *a*-axis was formed by DB-24-crown-8. The H-pdaz$^+$ or H-praz$^+$ with H_2O were included in the column. Isolate N-H•••O hydrogen bond was observed between H-pdaz$^+$ and DB-24-crown-8 in crystal 1, while H-praz$^+$ and H_2O molecules formed 1D hydrogen bonding chain in the crystal 2. In crystals 3a and 3b, H-bpy$^+$ and DB-24-crown-8 formed supramolecular cation structures through weak π•••π interaction between phenylene rings of DB-24-crown-8 and one of the pyridyl rings of H-bpy$^+$. Each suramolecular cation in crystals 3a and 3b was interacted through N-H•••N hydrogen bonding between H-bpy$^+$ cations, forming a 1D pseudo-polyrotaxane structure (Fig. 1).

Crystal structure and physical properties of these salts will be discussed in detail. [2]

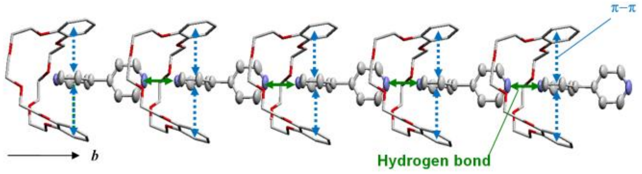

Fig. 1. 1D hydrogen-bonded polyrotaxane structure in **3a**.

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The authors appreciate to Prof. Tomoyuki Akutagawa and Dr. Norihisa Hoshino for the dielectric measurements and fruitful discussions. We also express gratitude to Dr. Shuhei Fukuoka for the measurement of magnetic susceptibility.

Spin-labeled graphene nanoribbons for organic electronics and spintronics

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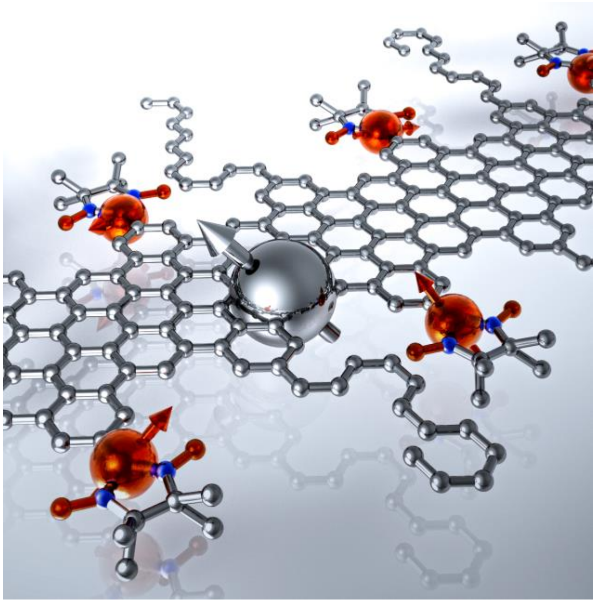
Graphene is a two-dimensional crystal demonstrating a unique set of optical, electrical and mechanical properties [1]. Moreover, by introducing magnetic edges in graphene nanoribbons, ferromagnetic couplings and superior spin filtering are predicted [2, 3].

To design magnetically active graphene-based systems, we proposed a directed synthetic approach including the synthesis of graphene nanoribbons with great purity and subsequent functionalization them with robust organic radicals. Using this approach, a spin-labeled graphene nanoribbon bearing nitronyl nitroxide substituents was prepared and completely characterized [4–6]. Using ESR spectroscopy and quantum chemical calculations, the degrees of spin labeling of the graphene nanoribbon with a stable nitronyl nitroxide were evaluated, as well as a full picture of the interactions between the magnetic radicals. It was shown that the coherence time reach microseconds at W-band frequencies at liquid nitrogen temperature, and sub-microseconds at room temperature. The co-existence of both localized radical spins and the magnetic edge state in the nanoribbon was clearly observed. Via DEER spectroscopy, a coupling between the edge state and the radical spins with characteristic two-qubit inversion time of 350 ns was determined. This finding is a milestone meaning that in properly designed spin-labeled graphene nanoribbons, quantum operations can in principle be performed via single-electron transport, and the spin states can be detected electrically.



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Acknowledgements

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Tuning the magnetic properties of Co(II)-based single-ion magnets by magnetic dilution

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Single ion magnets (SIM) are promising unit blocks for ultra-dense data-storage devices and quantum computers. The prerequisite for SIM behavior is large zero-field splitting (ZFS), an intramolecular property. In addition, intermolecular electron spin interactions can strongly influence the macroscopic magnetic properties of SIM bulk materials. When thinking of SIM as a self-sustained device, which can be addressed from outside, the distance between the individual SIMs is the parameter to be controlled when preparing SIM arrays. This urges for an unambiguous determination of inter- and intramolecular electron spin interactions. Spectroscopic methods alone are oftentimes not sufficient to reach this goal. Therefore, magnetic dilution of paramagnetic samples by complexes with diamagnetic ions is a routinely used approach. Yet, as will be shown herein, magnetic dilution, may not only change intermolecular interactions, but also intramolecular properties, determining SIM behavior.

We studied the magnetic properties of the SIM $[Co(piv)_2(2\text{-}NH_2\text{-}Py)_2]$ along with its magnetically diluted analogues with the general formula $[Co_xZn_{(1-x)}(piv)_2(2\text{-}NH_2\text{-}Py)_2]$ by XRD, X-band and Frequency-Domain Fourier-Transform THz-EPR (FD-FT THz-EPR) spectroscopy, AC magnetic measurements and quantum chemical calculations (QCC). FD-FT THz-EPR [1] allowed for direct determination of very large ZFS in $[Co(piv)_2(2\text{-}NH_2\text{-}Py)_2]$ and its Zn-diluted analogues down to 10% of Co(II) content. The ZFS was found to be almost constant in the range between 100% to 50% of Co(II) content. However, it drastically decreases from ~75 cm^{-1} to ~50 cm^{-1} while decreasing the Co(II) content below 50%.

The reason for this shift can be rationalized with the help of dilution dependent XRD analyses. XRD showed that dilution with Zn does not only change the average distance between paramagnetic ions, but induces also structural changes at the remaining Co sites. This indicates that $Co(piv)_2(2\text{-}NH_2\text{-}Py)_2$ molecules can be found in one of two geometries which correspond either to Co(II) or Zn(II) lattice. Further evidence could be obtained by QCC, which unveiled that the dilution-induced structural transition in $Co_xZn_{(1-x)}(piv)_2(2\text{-}NH_2\text{-}Py)_2$ leads to spin levels inversion of Co(II) ion forming true-SIM spin levels order. This observation was reliably confirmed by X-band EPR and AC magnetometry. The latter also allows one to determine the magnetic relaxation pathways for Co(II) ion spin system in both types of $Co(piv)_2(2\text{-}NH_2\text{-}Py)_2$ geometries.

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ORAL TALKS

Magnetic properties of π -conjugated phenoxyl-nitroxide radicals as designed for advanced molecular magnetism

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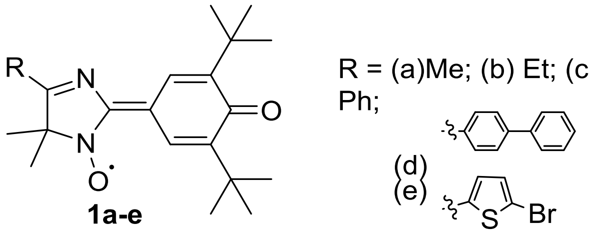
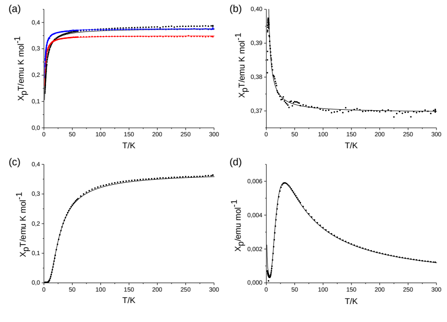
A series of stable and genuinely organic open-shell systems, π-conjugated phenoxyl nitroxide free radicals (hybrid phenoxyl nitroxide radicals) (Fig.1) have been synthesized and their magnetic properties in the crystalline state investigated, revealing their usefulness of new building blocks for molecular magnetic materials. The salient electronic structure of the hybrid phenoxyl nitroxide radiclas is extended π-spin delocalization from the nitroxide moiety, mediating the localization effect intrinsic to nitroxide radiclas. Five representative hybrid radicals containing an aliphatic, aromatic and heteroaromatic substituent with the side part of the compact hybrid radical centers were synthesized, and their molcular/crystal structures in the crystalline state were solved by X-Ray diffraction analyses. CW X-band ESR and ^{1}H-ENDOR spectroscopy and DFT calculations confirmed that an unpaired spin delocalizes over the whole molecular frames including the non-conjugated fragments, suggesting the possibility of tuning their electronic properties through substituent effects in the crystalline state. Significant influence of the joint phenoxyl moiety to the electronic structure was analysed in terms of the **g**-tensor calculations. The SQUID magnetization measurements revealed that the nitroxides bearing alkyl or aromatic substituents behave as 3D Curie-Weiss paramagnets with weak antiferromagnetic (AFM) (Θ = -1÷-2.6 K) or ferromagnetic (FM) (Θ = +0.33 K) spin-spin exchange interactions (Fig.1). On the other hand, heteroaromatically substituted hybrid phenoxyl-nitroxide showed significant AFM interactions with J/k_B = -25.6 K. The analyses of the bulk magnetic properties on the basis of the crystallographic data and DFT calculations revealed the occurrence of competition between the intermolecular AFM and FM interactions which originate from the C-O(phenoxyl)...Me(nitroxide) or (N)O-C(arom) infinity 1D head-to-tail chains and the C(arom)-C(arom) head-over-tail dimers forming 3D networks in their crystal lattices.



1a-e

R = (a)Me; (b) Et; (c) Ph;



Fiig.1.The SQUID magnetometry of the polycrystalline (solid) radicals **1a-e**: (a), (b) and (c) $\chi_{para}T$ vs. T χ_{para} vs. T plots for (a) **1a** (black);, **1b**(red); **1d** (blue); (b) **1c**; (c) and (d) **1e**. The dotted curves denote the experimental values and the solid curves the calculated Curie-Weiss curves in (a),(b) or Bleany-Bowers curve (J/k_B = -25.6K + Curie curve in (c) and (d).

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Novel 2,1,3-benzochalcogenadiazole based charge-transfer complexes

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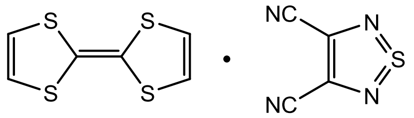
Chalcogen-nitrogen π-heterocycle are widely used as electron acceptors in synthesis of numerous charge-transfer (CT) complexes revealing electrical conductivity. Recently it was shown that 3,4-dicyano-1,2,5-telluradiazole and 1,2,5]thiadiazolo[3,4-c][1,2,5]thiadiazole as electron acceptors form CT complexes with such electron donor as tetrathiafulvalene (TTF) [1].

As extension of this approach the novel CT complexes **1-4** with 3,4-dicyano-1,2,5-thia(selena)diazole, fluorinated 2,1,3-benzothadiazole and 1,2,5-thiadiazoloquinoxalin were synthesized.

All this complexes are weakly-bonded and dissociates in diluted solutions. With DFT calculations, the largest value of CT between D and A was found for complex **4** to be 0.29e in the XRD structure. There are CT bands in the UV-Vis spectra of all complexes in long wavelength area that correspond to electron transition from HOMO, localized on D, to LUMO, localized on A. Gibbs free energies values of CT complex formation are small and slightly negative (-2.5 kJ mol^{-1} for complex **4**)



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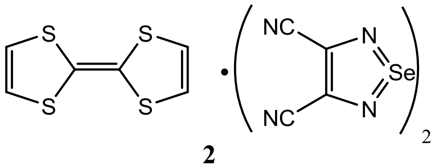

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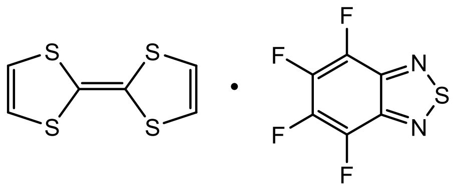

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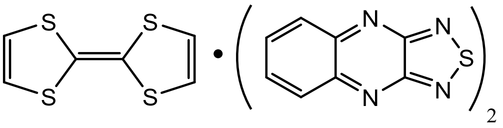

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Quantitative Topological Descriptor for Linear Co-oligomers Fusion

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Previously, conjugated rod-like co-oligomers (distyrylbenzenes, thiophene/ and furan/phenylene co-oligomers) were reported as highly-emissive semiconductors with moderate charge mobility. However, rigid and closely-packed annulated conjugated systems (acenes, fused polycyclic furans and thiophenes) were reported to show very high charge carrier mobility, albeit low emission efficiency due to aggregation quenching. Thus, searching an optimal annulated system with balanced optoelectronic performance is still a great challenge and hence strict and quantitative definition of annulation concept is required.

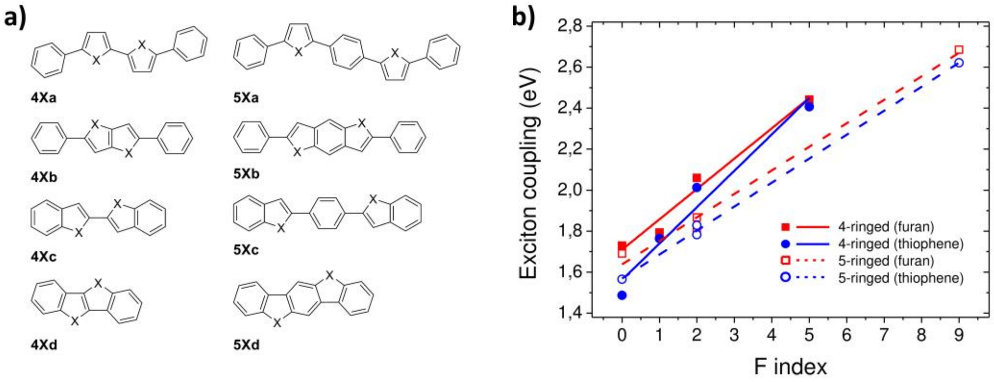

Fig. 1. (a) Chemical structure of studied compounds; (b) example of correlation between F-index and exciton coupling evaluated for model π-stacking dimers

In this work we propose F-index: intuitive, quantitative definition of annulation based on molecular topology applicable to the materials of strategic importance in organic opto-electronics. F-index evaluated for investigated compounds (Fig. 1a) showed excellent correlations with HOMO-LUMO gap, absorption energies, exciton coupling (Fig. 1b), electron affinity. Although some properties did not exhibit good correlations, further generalisation of the definition of F-index, with addition of other structural properties and electronic effects, may allow to apply it to a wider classes of conjugated compounds to estimate their optoelectronic performance without heavy quantum chemical calculations.

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Light-induced charge separation and spin-dependent recombination of charge transfer state in organic photovoltaic blends: insight from out-of-phase ELDOR

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The key process in organic solar cell operation is charge separation under light illumination. Due to low dielectric constant of organic materials the Coulomb attraction energy within interfacial charge-transfer state (CTS) is larger than room temperature thermal energy. Understanding the mechanism of charge separation at organic donor/acceptor interface still remains a challenge.

The aim of this work is to develop a technique allowing to observe photoinduced (CTS) – a weakly coupled electron-hole pair preceding to completely separated charges – in OPV composites so as to measure distance distribution of charges and how it evolves in time. Obtaining such an information for different composites is highly important for developing a general theory of charge separation.

Out-of-phase Electron Double Resonance (OOP ELDOR) is a reasonable choice to reach the goal. Interpreting ELDOR data one can estimate spin-spin interactions between hole and electron radicals, both the dipole and the exchange, and therefore find out the structure of the CTS. Also performing the experiment with different delays after photoexcitation gives an opportunity to observe CTS at different stages of charge separation and, thus, study kinetics of charge dissociation and recombination.

In this work the method of OOP ELDOR has been applied to OPV composites for the first time. The data have been measured for a set of polymers, including benchmark polymer P3HT and high-performance PCDTBT polymer, in conjunction with the PCBM acceptor. The data have been processed using the Tikhonov regularization approach and the corresponding electron-hole distance distributions have been obtained. The evolution of this distribution with delay afrer laser flash increase is interpreted in term of spin-dependent.

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Applying of Ink-jet Printing for creating organic electronic devices

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Ink-jet printing is a fast and material effective technique that allows to create the devices of any topology [1]. Ink-jet printing has many advantages over classic methods, but its use fraught with some difficulties. One of them is high requirements to physical parameters of the inks – viscosity, surface tension, solvents boiling temperature. Achieving the good values for all parameters is too hard task. The model of printing by low-viscosity inks was created [2]. The model allows to select printing mode for high-quality printing by non-optimal inks.

Many of the non-polar organic solvents, such as xylene and tetralen, are too “aggressive” for internal structure of the cartridge. More polar solvents should be used for ink-jet printing, in particular – alcohols. The choice of the luminofors is very restricted with alcohols as a solvent. But there are promising conjugated polymers that can be easily modified. The soluble in alcohols polyfluorens was synthesized [3].

The glass substrates coated by transparent layer of ITO was used for creating OLEDs. The PEDOT:PSS layer was formed by spin-coating method. For forming PFO (polyfluoren) and PFPO (modified polyfluoren) spin-coating method also was used. The PFO and PFPO layers were formed also by ink-jet printing method. To do this the inks were created. PFO was solved in 1,2-dichlorobenzene and PFPO in the mixture of n-butanol and glycerin. The cathode was formed by thermal vacuum evaporation.

The characteristics of the created OLEDs

OLED-structure	*V*th, V	*L*(100), cd/m^2	*j*(100), $мA/cm^2$	φ(100), cd/A
ITO/PEDOT:PSS(spin)/PFO(print)/LiF/Al	3.6	265	34	0.23
ITO/PEDOT:PSS(spin)/PFPO(print)/LiF/Al	5.1	578	16	0.64
ITO/PEDOT:PSS(spin)/PFO(spin)/ PFPO(spin) /LiF/Al	5.6	20	329*	0.02
ITO/PEDOT:PSS(spin)/PFO(spin)/ PFPO(print) /LiF/Al	4.5	27	286	0.04
ITO/PEDOT:PSS(spin)/PFO(print)/ PFPO(spin) /LiF/A	4.9	50	192	0.05

* Current density at a brightness 70 cd/m^2.

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Chemistry of Herz Radicals: A New Way to Near-IR Dyes with Multiple Long-Lived and Differently-Colored Redox States

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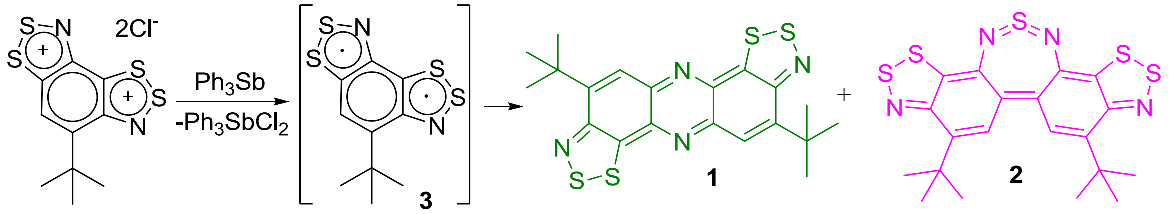
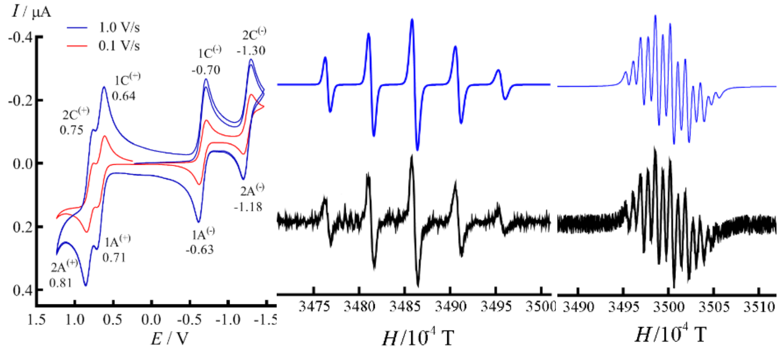
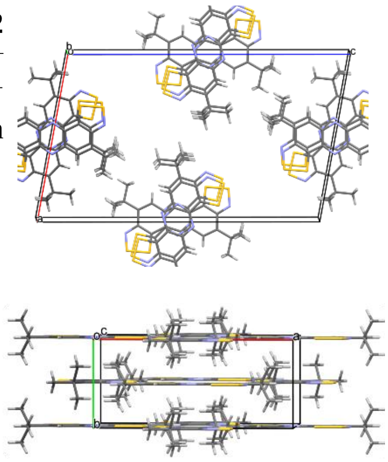
New polycyclic 1,2,3-dithiazoles **1** and **2** (stable in air up to 325 and 270 °C, respectively) were obtained by dimerization of the diradical **3** generated by reduction of the salt [**3**][Cl]$_2$. Intensive long-wave absorbtion of **1** (λ_{max} 689 nm and shoulder 760 nm) and **2** (λ_{max} 796 nm) runs to near IR region.



Compound **1** reveals five long-lived redox states. UV-Vis spectra of **2** and all five redox forms of **1** were analyzed with TD-DFT. $\mathbf{1}^{\bullet+}$ and $\mathbf{1}^{\bullet-}$ were studied by EPR spectroscopy. Radical cation $\mathbf{1}^{\bullet+}$ and dication $\mathbf{1}^{2+}$ as well as starting dication $\mathbf{3}^{2+}$ were characterized by X-ray diffraction in the form of stable salts of $GaCl_4^-$ and TfO^-.



CVA of **1** (left), EPR spectra of $\mathbf{1}^{\bullet-}$ (center) and $\mathbf{1}^{\bullet+}$ (right)



Packing of radical cations $\mathbf{1}^{\bullet+}$ in crystals of [**1**][$GaCl_4$]. Interplanar distance is 3.384 Å

Acknowledgements
The authors thank Dr. Elena A. Pritchina for CASSCF calculations, and the Russian Foundation for Basic Research (RFBR) and the Government of the Novosibirsk region (GNR) of the Russian Federation (projects RFBR 18-03-00596 and RFBR-GNR 18-43-540025), and the Deutsche Forschungsgemeinschaft (project BE 3616/6-2) for financial support.

Organic solar cells based on novel acceptor anthrathiophene molecules: vacuum-free fabrication

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Presently, researchers are looking for new kinds of acceptor molecules, which will lead to greater PCE of photovoltaic cells. Examples of such compounds are benzodithiophenes, which demonstrate PCE exceeding 10% [1]. We synthesized anthrathiophenes and functionalized them with acceptor moieties [2] (fig. 1). It was found that different pi-linker structure influences on electrochemical, optical and photovoltaic properties of fabricated devices. It is known that malononitrile groups improve acceptor properties by lowering LUMO energy by 0.3 – 0.4 eV and also increase solubility of compounds in organic solvents. In polymer/anthrathiophene blends charge separation was observed by light-induced EPR spectroscopy. For device fabrication we used traditional architecture ITO/PEDOT:PSS/Active layer/PFN/FM, where PFN is widely used electron transporting layer and FM – "Field's Metal Alloy" consisting of Bi/Sn/In eutectic alloy [3]. The cathode was fabricated by casting the melt at 90°C on the device through the mask. Voc was about 0.9 V, but Jsc and FF are low (~1 mA/cm^2 and 30% respectively). We suggest that morphology of active layer is not optimized and causes low PCE of fabricated solar cells.

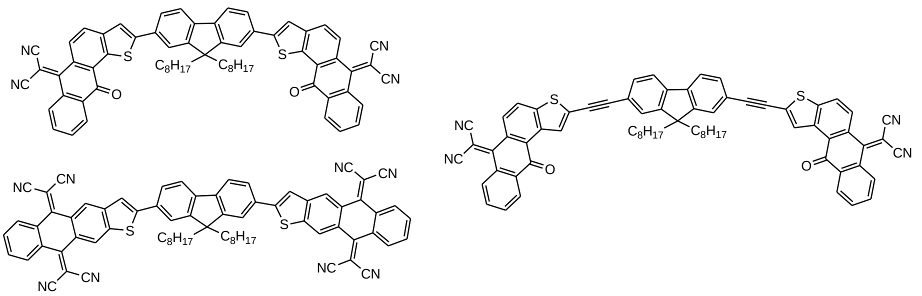

Fig. 1. Angular anthrathiophenes.

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Simulation of materials for organic light emitting diodes: photoluminescence efficiency and photodegradation mechanisms

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Rational design of novel materials for organic light emitting diodes (OLED) requires deep understanding of the processes accompanying device operation at the molecular scale, such as charge and energy transfer, generation and relaxation of excited states, photochemical reactions leading to the degradation of the material, etc. Modern computational chemistry provides versatile tools to study morphology and properties of the OLED materials that cannot be properly addressed with experimental techniques.

Photoluminescence (PL) efficiency of OLED materials depends on the relative rates of competitive radiative and non-radiative processes of energy relaxation occurring in the light emitting molecule. These rates can be estimated with first-order perturbation theory applied to adiabatic reference wavefunctions of the electronic states represented by multidimensional harmonic oscillators. This approach has been successfully applied to the prediction of PL quantum yields for a series of Pt(II)-based light emitting complexes [1].

Operational stability is one of the main issues for state-of-the-art blue OLED emitters. The exact mechanism of the degradation in any particular case is rarely known. Computer simulations of hypothetical chemical reactions can support scattered experimental evidences and shed light on this problem [2]. Intermolecular interactions and formation of exciplexes can also be responsible for the degradation. Calculated values of physically inspired parameters can be used to construct regression model possessing practically useful prediction power. Following this approach, combined with structure-based molecular fingerprints, we developed a model for prediction of photochemical stability of host OLED materials with Pearson regression coefficient R=0.85.

The methods useful for the simulation of OLED materials include molecular dynamics, density functional theory, multireference *ab initio* approaches (for prototypical molecules of moderate size), continuous theory of solvation, polarizable force fields and methods of chemoinformatics. They can be used to enhance our understanding or to construct a model for prediction of the desired property.

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Fused chalcogenadiazoles as a core central block in photovoltaic materials

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Materials based on 2,1,3-benzothiadiazoles play an important role as π-type building blocks for organic electronics, which include organic light-emitting diodes (OLEDs), organic solar cells (OSCs), organic thin film transistor and organic bistable memory devices.[1] Among these devices, OLEDs and OSCs are the most actively studied area of organic electronics. Other 2,1,3-benzochalcogenadiazoles (where chalcogen = oxygen and selenium), benzo[d][1,2,3]chalcogenadiazoles and 1,2,5-chalcogenadiazoles fused with heteroaromatic rings in combination with various anchoring groups and π-spacers are much less studied.[2,3] Meanwhile 1,2,5-chalcogenadiazoles fused with benzene and nitrogen heterocycles can be considered as one of the most perspective group of internal acceptors for the preparation of the systems (as well polycyclic, as polymeric) with high physical properties.

Novel approaches to the preparation of novel dyes on the ground of 2,1,3-benzochalcogenadiazoles, [1,2,5]chalcogenadiazolo[3,4-*c*]pyridines and [1,2,5]thiadiazolo[3,4-*d*]pyridazine will be presented. In addition, the application of the compounds obtained in organic light-emitting diodes and organic solar cells will be reported.

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Photophysical and Electroluminescent Properties of Organic Molecules with Thermoactivated Delaed Fluorescence

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According to quantum statistic under electrical excitation of organic compounds 75% of formed excitons are in nonradiating triplet state and only 25 % in singlet state. Thus, the most part of excitons is useless for OLEDs. The using of organic molecules with thermal activated delayed fluorescence (TADF) is the way to increase OLED's efficiency [1]. In such molecules there is process which converts triplet excitons into singlet excited states. One of the criteria for the effective process of the triplet states convertation into singlet states is the small energy gap between S1 and T1 states.

Spectral properties, luminescence under photo - and electro excitation have been studied here for three new organic compounds: 2,7-bis [N, N-di (4-tert-butylphenyl) amino] dibenzothiophene-S, S-dioxide (**L1**), 3,6-bis [N, N-di (4-methoxyphenyl) amino] dibenzothiophene-S, S-dioxide (**L2**), 3,6-bis [N, N-di (4-tert-butylphenyl) amino] dibenzothiophene-S, S-dioxide (**L3**).

To reveal the delayed fluorescence and phosphorescence the emitting of neat films of L1, L2 and L3 have been recorded with 0.1ms delay after excitation at room temperature and 77K . The energy difference (ΔE_{ST}) between the lowest singlet state (S1) and the lowest triplet state (T1) was equated to difference between maximums of fluorescence and phosphorescence spectra. The delayed fluorescence was detected for all compounds and the smallest ΔE_{ST}=0.15 ev belong to L2.

The spectral characteristics and the rate constants of photophysical processes such as radiative, nonradiative, intersystem and reverse intersystem crossing were calculated with TDDFT theoretical method. Calculated characteristics of ΔE_{ST} and rate radiative constants are in a good agreement with experimental ones.

The OLED structures ITO/PEDOT:PSS/NPD/**L**/BCP/LiF/Al, where **L** is one of the three compounds, were fabricated. Current-voltage, volt-brightness and spectral characteristics were obtained. The relation of OLED's efficiency and amount of ΔE_{ST} was analyzed. It was shown that the OLED's efficiency is close for structures where **L** is compound with high fluorescence quantum yield (**L1**) or one with the smallest ΔE_{ST} (**L2**).

The charge carrier mobility of this compounds was estimated by transient electroluminescence method. Rectangular electrical pulse was applied to the OLED's electrodes. Electroluminescence responses of devices to 7 V 400 μs pulses is shown in fig.1. Here we discuss the EL time evolution: a) - t_d, a delay time before light is detected; b) $t_{1/2}$, time when the EL intensity is half of the maximum; c) - t_q, time of the EL quenching after turning-off of an impulse.

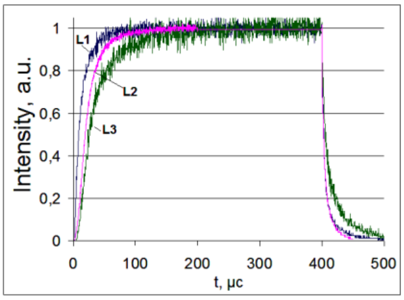

Fig.1. EL response of OLED devices to 7 V 400 μs pulses

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1,2,5-chalcogenadiazoles – efficient electron acceptors for the design of paramagnetics and anion receptors

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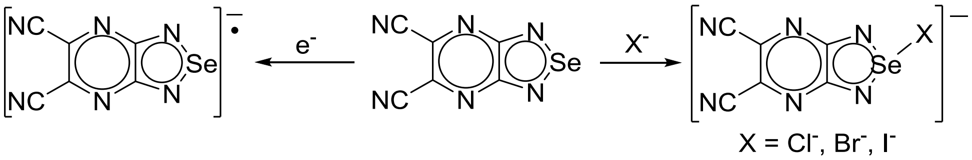
1,2,5-Chalcogenadiazoles (chalcogen: S, Se, Te) are of particular interest to the chemistry and materials science. The common property of these heterocycles is high positive electron affinity (EA) making them effective electron acceptors. Single-electron reduction of these compounds leads to the formation of stable radical anions (RAs), which can be isolated in the form of salts followed by characterization of the latter with XRD, EPR and SQUID magnetometry [1].

Another interesting property of 1,2,5-chalcogenadiazoles particularly significant for Se and Te heterocycles is an ability to coordinate anions via chalcogen bonding through two σ-holes on the chalcogen atom. Thermodynamic stability of these complexes varies in a wide range and depends strongly on the nature of anion and the structure of heterocycle. This allows for a selective binding of a certain anion in a competitive environment. One case of such a selectivity was recently demonstrated [2]. Coordination of anions (and other Lewis bases in general) leads to the change of spectroscopic properties of the system. Selectivity and spectral response open up a possibility for the design of 1,2,5-chalcogenadiazole based receptors and sensors for anions [3].

The present contribution describes DFT calculations-assisted molecular design, chemical synthesis and structural and functional characterization of novel paramagnetic materials based on 1,2,5-chalcogenadiazolidyl salts as well as synthesis, structural characterization and experimental and theoretical characterization of thermodynamics and binding in chalcogen bonded complexes. Two modes of reactivity are demonstrated with the most recent examples [2, 4]:



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Electronic Structure and Molecular Arrangement of the Cyclic Thiazyl Diradical BDTDA

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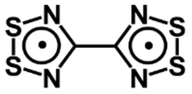
In recent years, organic semiconductors have received much attention in the field of organic electronics and spintronics. Most of studies, however, have been focused on closed-shell molecules like pentacene, and almost no attention has been paid to molecules with unpaired electrons, namely "organic radicals", though the radicals can be used as building blocks for semiconducting thin films and associated devices since the unpaired electrons has the ability to become charge carriers. We therefore focused the cyclic thiazyl radicals, which are stable and possess strong intermolecular interactions in 3D network crystal structures. In former study, we have fabricated highly oriented thin films of 4,4'-bis(1,2,3,5-dithiadiazolyl) (BDTDA) [1] consisting of π-stacking chains of radical dimers, and revealed steady-state photocurrent with a high on/off-gain of ITO/BDTDA/Al photocells at small reverse bias voltages and photovoltaic behavior with a giant transient photocurrent at zero bias voltage [3-5]. To understand the mechanism of charge transportation, we first carried out the *hν*-dependence of ultraviolet photoemission spectroscopy (UPS) of a BDTDA thin film on GeS(001) to obtain the knowledge of the electronic structure [6]. Stacked BDTDA dimers showed an energy band dispersion of about 0.3 eV for the highest occupied molecular orbital in the direction of the surface normal of the BDTDA solid film. However, the electronic structures of BDTDA on GeS(001) which is flat in atomic scale and have few defects may be different from those on the substrates used for the real devices, such as bumpy substrate, ITO. By measuring the band structures, we found that the HOMO of BDTDA on ITO substrate shows almost negligible dispersion. These results are indispensable evidences of the mechanism of transient photocurrent "double-layer model" [4-5]; most of the thin film is an insulator, and an anomalous transient photocurrent induced by an effective charge separation at the interface. That is, the interface property critically dominates the electronic properties of whole devices.



BDTDA

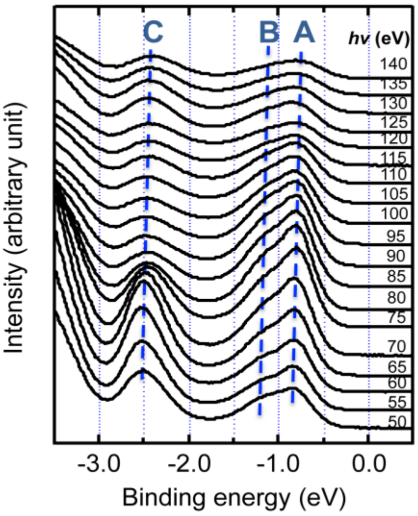


Figure. *hν*-dependence of UPS spectra of BDTDA thin film on ITO.

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Structure and Dynamics of Light-Induced Electron-Hole Pairs within the Composite DTS(FBTTh$_2$)$_2$:PC$_{71}$BM Observed by Electron Spin Echo

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The donor-acceptor composites based on organic π-conjugated semiconducting compounds are promising materials for active layers of advanced thin-film and flexible solar cells. The crucial step of photocurrent generation is light-induced electron transfer from donor to acceptor which occurs through electron-hole pair called as Charge Transfer State (CTS) [1].

In the present work an advanced approach of electron spin echo technique application has been developed to describe structure and dynamics of CTS in DTS(FBTTh$_2$)$_2$:PC$_{71}$BM organic photovoltaic composite at temperatures 20K - 70K. DTS(FBTTh$_2$)$_2$ is a non-polymer electron donor and PC$_{71}$BM is a fullerene-based electron acceptor.

Pronounced out-of-phase ESE signal was observed within first few microseconds after a laser flash exciting the composite. This implies correlation of unpaired electron spins of DTS$^+$ and PC$_{71}$BM$^-$ species constituting CTS. Low-temperature CTS lifetime of about 15 μs was obtained (at 20K). It decreases when the temperature increases. Non-exponential ESE decays of CTS with *DAF* increase are manifested due to a distribution within CTS lifetimes, which is in turn caused by a distribution of a primary charge separation distance. The characteristic transversal spin relaxation time T_2 = 2.6 μs was found for both DTS$^+$ and PC$_{71}$BM$^-$.

The distribution of distances within CTSs was obtained from magnetic interactions which determine out-of-phase ESE Envelope Modulation (ESEEM) [2]. Both magnetic dipolar and electron-hole exchange interactions within CTS were characterized from the numerical simulations of the out-of-phase ESEEM traces [3]. The most probable distances between DTS$^+$ and PC$_{71}$BM$^-$ within CTS were found within the range between 4.9 nm and 6.1 nm at different delays after the laser flash, whereas the electron-hole exchange interation is about J/h = 1.5 MHz for the smallest interspin distance obtained r_0 = 2.5 nm.

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Sulfur-containing monomers and polymers with a high refractive index for electro-optics and photonics applications

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Vitalii Basistyi[1, 2]

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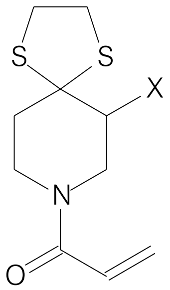
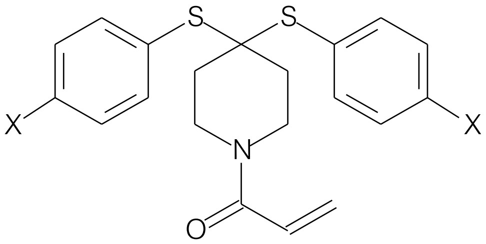
High refractive index polymers (HRIP) has a wide range of applications in optoelectronic products, such as display devices, optical encapsulants for OLED, antireflection coatings for optical components, a material for lenses, including ophthalmic, photoresists of 193 nm lithography, microlenses in charge coupled devices or complementary metal oxide semiconductor image sensors.

The some types of the sulfur-containing polymers are used in optics to achieve high refractive index materials [1-3]. One way to increase the refractive index of a polymer is introduction sulfur atoms into the monomer structure. Acrylamide monomers based on 4-piperidone derivatives containing 2 and 3 sulfur atoms were synthesized to obtain HRIP polymers.



1: X = H

2: X = SC_6H_5



4: X = H

Polymer films (0.4-1 mm thickness) were obtained from (1-5) monomers. The refractive index and Abbe number of monomers and polymers were measured using the Abbe refractometer DR-M4. The obtained values of the refractive index are varied in the range 1.58-1.64, the Abbe number – 31-33. The structure-properties relationships are discussed in the report.

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Synthesis and solid-state luminescence of silver(I) complexes with polydentate pyrimidine ligands

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In recent years, great interest of scientists in the field of materials science, photophysics and photochemistry has been focused on the study of luminescent coordination compounds. This interest stems mainly the fact that luminescent coordination compounds can be used as emitting layers in OLEDs. One of the appealing and interesting metals for the design of coordination compounds showing luminescence is silver. Silver complexes show a large number of possible transitions to excited states and subsequent radiative decay of these excited states. Such a behavior may result in the appearance of multiple emission bands and excitation-wavelength dependent emission. The goal of the present research is the synthesis of photostable silver(I) complexes and the investigation of emission properties the complexes at various excitation energies.

We have synthesized a series of silver(I) complexes with polydentate pyrimidine ligands (Fig. 1). The ligands, with various N-heterocycles in the positions 2 and 4 of the pyrimidine ring, can adopt various coordination modes. The substituents in the position 2 of the pyrimidine ring differ by their electronic properties (π-donor or π-acceptor) and can significantly influence on the stability and emission properties of the complexes.

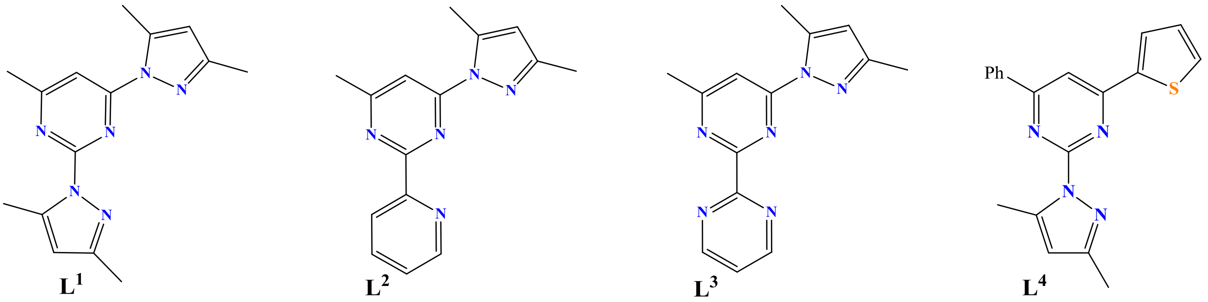

Fig. 1. Pyrimidine ligands

A series of silver(I) coordination compounds, $[AgL^1NO_3]$, $[AgL^1X]_n$ ($X = I^-, Br^-$), $[AgL^1(PPh_3)Y]$ ($Y = CF_3SO_3^-, BF_4^-, NO_3^-$), $Ag_2L^2I_2$, AgL^2I, $[AgL^3NO_3{\cdot}CH_3CN]_n$, $Ag(L^4)_2NO_3$ have been isolated and structurally characterized. The complexes $[AgL^1NO_3]$, $[AgL^1(PPh_3)Y]$ adopt mononuclear structures, whereas $[AgL^1X]_n$ and $[AgL^3NO_3{\cdot}CH_3CN]_n$ are polymeric compounds. The ligand L^1 adopts either N,N-bidentate ($[AgL^1X]_n$, $[AgL^1(PPh_3)Y]$) or N,N,N-tridentate ($[AgL^1NO_3]$) coordination mode. The silver(I) complexes exhibit photoluminescence in blue, green and red regions of visible spectrum. Importantly, some of them show excitation-wavelength-dependent emission.

Optoelectronic Conversion in MISIM Photocells using Photo-induced Pure Polarization Current without Carrier Transfer across Interfaces

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Organic optoelectronics devices have received attention recently by virtue of their low cost, light weight, and ease of fabrication. However, attempts to utilize organic materials in these devices generally encounter the most significant problem with organic materials: their poor mobility. Due to this and to an imbalance between hole and electron mobilities, space charges are always produced in organic photocells such as organic solar cells and photodetectors, thus limiting the photocurrent in these devices. However, it is also notable that photogenerated space charges can boost optoelectronic conversion through the generation of a highly efficient transient photocurrent [1].

Recently, we proposed a [metal|insulator|semiconductor|insulator|metal] (MISIM) photocell, as a novel architecture for high-speed organic photodetectors (Figure 1)[2]. The electric polarization in the S layer, induced by modulated light illumination, propagates into the outside circuit as a polarization current through the I layers, without any carrier transfer across the interfaces.

In the present work, we examined the MISIM photocells consisting of zinc-phthalocyanine(ZnPc)-C_{60} bilayers for the S layer and Parylene C for the two I layers, to understand the fundamental aspects of the MISIM photocells, such as current polarity and modulation-frequency dependence. It was found that, in such devices, the current polarity was primarily determined by the polarization in the S layer, which was induced by the donor–acceptor charge-transfer upon illumination. Furthermore, the ON and OFF current, which appeared in the periods of illumination-on and -off, respectively, exhibited significantly different dependence on the modulation frequency. This was well-explained by an imbalance between a quick polarization in the S layer during illumination and its slow relaxation in the dark.

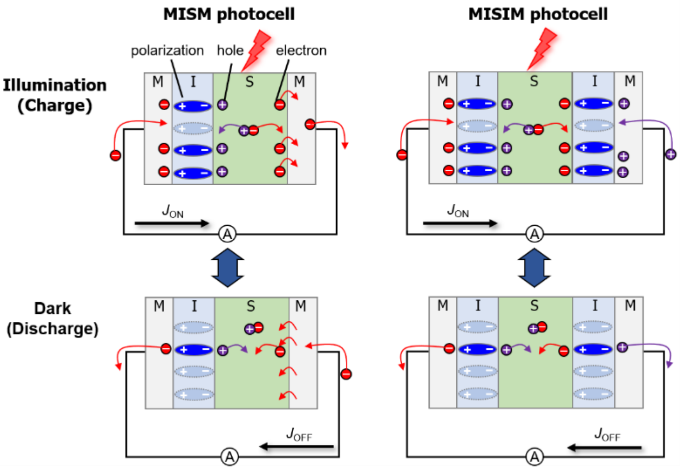

Figure 1 Comparison between the optoelectronic conversions in the MISM and MISIM photocells.

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2,1,3-Benzochalcogenadiazolidyls across O, S, Se, Te and Po pentad

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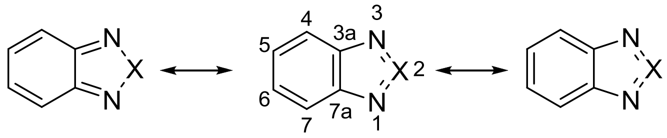
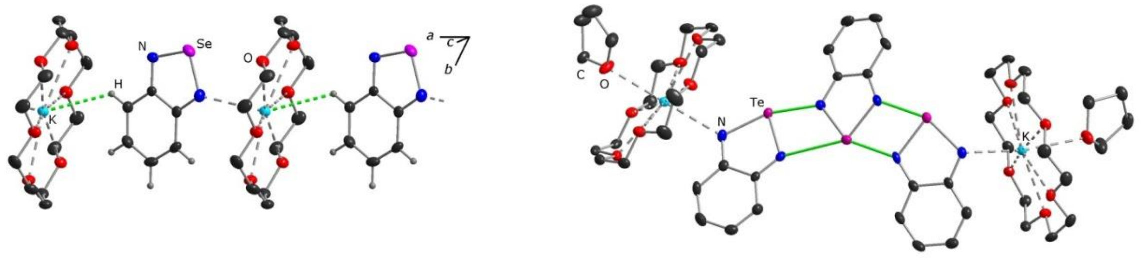
Radical-anion (RA) salts of chalcogen-nitrogen π-heterocycles, first of all derivatives of 1,2,5-chalcogenadiazole ring system, represent a new class of organic paramagnetics promising for functional materials science.

Recently, RA salts of 2,1,3-benzochalcogenadiazoles **2-4** (Scheme) were synthesized and characterized by XRD (Figure), solution and solid-state EPR, and quantum chemical calculations. In this talk their preparations, structures and properties are discussed in a broader context covering also still non-isolated RA of compound **1** and putative RA of compound **5** (Scheme) [1,2].



Scheme. 2,1,3-Benzochalcogenadiazoles **1-5** represented by superposition of quinoid (left) and benzenoid (middle and right) forms, X = O (**1**), S (**2**), Se (**3**), Te (**4**) and Po (**5**).



X = Se

X = Te

Figure. XRD structures of 2,1,3-benzochalcogenadiazolidyl salts with cations [K(18-crown-6)]$^+$ (X = Se) and [K(18-crown-6)(THF)]$^+$ (X = Te). For X = S, Se and cation [K(THF)]$^+$, salts are isomorphous.

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POSTER PRESENTATION

The effect of N-Benzyldimethylamine on the light scattering of films based on a thiol-siloxane compound

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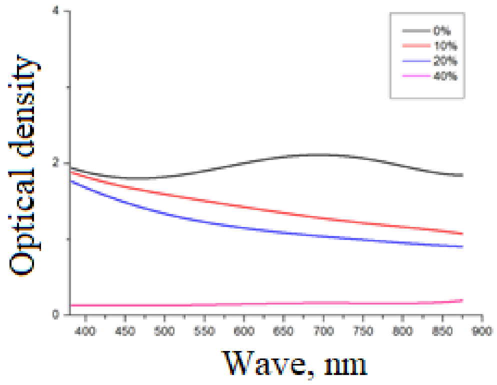

Figure 1. Absorption spectrum of a mixture of TS + BDMA at various amine

Currently, hybrid photopolymer materials (HFM) are being actively developed and investigated [1]. HFMs combine organic and inorganic structural blocks in their structure, which makes it possible to vary the properties of HFM for specific tasks [2]. As an inorganic block, thiol-siloxane oligomers (TS) can be used [3]. From literature data it is known that siloxane-containing compounds can undergo hydrolysis, which in turn can lead to increased light scattering and poor film formation [4]. It can be assumed that tertiary amines can affect the rate of hydrolysis of siloxane-containing compounds. shows the spectra of TS films with different contents of N-Benzyldimethylamine (0, 10, 20, 40 mol.%.). At the time of the experiment, the air humidity was 60%, and the temperature + 23°C. It can be seen from Fig. 1 that the addition of 40% BDMA significantly reduces the light scattering of the film.

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Synthesis of 2,8-disubstituted 1,3,7,9-tetraazaperylene

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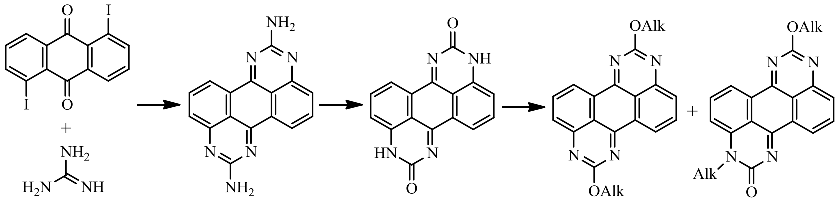
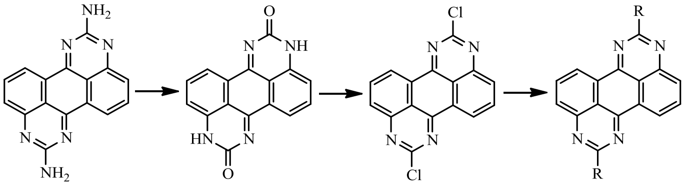
Polycyclic N-heteroaromatic compounds such as polyazaperylenes are of interest for organic electronics but are poorly understood [1]. The number of such compounds known to date is small and the methods for their synthesis are few [2].

Previously, we have developed a simple approach to synthesize 1,3,7,9-tetraazaperylenes. [3] The main advantage of our approach is one stage assembly of tetraazaperylene framework by condensation of 1,5-diiodoanthraquinone with guanidine in Ullmann conditions. The obtained 2,8-diamino-1,3,7,9-tetraazaperylene was transformed into corresponding anthradipyrimidone by simple diazotization reaction and then functionalized via regioselective N- or O-alkylation.



In this work, we report a synthesis of novel 2,8-substituted 1,3,7,9-tetraazaperylene derivatives from 2,8-diamino-1,3,7,9-tetraazaperylene. The preparation of series of 2,8-substituted 1,3,7,9-tetraazaperylenes functionalized by NR_2, Cl, alkoxy and phenoxy groups was achieved through the simple transformations such as diazotization, alkylation and nucleophilic aromatic substitution.



R = OAlk, OPh, $NAlk_2$

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Photoexcited optical chemical laser sensors

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The possibility to register the nitro groups is very important for human life and environment. The nitrogen-containing compounds are typical detectable substances (analytes) for photoluminescent methods due to their ability to form stable and reversible charge transfer complexes with substances that contain weakly bound electrons. In the resulting complex, the electron charge is transferred from the donor to the acceptor, and the donor (sensor) molecule loses the light-emitting ability.

The transition from the fluorescence mode (spontaneous emission) to the threshold lasing mode (transition from enhanced spontaneous emission to stimulated emission) is one of the ways to increase the sensitivity of optical molecular sensors [1-3]. Such a transition radiation mode is dependent on changes in the laser and active medium, as well as on the presence of a small amount of substances (ppb), causing the effect of luminescence which leads to a complete rupture of lasing.

Sensor properties of poly[9,9-dioctylfluorenyl-2,7-diyl] with dimethylphenyl end groups (ADS129) doped in the different materials were investigated using the fluorescence quenching due to complex formation between fluorophore and nitrotoluene molecules, since the prospect of using these compounds for the detection of nitrocompounds was shown in [3,4]. Then the sensory properties of fluorophore in a laser mode were study. Nitrotoluene (NT) was selected as analyte.

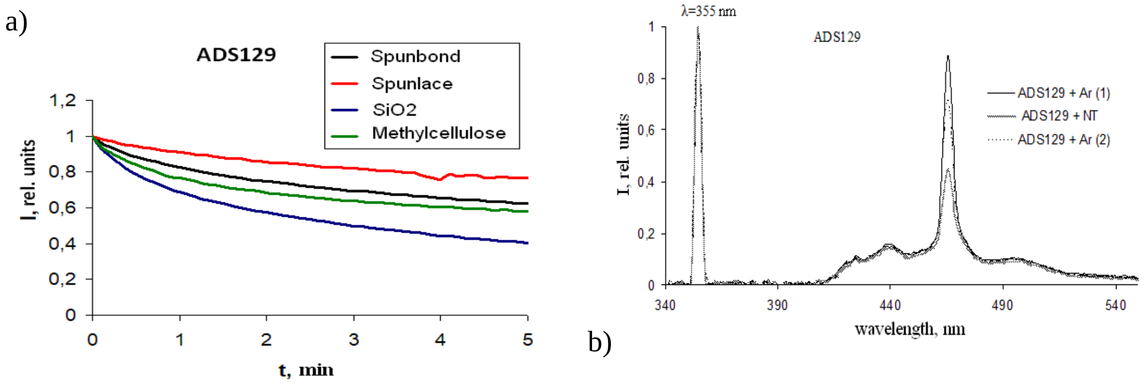

Fig. 1 a) Luminescence kinetics of the examined ADS129 on the substrate upon exposure to the NT vapors; b) Generation change spectra of the investigated ADS129 in chloroform (CLF) on a glass substrate when exposed to NT

Thus, in the sample based on ADS129 in CLF, a decrease in lasing intensity was registered by 50% from the initial level of lasing intensity after exposure to NT for 30 seconds, which is significantly faster compared with the results where the fluorescence quenching of the sample based on ADS129 on the SiO2 substrate under study was 43 % after 2 minutes exposure to NT vapor.

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The synthesis of sulfur-containing monomers based on piperidone

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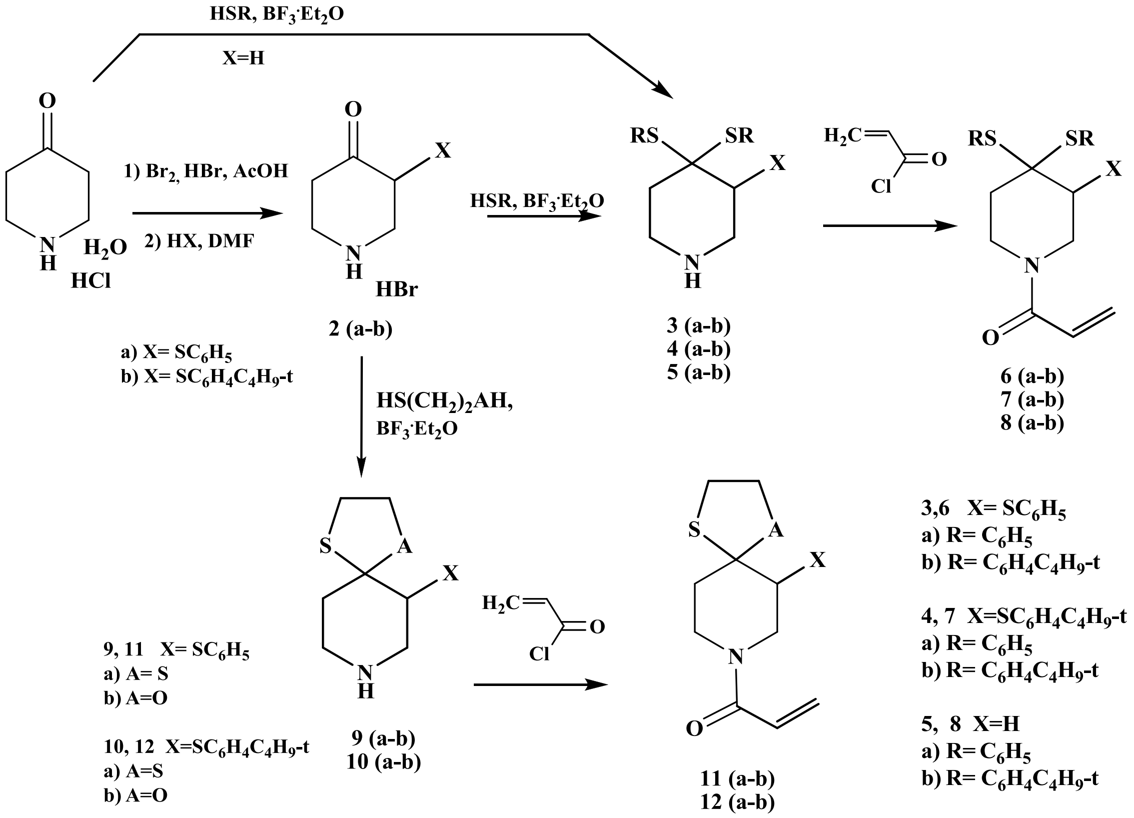
It is known that the introduction of sulfur atoms into a monomer molecule leads to an increase in refractive indices [1, 2]. We synthesized acrylamide monomers based on 4-piperidone containing 2 and 3 sulfur atoms in the molecule. Thiophenols, 1,2-ethanedithiol, 2-mercaptoethanol were used to introduce sulfur atoms in this work.



The measured values of the refractive indices of the some synthesized monomers are in the range 1.587-1.635.

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Hybrid materials of substituted zinc phthalocyanines as active layers of chemiresistive sensors

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Metal phthalocyanines (MPcs) are the class of compounds which are widely used not only as dyes but also as materials for various electronic and optoelectronic devices. The structure and properties of MPcs can be substantially altered by the introduction of different substituents in benzene rings. Electronegative fluorine substituents attract particular interest because their introduction leads to the substantial change of semiconductor properties and sensing behavior. Single walled carbon nanotubes (SWCNT) were used as a platform in various chemiresistive and electrochemical sensors due to their high conductivity and large surface area. We suggest that the hybrid structures of carbon nanotubes with MPc will enhance their properties, e.g. solubility, electrical conductivity, specific surface area, chemiresistive sensor response [1].

Hybrid structures of single-walled carbon nanotubes with symmetrically substituted $ZnPcR_4$ (R= $SC_{10}H_{22}$ and fluorinated analogue with R=$SC_{10}F_{17}H_4$) have been prepared and characterized by spectral methods and microscopy. It was shown by the methods of Raman spectroscopy and ICP-AES, that fluorosubstituted ZnPc has interacted to SWCNT more efficiently than that without fluoro substituent. To demonstrate the potential applications of the SWCNT/ZnPc hybrids towards gas sensing, a gas sensor device based on the hybrid materials has been fabricated. The comparative analysis of sensor response of SWCNT and SWCNT/ZnPc hybrid films to ammonia (1-200 ppm), carbon dioxide (100-500 ppm) and other gaseous analytes were carried out to demonstrate the synergetic effect between SWCNTs and ZnPc derivatives. The effect of fluoro substituents in phthalocyanine ring on sensor properties was also investigated.

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Photo - and Electroluminescence of the Metalorganic complexes on the Base of Zinc and Magnesium

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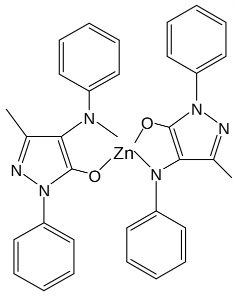
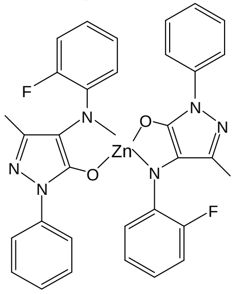
Research efforts on metal-coordinated organic materials with luminescent properties have been of great interest for decades because of their potential applications as components of electroluminescent diodes (OLED), lasers, and solar cells. The advantages of metal complexes with organic ligands as candidates for luminescent materials stem from the possibility of increasing the brightness and stability of emitters when a "purely" organic material is exchanged for a compound with optically inactive metal ions, such as zinc, aluminium, beryllium, etc. Of importance is the fact that luminescence of coordination compounds is a structure-sensitive property. Therefore, the observation of luminescence from these compounds can establish relationships between the composition and structure of organic metal complexes, their luminescence properties, and the properties of related materials.

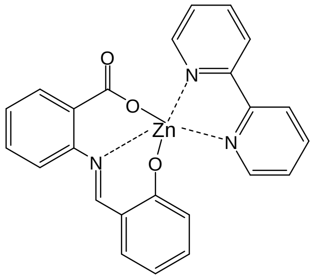
Spectral properties, luminescence under photo - and electro excitation have been studied here for four new metalorganic complexes:



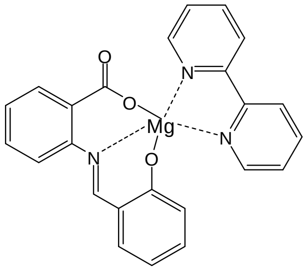
ZnH



ZnF



Zn-diPy



Mg-diPy

The nature of electronic transitions were studied with quantum-chemical calculations in the approximation TD-DFT taking into account the solvent of chloroform. The main weight in the absorption spectra is due to intraligand transitions and to a small extent interligand transitions. Any d-d or MLCT transitions were not found in our calculations.

The electroluminescent (EL) properties were studied for simple sandwich structures ITO/PEDOT:PSS/NPD/complex/LiF/Al by using complexes ZnH, ZnF, Zn-diPy and Mg-diPy as an emissive layer in the configuration. All complexes emit in the applied voltage. The electroluminescence spectrum of each of these compounds practically coincides with the corresponding photoluminescence spectrum for thin films obtained by thermo-vacuum deposition. It indicates that the EL and PL have the same origin. The maximum of EL spectra are 440, 454, 512 and 487 nm respectively. The maximum brightness of the ITO/PEDOT:PSS/NPD/Zn-diPy/LiF/Al device is about 600 cd/m^2 at a driving voltage of 12 V while maximum brightness for similar OLED structure with Mg-diPy reach only 120 cd/m^2. Thus, despite the fact that the Zn-diPy and Mg-diPy complexes have the same ligands, their electroluminescent properties differ markedly.

Acknowledgements
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Electroconductive structures on anodized aluminum substrates with the use of polyfluorochalcones as a photoresist layer

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In connection with the development of microelectronics, there are of great interest nano- and micro-dimensional systems composed of several components: "semiconductor-dielectric", "semiconductor-metal", "metal-dielectric" obtained by profiling surfaces through local anodic oxidation and metallization processes [1]. For example, anodized aluminum substrates that divert thermal power emitted by optical or microelectronic components. At the same time, the locality of electrochemical profiling of surfaces is ensured by the use of photoresists, the masking properties of which under conditions of liquid chemical etching in acids and alkalis, as well as under high (100-150 degrees) temperatures can be a limiting factor in the development of technologies in this area, therefore the search for photoresists with increased masking properties is an urgent task.

The object of the study are photoresist layers of polyfluorochalcone (TAFCh - triacrylamide-fluorochalcone) - 3-(4-(4-acryloylpiperazin-1-yl)-2,3,5,6-tetrafluorophenyl)-1-(2,4-bis(4-acryloylpiperazine-1-yl)-2,5,6-trifluorophenyl) -prop-2-en-1-one [2-4].

As a result of this work, approaches to the formation of electroconductive structures on aluminum and anodized aluminum substrates were investigated when photoresist was exposed through a photomask with a maximum resolution up to 10 μm using the contact photolithography method. The optimal electrolytes for anodizing and copper plating were selected: anodizing electrolyte - 15% H_2SO_4 + 15% H_3PO_4 + HF; copper plating electrolyte - $CuSO_4$ + H_2SO_4 + HF. Electroconductive structures were obtained using TAFCh photoresists and commercial SU-8 photoresist according to two schemes: on the surface of aluminum and dielectric anodized aluminum. The effect of aluminum surface quality on the resolution of the process of creating electrically conductive microstructures is shown. It has been experimentally shown that preliminary electrochemical polishing of aluminum substrates makes it possible to achieve a resolution of conductive copper tracks up to 10–15 μm using TAFH as a photoresist. It is shown that the SU-8 photoresist does not provide a resolution higher than 40 μm on the Al_2O_3 substrate.

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Conductive tracks formation by inkjet printing and laser sintering of silver ink

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The formation of conductive tracks is one of the key stages in the creation of electronic devices, in particular, for organic electronics, where polymer flexible films, glasses or composite materials often used as substrates. In this regard, it is important to develop methods for the formation of conductive elements and layers that allow plot wiring on various materials (including flexible ones).

During the work, ink compositions based on silver nanoparticles up to 50 wt.% were prepared by reducing solid silver carboxylates with hydrazine hydrate in benzyl alcohol at room temperature. The developed preparation method is cheap, easily scalable and allows the creation of nanoparticles with a low sintering temperature (110 – 180 °C in comparison with 200 – 300 °C for nanoparticles stabilized by carboxylic acids with the length of the hydrocarbon chain more than 10) [1]. The developed compositions make it possible to form films by different methods (spray, centrifugation and inkjet printing) with subsequent selective laser sintering and are suitable both for additive and subtractive technology of conductive tracks creation.

The developed ink was used for inkjet printing on a flexible polyimide substrate, followed by thermal annealing at 180 °C. The shape of driven pulse was simulated in specially developed program for simulating the response of a piezoelectric print head [2].

Regimes of laser sintering of ink for obtaining conductive paths on flexible polyimide substrates are selected. The most optimal two-pass sintering regime is established, when at the first pass, evaporation of the solvent is achieved, and at the second pass, sintering of the nanoparticles take place. The electrical resistance of films obtained by laser sintering is close to the resistance of films obtained by conventional thermal annealing (12 $\mu\Omega\times$cm). Inks from film areas not exposed by laser irradiation, can be removed with an aqueous-alcohol solution [3].

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Acknowledgements

This research was supported in part by the Program of Enhancement of Tomsk State University Competitiveness among the World's Leading Research and Educational Centers (Project No. 8.2.20.2018).

Molecular layer epitaxy of a 1,8:4,5-naphthalenetetracarbodiimide monomolecular layer on quartz wafers

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In recent years, the organic electronics has been developing significantly. It concerns the development of various electronic devices based on organic materials. At present, considerable progress has been achieved in the creation of organic light emission diodes. In addition, considerable efforts are directed to the development of efficient solar cells and FET transistors. Further progress in the field of organic electronics is associated with the development of molecular nanoelectronics. Nanoelectronics is based on the self-assembling of organic molecules [1]. Changing the chemical structure of synthesized molecules, the nature and distribution of functional groups, it is possible to control the process of molecular self-assembly. Therefore, it is possible to obtain nanostructures with unique properties. One of the most promising methods for obtaining structures for nanoelectronics is the molecular layer epitaxy method (MLE). This method is one of the epitaxial grow technique, which essentially relies on self-restricting self-assembly reactions in vapor phase, which utilize difference between chemi-and physi-sorption to build variety of robust artificial organic structure.

The growth of monomolecular layers of 1,8: 4,5-naphthalenetetracarbodiimide (NTCDI) was carried out on the special design setup. The growth chamber (reactor) of the setup contains three zones whose temperatures are set independently. The first input zone of the reactor contains sources (sublimers, bubblers) of organic precursors. In the second zone there is the sample holder. The temperature of holder is set independently from the reactor walls. The third zone is the zone of withdrawal of the carrier gas (Ar) from the reactor. The flow of the carrier gas through the system is controlled by a high-precision mass flow controllers and a baratron.

Quartz wafers were cleaned for 1 h in an ultrasonic bath in a hot (90 C) a piranhao solution. The template layer was obtained on precleaned hydroxylated substrates by liquid-phase silanization reaction with 3 mm (3-aminopropyl)trimethoxysilane. After the template layer was deposited the following film growth steps were conducted in the MLE reactor: The 1,8:4,5-naphthalenetetracarboxylic dianhydride precursor was vaporized at 200 C to react with the surface-bound amine; 1,6-diaminohexane precursor were vaporized at 40 C. Imidization in both steps was carried out at a substrate temperature of 295 C for 20 min at a total pressure of 0.02 Torr. The reactor walls were independently heated to 330 C. There is the laminar flow through MLE reactor setup (Reynolds number is 250) Following the assembly of each monolayer, the reaction zone was cleaned by resublimation of unchanged precursors under a Ar flow for 10 min.

After the formation of the monomolecular layer of the NTCDI the absorption spectrum of the samples was measured. The absorption spectrum was measured with the AvaSpec-2048x64 spectrograph. Experimental data showed that in the spectral range 300-400 nm the NTCDI absorption peaks at 360 and 380 nm are observed.

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9*H*-Thioxanthene-9-one-10,10-dioxide and 1*H*-thioxanthen-1,4,9-trione based redox active labels for electrochemical detection of DNA hybridization

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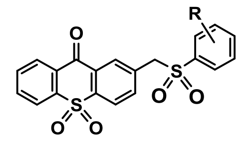
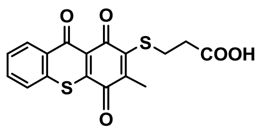
New redox-active oligonucleotide modifiers based on 9*H*-thioxanthen-9-one-10,10-dioxide (**1, 2**) and 1*H*-thioxanthen-1,4,9-trione (**3**) have been synthesized. Compounds **1, 2** were obtained by the reaction of 2-bromomethyl-*9H*-thioxanthene-9-one with o-, p-mercaptobenzoic acids with the following oxidation by H_2O_2. Compound **3** was synthesized by nucleofilic addition of 3-thiopropionic acid to 3-methyl-1*H*-1,4,9-thioxanthenetrione with the following oxidation by ammonium cerium nitrate.



R = 2-COOH (1), 4-COOH (2)

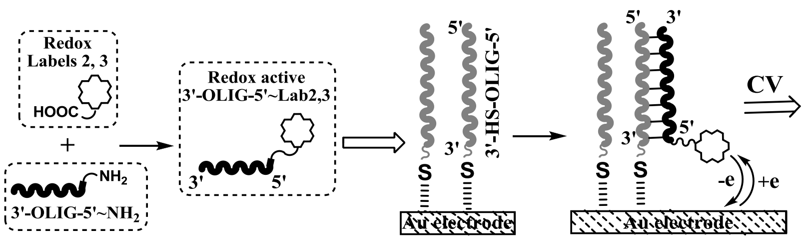


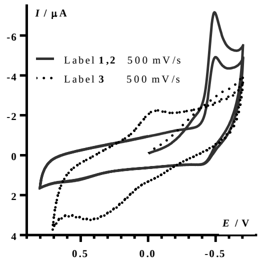
3

The first step of electrochemical reduction (ECR) of compounds **1, 2, 3** is reversible one-electron transfer process in aprotic solvents leading to the formation of the corresponding long-lived radical anions have been characterized by EPR. In binary DMF-H_2O mixtures and water buffers the first ECR step of **1, 2** retains reversibility, whereas one-electron transfer to the thioxanthene-trione fragment of compound **3** becomes slow and leads to the increased difference of anode and cathode peaks potentials in the corresponding cyclic voltammograms (CV). First peak potentials of compounds **1, 2** were found to be the same indicating one-electron transfer to 9*H*-thioxanthen-9-one-10,10-dioxide fragment only for both compounds. Electrochemistry of starting compounds for the synthesis of **1-3** was described in [1,2].

With the model thin-layer electrochemical DNA-sensor described earlier in [3], the formation of model DNA-duplexes containing redox active labels **1-3** has been detected by CV. Structures of the duplexes were the following:

HS-(CH2)6-3'-CCGTCTTCGATACGCTATACCC-5' (**OLIGOPROBE 1**)
Labels **1,2,3**,-CONH-5'-GGCAGAAGCTATGCGATATGGG-3' (**OLIGOPROBE 2**)





Oligoprobe **1** was immobilised on Au working electrodes of the sensor by SH anchor groups. Redox-active labeled oligoprobes **2** were used to form DNA duplexes. The results of electrochemical detection of the corresponding DNA duplexed demonstrated interpretable results of the detection with well-distinguished peak potentials of the labels **1,2** and **3**, respectively.

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Advances in synthesis of precursors for novel triarylpyrazoline chromophores

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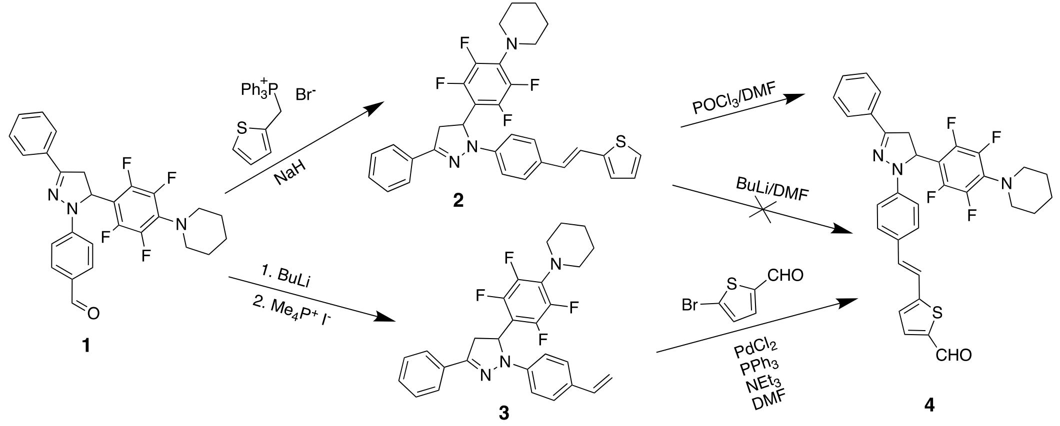
Triarylpyrazoline-based aldehydes are an area of interest as donor blocks in conjugated nonlinear chromophores for optoelectronics. Previously a range of triarylpyrazoline-based dyes were synthesized and described [1]. That chromophores had an absorption maximum around 510 nm. We hope, addition of thiophene bridge will allow to shift of absorption towards IR region.

Here we are reporting our last advances in the synthesis of triarylpyrazoline-based chromophores with thiophene conjugated bridge: aldehyde **4** can be used as a precursor for novel chromophores.



Synthesis of aldehyde **1** was well worked out previously, that’s why it was chosen as the starting material. Two approaches were taken:

1. Addition of thiophene fragment by Wittig condensation and further formylation
2. Addition of methylene fragment by Wittig condensation and Heck coupling with 5-bromo-2-thiophenecarboxaldehyde

Formylation of pyrazoline **2** with BuLi/DMF system leads to decomposition of molecule; Vilsmeier formylation of the same substrate with heating usually leads to overformylation: along with desired addition to thiophene fragment either double bond or phenylene ring were also formylated. However, necessary conditions were found and target aldehyde **4** obtained.

Heck coupling was performed on alkene **3** as a proof-of-concept using only $PdCl_2$ as a catalyst. So target aldehyde **4** was isolated with rather low yield which can be improved by the optimization of reaction conditions.

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Linear spirocyclic conjugated systems as new materials for optoelectronics

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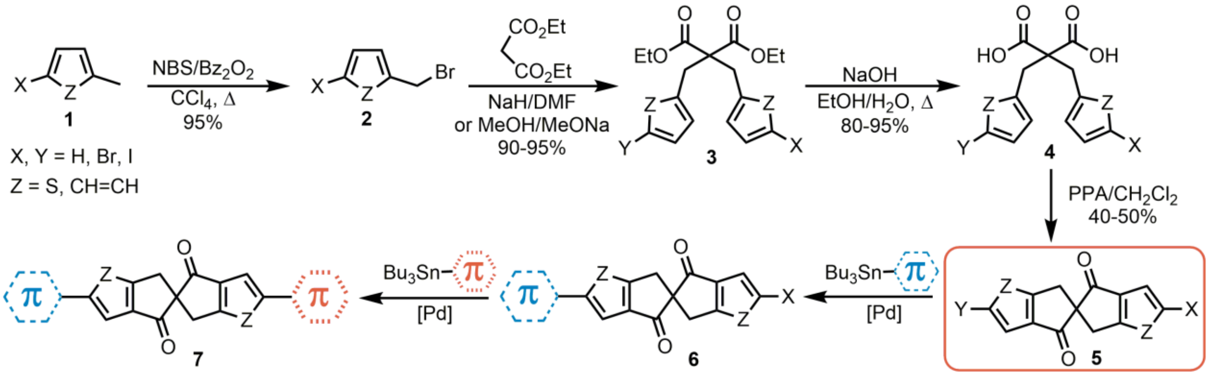
High-efficient organic light-emitting diodes (OLEDs), organic light-emitting transistors (OLETs) and organic electrically driven lasers require materials combining efficient electroluminescence and high semiconducting properties. However, synthesis of such compounds is challenging since the dense packing that is crucial for improved semiconducting properties causes quenching of luminescence due to the aggregation effects.

Thermally activated delayed fluorescence (TADF) is a promising way to increase electroluminescence efficiency of OLEDs and OLETs. This phenomenon is observed for molecules which energy difference between the first singlet (S_1) and triplet (T_1) excited electronic states is ~ kT. It facilitates reverse intersystem crossing (RISC) and allows harvesting all triplet excitons achieving almost 100% of the internal quantum efficiency of electroluminescence.

Herein we develop synthesis and study properties of linear conjugated spirocyclic compounds – 2,2'-spirobi[indene]s and 5,5'-spirobi[cyclopenta[*b*]thiophene]s – which combines rod-like structure with the orthogonality of two independent π-systems.



The synthetic route to spirocyclic dihalogenide **5** includes the sequential alkylation of malonic ester with the corresponding halogenides **2**, hydrolysis of the obtained ester **3**, and the intramolecular acid-catalyzed cyclization of the resulting acid **4** in the presence of polyphosphoric acid (PPA). Spirocyclic dihalogenide **5** was further decorated with linear conjugated systems based on thiophene or phenylene-thiophene moieties via Stille reactions.

DFT and TD DFT quantum chemical calculations were used for theoretical study of ground and excited states of the molecules obtained. As a result, it was shown that spiroconjugation could be effectively used for design materials with specific optical and electronic properties.

Acknowledgements

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Fused derivatives of 1,5-diaminoanthracene-9,10-dione and 1,4-diaminoanthracene-9,10-dione

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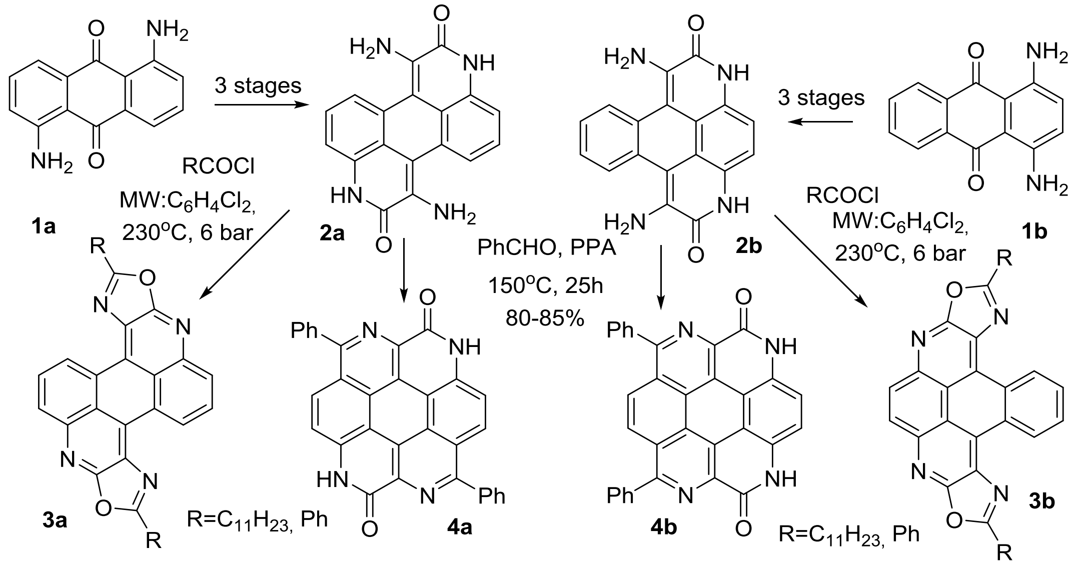
New polyfused heterocyclic systems **3,4 a,b** were prepared on the base of commercially available 1,5-diaminoanthracene-9,10-dione **1a** and 1,4-diaminoanthracene-9,10-dione **1b**. 1,8-Diaminoantra [1,9: 4,10] - and 1,7-diaminoantra [1,9: 5,10] dipyridones were synthesized from compounds **1a,b** in three stages as reported in [1]. Reaction of compounds **1a,b** with carboxylic acid chloride under microwave radiation were synthesized dioxazoles **2a,b** (R=$C_{11}H_{23}$, Ph). Tetraazocoronene derivatives **4a,b** were obtained by the Pictet-Spengler reaction of compounds **1a,b** with benzaldehyde in polyphosphoric acid [2]. The polyfused systems **3,4 a,b** are promising materials for organic electronics [3].



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Synthesis novel acceptors tienonaphthalimide-based small molecules

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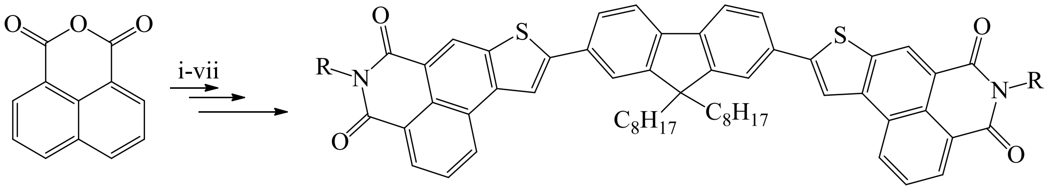
Organic semiconductors are the focus of research in the past decades, because of their various applications in organic light emitting displays, printable electronic circuits, and solar cells [1].

1,8-Naphthalimides bearing electron withdrawing substituents in the naphthalene moiety are well known organic fluorophores showing good photostability, strong absorption and emission in the UV/Vis region. Their derivatives are widely applied in design of molecular fluorescent device.also they are used as non-fullerene acceptors in organic photovoltaics [2].

In the present work we report synthesis of small molecular acceptor comprising a central fluorene core, two thiophene bridges and two 1,8-naphthalimide terminal groups. Aliphatic substituents in fluorene core have been used to make polycyclic molecule soluble in organic solvents.

The target naphthalimide analogue was synthesized via multistep reactions from commercially available starting material 1,8-naphthalic anhydride.



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Doping of furan/phenylene co-oligomer single crystals as an efficient way to control their optoelectronic performance

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Nowadays a number of extremely valuable organic crystalline materials combining good photoluminescence (PL) and semiconducting properties have been found. One of the most promising materials are furan-phenylene co-oligomers [1] due to their higher solubility, molecular rigidity and planarity leading to efficient charge and exciton transport [2]. Moreover, solution processing allows obtaining materials with a small amount of dopant appearing as a by-product of the synthesis [3] or added artificially [4]. In this work we have studied the doping of promising highly-luminescent organic semiconductor 1,4-bis(5-phenylfuran-2-yl)benzene (FP5) by it's synthetic by product 5,5'-bis(4-(5-phenylfuran-2-yl)phenyl)-2,2'-bifuran (FP8).

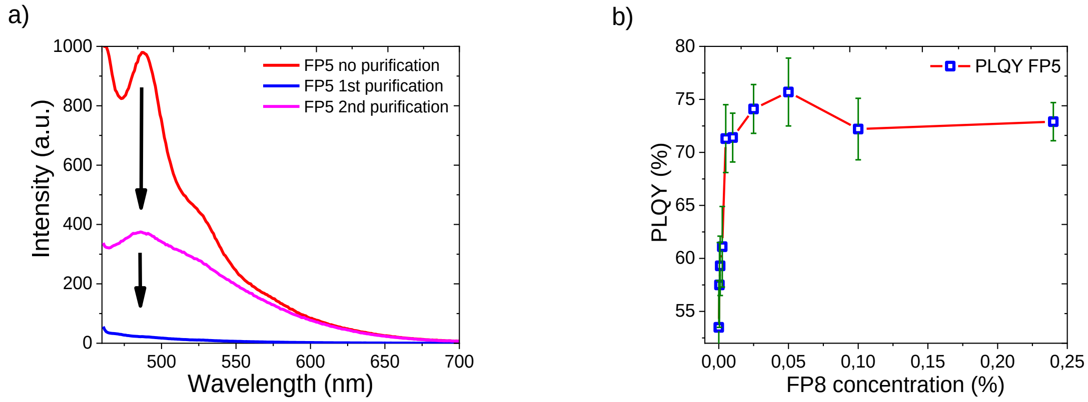

Figure 2. a) PL spectra of FP5 of different purity: raw material (red), purified by PVT (violet), twice purified by PVT (blue); b) PLQY for FP5 crystals doped by different amount of FP8.

By using a combination of separate synthesis of potential by-product FP8 and a PL spectroscopy of FP5 solution we demonstrated that a raw FP5 material contains ~0.2% of FP8. Two stage re-crystallization by a physical vapor transport (PVT) method allowed purification, the residual amount of FP8 being <0.002%. Furthermore, the intentional doping of solution-grown FP5 crystals was performed to elucidate the optimal doping level. Remarkably, the 0.05% of dopant was demonstrated to be enough for maximizing the PL efficiency of FP5 crystals. Single crystal field-effect transistors fabricated on doped FP5 crystals revealed the decrease of hole mobility and increase of threshold voltage upon doping, what is assigned to the generation of shallow and deep traps in the crystals.

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Electronic System for Modulating THz Radiation at Novosibirsk Free Electron Laser: Possible Applications and Technical Aspects

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Novosibirsk Free Electron Laser (NovoFEL) facility is able to produce high-power tunable laser radiation in quasi-continuous mode in the terahertz (THz) frequency range [1, 2]. The ability to save the peak power of this radiation together with the possibility to control radiation time is of great importance in a number of experiments. In this work we developed and implemented the approach allowing one to create THz macropulses at NovoFEL with any repetition rate and almost any individual pulse length. The proposed electronic modulation system is based on a periodic shift of the phase of electron bunch injection. Such a shift suppresses lasing and forms macropulses from quasi-continuous radiation of NovoFEL. The system is directly embedded into the electronic infrastructure of NovoFEL and can be triggered directly on user stations. Figure 1 shows the typical examples of macropulses with different lengths that were obtained by the electronic modulation system in the THz frequency range. In order to characterize EMS, series of macropulses with different durations from 10 to 400 μs were measured for three available frequency ranges. Using the rising and falling edges of typical macropulses the calculations of the gain and total losses were done for three optical resonators. The use of short macropulses was exemplified for TR EPR spectroscopy. The heating of copper(II) complex by the absorbed THz radiation and its subsequent thermal relaxation were measured.

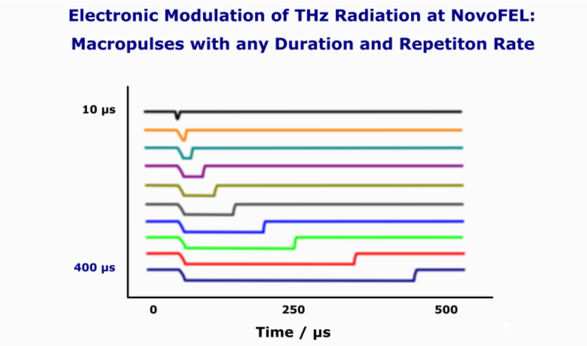

Fig. 1 Macropulses of THz radiation with 76.9 cm^{-1} wavelength created by the electron modulation system. Pulse durations are from 10 μs to 400 μs. Each subsequent pulse is vertically shifted.

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Electrical conductivity at elevated temperatures of polymer components in planar EO-polymer modulators

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Integrated optical devices based on the electro-optical active polymers are intensive developed today. Applications of the active polymers attracts by the opportunity to significant increase of both the device speed [1] and the sensitivity to control voltage [2].

The active polymers are the polymer-chromophore systems [3]. The polymer has a matrix function, while the chromophore is responsible for optical and nonlinear optical properties of the composition. A “guest-host” system is wide used; a system with covalent attachment of chromophores to polymer side chains has the prospect of improving the device’s performance.

A structure of multiple layers transparent materials including the active polymers with different refractive indexes fabricates to organize optical connections in planar integrated optical device [4]. One of inner layer, called a core, has refractive index higher than neighbor ones. It permits to localize a light propagation into the core. Formation of the core layer with some profile, like a rib for example, permits to fabricate light-guiding channels and complicated optical circuits based on it.

When creating such devices with a layer of polymer-chromophore composition, an important step is giving it second-order nonlinear optical properties. It is provided by orientation of chromophore molecules mainly in one direction. The molecules has a dipole moment thus it may be reorients by mean applicate strong electrical filed under high temperature elevated to near the glass transition temperature level when the chromophore’s rotation ability is noticeably rises (the poling procedure). An external electrical field usually produces by electrodes, which formed onto external surfaces of multilayer planar optical structure, so a several layers lies in a gap between electrodes.

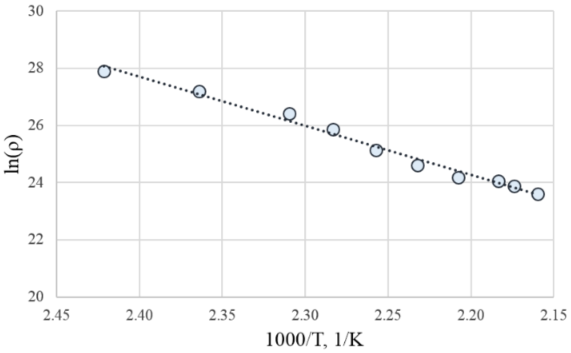
The electrical field directly in the layer of active polymer composition, and a result of the poling procedure, are substantially depend on the ratio of the conductivities of the layers between the electrodes because the conductivity of layer’s material is not typically zero. The chromophores brings noticeable contribution into the conductivity as polar objects, and electrical properties of the polymer-chromophore systems thus may differ from ones of the host polymer and from systems with other types of chromophores. Therefore, it is very important to know the electrical properties of used materials and its dependency of other conditions to increase an efficiency of the poling.

In this work, we measured the volumetric electrical conductivity of flat layers of polymeric materials used by us in the development of active integrated optical devices [5]; The specific conductivity at various temperatures of the material was determined, as well as the effect of the external electric field on this parameter.

For the measurements, we used glass substrates with a conductive coating (mixed indium-tin oxide), which served as the lower electrode. Single layers of polymer materials with a thickness of several micrometers were deposited to the lower electrode from the solution by centrifugation. Using a mask and the magnetron deposition method, several metal electrodes were formed on the upper surface of the layer. The lower and one of the upper electrodes were connected using an electrically conductive adhesive to the measuring circuit, which consisted of a constant voltage source, limiting resistance, and a microampermeter, so that the current flowed across the polymer layer in the region bounded by the upper electrode. The sample with the electrode system was uniformly heated to a predetermined temperature.

The method of measuring conductivity excluded the contribution of the current component arising in the circuit during reorientations of the chromophores. For this purpose, the sample included in the circuit, to which the specified voltage was applied, was heated to a temperature close to the glass transition temperature of the polymer composition, was held for 5-10 minutes, until the reorientation currents relaxed. Then the heating was turned off and the current measurements were performed during the sample cooling down.

Among others, the polymer composition based on the original synthesized polyimide (as a matrix) and commercial chromophore DR13 that covalently attaches to side chains of the polymer molecules was studied. The temperature dependence of the specific resistivity is of an Arrhenius character (fig.) with the activation energy of 1,5 ± 0,2 eV. Meanwhile, at 150 C, the resistance decreases with increasing external electric field strength, almost linearly in the range of 5-50 V/μm.



The temperature dependence of the resistivity of the original polyimide with a chromophore at an external electric field of 34 V/μm

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Acknowledgements

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Seeking a temperature shift of spin transition in the metal organic complex [Fe(1-bpp)$_2$][BF4]$_2$ induced by an external electrostatic field

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Spin-crossover can be induced by various external stimuli such as temperature, pressure and light irradiation. Structural and magnetic bistability is an appealing property of spin-crossover compounds which provides scope for potential application as an active element in memory storage devices and spintronics. Perhaps, the external electric field is the easiest way to implement spin state control in electronic devices based on spin-crossover materials. The theoretical foundation of the electric field effect on a magnetostructural transition has been described earlier [1].

In this work we investigate the influence of an external electrostatic field on the spin transition temperature in a spin crossover compound of iron(II). The sample was a single crystal of [Fe(1-bpp)$_2$][BF$_4$]$_2$ (1-bpp = 2,6-bis[pyrazol-1-yl]pyridine) [2]. Spin states of [Fe(1-bpp)$_2$][BF$_4$]$_2$ were controlled using variable-temperature mid Fourier transform infrared (FTIR) microscopy. In order to apply an external electric field we modified a Linkam FTIR600 sample stage. The object carrier (BaF$_2$ window) was equipped with parallel plate electrodes with a distance between them of 0.7 mm. The applied voltage results in an external electric field in the area where a single crystal is placed. The breakdown field strength was 87±0.2 kV/cm. FTIR spectra were measured in the temperature range of 258–262 K (which includes an area of temperature hysteresis in the spin-crossover transition) in steps of 0.1 K. We performed two series of the experiments: (i) without an electric field and (ii) with an applied electric field of different intensities lying in the range of 14 kV/cm to 86 kV/cm. It was shown that the spin transition temperatures of [Fe(1-bpp)$_2$][BF$_4$]$_2$ shifts to higher temperature values with increasing the electric field strength. The magnitude of the effect was 0.0015±0.0001 K·cm/kV for the high-temperature transition and 0.0024±0.0004 K·cm/kV for the low-temperature transition. The low sensitivity of the spin transition temperature in [Fe(1-bpp)$_2$][BF$_4$]$_2$ to the external electric field strength can be explained by the similar dipolar moments of the complex in its low and high spin states.

Currently, we are looking for new spin-crossover complexes with pronounced differences of dipolar moments in their low and high spin states in order to increase the temperature shift value.

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Acknowledgements

This work was supported by the Russian Foundation for Basic Research (Nos. 18-03-00362) and Russian Science Foundation (17-13-01412).

Dendroid NLO Chromophore with Polyfluorinated Triarylpyrazoline as Donor Block

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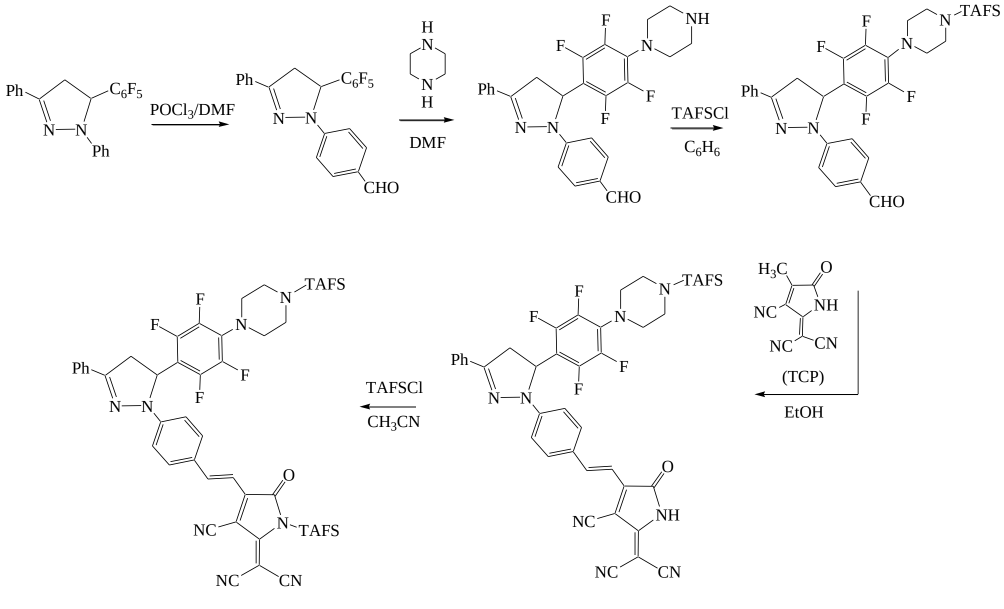
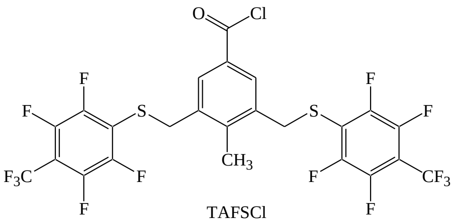
Asymmetric polymethine dyes possessing high molecular polarizability are promising compounds for the creation of nonlinear optical (NLO) materials used in electro-optical modulators. Such dyes contain strong electron-withdrawing and strong electron-donating groups as terminal fragments. N,N-Dialkylaminosubstituted aromatic aldehydes are usually used as donor fragments.

We used as donor block the derivative of polyfluorinated triarylpyrazoline which can be regarded as the heterocyclic analog of N,N-dialkilaminobenzaldehydes. Branched (dendroid) substituents improve the electro-optical properties of chromophores due to the separation of their molecules in the films. We introduced a dendroid substituent TAFS in both the donor and acceptor parts of the chromophore. The synthesis scheme is given below.





TAFSCl

(Toluic Acid, Fluorinated Sulfide, Cloroanhydride)

Acknowledgements

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Precise Measurements and of effective window sizes of ZIF-8 monitored by Electron Paramagnetic Resonance

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Metal-organic frameworks (MOFs) are highly perspective porous materials. Their structural and functional properties can be fine tuned by variation of metal clusters and bridging organic linkers, which opens prospects for many different applications. Also, many MOFs are able to change their properties upon application of external stimuli such as temperature, pressure etc. ZIF-8 is one of the most stable and extensively studied MOFs, and it is broadly available commercially. ZIF-8 has a 3D channel structure with large cavities (~11.6 Å) separated by small windows (~3.6 Å). Adsorption of various guest molecules and permeability of the windows of ZIF-8 were intensively studied, and several exciting applications of molecular separation were reported [1], [2]. However, significantly different conclusions on permeability of ZIF-8 windows were reached. In this work, we synthesized ZIF-8 with incorporated spin probe (TEMPO), that is too large (~8 Å) to leave the cavity. This material TEMPO@ZIF-8 allows us to study diffusion processes and guest-host interactions by Electron Paramagnetic Resonance (EPR) spectroscopy. Using this approach as a control, we have found the way to tune window apertures by temperature and applied it for efficient separation of xylenes. We also studied permeability of ZIF-8 windows for different other organic molecules. In summary, we have developed a new experimental in-situ approach for precise measurement of permeability and effective window apertures of ZIF-8.

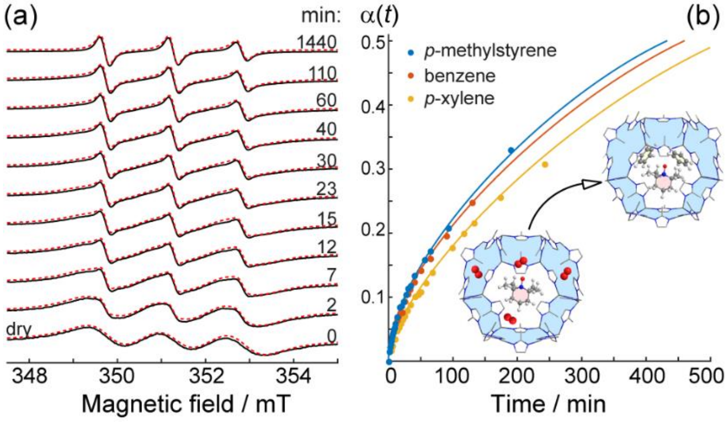

Fig.1. Time resolved EPR spectra of TEMPO@ZIF-8 under p-xylene (left). Obtained diffusion kinetic curves with different guest molecules (right).

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Charge transfer chemistry of novel strong electron acceptor – 5,6-Dicyano-1,2,5-selenadiazolo[3,4-b]pyrazine

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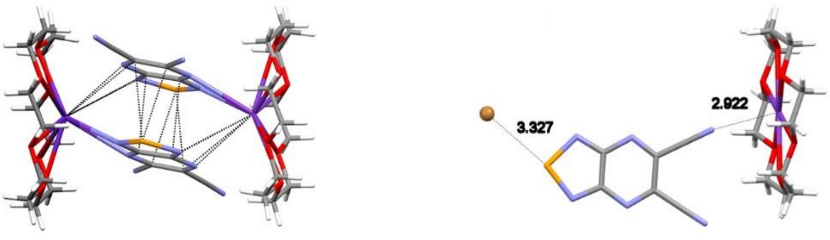
1,2,5-Chalcogenadiazoles are of interest to the fundamental chemistry and its applications in materials science. Their common property is high positive electron affinity (EA) making them effective electron acceptors. The transfer of electron density from the donor onto the heterocycle may be complete, leading to the thermodynamically stable radical anions (RAs), or partial one leading to charge transfer complexes (CTC) [1]. The present contribution covers synthesis and XRD structure of a novel highly acceptor molecule – 5,6-Dicyano-1,2,5-selenadiazolo[3,4-b]pyrazine (**1**) as well as two examples of the above reactivity of **1**.

Compound **1** was synthesized via cyclisation of the corresponding diamine with SeOCl2 and its structure was solved by XRD. Cyclic voltammetry of **1** revealed reversible single-electron reduction at –0.022 V vs. SCE. Reaction of **1** with potassium thiophenolate or sodium dithionite gives RA salts [K(18-crown-6)][**1**] (**2**) and [Na(18-crown-6)][**1**] (**3**) respectively. Salts **2** and **3** are EPR active in both solution and solid state. The latter is unexpected, because the π-dimerisation of RAs, present in these structures, typically leads to the loss of the EPR signal in the solid state [2].

Interaction of **1** with KBr or KI gives anionic complexes **4** and **5** respectively, which were isolated and structurally characterized by XRD. Formation of these complexes is a new example of the recently found reaction of anion coordination to chalcogenadiazoles, which was previously observed only for 3,4-dicyano-1,2,5-selena- and telluradiazoles[3]. The length of the Se…X bond in the anions **4** and **5** is by 1 Å longer than the sum of the covalent radii, but by 0.4 Å shorter than the sum of Van Der Waals radii, indicating that these are rather weak complexes. Properties of **2-5** are being investigated**.**



XRD structures of RA salt **2** (left) and CT complex **4** (right)

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Synthesis of fluorinated derivatives of benzo[1,2-b:4,5-b']bisbenzofuran

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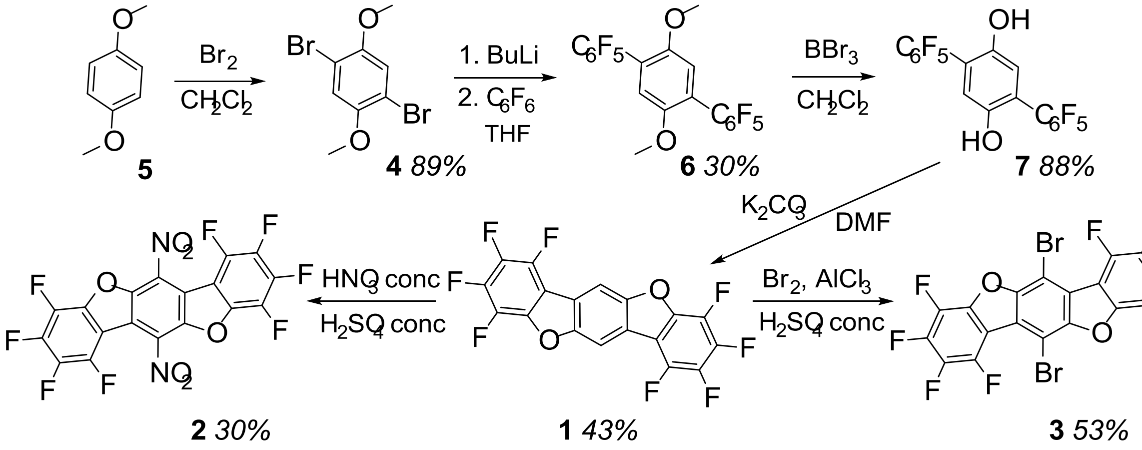
Fluorinated benzobisbenzofurans address the problem of increasing the efficiency of organic semiconductor materials. Firstly, furoacenes have a high fluorescence yield in solid, carrier mobility, stability, and good solubility [1, 2]. Secondly, fluorine atoms improve the resistance of the material to oxidation by atmospheric oxygen and increase the acceptor properties of the molecules, which is important for creating a π-conjugated donor-acceptor system.

Here we report the synthesis of fluorinated benzo[1,2-b:4,5-b′]bisbenzofurans **1-3**. Compound **4** is obtained by bromination of 1,4-dimethoxybenzene **5**. Fluorinated terphenyl scaffold **6** is synthesized by the reaction of the organolithium compound with hexafluorobenzene. Diol **7** is formed by removing the methyl groups from **6** and it is cyclized to the target benzobisbenzofuran 1. Using electrophilic addition reactions, nitro- (2) and bromo- (3) derivatives are obtained, which allows further modification of the central benzene fragment.



Electrochemical and spectroelectrochemical properties of new derivatives 1-3 are being investigated.

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Acknowledgments

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Stimuli responsive aggregation-induced emission of fluoren-ylidene capped thiophene/phenylene co-oligomer single crystal

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Aggregation-Induced Emission (AIE) materials are in the spotlight of current materials development due to their unique properties and potential applications in light-emitting devices, bio-imaging and sensors. AIE materials have low emission in solution and high emission in the solid state due to non-planar and non-rigid molecular structure.

In this work we synthesized and studied a novel luminogen based on bis(4-((9H-fluoren-9-ylidene)methyl)phenyl)thiophene (BFMPT) showing polymorph-dependent AIE (Fig. 1).[1]

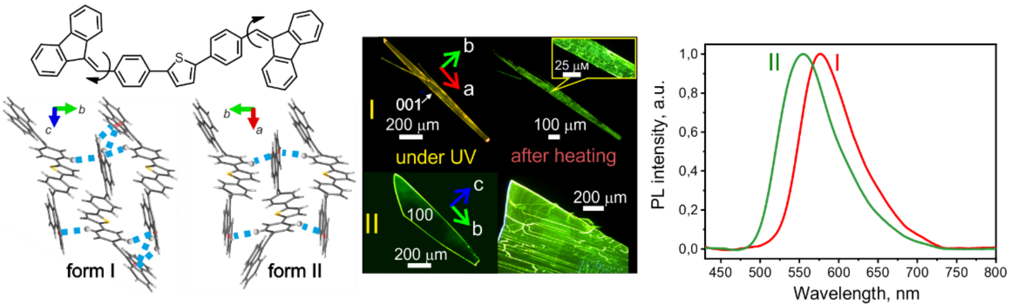

Figure 1. Chemical structure of BFMPT and fragments of crystal structures of polymorphs (left); optical images of polymorphic single crystals under blue laser irradiation (405 nm) and after heating at 280°C (center); PL spectra of polymorphic single crystals by integrating sphere (right).

BFMPT crystallizes in two concomitant polymorphs: orange needle-like crystals with orange emission (form I) and yellow plate-like crystals with green emission (form II). Both forms of crystals have the same photoluminescence quantum yield (PL QY) 40%. Form I undergo irreversible phase transition into form II upon mechanical and thermal stress over 230°C with retaining the crystals' shape. The PL efficiency of BFMPT single crystals does not significantly affected by thermal stress. Due to high intrinsic torsional freedom BFMPT-related compounds could serve as a basis for further molecular design of novel high-performance aggregation-induced emissive materials.

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New π-conjudated thieno[3,2-b]indole derivatives and charge carrier mobility in their thin films

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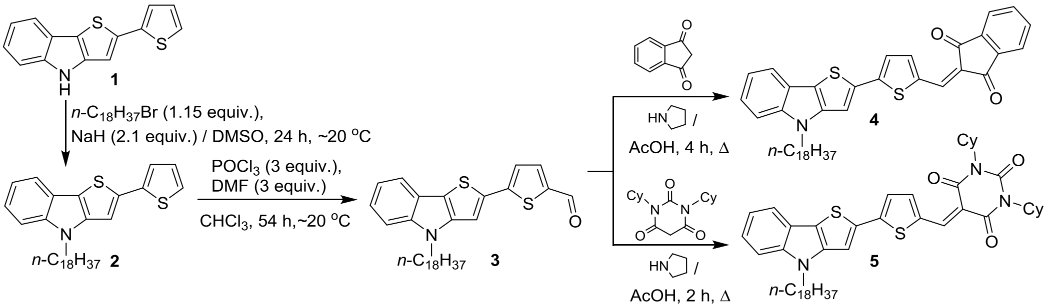
Recently, we have described an efficient approach towards 2-(hetero)aryl-substituted thieno[3,2-*b*]indoles, including 2-(thien-2-yl)-substituted derivative **1**, based on combination of the Fiesselmann thiophene synthesis and the Fisher indole synthesis, and used available sources, such as 3-(hetero)arylacrylates and arylhydrazines [1]. In this study, we synthesized two new push-pull chromophores based on thieno[3,2-*b*]indole. Thus, treatment of thieno[3,2-*b*]indole **1** with *n*-octadecyl bromide in the presence of sodium hydride and the subsequent formylation of derivative **2** using a Vilsmeier reagent at ~20 °C gave thienaldehyde **3**. The final step of chromophores **4** and **5** construction was the Knoevenagel condensation of thienaldehyde **3** with indan-1,3-dione and 1,3-di(cyclohexyl)barbituric acid. In addition, the same synthetic strategy was used by us to obtain new thieno[3,2-*b*]indole-based dyes, bearing 2-cyanoacrylic acid as an acceptor, which were used for dye-sensitized solar cells [2].



Based on new chromophores **4** and **5**, solid-phase layers with nanoscale thickness prepared by casting from a liquid solution and their optical and charge-transport characteristics were studied. Due to the presence of donor and acceptor fragments in the molecules acting as transport centers for holes and electrons, respectively, the obtained compounds exhibit ambipolar conductivity with balanced electron and hole mobilities. At the same time, due to the relatively narrow optical band gap, these compounds are promising candidates in the development of organic solar cells and photodiodes.

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Acknowledgements

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Sensing spin-state switching in a spin-crossover metal-organic material by dopant compounds

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Spin crossover (SCO) compounds exhibit reversible transitions between high- and low-spin states (HS and LS, respectively) upon application of temperature, pressure, light and some other external stimuli [1]. Spin state switching under light irradiation in many SCO compounds is followed by light-induced excited spin state trapping (LIESST) making them promising for potential use in data storage, sensors, molecular devices, etc. HS and LS states possess distinct geometries, magnetic and optical properties, resulting in large scientific interest in SCO systems for several past decades. An interesting way to influence the SCO properties is to introduce dopant molecules into the host lattice, but effect of such incorporation on SCO parameters is not well studied and might differ from classical magnetic dilution. Therefore, studying of SCO complexes containing metal ion dopants is important for understanding mechanisms behind temperature- and light-induced spin-state transitions and could be a first step toward designing a new type of magnetic materials.

We studied three compounds based on [Fe(bpp)2][BF4]2 (bpp = 2,6-di{pyrazol-1-yl}pyridine) host lattice with [Cu(bpp)2]2+, [Cu(terpy)2]2+, and [Co(terpy)2]2+ as dopants using variable-temperature Q-band EPR spectroscopy. [Fe(bpp)2][BF4]2 undergoes abrupt spin transition at 261 K and has T(LIESST) = 81 K [2], but, as in most cases, Fe(II) remains EPR silent in both spin states. Contrary, EPR spectra of Co(II) and Cu(II) can be very sensitive to the HS-LS transitions of the host lattice. We recorded EPR spectra in the temperature range 20 - 90 K after illuminating the compounds at 20 K. In this experiment we revealed that Co(II) ion not only follows the LS->HS spin state conversion of Fe(II) host lattice upon irradiation at 20 K, but also relaxes back to LS state near T(LIESST) ~ 80 K. Similar measurements were also made for the Cu(II) doped compounds. As was mentioned above, Cu(II) ions do not exhibit SCO phenomenon, but their g-values are very sensitive to the lattice strains and thus to the spin state of the host Fe(II) lattice. Namely, an increase of effective volume of coordination sphere upon LS->HS photoconversion at 20 K results in increase of all g-tensor components. At higher temperatures we also observe gradual changes of the g-tensors due to dynamic Jahn-Teller behavior, but the most pronounced jumps in g-values occur close to T(LIESST) of Fe(II) lattice. Hence, doping of Cu(II) and Co(II) into SCO compounds could offer a straightforward high-sensitivity measurements of SCO processes using EPR. Moreover, we have shown that doped Co(II) undergoes concomitant spin-transition in Fe(II), which might be used for designing new compounds with unique magnetic properties..

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Synthesis of fused benzo[b]thiophene derivatives

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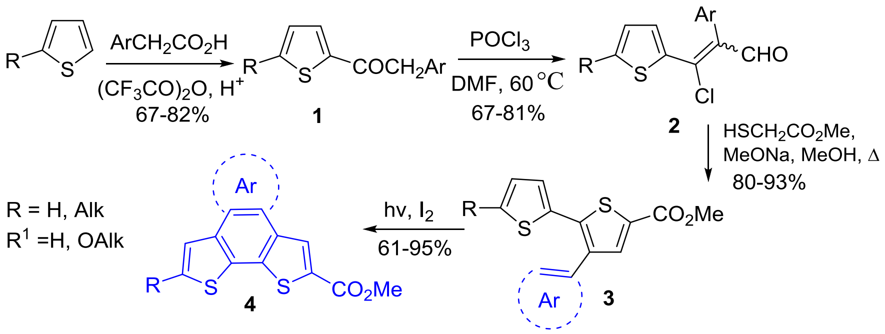
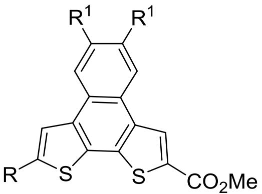
Recently we have developed a simple and efficient method for the synthesis of bi-, ter- and quaterthiophen derivatives, which contains a long alkyl chain, aryl or functional group in the C(3) position of the thiophenic ring [1,2]. Compounds **3** (R = H, Alk) were converted to fused benzo[b]thiophene derivatives **4** by photochemical cyclization. The obtained esters **4a-c** are promising building blocks for the synthesis of organic semiconductors [2-5].





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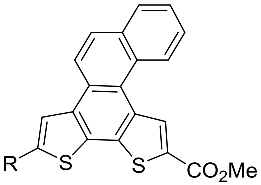

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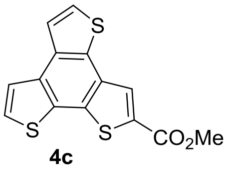

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Acknowledgements

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Minor formation of 1,2,3-benzoditiazolyls was detected by EPR spectroscopy in all cases studied

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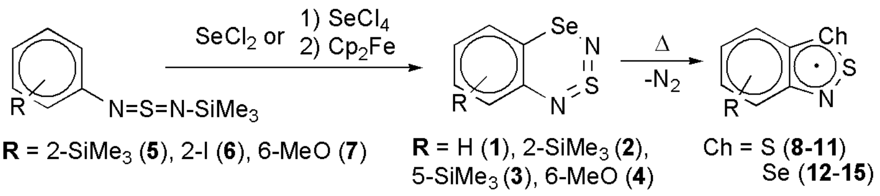
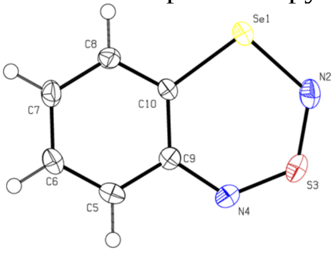
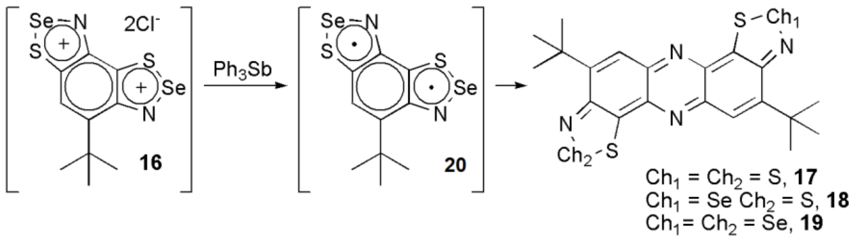
2,1,3-Benzothiaselenazolyl radicals **12-15** were generated by thermolysis of 3,1,2,4-benzothiaselenadiazines **1-4** prepared by electrophilic cyclization of Ar-N=S=N-SiMe$_3$ **5-7** under the action of SeCl$_2$ or SeCl$_4$, with H or SiMe$_3$ as the leaving groups. Radicals **13-15** are otherwise inaccessible. Minor formation of 1,2,3-benzodithiazolyls were detected by EPR spectroscopy in all cases studied.

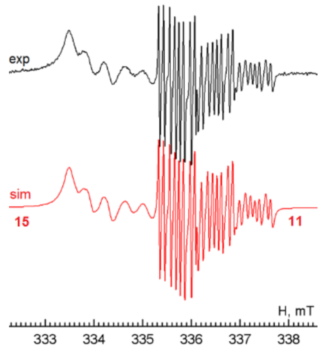
Similar partial replacement of Se atoms by S ones was observed also at irreversible dimerization of the benzobis[1,2,3]thiaselenazolyl diradical **20** giving a mixture of bis([1,2,3]dichalcogenazolo)phenazines **17-19** identified by ^{1}H NMR and HRMS spectroscopy.





XRD Structure of Compound **1**





Experimental and simulated EPR spectra from thermolysis of **4**

Acknowledgements
The authors thank the Russian Foundation for Basic Research (RFBR) and the Government of the Novosibirsk region (GNR) of the Russian Federation (projects RFBR 18-03-00596, 15-03-08970 and RFBR-GNR 18-43-540025) for financial support.

Crystal structure, magnetic properties and photoluminescence of lanthanide(III) (Eu, Gd, Tb, Dy) complexes with 4-(pyridin-2-yl)methyleneamino-1,2,4-triazole

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Lanthanide coordination compounds have attracted considerable attention owing to their unique luminescent and/or magnetic properties, which suggest their potential application in various photonic and electronic devices [1,2]. The properties of 4f element compounds can be controlled with the use of organic ligands, which form the coordination environment of the metal ion, determine the geometry of the molecule that affects magnetic behaviour, and enhance the emission of the lanthanide ion due to the transfer of the excitation energy due to a number of intrasystem nonradiative transitions.

Our work is aimed at investigating the reaction of lanthanide(III) nitrates with 4-(pyridin-2-yl)methyleneamino-1,2,4-triazole (L), as well as the magnetic and photoluminescent properties of the new compounds. The compounds $[Ln(NO_3)_3(H_2O)_3]\cdot 2L$ (Ln = Eu (1), Gd (2), Tb (3), Dy (4)) obtained in a mixture of MeCN/EtOH have the same structure, as shown by XRD. The metal atom is chelated by three nitrate anions and monodentately coordinated by three water molecules. The coordination polyhedron of the metal atom can be described as a distorted capped square antiprism. In the crystal, each mononuclear complex unit $[Ln(NO_3)_3(H_2O)_3]$ is linked to six L molecules through intermolecular hydrogen-bonding interactions to form a 2D polymeric supramolecular structure. An investigation into the optical characteristics of the Eu^{3+}-, Tb^{3+}-, and Dy^{3+}-containing compounds (1, 3, and 4) showed that these complexes displayed metal-centered luminescence. According to magnetic measurements, compound 4 exhibits single-ion magnet behavior, with $\Delta E_{eff}/k_B = 86$ K in a field of 1500 Oe [3].

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Novel indolin-2-one methanofullerenes for bulk-heterojunction solar cells

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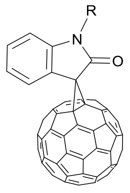
As an alternative to PCBM, we suggested indolinone-substituted methanofullerenes (IMF) recently were studied [1]. The principal advantages of IMFs are their easy synthesis and the possibility of structural variation due to substitutions in the nitrogen atom and aromatic ring. A series of IMFs (Fig. 1) were synthesized [2]. Our research showed that the increasing of the alkyl chain length from C3 to C9 has no strong effect on the solubility. The electrochemical data and calculated data for LUMO energy levels indicate that IMFs could be attractive acceptors for solution-processed organic solar cells.



IMF-C3	R = C_3H_7
IMF-C6	R = C_6H_{13}
IMF-C7	R = C_7H_{15}
IMF-C9	R = C_9H_{19}
IMF-C10	R = $C_{10}H_{21}$
IMF-C12	R = $C_{12}H_{25}$
IMF-C14	R = $C_{14}H_{29}$
IMF-C16	R = $C_{16}H_{33}$

Fig. 1 General structure of IMFs studied

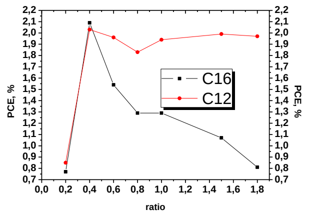
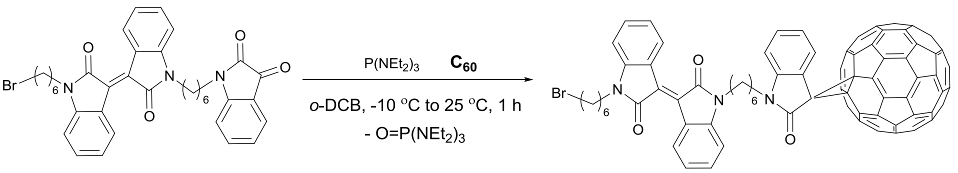


Fig. 2 PCE versus P3HT/IMF-C12 (C16) weight ratio

BHSCs with ITO/PEDOT:PSS/P3HT:IMF/CaAl using IMF-C9-C16 as electron acceptors were fabricated and characterized. The effect of the alkyl chain length on *J*sc, V_{oc}, FF and PCE was studied at P3HT:IMF 1 : 1 weight ratio. The data obtained showed that the promising compounds are methanofullerenes with the longest alkyl chain. We studied P3HT/IMF-C16 solar cells with various donor:acceptor weight ratio. We found that the P3HT:IMF-C16 1 : 0.4 w/w ratio results in the highest efficiency 2.1%. Further we tried to improve the absorption properties of the fullerene derivatives by introducing of a chromophore fragment. Using our experience in the chemistry of indigo dyes, fullerene C_{60} was functionalized with an isoindigo moiety [3]. As a result, optical absorption of isoindigo-based methanofullerene (IIMF-C6) is higher, and its solubility is 17 mg·mL^{-1}. Possibilities of IMFs for organic photovoltaics are discussed.



IIMF-C6

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Synthesis of metal-polymer complexes by Nitroxide Mediated Polymerization

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Metal-polymer complexes find variety of specific application in fabrication of modern electronic as they compare the mechanic stiffness of polymers with conductivity and light-emission ability of metal ions.

Hereafter we report application of metal cations as modificators of alkoxyamine reactivity. The latter are used as initiator in nitroxide mediated polymerization (NMP) that is a method of polymer synthesis. It has many advantages including defined molecular weight and ability to introduce target functionality. We used pyridine-functionalized alkoxyamines as initiators for synthesis of poly-styrene and poly-butyl acrylate and block-copolymers of thereof. Further on, alkoxyamines were used as ligand for preparation of variety of coordination compounds. [1] Depending on the structure of complex, the reactivity of alkoxyamines changed to enhance their initiator efficiency. When applied for polymerization these complexed forms of initiators allowed us to obtain metal-polymer complexes simultaneously. [2]

Thus, complexation of alkoxyamines increase their reactivity and opens an easy way for preparation of metal-polymer complexes with defined structure.

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Radical-labellled block-copolymers for organic electronic devices

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Radical polymers are useful materials for use in organic electronics. They are used by magnetic devices to flexible batteries. For the successful use of polymers, it is necessary to easily obtain the necessary molecular structures. It is hypothesized that this class will provide an opportunity for designing the unique optical and electronic properties of soft materials. However, there is a problem with the reproducibility of synthesis on a commercial scale.

Stable organic radical polymers are prepared via several alternative routes: (a) the direct route, which involves polymerization of monomers carrying Stable organic radical - SOR by nonradical techniques, (b) conversion of radical precursors into a SOR via different approaches such as oxidation of amines or the C — ON bond homolysis of alkoxyamines; (c) postmodifications of a polymer carrying an activated group. Several problems arise when using these methods. It is necessary to carefully monitor the purity of the solvent. Synthesis usually takes a lot of time and the final product is expensive. And one of the main disadvantage is that the properties of the polymer being obtained are not always well controlled. Experimental conditions might alter the integrity of the materials.

In the literature, methods for the preparation of radical polymers using nitroxide-mediated polymerization have not been described before. It seemed that the resulting radicals would be unstable. Free radical polymerization (RP) is a very important method for producing high molecular weight polymers. But this method has limitations, such as poor control over molecular weight, polydispersity, finite functional groups, chain architecture and composition. Radical controlled polymerization (or “live radical polymerization”) is very different from conventional radical polymerization. The main difference is a linear increase in molecular weight with conversion and low polydispersity. The resulting macromolecules have a narrow molecular weight distribution (1.05-1.5), which cannot be obtained by the method. RCP is also well suited, because it can be used under mild conditions to produce various polymers and block copolymers with the necessary substituents.

Block copolymers were obtained by radical polymerization controlled by nitroxyl radicals. First, 1,2-radical hydroxylamine (BlockBuilder) additions are available to the polyethylene glycol diacrylate monomer with followed formation of SG1-based dialkoxyamine. After that, the resulting product is used to initiate the copolymerization of styrene and a triarylmethyl radical. The preparation of a radical block copolymer was proved using gel filtration chromatography and electron paramagnetic resonance method [1].

Thus, the presented method makes it possible to further obtain various radical polymers. It combines simplicity, reduces the time and cost of the final product. If necessary, there is a chance of obtaining materials on an industrial scale

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19F-19F NMR coupling constants as potential tools for conformational analysis

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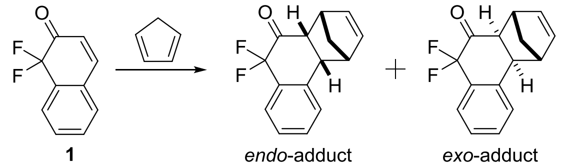
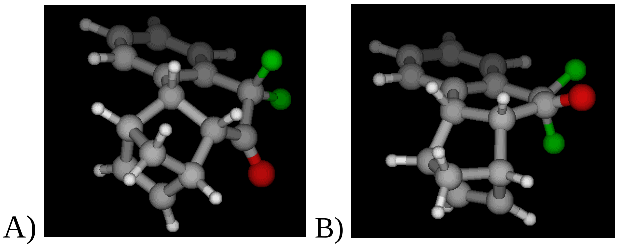
Selective and efficient methods for the synthesis of organofluorine compounds are nowadays subject of intensive research due to the increasing popularity of fluorine, especially in the materials design. The Diels-Alder reaction represents one of the most powerful synthetic methods for construction of cyclic backbones,[1] but it is rarely used for the synthesis of organofluorine compounds mainly due to lack of broad range of fluorinated synthons.[2]





During our investigation of the Diels-Alder reaction of 1,1-difluoronaphthalene-2(1*H*)-one 1 with various dienes DFT calculations showed that each of the diastereomeric cycloadducts can exist in two conformations: with keto-group pointing either towards (A) or away from the diene fragment (B). Moreover, calculated ^{19}F-^{19}F NMR spin-spin coupling constants correlate with experimental ones in case of using cyclopentadiene, cyclohexadiene and 1,3-diphenylisobenzofuran as dienes. The observed correlation presumably reflects the equilibrium state between conformers and can potentially be used for NMR conformational equilibrium analysis in case of CF_2-containing organic compounds.

DFT calculations were performed on B3LYP/6-31G(d) level for geometry optimization and B3LYP/aug-cc-pVZT-J (for fluorine) and cc-pVDZ (for other atoms) for SSCCs.

Diene	Cyclopentadiene				Cyclohexadiene				1,3-Diphenylisobenzofuran			
Adduct	*endo*		*exo*		*endo*		*exo*		*endo*		*exo*	
Conformer	A	B	A	B	A	B	A	B	A	B	A	B
SSCC calc., Hz	268	209	262	202	249	203	264	202	270	203	233	202
SSCC exp., Hz	260		258		259		262		272		258	

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Geometry optimization of X-band EPR resonator

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The microwave resonator is one of the key components in the modern Electron Paramagnetic Resonance (EPR) spectroscopy setup, as it largely determines the performance characteristics and limitations of the entire spectrometer. Dielectric microwave cavities became very popular in X- and Q-band due to their compact size, relatively high filling and Q-factors and well space separated E and H components of the electromagnetic field. However, this type of resonators suffers from paramagnetic impurities and defects in dielectric materials which manifest themselves in undesirable background EPR signals. In case of continuous wave (CW) EPR the background signals complicate the analysis of EPR spectra and in some cases limit the resulting sensitivity of the spectrometer. High purity bismuth germanate ($Bi_4(GeO_4)_3$, BGO) is proposed and implemented as alternative material for dielectric EPR resonators [1]. In this research note the possible way of resonator optimization is described. A detailed computer model describing the distribution of the electromagnetic field for Bruker 4118X-MD-5W1 design resonator has been developed. The resonator geometric parameters are optimized to achieve maximum sensitivity. According to the calculations, the optimized resonator structure has in 10 times greater sensitivity than the original MD-5 design [2].

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Synthesis and characteristics of reduced graphene oxide thin films

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The presence of practically confirmed unique properties of graphene is of particular interest in research into the applicability of this material. For example, graphene has high electrical conductivity, has great surface area (2640 m^2/g) is capable of withstanding the enormous current densities [1, 2]. Another advantage of graphene is the ability to modify its surface. For example, in the case of the graphene oxide contained on the surface of various functional groups which can be a substrate for the formation of metal nanoparticles, that allows to create new composite materials. Thus, the development of a technologically accessible and economically efficient method for producing graphene films is a very urgent task.

This paper presents the results of research work on the development of new techniques for the preparation of films from a reduced graphene oxide (RGO), through their formation during directed heat treatment of the surface of two immiscible liquids - an aqueous dispersion of graphene oxide (GO) and oils (Figure 1).

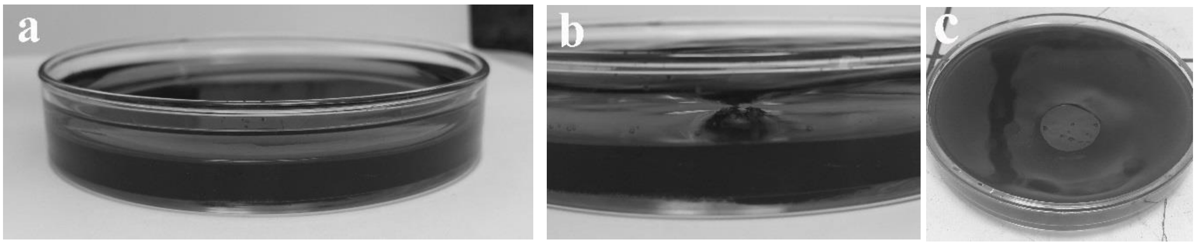

Figure 1(a, b, c) – Stages of formation reduced graphene oxide film: **(a)** heating of the oil layer; **(b)** formation at the interface of oil and water dispersion of reduced graphene oxide film; **(c)** transition reduced graphene oxide film through oil layer

For the synthesis of reduced graphene oxide films used water dispersion of graphene oxide (with concentration of 1 mg/ml) of lateral size from 0,1 to 4 microns and thickness up to 1,5 nm, which made by Hummers method. Method for the synthesized of reduced graphene oxide film (figure 1) was as follows: in a 1/3 petri dish its volume was filled with a water dispersion of graphene oxide. On a next step the petri dish poured at vacuum oil to form oil thin layer above the graphene oxide dispersion. Then, a heat gun was installed above the Petri dish with a function to control of the temperature and flow of the heated air directed to the surface of the liquid, after it was started. About reaching the set temperature, after 5-7 minutes occurred heating oils, and between oil and graphene oxide dispersion formed reduced graphene oxide film (Figure 1b). After 10 minutes of synthesis through oil formed reduced graphene oxide film. The films obtained are characterized by modern methods of analysis, the morphology of the surface, the structure of the bonds, the specific surface electrical resistance and thickness are investigated. It has been established that this method of synthesis allows to obtain films of multilayer reduced graphene oxide with a thickness of 0,5 to 12 μm and a specific surface electrical resistance of up to 1,45×106 Ohm/□, which can be widely used in modern micro - and optoelectronics, sensor technology, photovoltaics, the creation of microbatteries.

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EPR Study of Nitroxyl-Verdazyl biradicals

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Dynamic Nuclear Polarization (DNP) is an important method of NMR signal enhancement. Using this technique one can increase an NMR signal several times and use it in such previously inaccessible areas as a determination of proteins structure, an analysis of materials surfaces and a studying of short-lived biological structures. A promising DNP mechanism – cross effect mechanism - is based on the use of biradicals as polarizing agents. For an effective DNP generation in this approach one also must fine tune the properties of the biradicals: for instance a very important condition for the DNP realization is the long electronic relaxation time of radical fragments. Thereby, the development of new biradicals for DNP-NMR is impossible without the investigation of their properties by means of EPR spectroscopy.

The goal of this work is the investigation of magnetic properties of the new biradicals consisting of various nitroxyl and an verdazyl moieties.

By means of X-band (9 GHz) continuous wave (CW) and pulse EPR we studied the series of nitroxyl-verdazyl biradicals that are intraconnected by linkers of different length and stiffness. As a reference we also studied independent radical fragments with corresponding linker-substitutes. All studies were conducted in a toluene glass at 80 K. The analysis of CW EPR spectra of individual radicals and their numerical simulations demonstrated that the spectra of the biradicals are the accurate sum of the corresponding nitroxyl and verdazyl moieties EPR spectra. Hence, conformations of the biradicals in a solvent prevent the closing of the radicals moieties resulting in a relatively low exchange interaction. Moreover, using pulse EPR spectroscopy we managed to study longitudinal (T_1) and transverse (T_2) relaxation times of biradicals and their fragments together with analyzing temperature dependence of these times. Finally, we made a conclusion about the prospects of these biradicals as polarizing DNP-NMR agents.

Acknowledgements
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Impact of molecular packing rearrangement on solid-state fluorescence: polyhalogenated *N*-hetarylamines *vs* their co-crystals with 18-crown-6

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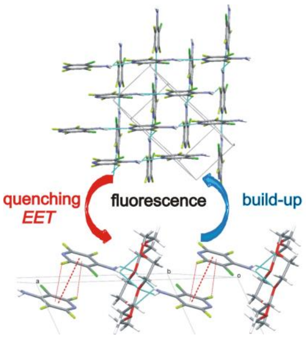
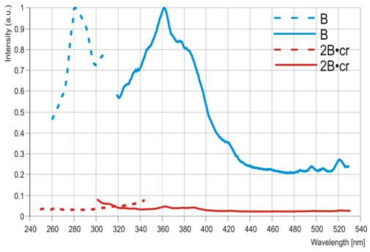
Organic co-crystals formed *via* non-covalent interactions exhibit photochromic, nonlinear optical, luminescent, magnetic, piezoelectric, nanomechanical properties so that they can serve as promising materials for various high-performance applications. Molecular packing modes and intermolecular electronic interactions play a key role in modulating properties of organic solids. We used the series of polyhalogenated hetarylamines and their co-crystals with 18-crown-6 ether to reveal the effect of co-crystallization on the supramolecular structure and fluorescence properties, as well as the relationship between these characteristics and peculiarities of the hetarylamine chemical structure (α- or γ-position of NH_2 group, number of Cl and F substituents, pyridine or quinoline framework, presence of a fluorophore fragment) [1]. Incorporation of crown ether into the crystal matrix of hetarylamine results in a significant rearrangement of the supramolecular structure. In all cases, the H-bonds $N–H\cdots N_{het}$ and $N–H\cdots F$ are replaced for the bond $N–H\cdots O_{crown}$. Changes in π-electron interactions that affect fluorescence characteristics depend on the amine structure. In the co-crystals of γ-aminopyridines, replacement of $C–F\cdots\pi_F$ interactions with $\pi_F\cdots\pi_F$ stacking causes the fluorescence quenching or a bathochromic shift of λ_{em}, whereas replacement of $\pi_F\cdots\pi_F$ or $\pi_F\cdots\pi_H$ stacking with $C–F\cdots\pi_F$ interactions or $\pi_H\cdots\pi_H$ stacking in the co-crystals of α-aminopyridines is accompanied by the hypsochromic shift of λ_{em}. γ-Aminopyridines show more pronounced changes in the fluorescence characteristics as compared to α-aminopyridines, the effect being depending on the nature of halogen substituents. The fluorescence properties of aminoquinolines, regardless of the amino group location, are insignificantly modified due to ability of the extended π-system to minimize interaction changes. Exploration of the nature of the excited states of isolated molecules, homocrystals and co-crystals using quantum mechanical calculations evidences that fluorescence quenching occurs due to EET, facilitated by the presence of crown ether molecules. The bathochromic and hypsochromic shifts of emission are caused by the change in a mutual orientation of the hetarylamine molecules with subsequent different stabilization of the ground and excited states. The revealed modification of the hetarylamines' fluorescence properties due to the formation of co-crystals with crown ether seems to be promising for use in solid-state supramolecular chemo and thermo sensors (indicators), i.e. co-crystals composed of signal (arylamine) and receptor (crown ether) components and exhibiting drastic fluorescent effect due to rearrangement of the molecular packing caused by the guest-to-receptor binding.





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4-Amino-2,1,3-benzothiadiazole derivatives: Synthesis, structure and luminescent properties

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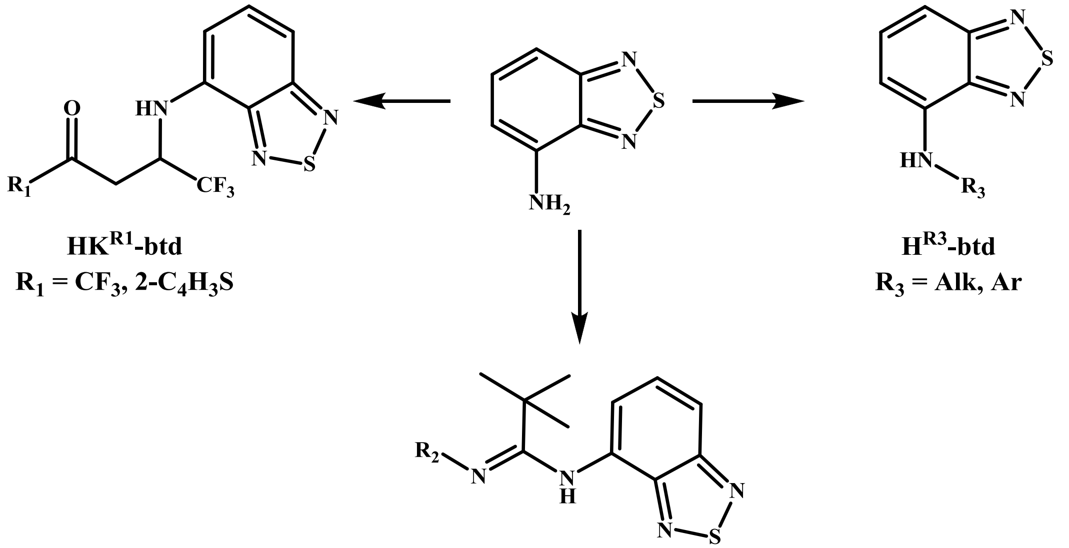
2,1,3-benzothiadiazole (btd) and its derivatives are known to have interesting photophysical and electron-withdrawing properties. [1] These properties are reported to allow using compounds on based 2,1,3-benzothiadiazole as components of dyes, organic light-emitting diodes and as fluorescent markers in biological research. [2] Coordination chemistry of btd derivatives is of particular interest, as it allows expanding the range of their functional properties. For example, the btd derivatives can act as antenna ligands sensitizing luminescence of lanthanides. [3]

One of promising btd derivatives is 4-amino-2,1,3-benzothiadiazole (NH_2-btd). Main advantages of NH_2-btd are application as a ligand in the coordination chemistry and possibility for its further functionalization. A number of Ag(I), Zn(II), Cd(II) and Ir(III) complexes with NH_2-btd has been prepared and their photophysical properties studied [3]. In the present work, we continue studying NH_2-btd derivatives. A novel compounds have been prepared: ketoimines (HK^{R1}-btd), amidines (HA^{R2}-btd) and secondary amines (HN^{R3}-btd).



HK^{R1}-btd
$R_1 = CF_3$, 2-C_4H_3S

H^{R3}-btd
R_3 = Alk, Ar

HA^{R2}-btd
R_2 = Ar

The complexation reactions have been studied for Zn(II) and Cu(I). The luminescent properties of organic compounds and the complexes have been discussed. The structures of new compounds were established by single-crystal X-ray diffraction..

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Lanthanide complexes for single and multiple electron transfer reactions and stabilization of anionic species

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For the studies of electroactive species on molecular level it is often very desirable to obtain X-ray diffraction data of reactive molecular species, which greatly helps in understanding reactivity and in evaluating the accuracy of quantum chemical calculations. Separation of reactive species, such as radical anions, can be challenging. We suggest the use of cationic lanthanide (Ln) complexes, which can form kinetically stable molecules with anionic species. Large size and coordination flexibility of Ln cations and bulky supporting ligands contribute to stabilization and adaptability of possible complex structures. Ln complexes serve as reductants and provide electrons for producing anionic species. In the first approach, Ln(II) complexes reduce a substrate (X) to its anionic form or derivative (Z), which is bound in large coordination sphere of Ln^{3+} cations: $k\,[Ln^{II}L_n] + X \rightarrow [(Ln^{III}L_n)_kZ]$. We are investigating the reducing complexes $[LnL_2(thf)_n]$ with N,N-chelating amidinate ligands (L = ArForm = $HC(NAr)_2^-$) as versatile ligand family, which can be easily functionalized at arene substituents (Ar), in order to attain required steric and electronic properties [1]. Second approach is the use of redox-active ligands, which can reversibly accept electrons while preserving the same composition: $k\,[Ln^{III}L_n] + X \rightarrow [(Ln^{III}L'_n)_kZ]$, where L' is an oxidized form of the ligand. These ligands can extend the number of electrons accessible per Ln atom (up to 4*e*), and make it possible to involve all the lanthanides, including those without easily accessible divalent state (2+). We are studying Ln complexes with *o*-iminobenzoquione (L = IQ) ligand, which can be reduced to iminosemiquinone radical (ISQ^-) or amidophenolate (AP^{2-}) forms.

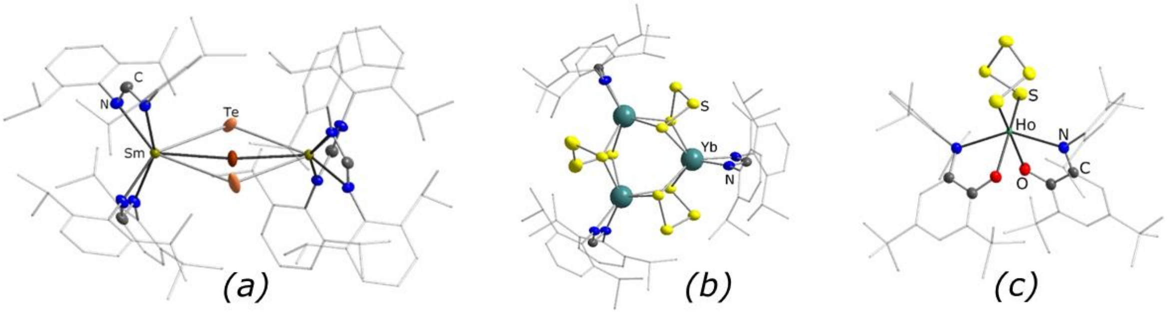

Figure. X-ray crystal structures of the complexes *(a)* $[(SmL_2)_2(\mu\text{-}Te)] + [(SmL_2)_2(\mu\text{-}Te_2)]$ co-crystal, *(b)* $[(YbL)_3(\mu\text{-}S_4)_3]$, *(c)* $[HoL_2(S_5)]^-$ (organic ligands are simplified)

Experiments on reduction of various chalcogenide sources demonstrated that mono- and dichalcogenide (for Q = S, Se, Te), as well tetra- and pentasulfide units can be stabilized in the coordination sphere of molecular Ln complexes (Figure). Composition of (poly-)chalcogenide anion formed, as well as structures of the complexes depend on the ligand type, reagent stoichiometry, and on reaction conditions. Proposed reaction routes include intermediate formation of radical species.

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Trityl-Aryl-Niroxide Based Genuinely g-Engineered Biradicals, as Studied by DNP, Multi-Frequency ESR/ENDOR, AWG Pulse MW Spectroscopy and Quantum Chemical Calculations

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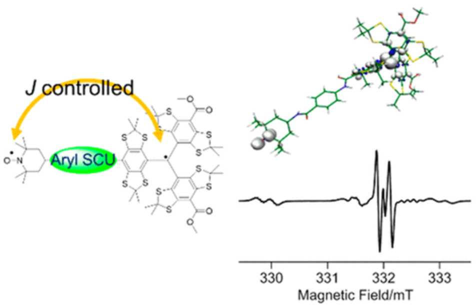

Trityl (Tr) and nitroxide (NO) radicals are connected by π-topologically controlled aryl linkers, generating genuinely g-engineered biradicals. The rationalized molecular design of the aryl likers bridging between the two stable radicals was underlain by the π -π topological symmetry argument of the electron network of the aryl linkers, i.e., *p*-phenylene (Ph) and 2,7-naphthylene (Nf). Ph and Nf give a positive and negative exchange interaction (J) between the Tr and NO radical moieties, respectively. The magnitude of J won't be sizable and the difference in the **g**-tensor of the radical site is significant. They serve as a typical model for biradicals in which the exchange J and hyperfine interactions compete with the g-difference electronic Zeeman interactions. The magnetic properties, including J's, underlying the biradical spin Hamiltonian for solution have been determined by multi-frequency CW-ESR (X-, Q- and W-band) and ^{1}H ENDOR (X-band) spectroscopies, comparing with those obtained by quantum chemical calculations. The signs of the J- values have been determined, being in good harmony with the quantum chemical calculations and with the topological argument for the molecular optimization. The g-engineered biradiclas have been tested as a prototype for AWG (Arbitrary Wave Generator) based spin manipulation techniques for GRAPE (GRAdient Pulse Engineering) microwave control of spins in molecular magnetic resonance spectroscopy, demonstrating efficient signal enhancement of selective and weakened hyperfine signals of the particular radical site occurring in the pulse ESR experiments. DNP effects of the biradicals for NMR signal enhancement have been examined, giving the efficiency factor of 30 for ^{1}H and 28 for ^{13}C, markedly reducing the measurement time of solid-state NMR spectroscopy.

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Theoretical modeling of Auger decay in thiophene

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Auger effect is commonly associated with core ionization. However, it was observed that Auger effect is also possible after inner-valence ionization of aromatic molecules [1]. Thiophene is one of the most important and well-studied heterocyclic aromatic compounds, a prominent building block of conductive polymers and oligomers, promising photochromatic molecular switches, organic semiconductors, solar cells, light-emitting diodes and field-effect transistors.

In most cases, experimental investigations of Auger spectra are quite complicated due to the rapid relaxation processes and degradation of final dications. Hence, theoretical modeling is required for spectra interpretation and clarification of the underlying processes. However, there are only few theoretical approaches that allow for such studies. The most practical of these computational schemes at the moment are the ADC(2) method for the two-particle propagator [2] and the EOM-CCSD method [3]. Since to the best of our knowledge a direct comparison of results of the ADC(2) and EOM-CCSD methods for double ionization energies (DIE) is still missing in the literature, in this work we compare the methods using the example of thiophene, for which recent experimental data obtained using time-of-flight photoelectron-photoelectron coincidence (TOF-PEPECO) spectroscopy are available [4] (see Table below).

Auger spectra assignment [4]		ADC(2)	EOM-CCSD
DIE, eV	2*h*	DIE, eV	DIE, eV
26.1	$2b_1^{-2}$	26.1	26.1
29.1	$6a_1^{-1}2b_1^{-1}$	28.2	28.4
31.9	$2b_1^{-1}4b_2^{-1}$ / $2b_1^{-1}1b_1^{-1}$ /$6a_1^{-2}$	29.1 / 30.2 / 31.2	29.4 / 31.2 / 31.5
33.1	$6a_1^{-1}1b_1^{-1}$ / $6a_1^{-1}4b_2^{-1}$ / $4b_2^{-2}$	31.2 / 32.1 / 33.4	32.0 / 32.4 / 33.7
36.4	$1b_1^{-1}4b_2^{-1}$ / $1b_1^{-2}$	32.3 / 32.8	32.9 / 34.1

The calculations were carried out using the cc-pVTZ basis set. Only singlet dicationic states were evaluated which are known to have the largest Auger intensities. In order to correct for the inaccuracy of the calculations, the theoretical spectra were shifted by 0.7 eV to higher DIE in the case of the ADC(2) and by 0.4 eV to lower DIE in the case of the EOM-CCSD calculations. In this way the lowest transitions in each spectrum were aligned with the experimental value. Within the energy interval considered, the ADC(2) and EOM-CCSD (relative) DIEs are in excellent agreement with each other and in good agreement with the experimental data. Both computational schemes therefore can equally well be employed for studies of the double ionization processes, the EOM-CCSD method providing slightly more accurate absolute DIE values that the ADC(2) scheme.

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Bis(diphenylphosphino)amine derivative of benzothiadiazole: coordination chemistry and photophysical properties

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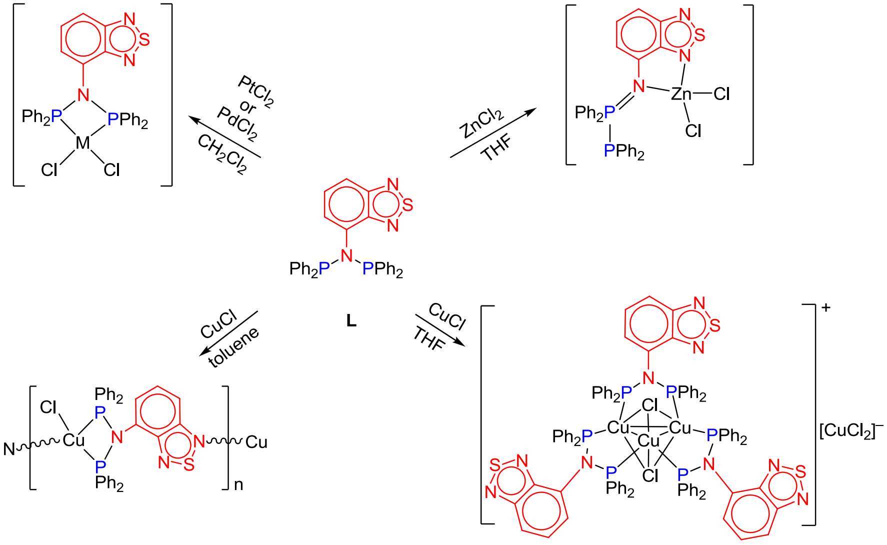
There is unceasing interest in the investigation of Ox-Red and optical properties, noncovalent interactions, electronic structure and charge transfer processes in 2,1,3-benzothiadiazoles (btd) [1, 2]. Due to these properties, btd derivatives are promising for creating devices of modern microelectronics. However, little attention is paid to phosphorus-containing btd compounds: their examples are mostly limited to derivatives with phosphate groups binded with btd unit *via* various linkers. Coordination chemistry of these derivatives is of particular interest: they are promising as hybrid ligands containing different donor atom types ("soft" phosphorus and "hard" nitrogen). Inclusion of phosphorus in the ligand provides an additional opportunity for metal coordination, allowing to further tune photophysical properties of the complexes.

Herein we report the synthesis and characterization of novel btd derivative, *viz.* N,N-bis(diphenylphosphanyl)-2,1,3-benzothiadiazol-4-amine (L). Its complexation behavior and multidentate nature are demonstrated by the example of different coordination compounds: $[PdLCl_2]$, $[PtLCl_2]$, $[ZnCl_2L']$, $[CuClL]_n{\cdot}nC_7H_8$ and $[Cu_3Cl_2L_3][CuCl_2]$.



The resulting compounds were characterized by XRD and other physical-chemical methods. Interestingly, P–N–P to P–P=N rearrangement of L occurred in the presence of Zn^{2+}. This type of rearrangement is known to be triggered by some Lewis acids, *e.g.* H^+ and Al^{3+} [3]. Photophysical properties of polycrystalline compounds synthesized were investigated. Positions of the bands in the emission spectra differ significantly implying strong influence of the metal and coordination type of the ligand.

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A novel synthetic approach to alkylated 1,3-diphenyl-2-propanones – key building blocks in design of graphene nanostructures

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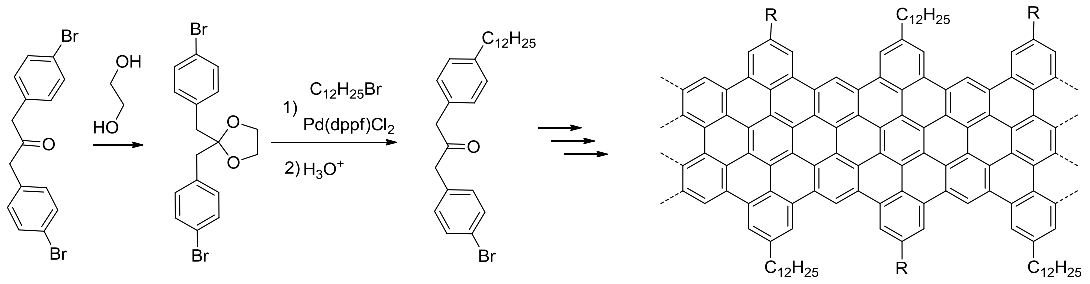
Molecular design of graphene nanostructures is a new actively developed field of study aimed on the preparation of new graphene nanoribbons and quantum dots with defined electronic, magnetic and optical properties [1]. Alkylated 1,3-diphenyl-2-propanones are key intermediate compounds in the synthesis of such graphene nanostructures. Here we developed a new advanced synthetic procedure to acquire mono- and dialkylated diphenyl-2-propanones through palladium-catalyzed cross coupling reaction of the dioxolane protected 1,3-di(4-bromophenyl)-2-propanone with dodecylmagnesium bromide which allows their large scale syntheses and opens the way to non-symmetrically substituted ketones useful for the synthesis of new functional derivatives of graphene nanoribbons.



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The first Single Ion Magnet based on Iron(II) and redox-active dpp-BIAN ligand

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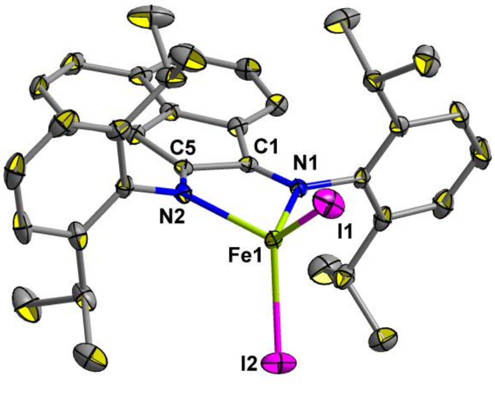
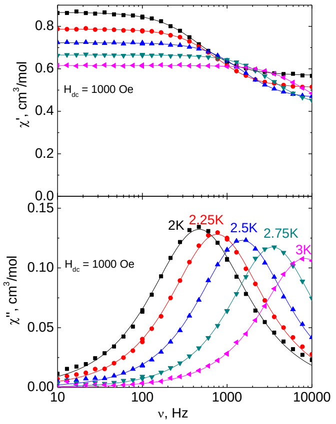
Future electronic devices based on quantum theory need memory modules with write/read speed much higher than nowadays chips based on silicon transistors. New materials of the future may be based on new compounds with a magnetic behavior depended on the temperature and applied magnetic field - such compounds exhibit slow reversal of magnetization below a certain temperature are called Single Molecule Magnets (SMMs). For over than 23 years after a publication an article about the Magnetic bistability in a Mn_{12} cluster [1] many scientists have been working on searching new effective SMMs.

Initially, the search for SMMs based on high-spin 3d metal ions was focused on the synthesis of spin-interacting centers in polynuclear molecules but in 2010 by Chang and co-workers was shown that isolated Fe(II) ion in the series of complexes exhibits slow magnetic relaxation – they called it Single Ion Magnet (SIM) [2]. After that work a wave of new SIMs based on 3d metal core were described but to our best knowledge there were not multifunctional compounds based on redox-active metal center and non-innocent ligand.

In this work we present the first SIM based on iron(II) and 1,2-bis[(2,6diisopropylphenyl)imino]acenaphthene (dpp-BIAN) - redox-active α-diimine ligand. The new compound $[(\text{dpp-BIAN})^0\text{Fe}^{II}\text{I}_2]$ exhibit slow relaxation of the magnetization up to 3 K under an applied dc field. This compound is also quite resistance in solid state to water and oxygen although it has Fe^{2+} core. Synthesis of complex, its structure, magnetic susceptibility and electrochemical behavior in solution will be discussed in the report in details.





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LEPR Study the Influence of Coumarin on Photoinitiation and Recombination of Spin Charge Carriers in the Copolymer-Methanofullerene Composite:poly(3-dodecylthiophene)/PCBM

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The paper presents the results of the direct Light-induced Electron Paramagnetic Resonance (LEPR) studies of magnetic, relaxation and dynamic parameters of photoinduced spin charge carriers arising in polymer photovoltaic composites based on poly(3-dodecylthiophene) (P3DDT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) when coumarin is added to the system. Coumarin is a photophysical activator of electron excitation energy transfer and has a high quantum yield of luminescence. The content of coumarin molecules in the composite ranged from 3 wt% to 21 wt%. The magnetic resonance parameters of the polarons and methanofullerene radical anions, photoinduced in the bulk heterojunctions of these composites under illumination by photons with an energy of 1.3 – 3.4 eV, were determined from the analysis of the contributions of these charge carriers to the total LEPR spectrum. It is shown that the concentration of both spin carriers is characterized by a nonmonotonic dependence on the energy of photo stimulating photons with an extremum in the region of 1.8 - 1.9 eV, close to the value of the energy gap of the polymer P3DDT. The greatest increase in the concentration of mobile charge carriers was observed in P3DDT/PCBM composites with coumarin content of 3 wt% and 6 wt%. Charge carriers of both types begin to recombine when the initiating light is turned off. A significant slowdown in this process was found when 3-6% coumarin weight was added to the initial composite. The temperature dependence of the concentrations of both the spin of the charge carriers, photoinduced in the composite P3DDT/PCBM with a content of 3 wt% of coumarin was investigated. It was found that these parameters are characterized by nonmonotonic dependence on temperature and show extreme growth at $T \approx 110$ K, more pronounced for mobile charge carriers. The data obtained allow us to conclude about the effect of coumarin on spin interactions in a polymer composite. This effect becomes more pronounced at the optimal concentration of coumarin, which is 3-6 wt%, at which its molecules are uniformly distributed in the bulk heterojunctions of the composite P3DDT/PCBM without forming a crystalline phase in them. This can lead to shorter distances between the photoinitiated spins, a deeper overlap of their wave functions and the appearance of additional energy barriers in heterojunctions as a result of this. In this case, it is possible to implement an intermediate mode of exchange interaction between the spin charge carriers of the composite, the concentration of which can increase due to the additional energy transfer of the excited coumarin molecules into the composite matrix. The results obtained in this work may indicate a significant effect of coumarin microadditives on the morphology of the composite and the exchange interactions of the spin charge carriers photoinitiated in it. There may be other processes occurring in the studied composites with coumarin, which will be studied in further studies.

Acknowledgements

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EPR and DEER characterization of new mixed weakly coupled nitroxide triradicals for molecular three-spin qubits

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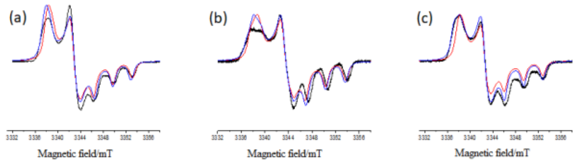
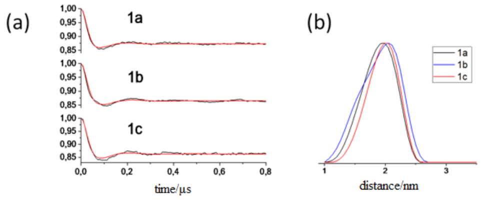
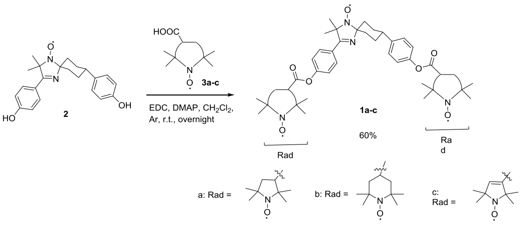
Three new mixed triradicals with small exchange coupling parameters ($J << A_N$) were obtained on the base of a coupling reaction between the derivative of spirofused 2,5-dihydroimidazol-type monoradical and the two mol. equivalents of carboxylic acid derivatives of PROXYL-, TEMPO- or 2,5-dihydro-1H-pyrrol –type nitroxides. Their intramolecular magnetic interactions were characterized in terms of comparison of the CW X, Q- and W-band EPR spectra with those of the monoradical precursors. The dipole-dipole coupling parameters of the triradicals were estimated on the base of the quantum chemical calculations at UB3LYP/6-31G(d) level of theory. Two types of the spin distances were found in the triradicals: short - with the distance of 13-17Å ($D \approx$ 11-24 MHz) and long - with the distance of 21-23Å ($D \approx$ 4-6 MHz). The long spin contacts (~2 nm) were detected between the side nitroxides by PELDOR and the short spin contacts (1.3-1.7 nm) between the central and the both side nitroxides were confirmed by the CW X-band EPR spectral analysis based on the well- established second moment approach.The longest spin-spin as well as spin-lattice relaxation times at 50 K were detected for the triradical carrying the two TEMPO fragments, indicating the potential usage of three-spin qubit models for quantum gate operations.







CW W-band EPR spectra obtained for the diluted (~10^{-4}M) and oxygen free THF solutions at 130K: (a) **1a**; (b)**1b**; (c) **1c**. Black lines – the experimental spectra; red lines – the spectra obtained as a superposition of the corresponding monoradical`s spectra; blue line – the spectra obtained as a superposition of the corresponding monoradical`s spectra (a) Background corrected time dependences of DEER. Black lines - experimental and red lines – simulated. (b) The corresponding distance distributions for **1a-c** obtained by Tikhonov regularization**.**

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Dy^{III}-based single molecule magnets with Schiff base ligand

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The design and synthesis of single molecule magnets (SMMs) containing lanthanide atoms are currently of great interest in chemistry of coordination compounds. Such magnetic molecules can be potentially used for creation of magnetic storage devices with high-density information, quantum computer, spintronics and magnetocaloric materials [1]. Considerable attention is paid to the synthesis of molecules containing ions of lanthanides [2], mainly because of the presence of large magnetic moments and significant magnetic anisotropy.

In the search for compounds having a single molecule magnets properties we synthesized new dysprosium complexes with Shiff base aromatic ligand, N'-(pyridin-2-ylmethylene)isonicotinohydrazide (HL). The ligand HL is an N,N,O-tridentate chelating ligand forming three type of mononuclear compounds with different structure and contain: $[Dy^{III}(H_2O)(MeOH)(NO_3)_2(HL)]$ (**1**) $[Dy^{III}(MeOH)(NO_3)(L)_2]\cdot Solv$ (**2**, Solv = MeCN, MeOH), $[Dy^{III}(L)_3]\cdot 2H_2O$ (**3**). According to structural and magnetic data as well as FD-FT THz-EPR spectroscopy data it was demonstrated that structure and coordination polyhedron geometry determine the value of $\Delta E/k_B$ that is changed from 51 K to 254 K in the H=1000 Oe.

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