

Structure of intercalates C₆₀ and C₇₀.

Agafonov S.S., Somenkov V.A., Filippov A.A.

"Kurchatov Institute", Moscow, Russia

To explore the possibility of creation of a safe keeping system for different gases and liquids, we carried out the research of structure, sorption properties and thermal stability of intercalation compounds of crystalline and amorphous fullerenes C₆₀ and C₇₀ with saturated and unsaturated molecules. We also studied intercalation of inert gases under low pressure. The analysis of structure by neutron scattering and precise thermogravimetry shows that sorption is determined by formation of solid solutions, superstructures or compounds on base of initial fullerenes.

Mole ratio fullerene/absorbate, equal 1/1, is characteristic for saturated molecules, while for unsaturated molecules it arrives at 1/2. This circumstance can be explained by specific interaction between p-electronic shells of unsaturated derivatives and the electronic structure of fullerenes and it can specify on possible using of fullerites for absorption and storage exactly of unsaturated matters.

The principles of reactivity of higher fullerenes

Amsharov K.Yu., Simeonov K., Jansen M.

Max Planck Institute for Solid State Research, D-70569 Stuttgart, Germany

A characteristic feature of all fullerenes which makes them interesting and defines their unique chemical and physical properties is the steric strain induced by the geometric peculiarities of the fullerene molecule. Single crystal X-Ray analyses which should provide information about molecular geometry rarely gives reliable data in the case of fullerenes because of their virtually spherical shape and rotational mobility in the crystal lattice. It was found that chlorinated fullerenes exhibit reduced rotational mobility and form high-quality single crystals. A number of chlorinated higher fullerenes $C_{76}(:1)Cl_{18}$ [1], $C_{78}(:2)Cl_{18}$ [2], $C_{78}(:3)Cl_{18}$ [2], $C_{78}(:5)Cl_{18}$ [3], $C_{80}(:2)Cl_{12}$ [4] were obtained via selective chlorination of the corresponding isomers. Analysis of the addition patterns of chlorine atoms in the halogenated higher fullerenes has made it possible to understand some principles of fullerene reactivity. It was found that adding chlorine atoms to specific sites on the fullerene „surface“, i.e. introducing sp^3 hybridized carbon atoms, minimizes the deviation from planarity for all remaining sp^2 carbons. Moreover the presence of triple hexagon junctions (THJ) which are characteristic only for higher fullerenes define this specific positions. The reduced sizes of the extended joint-hexagon fragments leave the strained THJ-carbon atoms „relaxed“ through flattening the local geometry. THJ-carbons decrease their deviation from planarity, which consequently unifies them in a chlorine-free „flat“ fragments. Actually, one might regard the addition pattern scenario as fencing off the „surviving“ areas (the islands of aromaticity). In other words, the system endeavours to release tension in the extended THJ-fragments by their “separation” from the pentagons which are responsible for fullerene curvature. This process might be defined as the initial step of exohedral derivatization. Depending on the conditions, the process might terminate at that stage or continue further. Namely, remaining pentagon-containing regions (which can be considered as C_{60} -fullerene fragments) could attach additional chlorine atoms in a similar manner like C_{60} fullerene. A prerequisite for the direction and extent of addition is the formation of a stable conjugated system.

- [1] K. Simeonov, K.Yu. Amsharov, M. Jansen, *Angewandte Chemie Int. Ed.* **46**, 8419 (2007).
- [2] K. Simeonov, K.Yu. Amsharov, E. Krokos, M. Jansen, *Angewandte Chemie Int. Ed.* **47**, 6283 (2008).
- [3] K. Simeonov, K.Yu. Amsharov, M. Jansen, *Chem. Eur J.* **14**, 9585 (2008).
- [4] K. Simeonov, K.Yu. Amsharov, M. Jansen, *Chem. Eur J.* **15**, 1812 (2009).

Influence of medium on C₆₀ reactivity in liquid phase oxidation of hydrocarbons

Bulgakov R.G., Ponomareva Yu.G., Sabirov D.Sh.

Institute of Petrochemistry and Catalysis RAS, Ufa, Russia

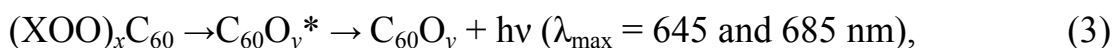
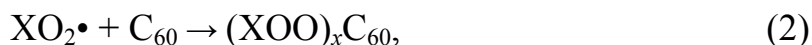
Investigation of C₆₀ reactivity toward RO₂• radicals generated upon liquid phase oxidation of hydrocarbons has two aspects of importance: first, RO₂• radicals are key intermediates of various chemical and biochemical processes of oxidation; second, there are contradictions in publications devoted to possibility of inhibition of thermo-oxidative polymer destruction and metabolism of viruses due to reaction of C₆₀ with RO₂•:



Using chemiluminescent methods and HPLC, we have found that C₆₀ does not inhibit liquid phase oxidation of different compounds (ethyl benzene EtPh; dodecane, cyclohexane, oleic acid) initiated by AIBN. So, inertness of C₆₀ toward RO₂• has been declared [1]. This conclusion is contradictory to [2] where *t*-BuO₂• generated by catalytic decomposition of *t*-BuOOH reacts with C₆₀ yielding fullerene mixed peroxide-epoxide derivative (*t*-BuOO)₄C₆₀O. It is worth to note that hydrocarbons with active hydrogen have been used as medium in [1] while benzene characterized with complicated H atoms alienation was a solvent in [2]. So, we can propose that medium significantly influences C₆₀ reactivity toward RO₂•, *i.e.* reaction (1).

Addition of RO₂• to C₆₀ does not occur in the medium of hydrocarbon with active C–H bond because it is depressed by concurrent reaction of RO₂• with hydrocarbon. Interaction C₆₀ + RO₂• occurs in benzene with strong C–H bond and in the case of low amounts of hydrocarbon being oxidized.

We have found a new type of C₆₀ derivatives chemiluminescence (CL) caused by thermal decomposition of fullerene peroxides generated in the system C₆₀–AIBN–O₂–EtPh–PhH by addition of RO₂• to C₆₀:



where X – alkyl, C₆₀O_y – fullerene polyketones.

The work was supported by the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (programme No. 1).

- [1] R.G. Bulgakov, Yu.G. Ponomareva, S.I. Maslennikov, E.Yu. Nevyadovsky, S.V. Antipina. *Russ. Chem. Bull., Int. Ed.* **54**, 1862 (2005).
 [2] L. Gan, Sh. Huang, X. Zhang, A. Zhang, B. Cheng, H. Cheng, X. Li, G. Shang. *J. Am. Chem. Soc.* **124**, 13384 (2002).

A new type of chemiluminescence: liquid phase oxidation of C₆₀H₃₆ fullerene hydride

Bulgakov R.G., Galimov D.I., Kinzybaeva Z.S., Sabirov D.Sh.

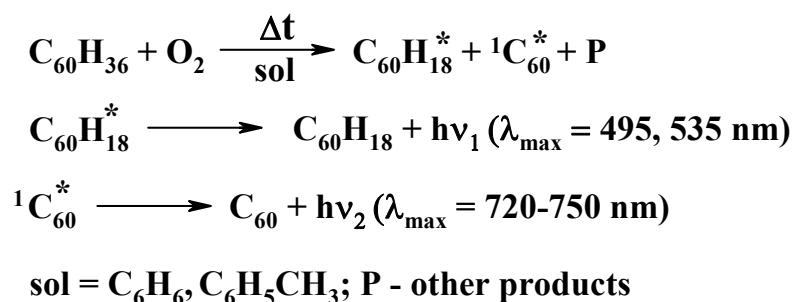
Institute of Petrochemistry and Catalysis RAS, Ufa, Russia

Study of properties of fullerene hydrides has both basic and applied interests which are explained with an opportunity of their use for hydrogen accumulation.

For the first time chemiluminescence (CL) upon oxidation of C₆₀H₃₆ fullerene hydride with oxygen in solutions has been found.

Fullerene hydrides have been synthesized by interaction of C₆₀ solutions with Zn–HCl and Zn/Cu–H₂O. Oxidation has been performed by O₂ bubbling through C₆₀H₃₆ 10⁻⁴ mol dm⁻³ solutions in toluene (or benzene). Reaction is accompanied with slowly fading CL characterized with intensities 1.4·10⁶ and 6.6·10⁷ photon s⁻¹ cm⁻³ at 23 and 70°C, respectively. CL is not observed at the O₂ action on both C₆₀H₂₋₆ and C₆₀ solutions under the same conditions (70°C, in dark). The addition of inhibitors ionol and galvinoxyl to the C₆₀H₃₆ + O₂ system does not decrease in the CL intensity that in contrast take place in the case of hydrocarbons oxidation.

CL spectrum in C₆₀H₃₆ oxidation (λ_{max} = 495, 535, 610, 720-750 nm) contains maxima (495, 535 nm) close to maxima of photoluminescence spectrum of C₆₀H₁₈ (480, 520 nm) and wide maximum at 720-750 nm which conterminous with area of C₆₀ photoluminescence. So, the most probable CL emitters are singlet ¹C₆₀* and electronically excited states of C₆₀H₁₈. Generation of CL can be describing with the simplified scheme below:



The work was supported by the Division of Chemistry and Material Sciences of the Russian Academy of Sciences (programme No. 1).

Effect of structure of monocyclic aromatic solvents on the consistency of fullerene C₆₀ solvation shell

Chubarova E.V., Melenevskaja E.Yu.

Institute of Macromolecular Compounds RAS, 199004 St.-Petersburg, Russia

Donor-acceptor interactions of fullerene C₆₀ with solvent molecules result in its good solubility in numerous organic solvents due to the formation of strong solvation shells. It could be proposed that coordination of solvent molecules by C₆₀ molecules will depend on structure of solvent molecules, and that such a forced coordination would lead to the packing density of solvent molecules in fullerene solvation shell different from that of molecules in pure solvent.

To verify these suppositions, the study of fullerene solutions in monocyclic aromatic solvents (AS) diluted by tetrahydrofuran (THF) was carried out using UV-spectroscopy. THF was chosen since it is transparent in UV-region, and it is a good solvent for AS and a poor solvent for C₆₀. In this case, the structure of fullerene solvation shell is determined by the quantity of AS molecules, which C₆₀ is able to retain in THF. Using calibration procedures, for every AS the value of its concentration was obtained from UV spectrum of (C₆₀+AS) in THF, which was compared with the value of AS concentration calculated for C₆₀ solution in this AS diluted by THF. The difference in these concentrations for each AS was attributed to the change of solvation shell density with respect to the density of pure solvent. It was shown that the presence of asymmetrical substituents in AS molecule results in loosening of solvent structure in solvation shell, while the absence of substituents or the presence of symmetrical substituents leads to compacting of solvent structure.

Polymer chain degradation during deformation of polystyrene-fullerene C₆₀ composite films

Lebedeva M.F., Melenevskaja E.Yu., Chubarova E.V.

Institute of Macromolecular Compounds RAS, 199004 St.-Petersburg, Russia

Hindered mobility of macromolecular chains due to polymer-filler interaction results in chain degradation during dissolution of polymer-fullerene composites prepared from mixed polymer and fullerene solutions [1]. Since interactions between PS and C₆₀ increase with removing of a solvent from mixed solutions (PS+C₆₀) [2], necessary conditions for chain degradation are created during preparation of PS-C₆₀ composites. In this work the possibility of chain degradation during preparation of PS-C₆₀ composite film by slow evaporation of the solvent from (PS+C₆₀) toluene solution was examined.

Mechanical properties of the film of pristine PS and of PS-C₆₀ composite film were investigated and compared. The films were obtained under the same conditions; PS molecular weight was M=280 kDa; C₆₀ content in the composite was approximately 8%. The data obtained show that insertion of fullerene into polystyrene matrix leads to plasticization of the composite. These results unambiguously point to chain degradation during preparation of the composite film. The morphology of the composite films prepared under different conditions allows us to suggest that the tendency of C₆₀ molecules to aggregate promotes chain degradation.

- [1] Chubarova E. V., Melenevskaya E. Yu., Sudareva N. N., Andreeva O. A., Malachova I. I., Ratnikova O. V. *J. Macromol. Sci.- Phys.* **44**(4), 455 (2005).
- [2] Chubarova E.V., Melenevskaja E.Yu., Fullerenes, *Nanotubes and Carbon Nanostructures* **16**(5&6), 640 (2008).

Influence of sonic and magnetic fields on fullerene and nanotube formation in carbon-helium plasma of high frequency at atmospheric pressure

Churilov G.N.*, Osipova I.V.*, Marchenko S.A.⁺, Gulyaeva U.E.⁺

**Kirensky Institute of Physics SB RAS, 660036 Krasnoyarsk, Russia*

⁺*Siberian Federal University, 660041 Krasnoyarsk, Russia*

The results of fullerenes and nanotubes investigation obtained in cooling plasma treated with sonic and magnetic fields. The chamber where the arc plasma was cooled was made as acoustic resonator and it had quartz windows for emission spectra registration.

The sonic influence changed the volume of plasma with optimal synthesis parameters (electron concentration N_e and temperature T_e) [1]. Near the resonance the area with the optimal parameters N_e and T_e was maximum, and the fullerene contents in soot amounted to 13%. Also the ratio of the C_{60} , C_{70} , and higher fullerenes in fullerene mixture changed depending on sound intensity and frequency. These results were obtained by the HPLC method. The investigations of plasma containing 3d metals had shown that sonic field influenced not only on the nanotube contents in obtained condensate, but on the defect amount in them too. These results were obtained by PES by comparison of carbon quantities with sp^2 and sp^3 hybridization. Magnetic field was most influencing on nanotube formation. It was shown by the EPR, PES, and Raman spectroscopy methods that in magnetic field one can separate paramagnetic and ferromagnetic particles directly at the synthesis process. In the area of high magnetic field the carbon condensate contained essentially more amount of defect nanotubes than in the area of weak magnetic field.

[1] G.N. Churilov, A.S. Fedorov, P.V. Novikov. *JETP Letters* **76**, 522 (2002).

The new molecular structures based on *exo*- and *endo*-fullerenes

Domratcheva-Lvova L.G.¹, Domrachev G.A.², Domracheva E.G.³, Huipe Nava E.¹, Spivak A.E.²

¹Universidad Michoacana de San Nicolas de Hidalgo, Morelia, Mich., Mexico

²G.A.Razuvaev Institute of Organometallic Chemistry RAS, N.Novgorod, Russia

³Institute for Physics of Microstructures RAS, N.Novgorod, Russia

In analogy to the formation of ferrocenes from carbon and iron atoms we have investigated Fe – C structure models with a number of fullerenes: C₂₀, C₆₀, C₇₀, C₈₀, C₁₂₀, C₂₄₀ as well as polymer chains with *hapta*-10 bond which consist of connecting ferrocene links and fullerene structures bonded by iron atoms at the *exo*- and *endo*- positions. The magnitude of Fe-atoms varies from one to five.

The molecular modeling and interconverting of the structures given have been carried out by the Molecular Mechanics (MM+) and Molecular Dynamics (MD) methods. The fullerene structures have been demonstrated to be the most stable ones which contain two *endo*- Fe- atoms forming one virtual axis.

The work has been supported by the Project of CONACYT, the Program “The Fundamental Research of nanotechnologies and nanomaterials” of the Presidium RAS and the RF President Grant SS-1396.2008.3

The effect of ligand variation on catalytic property of CoSALEN in hydroperoxidation of Fullerene C₆₀

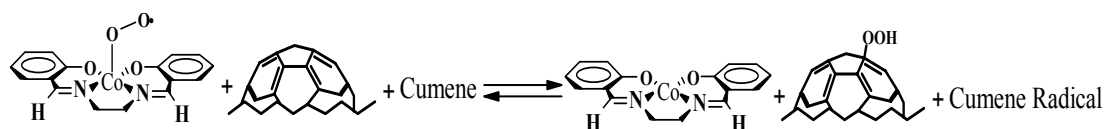
Ghanbari B.*, Tangeysh B.

Department of Chemistry, Sharif University of Technology, Tehran, P.O.Box 11155-9516, Iran

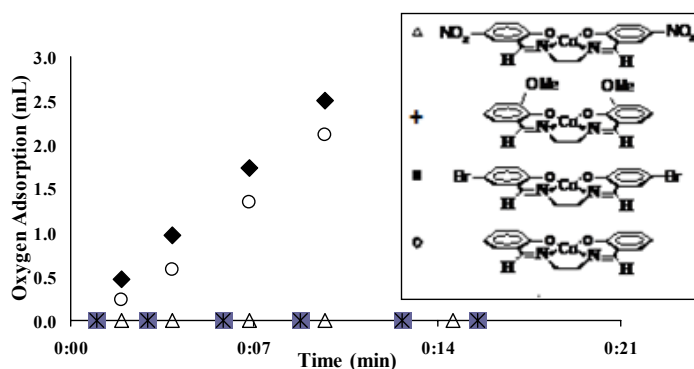
The oxygen-carrying property of synthetic cobalt Schiff bases have been studied extensively. The reversibility of dioxygen adduct formation was not demonstrated until 1938 when Tsumaki [1] showed that the color change observed upon exposing Cobalt(II)di-(salicylal)-ethylenediimine (CoSALEN) to air was due to reversible oxygenation. Then, Calvin et al. extensively studied on oxygen carrier properties of Co(II) complexes with SALEN-type ligands [2]. Furthermore in 1980's, Drago demonstrated the possibility of catalyzing the oxidation of phenols by metal-dioxygen adducts due to their ability to produce hydroperoxide radicals and oxidation initiation [3].

Furthermore, fullerene C₆₀ has already been known as to be efficient in trapping radicals [4]. The high affinity of this nanoparticle as well as its derivatives towards reaction with radicals makes it a potent candidate as radical scavengers [5]. The radical sponging property of C₆₀ could be considered in terms of its reaction with peroxy radicals [6]. Basically, a radical addition mechanism was proposed to explain the formation of C₆₀ peroxides [7].

In our previous work, we found that CoSALEN can act as a new catalyst in hydroperoxidation of C₆₀ in presence of O₂ and cumene as solvent, due to the mechanism shown below [8]:



Herein, the effect of ligand variation on catalytic activity of CoSALEN in hydroperoxidation of C₆₀ is investigated. Different types of CoSALEN complexes with having different substitution such as Br, NO₂, OMe and ... on the aromatic moiety of the ligand were synthesized and their effect on the catalytic process were explored. The results of these experiments significantly showed that such variations highly affected on the catalytic activity of CoSALEN complexes in hydroperoxidation of C₆₀. It was also observed that electron donor groups were capable in increasing the rate of hydroperoxidation, while electron withdrawing groups extensively terminated the hydroperoxidation of C₆₀. For instance, as is shown in Fig. 1, the existence of Br substitution, as a weak electron donor on the ligand aromatic ring, significantly increases the oxygen uptake while NO₂ group, as a strong electron withdrawing group, terminates the catalytic process:



This work was supported by Research Office of Sharif University of Technology.

- [1] Tsumaki, T. *Bull. Chem. Soc. Japan* **13**, 262 (1938).
- [2] Bailes, R.H., and Calvin, M. *J. Am. Chem. Soc.* **69**, 1886 (1947).
- [3] Zombeck, A, Drago, ., R.S., Corden, B.B., and Gaul, J.H. *J. Am. Chem. Soc.* **103**, 7580 (1981).
- [4] Gan, L., Huang, S., Zhang, X., Zhang, A., Cheng, B., Cheng, H., Li, X., and Shang, G. *J. Am. Chem. Soc.* **124**, 13384 (2002).
- [5] Singh. H. in *Encyclopedia of Nanoscience and Nanotechnology*, vol. 3, pp. 572 (2004).
- [6] Gan, L., *C.R. Chimie* **9**, 1001 (2006).
- [7] Huang, S., Xiao, Z., Wang, F., Gan, L., Zhang, X., Hu, X., Zhang, S., Lu, M., Pan, Q., and Xu., L. *J. Org. Chem.* **69**, 2442 (2004).
- [8] Ghanbari, B., Tangeysh, B. submitted for publication in *J. Coord. Chem.*

The effect of axial bases in catalytic activity of CoSALEN in oxidation of C₆₀

Ghanbari B.*, Abadi N.H.

Department of Chemistry, Sharif University of Technology, Tehran, P.O.Box 11155-9516, Iran

Oxygenation of fullerenes has received much attention since the early days of fullerene chemistry due to their bioactivity and possible applications in materials chemistry [1]. Mixtures of C₆₀O_n can be formed by electrochemical oxidation [2], photolysis [3], ozonation [4]. Furthermore, cobalt(II)di-(salicylal)-ethylenediimine (CoSALEN) was found to bind dioxygen reversibly [5], either in mononuclear superoxo- or dinuclear peroxy type complexes with dioxygen [6]. The superoxo-complex reacts very much like a radical and is usually assumed to be responsible for catalytic activity. In this study, the effect of axial bases on catalytic reaction of C₆₀ oxidation by CoSALEN was investigated in the presence of O₂ in cumene (Figure 1).

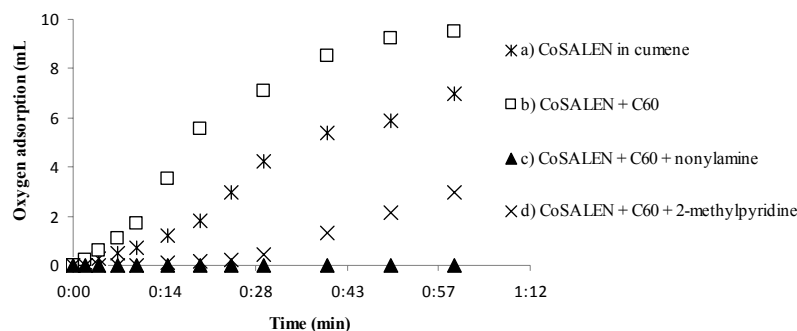


Figure 1. The effect of axial bases on the catalytic role of CoSALEN in oxidation of C₆₀

Experimentally, it was observed that the rate of oxygen consumption of the complex increases due to the oxidative capability of C₆₀ (compare Figures 1a with 1b). This was assumed as a result of scavenging the hydroperoxides produced by oxygenated CoSALEN by C₆₀[7]. Furthermore, as soon as nonylamine and 2-methylpyridine were introduced to the reaction mixtures (Figure 1c and 1d respectively) a sharp decrease in oxygen adsorptions was observed. Basically, it has been found that as the basicity of the ligand increases [8] as well as in non-polar solvents, a binuclear peroxy-bridged species should be dominating [6]. Conclusively, it is suggested that the axial bases are capable to reduce C₆₀ oxidation, due to their binding to CoSALEN and formation of inactive peroxy-bridged species which consequently decreases the rate of hydroperoxide formation. This is also in accordance to the observation that more basic axial base, nonylamine could reduce oxygen adsorption more efficiently than 2-Methylpyridine.

This work was supported by Research Office of Sharif University of Technology.

- [1] Huang, S., Xiao, Z., Wang, F., Gan, L., Zhang, X., Hu, X., Zhang, S., Lu, M., Pan, Q., and Xu., L. *J. Org. Chem.* **69**, 2442 (2004).
- [2] Thorp, H. H., Karlsbeck. *J. Electroanal. Chem.* **314**, 363 (1991).
- [3] Wood, J. M., Kahr, B., Hoke, S. H., Dejarne, L., Cooks, R. G., Ben-Amotz, D. *J. Am. Chem. Soc.* **113**, 5907 (1991).
- [4] a.Heymann, D., Bachilo, S. M., Weisman, R. B., Cataldo, F., Fokkens, R. H., b.Nibbering, N. M. M., Vis, R. D., Chibante, L.P.F. *J. Am. Chem. Soc.* **122**, 11473 (2000) and references cited therein.
- [5] Tsumaki, T., *Bull. Chem. Soc. Jpn.* **13**, 252 (1938).
- [6] Niederhoff, E., Timmon, J. and Martell, A.E. *Chem. Rev.* **84**, 137 (1984).
- [7] Ghanbari, B., Tangeysh, B. submitted for publication in *J. Coord. Chem.*
- [8] Fallab, S., and Mitchell, P. *Adv. Inorg. Bioinorg. Mech.* **3**, 311 (1997).

Organofullerenes with hydrocarbyl and trimethylsilyl groups prepared from lithium and sodium fullerides

Gorina E.A., Titova S.N., Kalakutskaya L.V., Domrachev G.A., Ketkov S.Y., Obiedkov A.M., Poddel'sky A.I., Lopatin M.A.

Razuvaev Institute of Organometallic Chemistry RAS, 603950 Nizhny Novgorod, Russia

Interaction of alkali metal fullerides $C_{60}M_n(THF)_x$ ($M = Li, Na$; $n = 4, 6, 8, 10, 12$) prepared as described earlier [1] with various electrophilic reagents gives fullerene polyadducts R_nC_{60} ($R = Me, n = 12$; $R = Et, n = 12$; $R = All, n = 6, 12$; $R = t-Bu, n = 4, 6, 8, 10, 12$; $R = i-Bu, n = 12$; $R = PhCH_2, n = 6, 12$; $R = Me_3Si, n = 4, 6, 8, 10, 12$), most of which being synthesized for the first time. All new compounds have been characterized by IR, 1H and ^{13}C NMR, MALDI mass spectrometry, and element analysis. The isomerically pure adducts were isolated by HPLC from the products obtained by reactions between $C_{60}Na_4(THF)_x$ and $t-BuBr$ ($t-BuC_{60}H$, four isomers of $t-Bu_2C_{60}H_2$, $t-Bu_3C_{60}H_3$), $C_{60}Li_{12}(THF)_x$ and $PhCH_2Br$ ($1,4,10,24-(PhCH_2)_4C_{60}$). They were identified by 1H NMR, UV/Vis spectroscopy and mass spectrometry. The charge transfer (CT) complexes of All_6C_{60} derivative with N-aromatic donors and hexamethylbenzene were investigated. The complexes have very weak CT-bands (λ_{max} 425-535 nm) showing hypsochromatic shift relative to complexes with unsubstituted fullerene. The DFT (B3LYP/3-21G, B3LYP/6-31G, PBE/TZ2P) and semiempirical (AM1) calculations were carried out to reveal the most stable R_nC_{60} configurations and to investigate the electronic structures of those and related fullerene systems. An essential decrease in the ionization energy (IE) and electron affinity (EA) on going from C_{60} to $R_{12}C_{60}$ was revealed, the difference in IE being 2-3 eV. To confirm the theoretical results, we have performed the redox-reactions of R_nC_{60} with various oxidants and reductants using X-band EPR monitoring. The experimental data are in consistence with the quantum-chemical studies.

This work was supported by the grant from the President of the Russian Federation (S.Sc.- 1396.2008.3, State Contract 02.513.11.0002) and programs of RAS.

[1] S.N. Titova et al. *Physics of the Solid State*. **46**, 1365 (2004).

Composite materials obtained on the basis of multi-wall carbon nanotubes

Obiedkov A.M., Gorina E.A., Kaverin B.S., Semenov N.M.,
Egorov V.A., A.I.Kirillov, Titova S.N., Domrachev G.A.,
Lopatina T.I., Gusev S.A.

Razuvaev Institute of Organometallic Chemistry RAS, 603950 Nizhny Novgorod, Russia

The fields of MWCNT's and MWCNT's-based composite applications are continuously extended. Nowadays they are employed as reinforcing components of composite and polymeric materials, electrodes for the technological processes, dealing with separation, isolation and purification of chemical substances, as well as a support for coating with various catalysts. The modification of the MWCNT's surface with inorganic or organic particles and coatings leads to appearance of new properties of modified MWCNT's. The MOCVD method makes it possible both to prepare MWCNT's and to modify MWCNT's for getting desired physical properties. We worked out methods of preparation of cylinders, where the cylinder walls consist of radial-oriented MWCNT's. We investigated the processes of vacuum deposition of pyrolytic chromium on the cylinders. MOCVD in static conditions produced coatings not only on the inner and outer surfaces of the cylinder but also on the individual nano-sized components of its walls. Organochromium liquid "Barchos" were used as organometallic precursors of pyrolytic metals. Various data on the structures and properties of the samples were obtained by X-RPD, TGA, SEM and HRTEM. It was found that the composite morphology depends strongly on the coating thickness and deposition conditions. The composite morphology depends largely on decomposition conditions of pyrolytic chromium coating. The occurrence of regular structures in the form of "beads" has been found. We consider the mechanism of their occurrence at the expense of bis-arene chromium compounds of intermediate viscous-ductile polymer phase formed in the process of pyrolysis as well as at the sacrifice of manifestation of Plato - Rayleigh instability.

This work was supported by the grant from the President of the Russian Federation (S.Sc.- 1396.2008.3, State Contract 02.513.11.0002) and programs of RAS.

New concept in SPM

New!

SOLVER NEXT™

Ease of performance!



Desktop SPM with full automation
Intuitive software for ease of operation
Ergonomic design
Best-in-class SPM (features, resolution and price)

www.ntmdt.com

 **NT-MDT**
Molecular Devices and Tools for NanoTechnology

NT-MDT Co.
Building 100, Zelenograd,
Moscow 124482, Russia

Tel.: +7(499) 735 03 05
Fax: +7(499) 735 64 10
E-mail: spm@ntmdt.ru

New fluorocycloalkyl derivatives of [60] and [70]fullerenes

Gruzinskaya N.I., Silin A.I., Pimenova A.S., Sidorov L.N., Troyanov S.I.

Chemistry Department, Moscow State University, 119991 Moscow, Russia

Fullerenes easily take part in radical addition and cycloaddition reactions. Radical addition to fullerenes produces a variety of compounds such as halides, perfluoroalkyl, amino, alkylsilyl, and metallated derivatives [1]. The cycloaddition reactions result, for example, in the formation of methanofullerenes [2]. There is only one report concerning the preparation of fluorocycloadducts of fullerenes [3]. Here we report the synthesis, isolation, and X-ray crystallographic characterization of new isomers of $C_{60}(C_4F_8)_n$, $n = 2-4, 6$ and $C_{70}(C_4F_8)_n$, $n = 1-3, 5$, and 6.

Mixtures of fluorocycloalkyl [60] and [70]fullerenes were synthesized by reactions of C_{60} and C_{70} with $C_2F_4I_2$ or $C_4F_8I_2$. Syntheses were carried out in sealed glass ampoules at 380-450°C. MALDI mass spectrometric analysis showed the presence of $C_{60/70}(C_2F_4)_n$ compounds with $n = 1-14$. Similar results were obtained with $C_4F_8I_2$ as reagent, the number of attached C_4F_8 groups varying from 1 to 6. The mixtures were subjected to separation by means of High Performance Liquid Chromatography (HPLC) using a Buckyprep column and toluene or toluene/hexane mixtures as the eluents. From some chromatographic fractions crystals were grown by slow removal of solvent. Crystal structures were determined by X-ray crystallography by using synchrotron radiation. Addition patterns of these new compounds are compared with the previously reported [3]. In the case of $C_{60}(C_4F_8)_n$ compounds, the C_4F_8 groups are attached in *ortho* or *meta* positions. In C_{70} derivatives, C_4F_8 groups are located in *ortho* or *para* positions on the fullerene cage. Relations between isomers with different number of attached groups are discussed in terms of possible formation pathways.

- [1] A. Hirsch, M. Brettreich, *Fullerenes: Chemistry and Reactions*, Wiley-VCH, Weinheim, p. 423 (2005).
- [2] A. Pimenova, A. Kozlov, A. Goryunkov, V. Markov, P. Khavrel, S. Avdoshenko, I. Ioffe, S. Sakharov, S. Troyanov, L. Sidorov, *Chem. Commun.*, 374 (2007).
- [3] A.S. Pimenova, L.N. Sidorov, E. Kemnitz, S.I. Troyanov. *Eur. J. Org. Chem.*, 4999 (2007).

Synthesis, structure and properties of allyl esters of methanofullerenes

Gubskaya V.P., Fazleeva G.M., Balandina A.A., Latypov S.K., Gubaidullin A.T., Saifina A.F., Nuretdinov I.A.

Arbuzov Institute of Organic and Physical Chemistry, KSC RAS, 420088 Kazan, Russia

Methanofullerenes are a subject of research of many scientists as they allow to receive practically useful substances and materials. Among them there are –components of solar cells and light-emitting devices and also biologically active substances.

We have received new allylic ethers of malonic and phosphonic acids and on their basis appropriate methanofullerenes. These compounds are interesting to obtain new polymeric materials and study of chemical transformations derivative of fullerenes. We have received and characterized appropriate new mono-, bis-, tris-, and hexa-adduct of methanofullerenes. The structure of the received substances is proved by spectral methods and by the x-ray-analysis, composition of the received products has been determined by MALDI mass-spectra and element analysis, and the purity has been checked by HPLC.

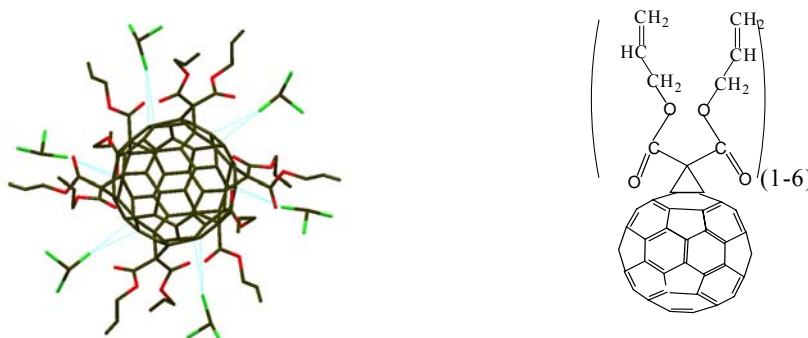


Figure. The structure of hexa-adducts of C₆₀ diallylmalonate.

In this report the NMR ¹³C results of received methanofullerenes are discussed.

The authors are grateful for support to the Programs of basic researches №27 and №18 Presidiums of RAS, RFBR (grant 08-03-01006. 09-03-00931) and Academy of sciences of Tatarstan.

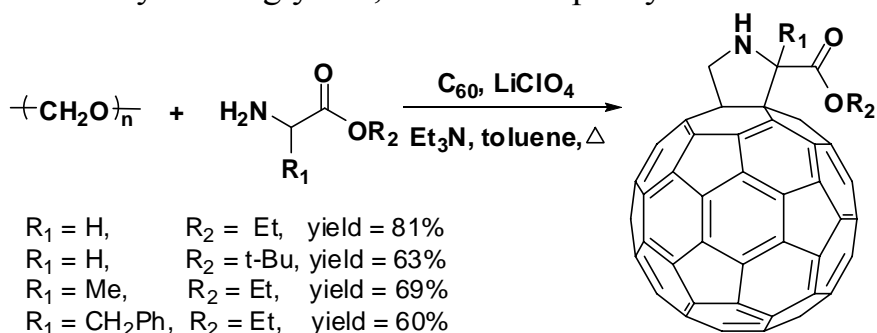
Application of metal-catalyzed 1,3-dipolar cycloaddition reactions for synthesis of substituted fulleroproline derivatives

Ioutsi V.A., Zadorin A.A., Ovchinnikova N.S., Yurovskaya M.A.

Chemistry Department, Moscow State University, 119991 Moscow, Russia

Di- or polypeptides with natural amino acid moieties fused to fullerene core attract much interest from the viewpoint of their biological activity [1]. 3,4-Fulleroproline (Fpr) provides an example of precursory compounds for peptide chain elongation on both amino and carboxylic sites.

Known method of synthesis of Fpr *tert*-buthyl ester is based on 1,3-dipolar cycloaddition reactions of azomethine ylides and C₆₀ fullerene as described in [2]. This method affords low yields of the desired ester, which is generally used in further reactions (including peptide synthesis) without isolation. Here we report an alternative method of synthesis of Fpr esters based on metal-catalyzed 1,3-dipolar cycloaddition reactions. Following this novel approach several substituted and unsubstituted Fpr esters have been obtained in rather high yields by means of lithium catalyzed cycloaddition of azomethine ylides generated from paraformaldehyde and glycine, alanine and phenylalanine esters.



A similar approach has been also applied to the synthesis of N-substituted fulleroprolines from N-methylglycine ester. It was found that lithium perchloride can be used as a catalyst in cycloaddition reactions of N-substituted azomethine ylides to fullerene C₆₀.

- [1] T. Da Ros and M. Prato, *Chem. Commun.*, 663 (1999).
 [2] A. Bianco, M. Maggini, G. Scorrano, C. Toniolo, G. Marconi, C. Villani, and M. Prato, *J. Am. Chem. Soc.* **118**, 4072 (1996).

Fractionation of fullerene containing copolymers

Yumagulova R.Kh., Medvedeva N.A., Kolesov S.V.

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia

The effect of fullerene C₆₀ on the formation of macromolecules for copolymerization of styrene with diallyl isophthalate (DAIP) has been studied. To achieve this purpose fractionation of the obtained products has been performed. All the copolymers under study are enriched by styrene (78-96%). In contrast to the fractions of copolymers obtained in the absence of fullerene C₆₀, the amount of DAIP in fullerene containing samples increases significantly. It must be noted for comparison that fullerene C₆₀ has exerts quite a different effect on the composition of copolymer made up of two vinyl monomers - styrene and methyl methacrylate (MMA). In this case a difference in the distribution of comonomers in various fractions has been observed.

Fullerene C₆₀ has a general effect on the formation of molecular characteristics of the non-fractionated samples of all the examined copolymers. This is due to the fact that in polymerization systems fullerene participates in the termination of the propagating chains. According to this finding it may be suggested that fullerene C₆₀ is mainly spend during the initial stages of polymerization and must be largely found in low molecular fractions of polymers.

However, its greater amount is found in high molecular fractions. Moreover, fullerene C₆₀ is found in all fractions of copolymers of styrene with DAIP including the deep stages of this process.

It should be noted that linear ratio between the amount of the bound fullerene C₆₀ and the quantity of allyl chains is observed. The level of fullerene C₆₀ is found to be constant in copolymers of styrene with MMA.

This indicates that there is certain difference in the mechanism of fullerene incorporation into polymer chains during copolymerization of styrene with vinyl and allyl monomers, and in the latter case this demonstrates that the presence of allyl monomers plays a decisive role in the chemical binding of fullerene. The possible way for fullerene incorporation into the chain is functionalization of allyl monomers or allyl chains of macromolecules which occurs under the conditions of radical polymerization parallel with the propagation of linear chains.

The work was supported by the Russian Foundation for Basic Research (project no. 07-03-00272-a).

Electronic structure and stability of C₈₀ fullerene IPR-isomers

Khamatgalimov A.R., Mukhametshafikova L.R., Kovalenko V.I.

Arbuzov Institute of Organic and Physical Chemistry RAS, 420088 Kazan, Russia

Only two isomers 1 (D_{5d}) and 2 (D₂) of seven IPR-isomers of fullerene C₈₀ have been produced and characterized as empty molecules. A third representative of the family, the isomer 5 (C_{2v}), was identified as its exohedral derivative C₈₀(CF₃)₁₂ [1]. Isomers 6 (D_{5h}), 7 (I_h) and presumably 1 (D_{5d}) exist as endohedral metallofullerenes [2].

Here the analysis of energy and geometrical parameters of molecules of seven C₈₀ fullerene IPR-isomers has been carried out by us on the basis of DFT calculations and earlier developed criteria [3].

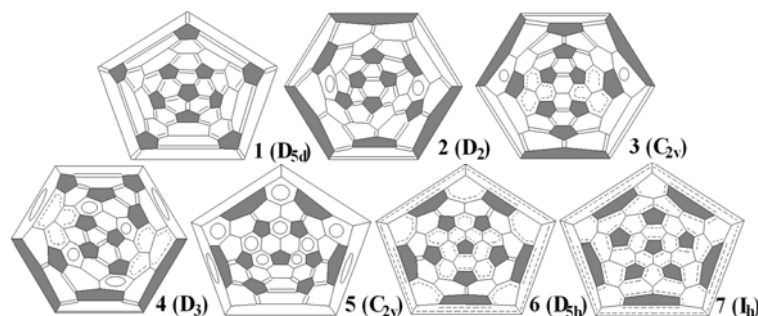


Figure 1. Schlegel diagrams of C₈₀ IPR-isomers

The distribution of single, double and delocalized pi-bonds in molecules of these isomers are shown (Fig.1). The reason of instability of "empty" isomers 3-7 is presence of various radical substructures like phenalenyl-radical whereas isomers 1-2 with the closed electronic shell are stable. Thus production of isomers 3-7 seems to be impossible as an "empty" molecules.

The distortions of hexagons and pentagons are most significant geometrical parameter directly connected with thermodynamic instability of closed electronic shell fullerenes and reflecting local strain of a molecule [4]. Analysis of geometry structures allows saying that the instability of isomers 3-7 are connected only with their radical nature.

This work was supported by the Grant of President of Russian Federation.

- [1] N.B. Shustova et al. *J. Am. Chem. Soc.* **128**, 15793 (2006).
- [2] S. Yang, L. Dunsch. *Chem. Eur. J.* **12**, 413 (2006).
- [3] V.I. Kovalenko, M.V. Semyashova. Abstr.4thWorkshop «Fullerenes and Atomic clusters» (IWFAC'99), St.Petersburg, 234 (1999).
- [4] A.R. Khamatgalimov, A.V. Luzhetskii, V.I. Kovalenko. *Int. J. Quant. Chem.* **108** (8), 1334 (2008).

Synthesis by *Prato* reaction and *in situ* UV-characterization of several fulleropyrrolidine derivatives

Jiménez Gómez M.A., Kharissova O.V.,* Kharisov B.I.,
Ortiz Méndez U.

CIIDIT, Universidad Autónoma de Nuevo León, Pedro de Alba s/n, Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, México, C.P. 66450.

1-methyl-2-phenylfulleropyrrolidine (**1**), 1-methyl-2-(4-(1-piperidyl)-phenyl)-fulleropyrrolidine (**2**), 1-methyl-2-(4-fluorophenyl)-fulleropyrrolidine (**3**) and 1-methyl-2-(3-hydroxy-2-naphtyl)-3,4-fulleropyrrolidine (**4**) were synthesized by *Prato* reaction and characterized *in situ* in the reaction mixture by UV-vis spectroscopy, high performance liquid chromatography (HPLC) and matrix assisted laser desorption ionization (MALDI). A comparison of theoretical and experimental UV spectra was carried out.

Keywords: Fulleropyrrolidine derivatives, HPLC, mass spectroscopy, UV spectra.

- [1] B.I. Kharisov, O.V. Kharissova, M.J. Jiménez Gomez, U. Ortiz Mendez. *Ind. Eng. Chem. Res.* **48**(2), 545 (2009).

Synthesis and properties of monometallic and bimetallic silver and gold nanoparticles

Guerrero-Dib X.E.¹, Ortiz-Méndez U.¹, Ferrer D.², Sepúlveda S.², Jose-Yacamán M.², Kharissova O.V.^{1*}

¹CIIDIT, Universidad Autónoma de Nuevo León, Av. Universidad s/n. Ciudad Universitaria, San Nicolás de los Garza, Nuevo León, C.P. 66451, Mexico

²University of Texas at San Antonio, USA.

Au, Ag monometallic, and Au-Ag bimetallic nanoparticles have been synthesized by two different methods, the first one was the polyol method and stabilized with poly(vinylpyrrolidone) (PVP), modifying the temperature of synthesis. Interesting structure changes were observed in the nanoparticles as the temperature was varied. The second method consisted of successive reduction of metal salts with ascorbic acid on pre-made seeds in the presence of a cationic surfactant, cetyltrimethylammonium bromide (CTAB).

In the first method at low temperatures no bimetallic nanoparticles were detected, but as the temperature increased bimetallic nanoparticles started to appear, commonly obtaining core-shell nanoparticles, always covered by the polymer. This originates the modification of the optical response of the system in the UV-visible region. An absorption peak centered at 520 nm at low temperatures was observed (100-110°C); at higher temperatures (130-170°C) there were non detectable absorption peaks, and finally at the two highest temperatures (180-190°C) the reappearance of an absorption feature centered at 510 nm was noticed. These UV-visible results indirectly imply the composition of the surface of the particle. The structure of the particles has been determined using transmission electron microscopy and high-angle annular dark field (HAADF), the latter being a powerful technique to determine the structural composition of the particles and allowing a direct correlation of the optical response with their structural composition. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) studies were also performed on the samples and their results support the idea of a Au-core-Ag-shell structure with the elements segregated from each other. The combination of these experimental techniques with calculated UV-vis absorption spectra allowed, in a reliable way, the elucidation of the nanoparticles structure and elemental distribution.

In the second method the coverage of the seeds is extremely uniform, although in some cases deviations from a spherical shape are observed with the formation of nanorods or nanoprisms. The evolution of the optical properties as further metal layers are deposited is very dramatic and can be modelled using Mie theory for multilayer spheres. However, preliminary results using high-resolution STEM-XEDS elemental mapping suggest that the actual distribution of the two metals within the multilayer spheres may involve (partial) alloying of the metals.

[1] O.V. Kharissova, B.I. Kharisov. *Recent Patents on Nanotechnology*. **2**(2), 103 (2008).

[2] B.I. Kharisov, O.V. Kharissova, M. José Yacamán, U. Ortiz Mendez. *Recent Patents on Nanotechnology*. **3**, in press (2009).

^{19}F NMR studies and DFT calculations of fluorocycloalkylated fullerenes $\text{C}_{60/70}(\text{C}_2\text{F}_4)$ and $\text{C}_{60/70}(\text{C}_4\text{F}_8)$

Khavrel P.A., Gruzinskaya N.I., Pimenova A.S.,
Ioffe I.N., Troyanov S.I.

Lomonosov Moscow State University, Chemistry Department, 119991 Moscow, Russia

First perfluorinated cycloalkyladducts of fullerenes $\text{C}_{60/70}(\text{C}_2\text{F}_4)_n$ and $\text{C}_{60/70}(\text{C}_4\text{F}_8)_n$ were isolated and structurally characterized only recently [1]. This branch of fullerene chemistry is interesting not only because of its novelty but also due to thermal and chemical stability of these compounds combined with high electron-withdrawing properties, analogous to those observed in trifluoromethylfullerenes, and easy synthesis. At the same time, addition of divalent perfluorinated carbon chains provides a considerable degree of structural diversity due to their ability to attach to *ortho*-, *meta*-, and *para*-pairs of sites as well as to form larger, oligomerized cyclic addends depending on synthetic conditions.

The aim of the current work consists in structural characterisation of a set of fluorocycloalkylated fullerenes by means of combination of ^{19}F NMR spectroscopy and quantum-chemical calculations. On the basis of the ^{19}F NMR spectra patterns, ^{19}F NMR chemical shifts values and relative isomer stabilities calculated at the DFT level of theory using the PRIRODA package (PBE exchange correlation functional, TZ2P basis set) [2], structures of the two isomers of $\text{C}_{60}(\text{C}_4\text{F}_8)$ and $\text{C}_{70}(\text{C}_4\text{F}_8)$ have been proposed. Accurate analysis of ^{19}F NMR spectrum of $\text{C}_{70}(\text{C}_2\text{F}_4)$ allowed unambiguous determination of its addition pattern, which is in agreement with X-ray crystallography findings.

- [1] A.S. Pimenova, L.N. Sidorov, E. Kemnitz, and S.I. Troyanov. *Eur. J. Org. Chem.*, 4971 (2007).
[2] D.N. Laikov. *Chem. Phys. Lett.* **281**, 151 (1997).

Fullerene-dendrimers with OPV moieties

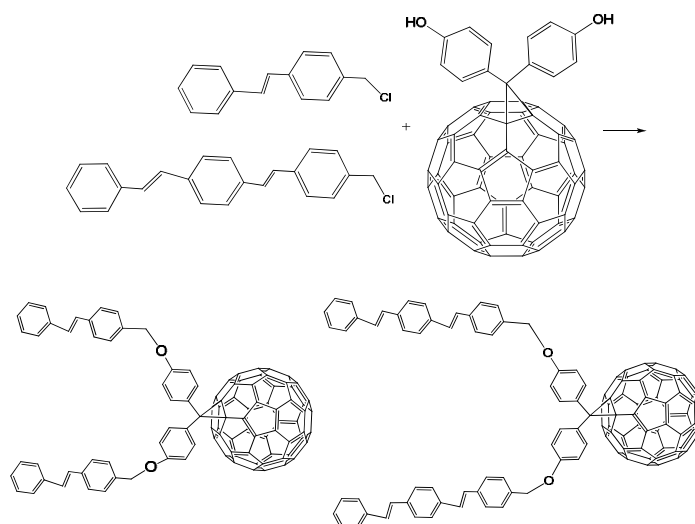
Lijanova I.^c, Klimova E.^b, Morales Espinosa E.^a,
Martínez-García M^{a*}

^aInstituto de Química, UNAM, Cd. Universitaria, Circuito Exterior, Coyoacán, C.P. 04510, México D.F. México

^bFacultad de Química, UNAM, Cd. Universitaria, Circuito Interior, Coyoacán, C.P. 04510, México D.F., México

^cInstituto Mexicano del Petróleo, Programa Ingn Mol, México City 07730, DF México, México

In the development of novel conjugated systems for optoelectronics, poly(*p*-phenylenevinylene) (PPV) and its oligomers have attracted much attention since 1990s due to their excellent electroluminescent and electroconductive properties. Control of size and structural order in π -conjugated systems is important because it enables tuning of macroscopic properties of electro-optical devices. Furthermore, if shape, dimension and size can be manipulated in a controlled fashion, these materials can presumably be used in nano-sized devices that are small, fast and can store high density information. Nanoarchitectures can be built-up through self assembly. Dendrimers are ideal building blocks for creating such structures because they have a well-defined architecture and can easily be modified with different functional core or end groups. Dendrimers with C₆₀ units in the periphery or as the central core have been reported recently. Several studies on fullerene derivatives have shown the great potential of this kind of materials for optical limiting applications. In the present work, we report the synthesis of fullerene-dendrimers with OPV moieties as dendritic branches.



The dendrimers were obtained from the OPV dendrons with 1,4-dihydroxy diphenylfullerene C₆₀. The reaction was carried out in acetone and K₂CO₃ at reflux for 3 days. The formation of the dendrimer was confirmed by ¹H, ¹³C NMR, UV-Vis, FTIR. FAB+ mass spectrometry and elemental analysis.

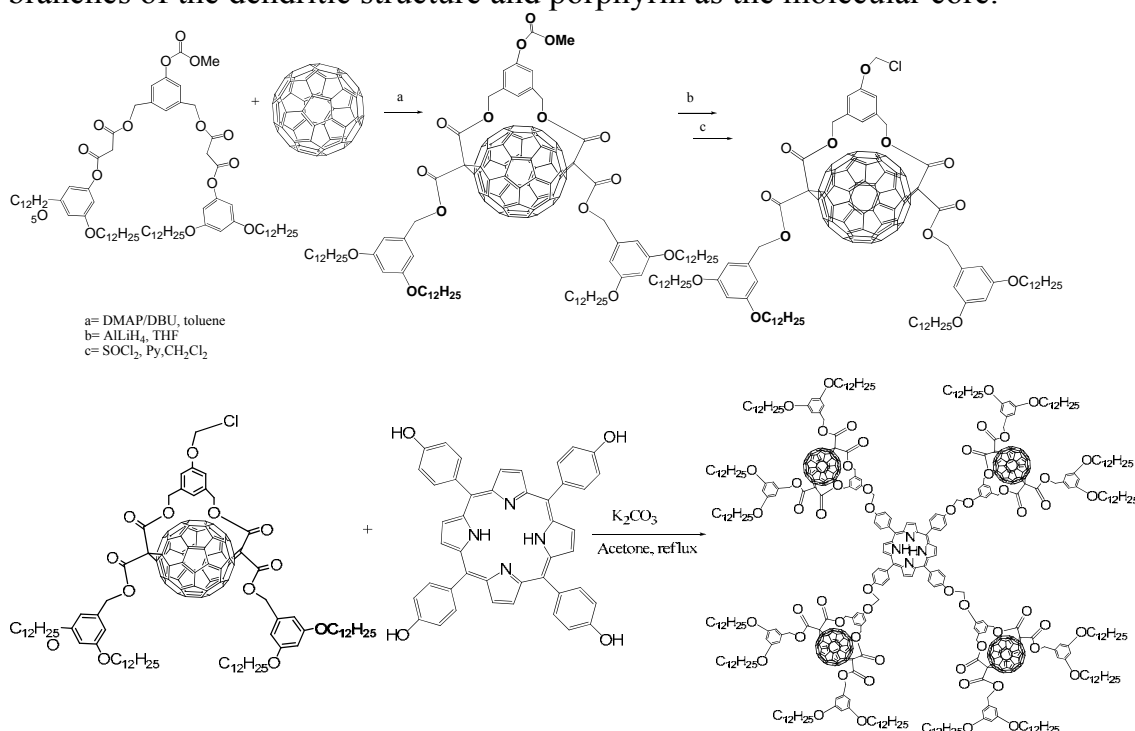
Synthesis of porphyrin dendrimers with fullerene C₆₀ units in the periphery

Sanchez-Montes K.E.^a, Klimova T.^b, Martínez-García M^{a*}

^a Instituto de Química, UNAM, Cd. Universitaria, Circuito Exterior, Coyoacán, C.P. 04510, México D.F., México

^b Facultad de Química, UNAM, Cd. Universitaria, Circuito Interior, Coyoacán, C.P. 04510, México D.F., México

Dendrimers have attracted increasing attention in the last decade due to their unique molecular structure. The synthesis of functional dendrimers is an area with unlimited possibilities for fundamental new discoveries and practical applications.¹ Among various electro- and photoactive chromophores utilized in dendrimer chemistry, C₆₀ appears to be one of the most versatile building blocks. This explains the growing interest in the development of fullerene-functionalized dendrimers, that is, fullero-dendrimers. In particular, the unusual chemical and physical properties of fullerene derivatives make fullerodendrimers attractive candidates for a variety of interesting features in supramolecular chemistry and material science. In the present work we report the synthesis of dendrimers with fullerene C₆₀ in the peripheral branches of the dendritic structure and porphyrin as the molecular core.



The dendrimer was obtained from dendrons with fullerene C₆₀ and porphyrin. The reaction was carried out in acetone and K₂CO₃ at reflux for 3 days. The formation of the dendrimer was confirmed by ¹H, ¹³C NMR, UV-Vis, FTIR. FAB⁺ mass spectrometry and elemental analysis.

[1] Newkome G.R, Moorefield C.N, Vögtle F. Dendritic molecules: concepts, syntheses, perspectives. VCH, Weinheim (1996).

Design of molecular and ionic complexes of fullerene C₆₀ with metal (II) octaethylporphyrins by using coordination M-N(ligand) and M-C(C₆₀⁻) bonds

Konarev D.V.*, Khasanov S.S.⁺, Mukhamadieva G.R.*, Lyubovskaya R.N.*

*Institute of Problems of Chemical Physics RAS, Chernogolovka, Russia

⁺Institute of Solid State Physics RAS, 142432 Chernogolovka, Russia

The formation of coordination bonds between metalloporphyrins and N-containing ligands or C₆₀⁻ was used to prepare molecular and ionic C₆₀ complexes with metal (II) octaethylporphyrins: {M^{II}OEP·DABCO}·C₆₀ (M = Zn (**1**) and Co (**2**)); {(MDABCO⁺)·M^{II}OEP}·(C₆₀⁻) (M = Zn (**3**), Co(**4**), Fe (**5**) and Mn (**6**)), (MQ⁺)·(Co^{II}OEP·C₆₀⁻) (**7**) and {(DMETEP⁺)·Zn^{II}OEP}·(C₆₀⁻)·(C₆₀)_{0.5} (**8**) (MDABCO⁺: the cation of N-methyldiazabicyclooctane; MQ⁺: N-methylquinuclidine; DMETEP⁺: the N,N'-dimethyl-N'-ethylthioethyl-piperazinium cation. Complexes **1-7** are isostructural and contain porphyrin channels accommodating zigzag fullerene chains. Complex **8** is a first example of fullerene complex containing simultaneously charged and neutral fullerene species arranged in zigzag chains and cavities formed by two (DMETEP⁺)·ZnOEP units. The coordination of DABCO, MDABCO⁺, DMETEP⁺, C₆₀ and C₆₀⁻ to M^{II}OEP was studied and their coordination abilities were compared. Only one N-containing ligand (L or L⁺) coordinates to M^{II}OEP in **1-6** forming five-coordinated L(L⁺)·M^{II}OEP species whereas fullerenes locate from the opposite side of the porphyrin macrocycle. The M...N(L or L⁺) bonds have the length of 2.18-2.39 Å. The M...C(C₆₀ or C₆₀⁻) distances are essentially longer (> 2.84 Å) and only in the case of complex with Co^{II}OEP (**4**) rather short Co...C distance of 2.51 Å is observed. C₆₀⁻ coexists with diamagnetic Zn^{II}OEP in **3** and high-spin Fe^{II}OEP and Mn^{II}OEP in **5** and **6**. The Weiss temperatures of -17.8, -42.0 and -2.5 K, respectively indicate antiferromagnetic coupling of spins in these complexes. Paramagnetic-diamagnetic transition is observed in **4** in the 250-50K range due to the formation of the coordination Co-C bond. The MQ⁺ cation is not coordinated to Co^{II}OEP in **7** assisting in the formation of stable Co-C(C₆₀⁻) bonds of 2.266(3) Å length and the diamagnetism of the complex.

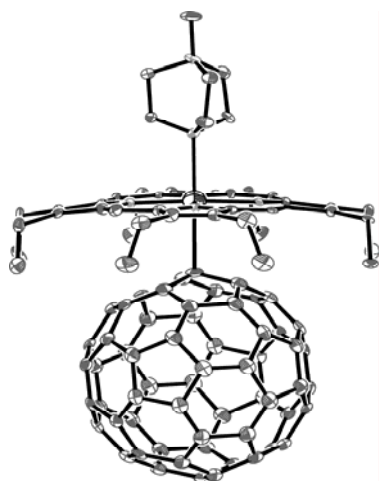


Figure 1. The {(MDABCO⁺)·Co^{II}OEP·(C₆₀⁻)} units.

- [1] [1] D.V. Konarev, S.S. Khasanov, G. Saito, and R.N. Lyubovskaya, *Cryst. Growth Des.*, **9**, 1170 (2009).