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“Design of polyfunctional structures: theory and synthesis”

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It is intended for scientific workers, teachers, post-graduate students and students specializing in the field of computational, inorganic and coordination chemistry, as well as in synthesis, characterization and computer modeling of functional materials.

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Content

Single ion magnets based on Co(II) Kramer's ion. Prospects for the development of new magnetic materials

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In the lecture, the structure and magnetic properties of single ion magnets (SIM) related to Co(II) complexes have been considered.

Particular attention has been paid to the results of experiments and theoretical modeling of hexacoordinated complexes of Co(II) with negative and positive magnetic anisotropy, which we have obtained recently [1, 2]. To analyze magnetic anisotropy of these complexes, additional experimental techniques, such as SQUID magnetometry and EPR spectroscopy have been used, as well as theoretical modeling using parametrized Griffith's Hamiltonian with parameters obtained from ab initio calculations. As follows from the analysis, magnetic anisotropy of these complexes is mainly triaxial, with different signs of axial components. Independently on the sign of the axial anisotropy, Co(II) complexes exhibit a slow paramagnetic relaxation in the constant magnetic (DC) field, i.e., belong to the class of field induced non-monoaxial single ion magnets (FI-SIMs). Such type of SIM behavior is due to Kramer's character of Co(II) ion [1, 2]. Possibility to produce new magnetic materials based on these compounds is being discussed.

The work was financially supported by the Ministry of Education and Science of Russian Federation (Agreement No. 14.W03.31.0001-Institute of Problems of Chemical Physics of RAS, Chernogolovka).

References

[1] A. V. Palii, D. V. Korchagin, E. A. Yureva, A. V. Akimov, E. Ya. Misochko, G. V. Shilov, A. D. Talantsev, R. B. Morgunov, S. M. Aldoshin, B. S. Tsukerblat, Inorg. Chem., **55**, 9696-9706 (2016).

[2] D. V. Korchagin, A. V. Palii, E. A. Yureva, A. V. Akimov, E. Ya. Misochko, G. V. Shilov, A. D. Talantsev, R. B. Morgunov, A. A. Shakin, S. M. Aldoshin, B. S. Tsukerblat, Dalton Trans., **46**, 7540-7548 (2017).

Improved cyclic performances of LiCoPO4/MOF cathode material for high-cell-potential lithium-ion batteries

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LiCoPO4/MOF composites were synthesized through a assisted Microwave-solvothermal. X-ray diffraction patterns demonstrate the phase formation of LiCoPO4. For the electrochemical measurements of LiCoPO4/HKUST composites in Li test cells. The discharge capacity of LiCoPO4/HKUST composites was 163 mAh g-1 for first cycle. The inherent stabilities studied by DFT with VASP for pure and mixed transition metal olivine phosphates of LixMPO4 (Fe,Co) and various LixCoyFe1-yPO4 compositions were evaluated as a function of the transition metal, y, and lithium content, x. In the pure compounds, LixCoPO4.

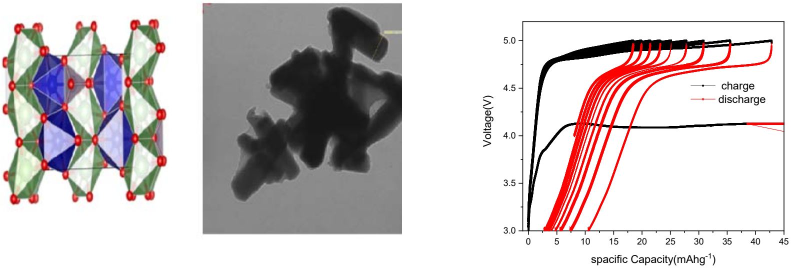

Figure: displays the structure of LiCoPo4, TEM for the compensation and electrochemistry

References

[1] W.L. Liu, J.P. Tu, Y.Q. Qiao, J.P. Zhou, S.J. Shi, X.L. Wang, C.D. Gu, J. PowerSources 196 (2011) 7728e7735

Electrically Switchable Magnetic Exchange in the Vibronic Model of Linear Mixed Valence Triferrocenium Complex

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In this report we discuss a possibility to control the magnetic properties of linear mixed valence triferrocenium complex Fe^{III}-Fe^{II}-Fe^{III} by the external electric field. It is shown that electric field of attainable strength is able to significantly increase the antiferromagnetic exchange coupling between the two terminal Fe^{III} sites.

Along with the electronic interactions such as electron transfer between the iron ions in different oxidation degrees and Coulomb repulsion between the extra holes, the proposed model of triferrocenium complex also takes into account the vibronic coupling which is an inherent ingredient of the problem of mixed valency. The last is described by the conventional Piepho- Krauzs-Shatz model adapted to the trimeric Fe^{III}-Fe^{II}-Fe^{III} complex. By introducing symmetry adapted molecular vibrations composed of the local “breathing” displacements, the three-mode vibronic problem is reduced to the two-mode problem involving interaction with even and odd molecular vibrations of the linear centrosymmetric complex.

The vibronic coupling is shown to play a decisive role in the degree of localization of the two holes among the three iron centers. This coupling is also shown to produce a pronounce effect on the electric field dependences of the hole density distributions and electrically switchable magnetic exchange in the considered triferrocenium complex. Particularly, vibronic coupling significantly influences the field induced stepwise transformation Fe^{III}-Fe^{II}-Fe^{III} ↔ Fe^{III}-Fe^{III}-Fe^{II} increasing the abruptness of the field dependences of the singlet-triplet gap and the hole densities.

Ultrasound dispersing of fullerene C60 in aqueous solutions of the surfactants mixtures

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In the processes of fullerene C60 dispersions preparation by means of ultrasonic treatment, the use of the surfactants as dispersing and stabilizing agents is promising. The main purpose of this work is the investigation of nonionic and anionic surfactants and their mixtures ability to fullerene C60 disaggregation and stabilization in aqueous solutions. We have studied the influence of nonionic (nonylphenol ethoxylates with various ethoxylating degree) and anionic (sodium dodecyl sulfate and sodium dodecylbenzene sulfonate) amphiphilic compounds and their mixtures on the colloidal properties of fullerene dispersions.

Dispersions of C60 in water and in aqueous solutions of the surfactants were obtained by ultrasonication (42 kHz, 50 W). Concentration, particle size and electrokinetic potential measurements of C60 dispersions were developed by absorbance spectroscopy, dynamic and electrophoretic light scattering.

The nature of the surfactants and ethoxylating degree were shown to influence the quality of dispersing and stabilization of colloid systems obtained. Our study revealed the connection between polar chain contraction and the dispersing activity of nonionic surfactants. Ethoxylated alkylphenol was established to be the most effective dispersing agent. Effective mixtures of the surfactants were obtained. The optimization of colloid and chemical properties of C60 dispersions was carried out.

The results of the study can be useful in the processes of fullerene C60 dispersions preparation for biochemical and biomedical studies and as modifying additives for composite materials.

The study was supported by the Russian Foundation for Basic Research,project No. 17-03-00600 a.

Field electron emission from closed carbon nanotubes

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It is noted the process of electron emission from carbon nanotubes (NT) occurs from the tip of a NT. The localization of electrons on the tips of the NT can be explained by the existence of emission molecular orbitals (EMO) forming as a result of special type of p electrons conjugation - in plane electron conjugation [1]. EMO is a prerequisite for the electron emission process. The existence of EMO in open ultra short single walled carbon nanotubes (usSWCNT) has been shown previously [2].

In this paper we calculate the electron structure of the closed usSWCNTs of chirality (n,n) for n=3-5 and (n,0) for n=5-9 in constant electric field with intensity E (from 0.0 to 1.5 V/Å). Electron structure of SWCNTs were calculated by B3LYP DFT in 6-31G basis set (Firefly package).

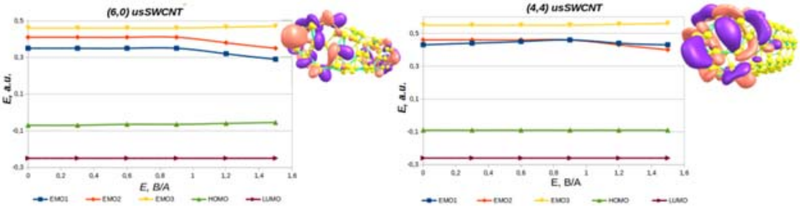

Fig. 1 Structure of EMO and Dependences of εEMO, εHOMO, εLUMO from E.

As a result we note that if the intensity of the applied field is increased, the energy of the EMO is decreased, leading to an increase in the population of emission level and therefore promotes an increase in the magnitude of the emission current, which corresponds to theoretical and experimental data.

References

[1] A.A. Fokin, J. Haijun, P.v.R. Schleyer (1998) From Dodecahedrapentaene to the “[n]Trannulenes”. A New In-Plane Aromatic Family. J. Am. Chem. Soc. 120, 9364-9365, (1998).

[2] O.B. Tomilin, E.V. Rodionova, E.A. Rodin, E.E. Muryumin (2018) FInfluence of admixture atom chemosorption on properties of p-electron conjugated system of open carbon nanotubes. NANOSYSTEMS: PHYSICS, CHEMISTRY, MATHEMATICS 9, 70-72, (2018).

Theoretical modeling of exchange coupling in the magnetic sublattice of bifunctional compounds

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For modeling of the magnetic sublattice of bifunctional compounds, quantum-chemical calculations of complexes $[(L)_2M1^{III}(L)M2^{II}(L)_2]^{5-}$ (I) have been performed ($M1^{III}$ and $M2^{II}$ are tri- and divalent atoms of 3d and 4d transition metals M_1 (Cr, Fe) and M_2 (Ni, Co, Pd), L is dithiooxamide or oxalate). We suggested that transfer from 3d to 4d transition metals is accompanied by an increase of the exchange coupling constant J between metals $M1^{III}$ and $M2^{II}$. Calculations of the complexes' geometric structure were performed by using the GAUSSIAN-03 [1] program (the B3LYP/LANL2DZ level of theory) and of J constants by using the ORCA program [2] (the B3LYP/TZV level of theory). The replacement of a divalent atom of 3d metal by a divalent atom of 4d metal leads to J increase, whereas replacement of a trivalent atom of 3d metal by a trivalent metal atom of 4d metal does not change the constant value. It has been found out that there was the correlation of J with the total change of the spin density on the M1 and M2 metals in the complex structures compared to the $M1^{3+}$ and $M2^{2+}$ isolated cations.

References

[1] Licence to Use Agreement: Gaussian, Inc., 340 Quinnipiac Street, Building 40, Wallingford, CT 6492.

[2]F. Neese, ORCA-An ab initio, DFT, and Semiempirical Program Package 2.7–00, Universität Bonn, Bonn, 2009.

A comparative study of the Cr_2O_n and $Cr_2O_n^-$ series, n =1−14

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The object of research is new complexes of chromium oxides. The aim of the work was to determine the criteria of stability of these complexes, conditions of their presence, ferromagnetic or antiferromagnetic properties. To answer these questions the geometrical and electronic structures of the Cr_2O_n and $Cr_2O_n^-$ clusters are computed using density functional theory with a generalized gradient approximation in the range of $1 \leq n \leq 14$ [1]. Local total spin magnetic moments, polarizabilities, binding energies per atom, and energies of abstraction of O and O_2 are computed for both series along with electron affinities of the neutrals and vertical detachment energies of the anions. In the lowest total energies states of Cr_2O_2, Cr_2O_3, Cr_2O_4, Cr_2O_{14}, $Cr_2O_3^-$, $Cr_2O_4^-$, and $Cr_2O_{14}^-$, total spin magnetic moments of the Cr atoms are quite large and antiferromagnetically coupled. In the rest of the series, at least one of the Cr atoms has no spin-magnetic moment at all. The computed vertical electron-detachment energies of the $Cr_2O_n^-$ are in good agreement with experimental values obtained in the $1 \leq n \leq 7$ range. All neutral Cr_2O_n possess electron affinities larger than the electron affinities of halogen atoms when $n > 6$ and are thus superhalogens. It is found that the neutrals and anions are stable with respect to the abstraction of an O atom in the whole range of n considered, whereas both neutrals and anions became unstable toward the loss of O_2 for $n > 7$.

References

[1] G.L. Gutsev, K.V. Bozhenko, L.G. Gutsev, A.N. Utenyshev, and S.M. Aldoshin. Transitions from Stable to Metastable States in the Cr2On and Cr2On− Series, n =1−14 J. Phys. Chem. A, 2017, 121, 845−854. doi: 10.1021/acs.jpca.6b11036.

Effect of Zn2+ replacement with Co2+ in ZIF-8 structure on success of iodine capping

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Nuclear power plant accidents and nuclear weapon tests lead to the contamination of the environment by two radioactive iodine isotopes – ^{131}I and ^{129}I. Both Iodine isotopes are absorbed by the body and preferentially concentrated in the thyroid. As radionuclides decay, it may cause diseases associated with prolonged irradiation of the body from within, like thyroid cancer [1, 2].In this point of view, iodine capping is of paramount importance.ZIF-8 is one of the best candidates for iodine sorption as it demonstrates both high iodine uptake and high temperature of iodine release [3]. ZIF-8 framework strongly binds iodine molecules, while I_2 located on the surface of ZIF-8 are restrained by traditional iodine−organic complexes. In the present work we have investigated effects of metal sites composition on the iodine sorption properties. For this aim, we have replaced zinc ions in ZIF-8 structure with cobalt ions. So, we tested for iodine sorption two mono-metal ZIFs – ZIF-8 and ZIF-67 and for the first time tree bimetallic ZIFs, containing both metal in the structure in various ratio. This allowed us to observe important trends caused by metal sites composition.

Authors acknowledge RFBR (research project No 18-33-00584) for financial support.

References

[1] Z. Jaworowski, Dose-Response, 8 (2010) 148-171.
[2] V.S. Kazakov, E.P. Demidchik, L.N. Astakhova, Nature, 359 (1992) 21-21.
[3] D.F. Sava, M.A. Rodriguez, K.W. Chapman, P.J. Chupas, J.A. Greathouse, P.S. Crozier, T.M. Nenoff, J. Am. Chem. Soc., 133 (2011) 12398-12401.

Defects in MOFs: new way to tune properties

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Metal–organic frameworks (MOFs)[1]are a new class ofporous materials with high specific surface area attracting attention dueto their numerous potential applications [2, 3].MOFs have module structure – the framework is constructed from two parts. Inorganic parts – metals and metal clusters – connected to each other with organic molecules – linkers. Due to the complex structure real MOFs always have some distinctions from ideal framework – defects. The control of the defect chemistry in MOFshas been investigated to achieve betterperformances in many applications. This approach has beennamed"defect engineering" as a shorthand for the ability tomanipulate defects by a synthetic and controlled way. Manyauthors have recently shown with their works severalfascinating ways to achieve this kind of defect control[4-6]. The research was supported by Mega-Grant of Ministry of education and Science of Russian Federation (14.Y26.31.0001).

References

[1] H. Furukawa, K.E. Cordova, et al. Science, 341 (2013) 974.

[2] J.R. Li, R.J. Kuppler, H.C. Zhou, Chem. Soc. Rev., 38 (2009) 1477-1504.

[3] L.J. Murray, M. Dinca, J.R. Long, Chem. Soc. Rev., 38 (2009) 1294-1314.

[4] Z.L. Fang, B. Bueken, D.E. De Vos, R.A. Fischer, Angew. Chem.-Int. Edit., 54 (2015) 7234-7254.

[5] G.C. Shearer, S. Chavan et al. Chem. Mat., 26 (2014) 4068-4071.

[6] C. Atzori, G.C. Shearer et al., The Journal of Physical Chemistry C, 121 (2017) 9312–9324.

Gold nanoparticles in porous materials

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This contribution summarizes our studies on growth and characterization of gold nanoparticles immobilized on surface of different porous solids. The supporting materials are selected as representatives for amorphous inorganic and crystalline inorganic types. Such selection allows to form a common ground for a comparative analysis of different properties of the resulting nanocomposites.

We will start considering incorporation of gold into the mesoporous silica glass, produced by a sol-gel method. The resulting composite has the same optical profile as colloidal gold solution, but it is stable over time and particle surface is accessible for gas probes [1]. Such properties are relevant for sensing applications like optical gas sensing and detection of ultra-small quantities of molecules by SERS.

The second group comprises zeolites, where gold nanoparticles were formed by chemical or thermal reduction. The process of thermally-induced formation of gold nanoparticles in Zeolite Y was monitored with High-Resolution X-Ray diffraction at ESRF (Grenoble). This has been done with purpose to study how change in size influences catalytic activity of small gold nanoparticles in a model reaction of CO oxidation.

All obtained materials were characterized with a set of laboratory techniques, including XRD, TEM, BET, UV-Vis, FTIR and some others. This work has been done with support of Mega-grant (N 14.Y26.31.0001).

References

[1] A. Budnyk, S. Cherkasova, A. Damin (2017). One-pot sol-gel synthesis of porous silica glass with gold nanoparticles. Mendeleev Commun., 27, 531-534 (2017).

Time-resolved operando study of palladium nanocatalyst

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Formation of hydride and carbide phases in the bulk and at the surface of the palladium nanoparticles is a critical process that governs catalytic activity and selectivity in hydrogenation reactions. We present the time-resolved operando X-ray absorption spectroscopy study of the industrial palladium catalysts consisted of 2.6 nm palladium nanoparticles supported on carbon. By applying modulation excitation approach switching between pure hydrogen and ethylene gas feeds, we demonstrate formation of three different phases: reversible palladium hydride, reversible surface palladium carbide and irreversible bulk palladium carbide. The relative fraction of the three phases is temperature dependent, with favorable formation of bulk carbide at high temperatures. At the same time, ethane formation was detected, explained by hydrogenation of the surface adsorbed ethylene in the case of ethylene-to-hydrogen switch, and hydrogenation of ethylene by the hydrogen accumulated in palladium in the case of hydrogen-to-ethylene switch.

References

[1] Bugaev, A. L., A. A. Guda, A. Lazzarini, K. A. Lomachenko, E. Groppo, R. Pellegrini, A. Piovano, H. Emerich, A. V. Soldatov, L. A. Bugaev, V. P. Dmitriev, J. A. van Bokhoven and C. Lamberti (2017). "In situ formation of hydrides and carbides in palladium catalyst: When XANES is better than EXAFS and XRD." Catalysis Today**283**: 119-126.

[2] Bugaev, A. L., A. A. Guda, K. A. Lomachenko, V. V. Shapovalov, A. Lazzarini, J. G. Vitillo, L. A. Bugaev, E. Groppo, R. Pellegrini, A. V. Soldatov, J. A. van Bokhoven and C. Lamberti (2017). "Core–Shell Structure of Palladium Hydride Nanoparticles Revealed by Combined X-ray Absorption Spectroscopy and X-ray Diffraction." The Journal of Physical Chemistry C**121**(33): 18202-18213

Computational study of bimetallic magnetically-active complexes bearing functionalized catecholate ligands

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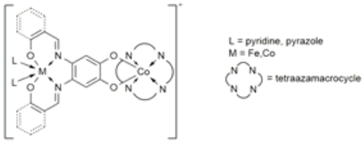
The possibility of controlling magnetic properties of coordination compounds under the action of external stimuli makes them suitable objects for the structural design of dynamic materials for the needs of molecular electronics and spintronics. Spin-crossover and valence tautomerism (or redox-isomerism) represent the most efficient mechanisms driving the changes of spin states of transition metal complexes. The spin-crossover phenomenon caused by the electronic rearrangement within a metal ion between its low-spin and high-spin states is mainly studied in the case of iron complexes with N6 or N4O2 environment, but it also occurs in cobalt systems. On the other hand, valence tautomerism – an intramolecular process consisting in reversible electron transfer between a metal ion and a redox-active ligand – has been most thoroughly studied in the case of cobalt complexes with o-quinones.

In the search for the ligands with the structure suitable for the formation of the transition metal complexes potentially prone to switching their spin states through SCO and also VT rearrangements combining in their molecules both redox- active and N-donor centers, we turned our attention to functionalized catechols. In present work we performed a DFT theoretical modeling and attempts to synthesis of binuclear Co-Fe systems bearing functionalized polydentane ligands.



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Computer modelling of electronic and optical properties of Cu-doped SiO_2 glass

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This study is devoted to the computer modeling of optical and electronic properties of composites containing copper complexes distributed across the volume of a porous silica glass. To understand the structure of copper sites on silica glass, several models have been constructed. These models consider the position of copper with respect to the SiO_4^{4-} tetrahedra. Quantum chemical calculations were carried out in the Gaussian 09 program [1] by using DFT. The stability of the wave function was checked for each calculated model, and the vibration frequencies and optical transitions were calculated. To simulate the optical spectra time-dependent DFT calculations were carried out. The theoretical results were compared with the experimental UV-Vis spectra (Fig.1). Obtained results play an important role in understanding of the samples structure and the possibility of their practical application. Moreover, it was found that even four SiO_4^{4-} tetrahedra are sufficient to describe the experimental spectrum.

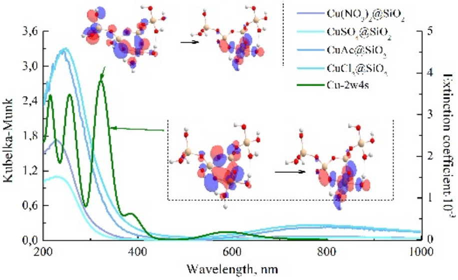

Fig.1 Experimental spectra (blue) and the theoretical one (green) of Cu-SiO2

References

[1] M.J. Frisch *et al*. (2009). Gaussian 09, Revision A.02 Gaussian, Inc., Wallingford CT, (2009).

Effect of thermal treatment on the atomic structure of plasmonic Au nanoparticles in glass matryx by EXAFS spectroscopy.

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Plasmonic nanoparticles make it possible to localize the electromagnetic field at scales smaller than the optical wavelength. This property is useful for the application of same objects for the creation of nanodetectors, in the processes of energy conversion and storage, in the tasks of data processing and transmission. In particular, the creation of computer chips with plasmonic elements instead of traditional semiconductors will increase their performance and energy efficiency. Our main purpose is obtaining implanted in the matrix of glass the arrays of plasmonic nanoparticles with controlled optical properties [1, 2]. Their properties can be varied by changing the conditions of their synthesis and post-processing. One of the proposed methods is long-term heating at 300 ℃ of already synthesized samples. This research presents the study results of the effect of temperature treatment on the atomic structure of nanoparticles. This is necessary for studying of their optical properties and searching for the optimal synthesis method.

Research performed by support of grant RFFR 18-32-00818 mol_a «Effect of component consist and architecture of bimetallic nanoparticles AuAg of their optical properties»

References

[1] M. Dubiel, M. Heinz, et al., Generation and characterization of plasmonic nanostructures in glass surfaces by means of excimer and solid state laser irradiation, International Society for Optics and Photonics, Volume 9163, August 2014, p. 91631M

[2] Y.-H. Su, W.-L. Wang, Surface plasmon resonance of Au-Cu bimetallic nanoparticles predicted by a quasi-chemical model, Nanoscale Research Letters, 2013, Volume: 8, Issue: 1, p. 408

Unidirectional migration of a bromine atom over the five-membered ring under application of the rotating electric field

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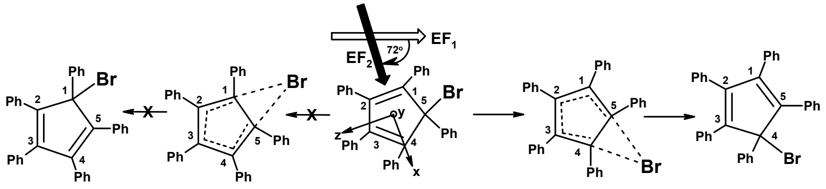
Fluxional cyclopentadienes prone to circumambulation of organic and organometallic groups along the perimeters of the cyclopentadiene ring may be considered as molecular prototypes of gear rotary motors. To impart the cyclopentadiene systems with the properties of a molecular motor it is necessary to ensure the conditions for unidirectional migration of the functional group 1. We have shown by means of dynamic 1H NMR and 13C methods that in 5-bromo-1,2,3,4,5-pentaphenylcyclopentadiene 1 sigmatropic shifts of a bromine atom along the perimeter of the five-membered ring occur fast with the energy barrier $\Delta G{\neq}298$ 17.0 kcal/mol. The DFT, B3LYP/Gen, 6-311++G(d,p)/SDD calculations of the reaction paths of circumambulatory rearrangement of 5-bromo-1,2,3,4,5-pentaphenylcyclopentadiene showed that under application of the rotating electric field the molecule behaves as a rotor type molecular motor with unidirectional motion of bromine atom along the perimeter of the five-membered ring ($\Delta G{\neq}298$ 7.4 kcal/mol).



1e **TS2** **1a** **TS1** **1b**

This work was financed by the Russian Government grant to support scientific research under the supervision of the leading scientist (Megagrant no. 14.Y26.31.0016).

References

[1] G.A. Dushenko,I.E. Mikhailov, O.I. Mikhailova, R.M. Minyaev, V.I. Minkin. Mendeleev Communications, vol. **25**,p.21-23 (2015).

Modeling of charging ordering in cuprate superconductors and its influence on the spectrum of delocalized charge carriers

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Charge ordering in cuprate superconductors is considered in two cases: in the case of only electronic bipolarons and in the case of coexistence of both electron and hole bipolarons. It is shown that the most favorable placement of bipolarons is the placement of a "checkerboard". The results are consistent with the experiment. The aim of the future work is to attempt to explain the appearance of a "pseudogap" in the spectrum of delocalized carriers in doped cuprates by taking into account their interaction with an additional periodic potential due to bipolarons.

References

[1] E. de Silva Neto et al. Charge ordering in the electron-doped superconductor Nd2-xCexCuO4. Science. 347, 282 (2015).

[2] J. Graf et al., Phys. Rev. Lett. 98, 067004 (2007).

Elaboration of original synthetic approaches to formation of 3d-4f heterometallic carboxylate coordination compounds

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Search for new and original synthetic approaches for simple preparation of heterometallic coordination compounds is one of the most interesting tasks of the modern coordination chemistry. Complexes, containing two and more metals of different electronic structure are especially interesting because they can be directly used for creation of new functional materials with unique magnetic, luminescence, and/or catalytic properties, as well as they are considered as promising stoichiometric precursors for the preparation of heterometallic compounds by thermal decomposition.

In the report a wide series of tri- and tetranuclear 3d-4f-complexes based on various carboxylate anions and N-donor ancillary ligands were synthesized and structurally characterized. Capabilities of the several synthetic routes for obtaining such type compounds were evaluated. The correlation of molecular and crystal structures, luminescence [1, 2] and SMM properties of obtained heterometallic complexes are analyzed in detail.

This work was financially supported by the Russian Science Foundation (projects 14-23-00176 and 16-13-10537).

References

[1] A. Goldberg, M. Kiskin, O. Shalygina et al., *Chem. Asian J.***2016**.V.11.P.604–612.

[2] S. Kiraev, S. Nikolaevskii, M. Kiskin et al., *Inorg. Chim. Acta*.**2018**. V.477. P.15–23.

Modified triangulenes: a DFT study

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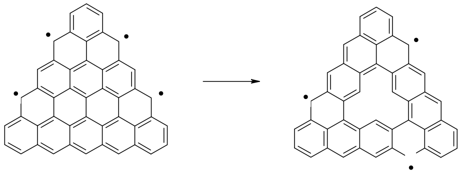
Triangulenes are alternant non-Kekulé hydrocarbons with high spin depending of the molecular size (structure 1). They are also could be described as triangular graphene-like flakes. Whereas carbon triangulenes are fairly well studied, their main group element analogues received much less attention. Various triangulene compositions of the group 14 elements were studied recently.1 The next modification of the triangulenes is holes in the skeleton2 and it is demonstrated at structure 2 with new spin value S.

In this work we present DFT calculations on structures and properties of a series of group 14 element (C, Si, Ge) triangulenes 2.



1 (S=2) 2 (S=3/2)

Figure 1. Modification of triangulenes.

Acknowledgements. This work was supported by the Russian Government grant (Megagrant no. 14.Y26.31.0016).

References

[1] O. A. Gapurenko, A. G. Starikov, R. M. Minyaev, V. I. Minkin (2015). Germanium, carbon-germanium and silicon-germanium triangulenes.J. Compt. Chem., 36, 2193-2199 (2015).

[2] Y. Morita, S. Suzuki, K. Sato, T. Takui (2011). Synthetic organic spin chemistry for structurally well-defined open-shell graphene fragments. Nat. Chem., 3, 197-204 (2011).

The dynamic light scattering as a cross-method for carbon nanotubes characterization in dispersions

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Computational methods for the characterization of cylindrical particles in dispersions are presented in [1] and [2] on the basis of average hydrodynamic size data. They can be usefull for determining the geometric parameters of carbon nanotubes (CNT). The purpose was to evaluate the applicability of computational methods on the basis of average hydrodynamic size data for characterizing the geometric parameters of multiwalled CNTs in dispersions.

Dispersions of CNTs in water and in aqueous solutions of the surfactants were obtained by ultrasonication. The resulting dispersion samples were examined by dynamic light scattering (DLS) and scanning electron microscopy (SEM).

It was shown that the values of CNT lengths calculated on the basis of average hydrodynamic size (AHS) data are 2 or more times shorter than it was obtained by SEM. It can be explained by the curvature of CNTs in the dispersion. AHS and polydispersity index (PdI) of the CNT dispersions were found to decrease with increasing the surfactant concentration. Constant minimum values of AHS and PdI indicates the limiting degree of dispersing of CNTs in the system. It follows that DLS method can be used as an express method for estimating the quality of CNT dispersion in liquid media from the values of AHS and PdI if the exact values of the average diameter and length of CNTs are known by other methods.

The study was supported by the Russian Foundation for Basic Research,project No. 17-03-00600 a.

References

[1] N. Nair, W. Kim, R.D. Braatz, M.S. Strano. Dynamics of surfactant-suspended single-walled carbon nanotubes in a centrifugal field. Langmuir, 24, 5, 1790-1795 (2008).

[2] R. Xu. Particle characterization: light scattering methods. Kluwer Acad. Publ., 403 p. (2002).

Molecular dynamics study of a new metastable allotropic crystalline form of gallium – supertetrahedral gallium

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A new metastable crystalline form of gallium has been computationally designed using density functional calculations with imposing periodic boundary conditions. The geometric and electronic structures of the predicted new allotrope were calculated on the basis of a diamond lattice in which all carbon atoms are replaced by gallium Ga_4 tetrahedra. This form does not have any imaginary phonons, thus it is a metastable crystalline form of gallium. The calculated density of the supertetrahedral gallium is equal to 1.74 g/cm^3, which is considerably lower than that of the usual structure of gallium 5.9 g/cm^3. The bulk, shear, and Young's moduli of polycrystalline supertetrahedral gallium are 11.05, 2.95 and 8.12 GPa, respectively, and its Poisson's ratio is 0.3776. Energy band gap is absent, i.e., supertetrahedral gallium is a good electric conductor. The minimum optical absorption is observed at 535 nm (2.32 eV) in the green region of the spectrum. Molecular dynamics simulations show that this form of gallium will melt at about 273 K with a sharp increase in temperature in the system during the melting process from 273 K to 1800 K. This melting process is very different from conventional melting, where temperature stays the same until complete melting. That unusual melting can be explained by the fact that supertetrahedral gallium is a metastable structure that has an excess of strain energy released during melting. If made this new material may find many useful applications as a new low density metal with stored internal energy.

Acknowledgements

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Theoretical study of physical adsorption of the $C_{60}F_{18}$ polar molecules on different surfaces

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For adequate description of the adsorption and self-assembly of $C_{60}F_{18}$ polar molecules on the Au(111) surface, quantum-chemical studies of the electronic and electrical properties of a single molecule are performed. Using various procedures of density functional theory [1], the electric dipole moment of the molecule, distributions of the electrostatic potential, electric field magnitude and electron density are calculated with controlled accuracy for the first time. An improved accuracy of the electric dipole moment value of the $C_{60}F_{18}$ molecule is obtained. The known approximation of a point dipole for electric field strength is shown to be fulfilled within an accuracy of 30% even at distances twice greater than the lateral size of the molecule. The structural fragments of the calculated lowest unoccupied and highest occupied molecular orbitals are assigned to their experimental images previously obtained using scanning tunneling microscopy and spectroscopy.

Quantum-chemical calculations of $C_{60}F_{18}$ molecule on highly oriented pyrolytic graphite (HOPG) substrate are performed using cluster model and various methods. Based on the results on scanning of a potential energy surface, a theoretical modelling using MP2 method indicated that a physical adsorption of a $C_{60}F_{18}$ molecule on HOPG takes place. The absence of the chemical adsorption of $C_{60}F_{18}$ on HOPG was also shown using the molecular orbital theory.

The information about the electronic and electrical properties of a single molecule opens the way to the better understanding of the adsorption of molecular ensembles on various surfaces.

References

[1] Kohn W., Sham L.J. Self-consistent equations including exchange and correlation effects. Phys. Rev. A. 1965. V. 140. №4.P. A1133-A1138.

Coordination compounds with non-symmetrical tetrapyrrolic ligands as basis for novel hybrid functional materials

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The elaboration of original synthetic approaches towards low-symmetry tetrapyrrolic ligands and their metal complexes, including sandwich compounds are of great interest for the design of novel hybrid organic-inorganic systems, which reveal prominent optical, catalytic and sensor properties.

The introduction of special functional groups into such molecules allows their further grafting on the surface of various nanomaterials: metal oxides, metal nanoparticles, quantum dots, carbon nanomaterials, as well as provides new coordination compounds with unique optical and physicochemical properties.

In the present talk the achievements in the field of design and synthesis of low-symmetry porphyrinoids and their coordination compounds will be discussed. The special attention will be paid for optical properties of such molecules and hybrid materials on their basis. The obtained results contribute to the development of novel optical materials for future nanoelectronic and optical device applications.

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Stabilization of non-standard planar configurations of cyclooctatetraene and cyclodecapentaene by metalcarbonyl annelation

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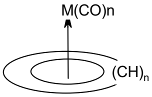
The effectiveness of the stabilization of anti-aromatic cycles by π-interaction with metalcarbonyl substituents is well known. For instance, the interaction of the $Fe(CO)_3$ group with the anti-aromatic cyclobutadiene fragment stabilizes the square configuration of the basal ring with equalized CC bond lengths **1**. At the same time, the possibility of the stabilization of non-standart planar configurations of the annulene rings using σ–localized peripheral metalcarbonyl substituents has not been studied.



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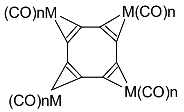

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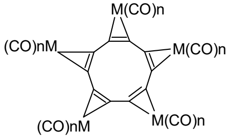

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In this work, we studied the possibility of stabilizing the cyclooctatetraene and cyclodeacapentene rings by multiple peripheral σ-interactions with metalcarbonyl substituents $Cr(CO)_5$, $Fe(CO)_4$, $Ni(CO)_3$, $Ti(CO)_4$, and $Ni(CO)_2$. The DFT-calculations performed reveal a new family of organometallic compounds **2** and **3** represented by metalcarbonyl-annelated cyclooctatetraene and cyclodecapentaene derivatives with planar core cycles. In spite of the planar structures the functionalized cyclooctatetraenes display clearly defined anti-aromatic character, whereas the cyclodecapentaene derivatives are aromatic. Stabilization of the non-standard planar forms of metalcarbonyl-annelated compounds is due to the sterically enforced flattening of central cycle and its π-interaction with the metalcarbonyl units.

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In situ characterization of ceria based nanocatalysts

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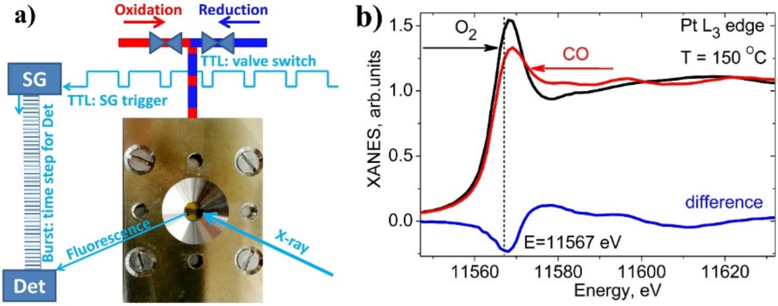
Performing a catalytic reaction, the atoms in the catalyst's active site periodically change their local coordination and often the oxidation state. Detection of intermediate species and distinguishing them from inactive spectators allows unravelling the reaction mechanisms and helps the rational design of better catalysts. This type of research requires the development of highly sensitive spectroscopic methods combined with advanced theory.



In our work we have applied time-resolved fluorescence detection scheme [1] to achieve millisecond time resolution for the CO oxidation reaction on CeO_2/Pt, CeO_2/Cu and $CeZrO_2$/Pt. Laboratory setup for in situ FTIR was developed to analyse active sites of the catalysts under study. Computer modelling was used to predict adsorption energies and frequency shifts for CO on the metal nanoparticles on ceria.

References

[1] A.A. Guda, A.L. Bugaev, R. Kopelent et.al., Journal of Synchrotron Radiation 2018 25 989-997.

Effect of ammonia exposure on carbon nanotubes growth by PECVD

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Carbon nanotubes (CNTs) have been extensively studied over the past decades, since their unique properties can be useful in various applications. Nevertheless, the industrial production of CNT for the needs of microelectronics is hampered by problems associated with controlled and reproducible fabrication of these structures directly on the substrate in a single technological process. The method of plasma-chemical deposition from the gas phase (PECVD), possessing the possibility of controlled production of CNT arrays with specified parameters directly on the substrate at relatively low temperatures, is promising for the introduction of CNTs into the microelectronic industry. However, the task is to work out the regimes for obtaining CNTs by this method, in particular the influence of the time of the action of ammonia on the process of reduction from the metal oxide of the catalytic layer. In this work, a Si (100) substrate was used to study the growth of CNTs with sputtered metal layers Cr and Ni 20 and 10 nm thick, respectively, using magnetron sputtering. Then, the influence of the time of the "activation" stage was studied, at which 210 cm3 / min of ammonia was supplied to the chamber, as well as the growth stage, in which acetylene was also fed into the chamber.

Conclusion

Experimentally revealed regularities of the time of ammonia exposure will allow to optimize the process of CNT growing by PECVD method.

The financial support was provided by Russian Foundation for Basic Research (projects № 16-29-14023 ofi_m and № 18-32-00652 mol_a).

References

[1] Qiang Zhang [et al.]. "Carbon Nanotube Mass Production: Principles and Processes". ChemSusChem, 4, pp. 864-889 (2011).

Formation of active Pd-sites in UiO-67 metal-organic frameworks

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Metal-organic frameworks (MOFs) are new promising porous materials, constructed from organic linkers and metal-oxide units. Additional useful properties can be achieved by the functionalization of MOFs, which allows obtaining new structures with specific functions.

One of the most promising MOFs is the UiO-66/67/68 family, that shows an incredible thermal and chemical stability. Also, in the case of UiO-66/67/68, functionalization has played an important role in enhancing the material potentialities, by insertion of other metals in the inorganic cornerstones and by functionalization of linkers by additional metals.

In this study, we focus on the evolution of Pd-species in the UiO-67 functionalized by palladium. Pd K-edge X-ray absorption spectroscopy (XAS), was used as the main experimental technique, because of its sensitivity to the local atomic environment around palladium atoms. Detailed analysis of extended X-ray absorption fine structure (EXAFS) spectra allowed us to track the formation of active Pd nanoparticles during the temperature programmed reduction in H2. In particular we observed almost simultaneous disappearance of Pd-Cl and Pd-N contribution with the growth of Pd-Pd one starting from around 200 °C. Around 300 °C, the Pd-Pd coordination number stabilized at NPd-Pd = 9. Further stepwise increase of Pd-Pd coordination number to NPd-Pd ≈ 12 indicated the aggregation of Pd nanoparticles to much bigger particles, with possible destruction of UiO-67 crystal structure.

A room-temperature synthesis and investigation of the gold nanoparticles synthesis on HKUST-1

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Metal–organic frameworks (MOFs) are new materials representing the next generation of porous materials characterized by a high surface area and huge variety of structures. Their crystal lattice can be described as periodical repetition of interconnected organic and inorganic units. Organic units act as linker binding the inorganic parts into a uniform framework. Inorganic cluster entities, called secondary building units (SBUs), are capable to coordinate polytopic linkers into an organized 3D network [1].

In this study, we observed for the first time that the presence of gold NPs was found influential on further phase transformation of MOF-199 into [Cu2(OH)(BTC)(H2O)]n under a MW heating. Stimulated by this observation we decided to perform a systematic study to follow such phase transition along the MOF solvothermal synthesis, extracting portions of reaction mixture through a special valve into an ice-cooled beaker at different steps of the synthesis for phase analysis. The properties of resulted materials were probed by different structural and spectroscopic techniques, including Cu K-edge X-ray absorption near edge structure (XANES) spectroscopy.

References

1. Yaghi OM, O'Keeffe M, Ockwig NW, Chae HK, Eddaoudi M, Kim J (2003) Reticular synthesis and the design of new materials. Nature 423:705. doi:10.1038/nature01650

DFT modeling of chain hydrogenation of graphene and chain dehydrogenation of graphane

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Theoretical study of systems, which constructed on base of graphene and graphane by chain hydrogenation and chain dehydrogenation correspondently, has been performed by DFT calculations with using supermolecular modeling and with imposing periodic boundary conditions. The supermolecular modeling calculations were carried out using Gaussian 16 program [1] with HSEH1PBE/6-31g(d,p) and PBE1PBE/6-31g(d,p) methods. The calculations with imposing periodic boundary conditions have been completed using Vienna ab initio simulations package [2] with PAW pseudopotentials and the PBE.52 density functional. The plane-wave cutoff energy 414 eV of the associated pseudopotentials was used. The Brillouin zone has been sampled by Monkhorst–Pack method with 15x15x15 grid. The calculated geometric characteristics have been visualized by using Vesta program and presented in Fig. 1.

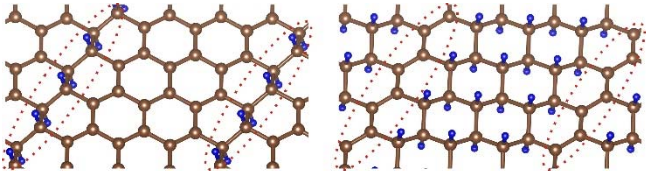

Fig. 1. Graphene with chains of hydrogen (left) and graphane without chains of hydrogen (right). Red ellipses indicate the corresponding chains.

The results of calculations show that these systems are stable and theoretically may be existed. Currently, the study of conductive characteristics continues.The work was supported by the by Russian Government grant by decree № 220 (agreement № 14.Y26.31.0016).

References

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al. Gaussian 16. Revision A.03. Gaussian, Inc., Wallingford CT (2016).

[2] G. Kresse, J. Furthmuller. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. Phys. Rev. B, 54, 11169-11186 (1996).

Character of chemical bonds in new materialstheoretically simulated with using of tetrahedral units X4 (X=B, C, Al)

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The acquisition of new materials with new unusual properties is an actual problem of modern material science. In [1-4] the several new materials was theoretically constructed on base of graphene and diamond in which atoms of carbon have been replaced by tetrahedral units X4 (X=B, C, Al) and analogues.

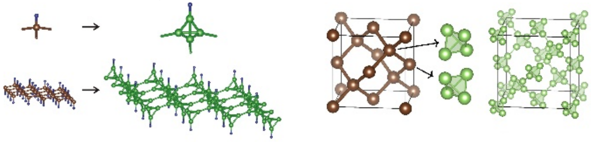

Fig. 1. Construction of 1D, 2D and 3D structures on base of graphene (left) and diamond (rigth).

One of the main theoretical questions was a character of chemical bonding in these structures. It was shown that atoms in the same tetrahedron are bound together by three-center two-electron 3c-2e bonds despite on type of atoms. The character of bonds between tetrahedrons is 2c-2e and also not depends on type of atoms although the properties of these bonds are slightly varying.

The authors greatly appreciate financial support of Russian Government grant by decree № 220 (agreement № 14.Y26.31.0016).

References

[1] I.V. Getmanskii, R.M. Minyaev, D.V. Steglenko, V.V. Koval, S.A. Zaitsev, V.I. Minkin. From Two- to Three-Dimensional Structures of a Supertetrahedral Boran Using Density Functional Calculations // Ang. Chem. Int. Ed., 56, 10118-10122 (2017).

[2] D.V. Steglenko, S.A. Zaitsev, I.V. Getmanskii, V.V. Koval, R.M. Minyaev, V.I. Minkin. Boron, carbon, and aluminum supertetrahedral graphane analogues. Russ. J. Inorg. Chem., 62, 802–807 (2017).

[3] I.V. Getmanskii, V.V. Koval, R.M. Minyaev, A.I. Boldyrev, V.I. Minkin. Supertetrahedral Aluminum – A New Allotropic Ultralight Crystalline Form of Aluminum. J. Phys. Chem. C., 121, 22187–22190 (2017).

New spiropyran salt containing carbomethoxy group

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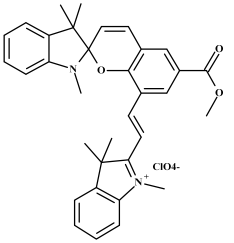
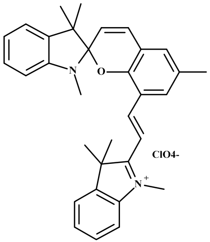
Spiropyrans are organic photochromic compounds perspective for creation of smart materials with controlled optical, physical and biological properties.

We are reported there about the synthesis of the new spiropyran salt (1), containing both carbomethoxy substituent and cationic fragment in benzopyran moiety.



(1)



(2)

Cationic spiropyrans are of particular interest as structural elements of molecular magnets with photocontrolled properties. In this work, we compared the photochemical properties of the target compound (1) and the similar ones spiropyran (2), described earlier [1]. During photochemical studies it was found that compound (1) shows a hypsochrome shift of the absorption maximum of the open form in comparison (2) (642 and 728 nm accordingly). Also, it was shown, that merocyanine form is stabilized by the carbomethoxy substituent. As the result compound (1) is thermally decolorized incompletely.

The work was supported by the by Russian Government grant by decree N 220 (agreement N 14.Y26.31.0016).

References

[1] Tkachev V.V. et al. Investigation of a new product of a condensation reation between 1,2,3,3-tetramethylindolenilium perchlorate and 2,6-diformyl-4-methyl-phenol. Journal of Structural Chemistry, V. 57, № 6, PP. 1270-1271 (2016).

Synchrotron-based X-ray diagnostics of nanoscale structure of geological materials

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X-ray absorption near-edge structure (XANES) spectroscopy is an effective modern technique providing unique information on the 3D local atomic (bond lengths and bond angles) and electronic structure of different classes of compounds without long-rang order in atomic arrangement including geological materials.

The investigation of atomic and electronic structure of different classes of terrestrial and extraterrestrial geological materials has been performed by the instrumentality of synchrotron-based XANES spectroscopy and computer modeling.

Local atomic structure of Ti-bearing hibonite, the mineral found in some calcium-aluminum-rich inclusions in chondritic meteorites has been studied. The probability of different structural models of Ti-bearing hibonite has been estimated. The limitations of hibonite as a single-mineral oxibarometer for early solar system processes have been discussed [1]. The oxidation state of lanthanides in some lanthanide-containing silicates has been determined. The complex X-ray diagnostics of the ordinary chondrites Markovka, Polujamki and Jiddat Al Harasis 055 has been done. The change in Fe oxidation state and coordination numbers has been estimated for the genetic series of tektites and impactites. The Fe2+ oxidation state has been determined for the australasian, moldavite, and Muong-Non tektites and the highest value Fe2.6+ for the silica-poor zhamanshinites.

The authors thank the Ministry of Education and Science of the Russian Federation for the award of grant 16.3871.2017/4.6.

References

[1] A.J. Berry, P.F. Schofield, A.N. Kravtsova et al. (2017). The limitations of hibonite as a single-mineral oxynarometer for early solar system processes. Chemical Cheology, V. 466, page 32-40.

Properties of Magnetic Nanoparticles for Theranostics in Oncology

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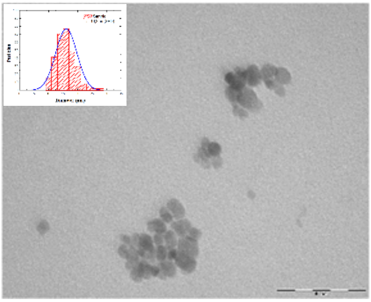
Nowadays one of the most important research field is the application of magnetic nanoparticles for theranostics in oncology (contrast agent for MRI (Magnetic Resonance Imaging) and active material for Magnetic Hyperthermia treatment).



Magnetic iron oxide nanoparticles were synthesized by a modified method of co-precipitation of iron (II) sulfate and iron (III) chloride with sodium carbonate followed by precipitation by addition of citric acid solution using micro-wave irradiation of SP-Discovery Microwave CEM, USA). Physicochemical characteristics (shape, dimensions, structure) were studied using a number of experimental techniques: TEM, XRD, DLS, VSM, XANES. The synthesized magnetic nanoparticles were almost spherical in hape, less than 20 nm in size.(TEM), with the average size of crystallites 16.2 nm (XRD), and were partially agglomerated as their averaged hydrodynamic radius is of 33.6 nm (DLS). The structure of the obtained nanoparticles was shown to be close to the γ-phase of iron (III) oxide (γ-$Fe2O3$, maghemite) (XRD, XANES).

The results of toxicity tests indicated that the synthesized nanoparticles were non-toxic for biological tissues. Moreover, obtained nanoparticles are heated in an alternating magnetic field to temperatures above 40 ° C. Therefore, magnetic nanoparticles of iron oxide are promising candidates for the hyperthermia in oncology.

The authors are grateful to the Ministry of Education and Science of the Russian Federation for the award of grant 16.3871.2017/4.6 ("Picometre diagnostics of parameters of 3D atomic structure of nanomaterials on the basis of XANES spectroscopy")

Named Intermolecular Interactions

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The past few years have seen a precipitous growth in the number of publications related to various aspects of weak interactions, both in chemistry and biology. A special issue of *Chemical Reviews* devoted exclusively to non-covalent interactions in chemistry was published in 2016, highlighting the cutting-edge nature of this project.

Compared to covalent bonds, intra- and intermolecular non-covalent interactions are weak. They have much lower energy, fluctuating in the range from several units to several tens of kcal/mol, as well as less directed orientation. Depending on specific chemical elements or building blocks based on these elements, non-covalent interactions are classified into hydrogen, halogen, chalcogen, pnictogen, metallophilic, lp-π interactions, π-stacking, and a number of others; this classification is continuously expanded and refined. Crystal engineering makes extensive use of interactions between multiple non-covalent bonds, allowing the design and production of associates, clusters, extended supramolecular systems and ultimately functional materials.

Despite the low energy of non-covalent interactions, in many cases they act collectively and the sum of their actions can play a significant role in the various transformations of chemical compounds, synthesis and catalysis, including organic catalysis.

The talk will consider such types of weak interactions as halogen and chalcogen bonds with special emphasis on how these non-covalent interactions affect the reactivity of chemical compounds.

A special emphasis will be placed on the achievements of the International Group established at Saint Petersburg State University under the Russian Science Foundation project 14-43-00017P.

Summary of 5-years of nanoscience research at SFedU and beyond

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In this lesson, I will summarize the cultural, educational, instrumental and scientific improvements done in the MegaGrant quinquennium 2014-2018 on the three main topics pursued in the project: metal nanoparticles [1], zeolites [2] and MOFs [3]. For the three class of materials the group was involved in the synthesis [4], in the characterization with advanced methods (most based on synchrotron radiation) [5] and in the interpretation of the results via the state of the art of theory [6]. Advises on how I recommend to continue the research in the next years will be provided.

References

[1] A. L. Bugaev et al., J. Phys. Chem. C, 2014, 118, 10416; Catal. Today, 2017, 283, 119; Faraday Discuss., 2018, 208, 187.

[2] K. A. Lomachenko, et al., J. Am. Chem. Soc., 2016, 138, 12025; J. Am. Chem. Soc., 2017, 139, 14961; Chem. Sci., 2015, 6, 548.

[3] L. Braglia et al. Phys. Chem. Chem. Phys., 2017, 19, 27489; Faraday Discuss., 2017, 201, 265; V. V. Butova, et al. Russ. Chem. Rev., 2016, 85, 280.

[4] V. V. Butova, et al., Cryst. Growth Des., 2017, 17, 5422; M. A. Soldatov, et al., J. Phys. Chem. C, 2018, 122, 8543; Polyhedron, 2018, 154, 457.

[5] A. L. Bugaev, et al., J. Phys. Chem. C, 2018, 122, 12029; 323; M. A. Soldatov, et al., Polyhedron, 2018, 155, 232; E. Groppo, et al., ACS Catal., 2018, 8, 6870.

[6] S. A. Guda, et al. J. Chem. Theory Comput., 2015, 11, 4512; A. Martini, et al., Chem. Sci., 2017, 8, 6836; E. Gallo, et al., Inorg. Chem., 2017, 56, 14408.

Co,Zn–ZIF-derived Fe-containing active carbons for the ORR

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Air-hydrogen low temperature fuel cells are promising devices for a sustainable energy supply. Nowadays, attention has been moving towards Pt-free catalysts like metals-doped carbons. We prepared Co,Zn/Fe/N/C catalysts from bimetallic zeolitic imidazolate frameworksaccording to Fig. 1 [1,2]. We found that Co and Fecontent influences both the morphology of catalyst and its catalytic activity in the oxygen reduction reaction (ORR). Electrochemical properties were probed by cyclic voltammetry and linear sweep voltammetry to outline performance and stability of the catalyst.

This work was supported by the Russian Science Foundation (grant №17-73-10386).

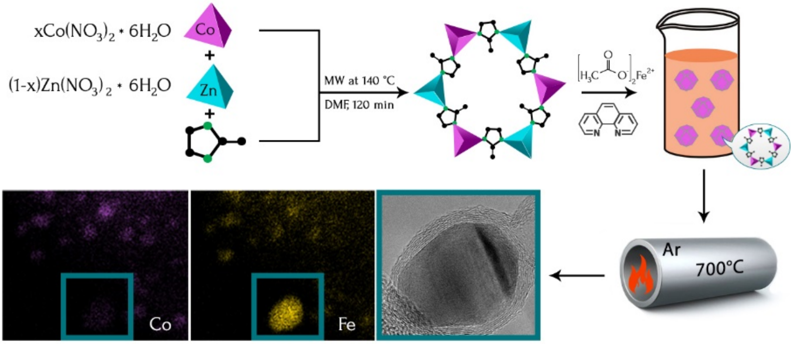

Figure 1. Schematic illustration of the preparation path for the Co,Zn/Fe/N/C catalysts.

References

[1] T. A. Lastovina*et al*. J. Phys. Conf. Ser. 829 (2017) 012007.

[2] T. A. Lastovina*et al*. Electrochem. Commun. 88 (2018) 83.

Unraveling structural, orbital, and optical properties of luminescent structurally sophisticated d0 titanocene

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The diverse titanium complexes represent a major class of compounds widely used in many fields of modern molecular science. Modeling of electronic spectra and orbital properties of coordination compounds remains to be a fundamental challenge. The present contribution systematically evaluates ability of quantum-chemical methods at different levels of theory to correctly simulate geometry, molecular orbital characteristics, and electronic spectra of a structurally sophisticated organometallic species with use of emissive d^0-titanocene dicarboranyl $Ti(\eta^5{:}\eta^1\text{-}CpCMe_2CB_{10}H_{10}C)_2$.

We have tested eleven HF methods and 147 density-functional/basis set combinations for their ability to reproduce the experimental bond distances and bond angles. The principal finding is that the structural parameters can be calculated with acceptable accuracy by the HF and the most DFT methods assessed. The most adequate for the geometry prediction are the Hartree-Fock (HF) methods and the DFT methods employing CAM-B3LYP, B3LYP, M06, M06-2X, M11, HISSbPBE, ωB97, B97-D, VSXC, and B98. We have not got the best fit with the experiment (bond lengths, angles), although this is hardly possible at this state of the art. The assessed time-dependent HF and DFT methods based on the functionals M06-HF, BMK, VSXC, N12, N12-SX, M06-L, M06, CAM-B3LYP, M11, LC-ωPBE, HISSbPBE, BP86, and partly M06-2X provide inaccurate descriptions of the ligand-to-metal charge transfer (LMCT) excitations of the model titanocene dicarboranyl. The TDHF errors in energy exceed 1.1 eV. On the contrary, popular functional B3LYP is a suitable choice to perform a reliable LMCT excitations study of titanocene complexes.

G.V. Loukova greatly appreciates receiving financial support from the FASO (the state contract 0089-2014-0008) and the RFBR (project 18-03-00359). V.I. Minkin acknowledges receiving financial aid from the SFU via the state contract 1.5056.2017.VU. A.A. Milov participated in the study in the framework of the SSC RAS state contract 01201354239.

Nature of ligand-to-metal charge transfer excited states in the metallocene dicarboranyl triadM(η5:η1-CpCMe2CB10H10C)2

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Group 4 bent metallocene complexes $(\eta^5\text{-RCp})_2MX_2$ (Cp = C_5H_5, M = Ti, Zr, Hf) have a particular importance for catalytic polymerization of unsaturated hydrocarbons, activation of small molecules, and in antitumor therapy. In the present work, photophysical and quantum-chemical methods were used to study the orbital properties and extremely rare ligand-to-metal charge transfer (LMCT) excited states of d^0 double-bridged metallocenes bearing carboranyl σ-ligands: $M(\eta^5{:}\eta^1\text{-CpCMe}_2CB_{10}H_{10}C)_2$ (M = Ti, Zr, Hf).

According to our computation data, despite the presence of metal–carbon σ-bonds, structurally complex d^0 metallocene dicarboranyls, in contrast to the related metallocene dimethyls, possess LMCT excited states with charge transfer predominantly from the aromatic π-ligands to the metal, a high electric dipole moment, and photoluminescent (we consider: phosphorescent) properties, making them similar to the dichloride analogs lacking M–C σ-bonds. We demonstrate the functional relationship between experimental energies of the HOMO-to-LUMO electronic transition in the isostructural complexes of the triad, and the fourth gas-phase ionization potential (IP_4) of the metal (Ti, Zr, Hf). The existence of the correlations is a consequence of the fact that, according to our calculations, the principal contribution to the LUMO in these molecules, where electronic changes are localized, comes from the metal AOs, while the Cp-based HOMO energy remains practically unchanged when varying the metal ion.

G.V. Loukova greatly appreciates receiving financial support from the FASO (the state contract 0089-2014-0008) and the RFBR (project 18-03-00359). V.I. Minkin acknowledges receiving financial aid from the SFU via the state contract 1.5056.2017.VU. A.A. Milov participated in the study in the framework of the SSC RAS state contract 01201354239.

Synthesis and study of new indoline spiropyrans containing a free hydroxyl group in the naphtopyran fragment

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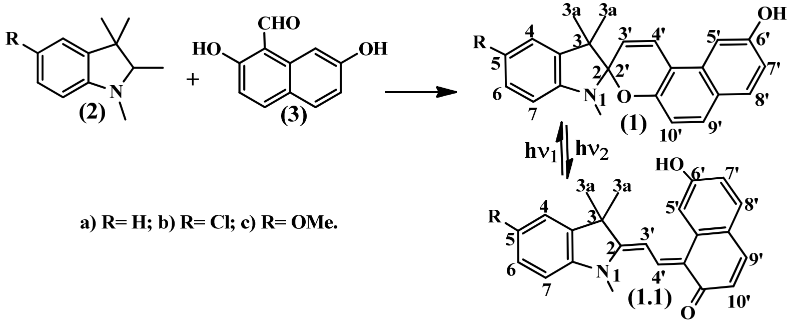
Stimuli-responsive materials have found widespread applications, as the need to create novel "smart" systems often requires materials that can change their chemical or physical properties by changing an external parameter. Spiropyrans represent one of the classes of photo-responsive molecules that can undergo reversible photoisomerization between spirocyclic and merocyanine forms upon UV irradiation. This phenomenon is accompanied by the dipole moment or lipophilicity changing. This paper presents the results of the synthesis of a number of indoline spiropyrans (1 a-c) containing various substituents in the hetarene moiety of the molecule. Changing the nature of the substituent in the naphthalene moiety, it becomes possible to control the stability of the spirocyclic isomer. In this study new spiropyrans of the indoline series (1) were synthesized by the interaction of the Fischer base (2) and aldehyde (3).



This work was supported by the joint program Mikhail Lomonosov of the Ministry of Education and Science of the Russian Federation and German academic exchange service DAAD (project no. 4.12815.2018/12.2).

Synthesis and study of new spiroindolinonaphtopyrans containing a free hydroxyl group

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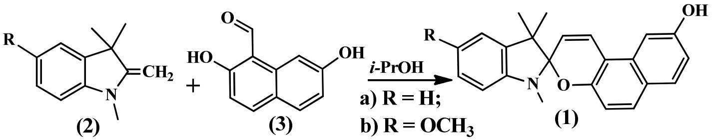
The self-assembly of photo-responsive molecules on metal nanoparticle surfaces has received considerable attention in recent years because it provides the opportunity of using switching devices as photo-responsive components in applications of optical storage, molecular recognition, photo-switchable surface wettability and drug delivery [1].

Spiropyrans represent one of the classes of photo-responsive molecules that can undergo reversible photoisomerization between spirocyclic and merocyanine forms upon UV irradiation.

In this study new spiropyrans of the indoline series (1) were synthesized by the interaction of the Fischer base (2) and aldehyde (3).



The NMR ^{1}H and NMR COSY ^{1}H–^{1}H spectra helped to determine the structure of the target compounds which exist preferably in the form of spirocyclic isomers in the solution at room temperature. Free hydroxyl groups in the 2H-chromene fragment are very promising for modifying the structure of spiropyran with various substituents, for example, by esterification or alkylation reactions.

The work was supported by the by Russian Government grant by decree N 220 (agreement N 14.Y26.31.0016)

References

[1] A.Ghavidast, et all., (2016). A comparative study of the photochromic compounds incorporated on the surface of nanoparticles. Journal of Molecular Liquids, 216, 552-564.

Cu-oxo species in Zeolites: Preliminary Results by Wavelet Analysis

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Recently, Cu-exchanged chabazite (Cu-CHA) and mordenite (Cu-MOR) are attracting increasing attention for the direct conversion of methane to methanol (MTM) [1]. A key step to understand their potential in this reaction is the reliable determination of Cu-speciation in O_2-activated materials. From a qualitative analysis, the experimental XAS data reported in the literature for O_2-activated Cu-CHA and Cu-MOR do not show sharp differences [1, 2]. However, the interpretation of the EXAFS signal significantly differs for the two topologies. We employed Wavelet Transform analysis (WTA) [3] on a series of simulated EXAFS spectra referring to different Cu moieties. We proved that this new kind of signal representation is able to single out different contributions from scattering atoms with different Z that, from classical FT-analysis, appear of ambiguous identification. In particular, for the case of Cu-dimers, WTA allowed to have a clear visualization of their contributes, shedding light on the long-standing question about nuclearity of Cu-species.

References

[1] D.K. Pappas et al., Methane to Methanol: Structure–Activity Relationships for Cu-CHA, J. Am. Chem. Soc., 139 (2017) 14961–14975.

[2] E.M.C. Alayon et al., Reaction Conditions of Methane-to-Methanol Conversion Affect the Structure of Active Copper Sites, ACS Catal., 4 (2014) 16-22.

[3] M.A. Soldatov et al., The Insights from X-ray Absorption Spectroscopy into the Local Atomic Structure and Chemical Bonding of Metal-organic Frameworks, Polyhedron, 155(2018)232-253.

Heating efficiency of various iron oxide nanoparticles for magnetic hyperthermia

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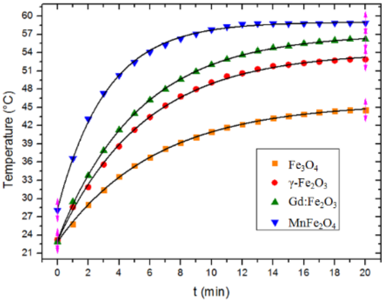
The method of local magnetic hyperthermia is based on the direct delivery of magnetic nanoparticles (MNPs) to the target tissue (malignant tumor) with subsequent heating using external alternate magnetic field [1-2]. The target tissue being exposed to high temperatures dies or becomes more susceptible to other therapeutic methods. Various types of NPs can be used for magnetic hyperthermia treatment: NPs of magnetic alloys (Fe-Co, Fe-Ni, Co-Ni), NPs of metal oxides (Fe_3O_4, γ-Fe_2O_3, NiO, Co_3O_4), ferrites with spinel structure ($MnFe_2O_4$ etc). The method has been developed allows to determine heating parameters such as specific absorption ratio (SAR) and intrinsic loss power (ILP). This research was supported by RFBR (project№ 18-32-01029).



References

[1] Z. Hedayatnasab, et al., Materials and Design 123 (2017) 174–196.

[2] J. Beik, et al., Journal of Controlled Release 235 (2016) 205–221.

MIL-88a as a carrier material for targeted drug delivery: impregnation with hormones

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To investigate the possibility of using metal-organic framework with flexible crystal lattice MIL-88a (MIL = Materials of Institute Lavoisier)[1] as a carrier material for hormonal treatment, serotonin and dopamine were encapsulated. The microcrystals of MIL-88a were obtained during the hydrothermal synthesis, pre-activated in a muffle furnace and then placed in aqueous solutions of hormones. Encapsulation process was occurred with constant stirring for 12, 24, 48 and 72 hours to determine the most optimal impregnation time. The analysis of hormone-impregnated samples was performed by XRD and FTIR.

To release the absorbed hormones, the obtained substance was placed in a phosphate-buffer solution, where the microcrystallites of MIL-88a were stirred for 1, 2, 4, 16 and 24 hours, after which the concentration of the released hormone in the final solution was determined by UV-vis.

References

[1] D. Cunha, M. Ben Yahia, S. Hall, S.R. Miller, H. Chevreau, E. Elkaim, G. Maurin, P. Horcajada, C. Serre, Rationale of Drug Encapsulation and Release from Biocompatible Porous Metal-Organic Frameworks, Chem. Mat., 25 (2013) 2767-2776.

PtCuAu/C catalysts of different structures for oxygen electroreduction and methanol electrooxidation reactions

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Carbon-supported platinum-based catalysts are currently the most important component of low-temperature fuel cells. Fuel cells are of great interest due to their high efficiency, but the cost of energy from low-temperature fuel cells is still high. To reduce the cost of power produced by low temperature fuel cells, it is necessary significantly reduce the noble metal loading in the catalyst layer. Composite materials containing Me@Pt (Me = Cu, Ni, Co) nanoparticles with «core-shell» structure deposited onto supports are most promising solutions of this problem [1-2].

The aim of this work is to obtain PtCuAu nanoparticles with different architecture of nanoparticles, deposited on a highly disperse carbon carrier, as a highly efficient material for low-temperature fuel cells.

Synthesis of PtCuAu/C catalysts with different architecture of nanoparticles [1] was carried out.

The characterization of prepared PtCuAu/C materials was performed by HRTEM, XRD, CV, LSV and Pt, Au L3- and Cu K-edge extended X-ray absorption fine structure (EXAFS).

Prepared "gradient" PtCu/C and PtCuAu/C materials demonstrated higher corrosion-morphological stability and activity in oxygen redaction reaction (ORR) and methanol electrooxidation (MOR) compared to Pt/C. These materials are promising for further study.

This work was supported by Russian Science Foundation (project no. 18-73-00161).

References

[1]A.A. Alekseenko, V.E. Guterman, S.V. Belenov, etc., Pt/C electrocatalysts based on the nanoparticles with the gradient structure, Int. J. of Hydrogen Energy, 43 (2018) 3676 – 3687.

[2] X. Wang, L. Zhang, H. Gong, Y. Zhu, H. Zhao, Y. Fu, Dealloyed PtAuCu electrocatalyst to improve the activity and stability towards both oxygen reduction and methanol oxidation reactions, Electrochimica Acta, 212, 2016, pp. 277-285.

Quantum-chemical study of increase of acene chains stability upon doping with metal atoms

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With use of the density functional theory calculations B3LYP/6-311++G** and PBE0/6-311++G**, properties and stability of acene chains before and after the lithium atoms dopingwere studied.

As shown by the calculations for various electronic states (upon the transition from pentacene to longer acene chains), the singlet biradical appears to be the most stable state. At the same time, the energy difference between the biradical and closed-shell systems increaseswith the growth of the acene chain length.

The doping of an acene chain with two lithium atoms leads to unusual results. So, for example, except for the 1, 2 and 1,3-isomers, the composition of the HOMO and the LUMO does not change as referred to the initial molecules. At the same time, depending on the arrangement of lithium atoms, all thus obtained isomers give the different values of the energy gap and stability.

The complete doping of the extended acene chains with lithium atoms leads to complete loss of their unique properties.

The work was supported by the Russian Ministry of Science and Education (agreement No. 14.Y26.31.0016).

Influence of the bimetallic nanoparticles architecture on the degradation degree of platinum containing electrocatalysts

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The low-temperature fuel cell is a complicated mechanism where a platinum containing electrocatalyst, distributed evenly upon the surface of a carbonic carrier, provides the course of cell reactions in anode and cathode spaces at high speed[1].

The study is aiming at examining the influence of alloying with d-metal on the platinum containing catalyst stability within different testing conditions. Degradation of the previously received catalysts (O1 - gradual precipitation of platinum and copper, followed by decreasing copper amount; O2 - simultaneous precipitation of precursors [1]) and commercial samples was studied in the potential range 0.6-1.0 V, 0.6-1.4 V under normal conditions, with 0.1 M perchloric acid used as the electrolyte. Speed of the potential sweep during the cycling process was equal to 100 mV/s, with the number of cycles being equal to 5000, 500 respectively. The data obtained were recorded in the Table 1.

Table 1. Electrochemical characteristics of electrocatalysts

Substance name	EASA (electrochemically active surface	EASA after the stress test		Stability, %	
		0.6-	0.6-	0.6 -1.0V	0.6 -1.4V
O1	103±10	84±	83±	82	81
O2	82±8	57±	69±	70	84
JM	96±10	61±	16±	64	17

The study resulted in manifesting the positive influence of the alloying component on the catalysts stability. It is connected with formation of the three-phase system Pt – Cu – C, due to which the adhesion of nanoparticles with the carrier rather improves.

References

[1] Junga N. 2014. Pt-based nanoarchitecture and catalyst design for fuel cell applications // Nano Today. 2014. V. 9. P. 433–56. 2014

β-amyloid peptide aggregation.Multi-scale simulations and XAS measurements

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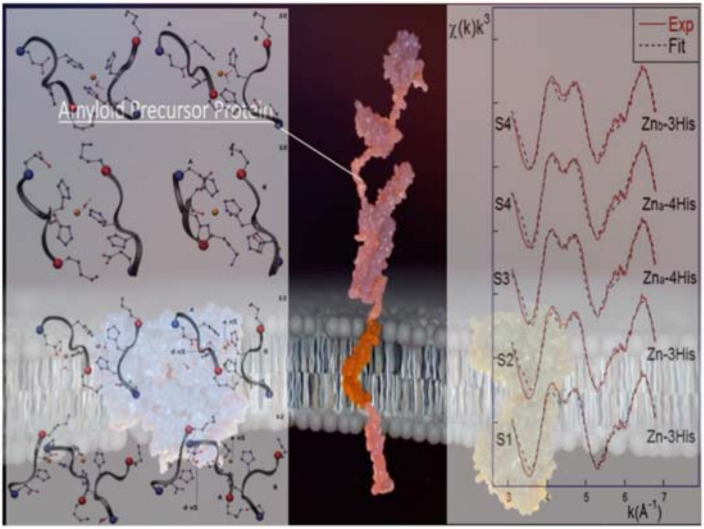
In this seminar I want to stress the special importance of understanding misfolding for the large class of protein involved in conformational diseases to which, among others, all neurodegenerative diseases belong. Our investigation is based on the experimental evidence that metal ions are involved in the misfolding and aggregation processes that are fingerprints of the diseases.



The complexity of the problem in which the dynamics of a protein in complex with a metal ion needs to be elucidated, requires a combined and synergic use of numerical and experimental methods [1][2]. From the experimental point of view X-ray Absorption Spectroscopy has proved to be an invaluable tool to deal with the highly diluted biological samples that are of relevance here. At the same time to correctly interpret experimental data and be able to extract the desired information, numerical (both classical and ab initio) large-scale computations are mandatory.

Despite the many efforts in the literature the problem of deciphering how misfolding, aggregation and disease are related is far from being solved. We will, however, show that some understanding on the role played by metal ions [3] in the misfolding and aggregation processes of these kind of proteins can be reached.

References

[1] S. Morante, G.C. Rossi (2014). Metals in Alzheimer’s Disease: A Combined Experimental and Numerical Approach. in Advances in Alzheimer’s Research Volume 2: 100-147.

[2] P. Giannozzi, K. Jansen, G. La Penna, V. Minicozzi, S. Morante, G.C. Rossi, F. Stellato (2012) Zn induced structural aggregation patterns of □-amyloid peptides by first-principle simulations and XAS measurements. Metallomics. 4(2):156-165.

[3] E. De Santis, V. Minicozzi, O. Proux, G. C. Rossi, K. I. Silva, M.J. Lawless, F. Stellato, S. Saxena and S. Morante (2015). Cu(II)-Zn(II) cross-modulation in amyloid-beta peptide binding: an X-ray Absorption Spectroscopy study. J. Phys. Chem. B. 119, 15813−15820

Compact model of a CMOS transistor for the effect of full dose radiation

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Full-scale experiments to analyze the effects of ionizing radiation on very-large-scale integration quite laborious and often not informative with respect to the physical processes taking place, so a good alternative is to include the effects of ionizing radiation in a compact device models used in circuit simulators. The inclusion of these effects requires knowledge of the physical processes that contribute to the occurrence of defects due to ionizing radiation, and influence of effects have on the electrical characteristics of the components in advanced CMOS technologies.

Efficiency of simulation of CMOS transistors operating under conditions of radiation exposure depends on the accuracy of transistors analytical models. Degradation of electrical parameters, as well as the resulting functional failures, largely determined by the dose rate of the radiation.

The effect of the absorbed radiation dose on the model based on the surface potential implemented by renormalizing the surface potential equation [1].

Model testing showed a good correlation with the experimentally obtained *drain current* - *gate voltage characteristics*.

References

[1] A.G. Mustafaev, G.A. Mustafaev, N.V. Cherkesova (2018). Consideration of the Effect of the Total Dose of Radiation in the Compact Models of the CMOS Transistors. Nano- i Mikrosistemnaya Tehnika, vol. 20, pp.396-402.

Strong long-range electron-phonon interaction as the driving force of charge ordering in cuprate superconductors

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The electronic structure of cuprates demonstrating high-temperature superconductivity is investigated more than 30 years, but so far remains not clear. Recently the experimental evidence of charge ordering in cuprates, arising at doping both with electrons and holes were obtained [1,2]. We adopt the variational method to look for the ground state of system with strong long-range electron-phonon interaction at high density of charge carriers. The method suggested allows taking into account coexistence of autolocalized and delocalized carriers. The charge ordering period in the model is the bipolaron diameter. We calculate the radius of an isotropic and anisotropic bipolaron in such system as function of doping level, and determine the temperature and doping region of the charge ordering existence. Results of calculation are in good consent with experimental data obtained with methods of resonant elastic X-ray scattering (REXS) and the scanning tunneling microscopy (STM)[1,2].

References

[1] E. de Silva Neto et al. Charge ordering in the electron-doped superconductor Nd2-xCexCuO4. Science. 347, 282 (2015).

[2] R. Comin, A. Damascelli. Resonant X-ray scattering studies of charge ordering in cuprates. Annual Review of Condensed Matter Physics. Vol. 7, 369-405 (2016.)

Search for magneto-structural correlations in a series of heterometallic carboxylate {Co2Ln} complexes shoving SMM behaviour

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Heterometallic carboxylate complexes containing 3d- and 4f-metal ions in one polynuclear core are the promising objects for design of magnetic materials. Identification of the factors that make influence on physico-chemical properties in such type of compounds is a part of the current interest in modern coordination chemistry. In this regard the properties of compounds with similar structures can be modified by variation of the electronic structure of 4f- metal ions. Studies of the rows of similar compounds can allow to investigate "structure-property" relationship.

We carried out the synthesis of coordination compounds $[Co_2Ln(NO_3)(Piv)_6(R\text{-}Py)_2]$ (Ln = Y, La–Nd, Sm–Lu; Piv – pivalate anion; Py – pyridine; R = H, 2-phenyl, 2-ethynyl, 2.3-cyclododecen). It was shown that the compounds containing diamagnetic Y^{3+}, La^{3+} and Eu^{3+} (in diamagnetic ground state) ions revealed single-molecule magnet behavior below 4 K upon application of external DC magnetic field. For compounds $[Co_2Ln(NO_3)(Piv)_6(Ph\text{-}Py)_2]$ the parameters τ_0 and $\Delta E_{eff}/k_B$ were estimated, $\tau_0 = 2.0\cdot10^{-8}$, $2.5\cdot10^{-8}$, $1.0\cdot10^{-8}$ s and $\Delta E_{eff}/k_B = 26, 24, 29$ K for Ln = Y, La, Eu, respectively. It is worth to note that change of the substituent in pyridine cycle from phenyl to another ones led to noticeable change of several geometrical parameters. From magnetochemical point of view change of the substituent led to noticeable decrease of the relaxation barrier from 24 to 7 K (on example of R = 2-ethynyl) for Co_2La complex on the reason of strong sensitivity of Co(II) magnetic anisotropy to the distortion of their coordination polyhedron.

Synthesis of the title coordination compounds, peculiarities of their structures and results of their magnetic behaviour investigation will be discussed in the report in details.

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Study of thermochromic transformations of bis-spiropyrans using dynamic NMR spectroscopy

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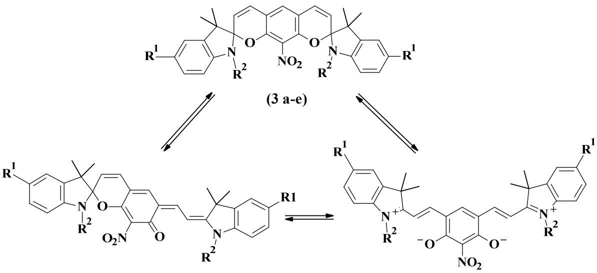
Most studies of photochromic properties of spirocyclic systems involve the irradiation of solutions of photochromes and the registration of their photoinduced changes in absorption spectra. However, it is extremely difficult to draw conclusions about the mechanisms of photochromic processes by methods of photochemistry only.

In this work, we synthesized a series of symmetrical indoline bis-spiropyrans **3** (BSP) and carried out preliminary studies of their thermochromic behaviour using dynamic NMR spectroscopy which confirmed demonstration of negative thermochromic activity of spirocompounds in their chloroform solutions.



Further investigation of these compounds using *in-situ* irradiation NMR technique could reveal unknown details of the mechanisms of photoinduced transformations of chromogenic systems. This information is of great significance for the practical use of photochromic compounds and for direct synthesis of compounds and materials with predetermined properties.

This work was supported by the joint program Mikhail Lomonosov of the Ministry of Education and Science of the Russian Federation and German academic exchange service DAAD (project no. 4.12815.2018/12.2).

XAS operando study of mixed Cu-Fe exchanged zeolites under the NH3-SCR conditions

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Mono-nitrogen oxides (NO_x) are among the main pollutants present in the exhaust from the popular and efficient Diesel engines. NH_3-assisted Selective Catalytic Reduction (NH_3-SCR) catalysed by metal-exchanged zeolites is a promising way to remove hazardous NOx from diesel engine exhaust gases.Fe-zeolites exhibit a higher activity in the high temperature range, while Cu-zeolites are more performing in the low temperature range.

In this work we present the results of operando study of the mixes Cu-Fe exchanged zeolite by means of simultaneous acquiring of both Cu K-edge and Fe K-edge XAS data. There are almost no changes has been observed during the activation as well as under the SCR conditions in the XAS spectra collected in whole temperature range (from 450 °C to 100 °C). Iron active sites is represented in the form of Fe_2O_3 clusters hosted in the cages of MOR, showing only minor reduction at higher temperatures most likely due to OH^- elimination from the surface of the clusters.

Conversely, more informative Cu K-edge XAS data in conjunction with a linear combination fit provides an important information about the temperature evolution of the different Cu sites upon SCR conditions. It was demonstrated that Cu-Fe-mix exhibit higher reducibility of Cu sites in the low temperature SCR mode with respect to the pure Cu-CZC catalysts being less reduced at high temperature SCR. Being more efficient in interaction with an oxygen iron-oxide clusters could change the gas feed composition in the cages of catalyst resulting in the lack of oxygen feed in the proximity of Cu sites and thus prevent a re-oxidation process at low T.

References

[1]M. H. Groothaert, et. al., J. Am. Chem. Soc., 125 (2003) 7629]

[2] K. A. Lomachenko et. al., JACS, 138 (2016) 12025

Functionalized o-aminophenols in the design of metal complexes bearing redox-active iminoquinone type ligands

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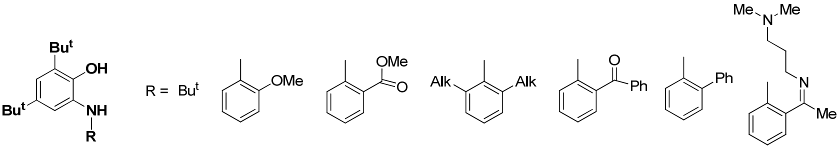
The investigation of metal complexes with redox-active ligands is a rapidly developing field of coordination chemistry.[1] The most common redox-active ligands are o-quinones, α-diimines and the variety of their organic derivatives. One of the features of the above ligands is their ability to coordinate the metal in a radical form, which provides a prerequisite for the use of compounds based on radical forms of redox-active ligands as elements of spin devices and molecular magnets. o-Aminophenols (o-imin oquinones)[2,3] are vivid examples of organic ligands that possess redox-active properties in metal complexes. In addition, they have excellent capabilities for various modifications which further allows to manage the properties of the target coordination compounds.

This report presents the recent results of the synthesis and study of chemical and physicochemical properties (spectral features, magnetism) of metal complexes bearing redox-active ligands based on various functionalized o-aminophenols (Scheme 1).



Scheme 1.

References

[1] G.A.Abakumov, A.V.Piskunov, V.K.Cherkasov et al. Russ. Chem. Rev. **87**, 393-507 (2018).

[2] A.I. Poddel'sky, V.K. Cherkasov, G.A. Abakumov. Coord. Chem. Rev. **253**,291-324 (2009).

[3] M.G. Chegerev, A.V. Piskunov. Russ. J. Coord. Chem. **44**, 258-271 (2018).

Antimony(V) complexes with redox-active o-quinone ligands: from the phenomenon of reversible O2 bindingto the O2-active polymer materials

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The binding of molecular oxygen is the process widely distributed in the chemistry of transition metals. In the chemistry of main group elements it was not known till 2005 when the reversible binding of O_2 was observed in investigations of triphenylantimony(V) o-amidophenolates and some catecholates. The conditions of process have been investigated in details, and the factors determining the O_2-activity of this class of antimony(V) compounds have been identified. On the basis of O_2-active antimony(V) complexes, the bulky copolymer containing antimony(V) complex centres based on o-quinone-methacrylate which is able to absorb molecular oxygen was prepared. Later novel porous polymers with 4-ethoxy-3,6-di-tert-butyl-o-benzoquinone grafted to the porous surface have been prepared, and these quinone-functionalized polymers have been applied for the synthesis of triphenylantimony(V) catecholate-containing polymers. The obtained antimony-containing porous polymeric material is able to bind molecular oxygen in nearly quantitative yield and in a reversible manner. The rate of molecular oxygen sorption is 900 times higher for the porous material than that for the same film material and comparable with the rate of process in solution.

In the present report we will discuss the structure and O_2-binding properties of antimony(V) catecholates and o-amidophenolates, bulky and porous polymeric materials based on these complexes, and propose the possible ways of complexes modifications and applications.

The work was performed with support of RFBR (grant N 16-33-60157 mol_a_dk).

Bimetallic ZIFs for iodine and clorine adsorption

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Zeolite imidazolate frameworks (ZIFs) have unique structural properties and unexpected thermal and chemical stability. Widespread application of ZIFs is associated with gas sorption and storage, primarily due to porous ZIFs structure. Recently it was shown that ZIF-8 could be effectively used for sorption of iodine, which is a volatile gaseous fission product [2]. Elemental halogens plays an important role in industry. On the other hand, they are toxic and volatile. That's why, the developing of reliable methods for safe handling, storage, and transportation of halogens is important research task[3]. In this study, we have shown the application of bimetallic $Zn_{1-x}Co_xC_8H_{10}N_4$ ZIFs structures for I_2 and Cl_2 sorption.

In present work the bimetallic ZIF $Zn_{1-x}Co_xC_8H_{10}N_4$ (x = 0.05, 0.25, 0.75) samples were synthesized [4]. Using XRD and XANES techniques the structure of $Zn_{1-x}Co_xC_8H_{10}N_4$ samples before and after interaction with volatile I_2 and Cl_2 was studied.

Analysis of the obtained data allowed us to conclude that interaction with iodine does not result in the collapse of ZIF structure, moreover ZIF structure adsorbs iodine in the pores. On the contrary, according to the XRD and XANES data interaction of $Zn_{1-x}Co_xC_8H_{10}N_4$ samples with Cl_2 leads to transformation of the initial sodalite structure apparently by addition reaction of Cl_2 and linker.

Acknowledgements

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References

1. Sava, D.F., et al., Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8. Journal of the American Chemical Society, 2011. 133(32): p. 12398-12401.

2. Butova, V.V., et al., New microwave-assisted synthesis of ZIF-8. Mendeleev Communications, 2016. 26(1): p. 43-44.

Effect of functional groups of MOFs with ZIF-8 structure on their sorption properties

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ZIFs are subclass of metal-organic frameworks (MOFs) with zeolite topology and high specific surface area. ZIFs were tested for specifically sorption applications [1]. Linker functional groups have strong effect on the sorption properties of resulting material. In particular, ZIFs with nonpolar functional groups can adsorb and retain nonpolar molecules, while polar functional groups provide specific sorption of polar molecules to ZIF structure. In the present work we have focused on two isostructural ZIFs – ZIF-65 and ZIF-8 [2, 3]. As the only difference between them is linker functional group in 2-position of Imidazole ring, it allowed us to highlight effect of functional group polarity on the specific adsorption properties of selected ZIFs. In this way, ZIF-65 and ZIF-8 were tested for iodine adsorption and retain. The research was supported by the Mega-Grant of Ministry of Education and Science of the Russian Federation (14.Y26.31.0001). V.V.B. and E.A.B. acknowledge RFBR (research project № 18-33-00584) for financial support.

References

[1] D.F. Sava, M.A. Rodriguez, et al. Capture of Volatile Iodine, a Gaseous Fission Product, by Zeolitic Imidazolate Framework-8, J. Am. Chem. Soc. 133(32) (2011) 12398-12401.

[2] K.S. Park, Z. Ni, et al. Exceptional chemical and thermal stability of zeolitic imidazolate frameworks, Proc. Natl. Acad. Sci. U. S. A. 103(27) (2006) 10186-10191.

[3] M. Tu, C. Wiktor, et al. Rapid room temperature syntheses of zeolitic-imidazolate framework (ZIF) nanocrystals, Chem. Commun. 50(87) (2014) 13258-13260.

Merocyanine isomer in the crystalline state

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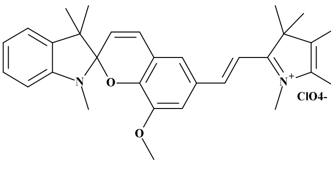
Spiropyrans are important class of organic photochromic compounds, which can be used for creation of new materials with controlled physical and biological properties.

Spiropyran salt **(1)** was synthesized using method [1]. Structure of this compound hasstudied due to NMR ^{1}H and ^{13}C. As a result it was shown, that in solution the compound **(1)** exists as a mixture of spiropyran and merocyanine with the ratio 3:2. Therefore, the structure was confirmed using XRD-method.



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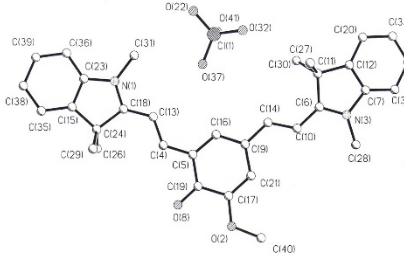

It was found that the compound **(1)** exist as merocyanine isomer in the crystalline state. This circumstance is quite atypical for spiropyrans.

ThisworkwassupportedbyPresident RF Grant № MK-439.2017.3

References

[1] M.B.Lukyanova et al. Structure investigation of new condensation products of 1,2,3,3-tetramethylindolenium with metoxysubstituted diformylphenols. Journal of Structural Chemistry. Vol. 59, No. 3, pp. 565-570. (2018)

Machine learning assisted study of uv/vis data of agglomerates of gold nanoparticles in glass

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In recent years, gold nanoparticles in glasses or on glass surfaces have been intensively studied because of their unique optical properties. Such nanoparticles find wide applications in photocatalysis and electrocatalysis as sensors in chemistry and biology, in medicine, and in a variety of optical devices due to their linear and nonlinear optical properties, such as the surface plasmon resonance (SPR). The presence of the SPR in their optical extinction spectra enables the localization of the electromagnetic field within nanometer distances. Shape and wavelength position (λSPR) of SPR depend on the size and shape of the nanoparticles, degree of their agglomeration [1,2]. Important part of our study is the modelling of optical extinction spectra and further fitting of the experimental data. Usual methods of fitting require long-time and often give different results. In recent years, machine learning allows to take the solve of this problems in XANES data analysis[3].

We apply boosting machine learning algorithms to predict the UV/vis spectra from agglomerate of two or three nanoparticles and avoid expensive calculation of spectrum. The training and testing datasets were produced using T-matrix approach which accounts for plasmonic interaction between neighbor particles. The speedup allowed to describe experimental UV/vis spectra of gold nanoparticles in glass and provided information about structure of agglomerates of nanoparticles, like average size of gold particles, average inter-particle distance and deviations from such average values.

This work was supported by grants from the Russian Foundation for Basic Research № 18-32-00818 мол_а.

References

[1] M. Heinz, V. V. Srabionyan, L.A. Avakyan, A.L. Bugaev, A. V. Skidanenko, V. V. Pryadchenko, et al., Formation and implantation of gold nanoparticles by ArF-excimer laser irradiation of gold-coated float glass, J. Alloys Compd. (2017). doi:10.1016/j.jallcom.2017.11.122.

[2] M. Heinz, V. V. Srabionyan, L.A. Avakyan, A.L. Bugaev, A. V. Skidanenko, S.Y. Kaptelinin, et al., Formation of bimetallic gold-silver

nanoparticles in glass by UV laser irradiation, J. Alloys Compd. 767 (2018) 1253–1263. doi:10.1016/j.jallcom.2018.07.183.

[3] J. Timoshenko, A. Halder, B. Yang, S. Seifert, M.J. Pellin, S. Vajda, et al., Subnanometer Substructures in Nanoassemblies Formed from Clusters under a Reactive Atmosphere Revealed Using Machine Learning, J. Phys. Chem. C. 122 (2018) 21686–21693. doi:10.1021/acs.jpcc.8b07952.

In-situ TEM heating applications for characterization of new Materials, Oil&Gas rocks and carbon nanomaterials

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In-situ Thermal impact experiments in Transmission Electron Microscopy is a very important tool for characterization of the behaviour of new Materials phases and interfaces, unconventional Oil&Gas reservoirs and carbon nanomaterials, which all could be impacted by heat during lifecycle. In the present work there will be reviewed the three examples of in-situ TEM heating application. First, is predicting the thermal behaviour of chemical elements interdiffusion and interface structure of Ti micro- and nanocarbides in nickel-based alloy (CERMET). Second - the observing of phase transitions and organic matter decomposition in nanostructured unconventional reservoir rock of Bazenov formation. The third case is related to development of the heat cleaning procedure of carbon nanotubes films from iron-based catalyst. In the presented report it is discussed the workflow from the sample preparation technique by FIB/SEM to time series images post-processing for detection of every feature of heat impact on the material's nanostructure during extremely dynamic experiment.

Modeling of viral capsid maturation

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The study of viral capsid maturation is very important for the possible applications of them as nanocontainers or for the treatment of viral infections by impairingthe capsid that protects the virus genome.

In this work thechanges in the environmental pH that induce morphological changes in empty shells of bacteriophages are modeled. They are very similar to the changes that occur in viral capsids in vivo after encapsidation of DNA. Using the non-obvious symmetry [1, 2] of procapsids and charge distribution on it the simple electro-mechanical model explaining the reconstructions of the shell in vitro is suggested. It combines the approaches of the elasticity theory of thin icosahedral shells with the recent results on dependence of the protein charges on the bathing solution acidity. The procapsids shape is obtained by minimization of the total electro-mechanical free energy and depends on both the positions of the protein charges and their magnitudes. Using the approach proposed, we model the reversible transition which takes place between the Prohead II and Expansion Intermediate II states of the bacteriophage HK97 procapsid due to the change in pH.

References

Roshal D.S., et al. Assembly of the most topologically regular two-dimensional micro and nanocrystals with spherical, conical, and tubular shapes. Phys. Rev. E., 94, 052605 (2016).

Rochal, S. B., Roshal, D. S., Myasnikova, A. E., & Lorman, V. L. Commensurability between protein nanotubes in contractile ejection nanomachines. Nanoscale, 10(2), 758-764 (2018).

Underlayer material effect on carbon nanotubes growth

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Practical use of unique properties of carbon nanotubes (CNTs) leads to the need to obtain orientedCNTs located at a given location of the substrate. One of the mostpromising methods for creating oriented CNTs is plasma enhanced chemical vapor deposition (PECVD). It makes it possible to form CNTs at specified locations of the substrate at catalytic centers (CC), as well as such advantages as synthesis at low temperatures and the possibility of varying the geometric parameters of carbon nanotubes in a wide range.

One of the most important factors for the growth of CNT by the PECVDmethod is the combination of materials of the catalytic layer and underlayer[1]. This sublayer works as a diffusion barrier to prevent the material of the catalyst layer from interacting with the substrate material.In this paper, the effect of underlayer material on the parameters of CNT grown is investigated. An underlayer of 20 nm thickness from various metals (Zn, Ti, Ta, Pt, Pd, Cr) and a Ni film10 nm thickas the catalyst layer was formed on the surface of the Si substrate by magnetron sputtering.

Thus, the results of the conducted studies have shown that Cr is the most suitable material for use as a buffer layer between the Si substrate and the catalyst layer of Ni during the PECVD process. When this contact is used, CNT grows with the most ordered and vertically oriented structure.

This work is supported by theRussian Science Foundation under grant№ 18-79-00176.

References

[1] Khurshed A. Shah, Bilal A. Tali. Synthesis of carbon nanotubes by catalytic chemical vapour deposition: A review on carbon sources, catalysts and substrates. Materials Science in Semiconductor Processing, 41, pp. 67-82 (2016).

Investigation of CO oxidation kinetics on Pt/CeO2 catalysts with mass spectrometry

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Pt nanoparticles over Ce-based supports show higher performance at low temperature CO oxidation than Pt NPs over non-reducible supports. That happens due to the ability of Ceria to provide oxygen at the metal-support interface. [1] Reducibility of Ceria could be also tuned by making a solid solution with oxides of zirconia and tin. [2]

It was reported that reductive pre-treatment of Ceria-based catalysts has positive affect on CO oxidation. We observed spikes of activity in Pt/CeO_2, $Pt/CeSnO_4$ and $Pt/CeZrO_2$ catalysts after reductive pre-treatment. With time activity decreases to the values of pre-oxidized catalyst. It is proposed that Ceria as a source of oxygen boosts the conversion.

In this work we used mass spectrometry to quantify the amount of CO_2 produced during the spike. Our setup consisted of a custom designed cell, mass flow controller setup and Pfeifer mass spectrometer. After reductive pre-treatment we switched to mixtures of CO and O_2, observing different spikes in activity. These experiments were made as supplementary to the XAS study of these catalysts in attempt to corelate changes in oxidation states of Ce to CO_2 conversion.

References

[1] Kopelent, R.; Van Bokhoven, J. A.; Szlachetko, J.; Edebeli, J.; Paun, C.; Nachtegaal, M.; Safono-va, O. V. Catalytically Active and Spectator Ce3+ in Ceria-Supported Metal Catalysts. Angew. Chem. - Int. Ed. 2015, 54 (30), 8728–8731.

[2] Gupta, A.; Waghmare, U. V.; Hegde, M. S. Correlation of Oxygen Storage Capacity and Struc-tural Distortion in Transition-Metal-, Noble-Metal-, and Rare-Earth-Ion-Substituted CeO2 from First Principles Calculation. Chem. Mater. 2010, 22 (18), 5184–5198.

Study of structure of monometallic nanoparticles using machine learning algorithms

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For many years the study of metallic nanoparticles attracted much attention due to their high level of efficiency in catalyzing of reactions. Today there is a fairly wide range of methods for diagnostic of the structural characteristics of such materials; among them is the analysis of XANES spectra. Investigation of materials with catalytic properties is often associated with high temperatures which lead to defects in the 3D arrangement of atoms. XANES in contradistinction to EXAFS is less affected by structural and thermal disorder which severely reduces the quality of EXAFS data and complicates their interpretation.

The current study is dedicated to development of a system that takes as an input data the theoretical XANES spectrum of monometallic nanoclusters and allows to automatically determine the average coordination numbers of the first four coordination spheres which are the most sensitive towards the nanoparticle morphology.

To develop a similar system we used machine learning algorithms, namely the supervised machine learning (SML) for multilayer neural network. Using the Python library ASE we modeled a large number of monometallic nanoclusters, theoretically calculated their XANES spectra and average coordination numbers of the first four coordination spheres, thus creating a training sample for the neural network. Further, in a series of theoretical experiments on learning models with different architectures we extracted the model that gives good predictions and also improves it, obtaining a system that gives stable predictions with small structural deformations of the cluster.

Further we are going to test the system's performance on experimental spectra and to develop an expert system that allows to determine various parameters of the materials under study using a combination of experimental data, such as XANES data, small-angle X-ray scattering and optical extinction spectra, and to generalize the study to the case of bimetallic nanoclusters.

Acknowledgments. The research is supported by the “Multiscale diagnostics of the structure of nanocomposite materials containing mono- and bimetallic nanoparticles using machine learning algorithms” grant No. 18-71-00092 of the Russian Science Foundation.

Operando XAS, XRD and Mossbauer spectroscopy studies of mixed d-metal olivine cathode materials for Li-ion batteries

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Mixed d-metal olivines (general formula $LiFe_{1-x}M_xPO_4$), which are now considered as promising cathode materials for Li-ion rechargeable batteries since they keep benefits from both d-metal components while having increased stability over the commercially used single d-metal cathodes. In this study we investigated a set of Co and Mn doped LiFePO4 samples obtained by mechano-assisted and solvothermal synthesis by the Group of Materials for Lithium-ion Batteries of the Institute of Solid State Chemistry and Mechanochemistry SB RAS [1,2].

The samples were studied with operando XAS, XRD and Mossbauer spectroscopy using both laboratory equipment and synchrotron radiation (BM31 beamline at ESRF, France). To achieve best results we used our self-developed electrochemical operando cell equipped with ultra X-Ray transparent conductive glassy carbon windows and spring-loaded adaptive anode.

The results we used to analyse the dynamics of local atomic and electronic structure of mixed d-metal olivines based cathodes depending on a cell SOC, as well as the origin of different electrochemical behaviour of samples obtained with different synthesis routes. Further analysis was performed also to reveal the mechanism of Li (de)intercalation for this class of cathodes and haw does the synthesis condition affect this mechanism, making possible the transition between homogeneous and heterogeneous processes.

References

[1] N.V. Kosova et al, 2014, J. Mater. Chem. A, 2, 20697
[2] N.V. Kosova et al, 2012, Solid State Ionics, 225, 564–569

Design of hexa- and heptacoordinated Fe(II), Co(II), Ni(II) coordination compounds with high magnetic anisotropy

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Search for the single-ion (SIM) and single-molecule magnets (SMM) with high blocking temperature (T_B) is one of the most challenging problems in coordination chemistry and it is a keyway to developing materials for ultra-high density memory storage, molecular electronic and spintronic devices. Ability to efficiently preserve induced magnetic moment within one molecule is determined by the height of the potential barrier between the states with opposite orientation of the spin moment in respect to the external magnetic field (Orbach barrier) which is, in turn, proportional to the product of the total spin of the molecule squared and the axial magnetic anisotropy parameter: $U_{eff} \sim |D| \cdot S^2$

Numerous attempts to build up SMMs with high T_B by maximizing the total spin demonstrated that this approach is not so straightforward, because (as it was shown in [1]) of the approximate reverse proportionality of $|D|$ and S^2. Therefore, developing of the coordination compounds with high axial magnetic anisotropy now is the most promising way to obtain SIMs and SMMs with high U_{eff}. and blocking temperatures.

In the current contribution some ideas of the of design, results of experimental and quantum-chemical (CASSCF/NEVPT2) studies of Fe(II), Co(II) and Ni(II) coordination compounds with distorted square and pentagonal bipyramidal coordination polyhedra is presented.

Acknowledgments

The work was supported by SFedU development program (grant No. VnGr-07/2017-29)

References

[1] O. Waldmann (2007) A Criterion for the Anisotropy Barrier in Single-Molecule Magnets, Inorg. Chem., **46**,10035-10037.

Atomic structure of bimetallic PtCu “gradient” nanoparticles in the composition of PtCu/C electrocatalysts

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Composite materials based on multicomponent platinum-containing nanoparticles are widely studied because they are promising catalysts for the electroreduction reaction of oxygen in low-temperature fuel cells. Platinum-containing nanoparticles are very promising due to high thermodynamic stability of platinum and due to specific chemical activity of this metal. However, the cost of pure platinum particle is one of the main factors restricting the wide application of low-temperature fuel cells. Such expenses can be decreased by using multimetal nanoparticles or non-paltinum nanoparticles.

In this research, the platinum-copper bimetallic electrocatalyst with initial composition of Pt0.8Cu/C was obtained by the methods of successive multistage reduction of platinum and copper from solutions of their precursors with a gradual increase in the concentration of atoms platinum in the mother solution . The composition and structural characteristics of this material were compared with the Pt0.1Cu/C catalyst based on solid solution nanoparticles which was obtained by combined single-stage chemical precursor reduction.

Structural analysis was performed using Pt L3- and Cu K- EXAFS spectra using the technique of determining local parameters of the structure of absorbing atoms that have a short-range environment consisting of Pt and Cu atoms. Based on the obtained structural data and on the composition of the investigated catalysts, the cluster models of PtCu nanoparticles are constructed, which demonstrate the features of the distribution of metal atoms in the volume of the "average" nanoparticle.

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Theoretical investigation of Pt and Pd species during activation process of Pt- and Pd- functionalized UiO-67 MOFs

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In order to describe the behavior of UiO-67 metal-organic frameworks (MOFs) functionalized with palladium and platinum activated in inert and H_2 atmospheres, we have performed DFT-calculations and XANES simulation by FDMNES code which were compared with experimental data. The atomic models used for XANES calculations included a standard MCl_2bpydc (M= Pd, Pt) linker, a linker with two chlorines substituted by hydrogen atoms with formation of Cl_2molecule, one chlorine substituted by hydrogen atom with formation of HCl molecule, detachment of two chlorines with formation of two HCl molecules, detachment of MCl_2fragment from the linker with its substitution by two hydrogens bond to nitrogen atoms of the linker, simple detachment of MCl_2fragment, and detachment of chlorines with formation of Cl_2molecule [1].

The calculated energy differences between the starting MCl_2bpydc linker and each of the structures showthat Pd nanoparticles (NPs) tend to be formed for both inert and H_2 atmospheres, while for $PtCl_2$bpydcformation of Pt NPs and isolated Pt sites is preferable in H_2- and inert atmospheres, respectively. Thus, the calculated XANES spectra allowed verifying and describing transitional experimental spectra.

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References

[1] A. Bugaev, A. Skorynina, et al. Evolution of Pt and Pd species in functionalized UiO-67 metal-organic frameworks. Catal. Today, submitted.

Iron coordination dynamics in the activation process of MIL-88a revealed by X-ray absorption and Mössbauer spectroscopies

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MIL-88a (Materials Institut Lavoisier) is an iron fumarate Metal-Organic Framework[1] that shows significant changes in unit cell parameters upon the activation process [2].The Mössbauer and X-ray absorption spectra (XAS) of MIL-88a sample were collected before and after activation (Fig. 1). Wavelet transform and theoretical XANES analysis were performed for XAS data, Mössbauer spectrum were analysed using standard procedures.

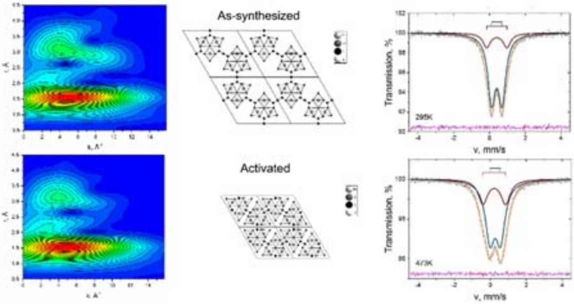

Figure 1a) Modulus of EXAFS signal wavelet transform before and after activation of MIL-88a. b) Structure dynamics. c) Mössbauer spectra.

X-ray absorption and Mössbauer spectroscopies revealed local atomic coordination dynamics of iron in the activation process of MIL-88a.

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References

[1] V.V. Butova, et al. Russian Chemical Reviews 85, 280-307 (2016)
[2] C. Serre et al. Science 315, 1828-1831 (2007)

Towards picometer resolution at femtosecond scale - novel research infrastructure horizons

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Fine details in the nanoscale local atomic, electronic, and magnetic structures determine most of the properties of advanced functional materials without long-range order in the atoms positions. To gain deeper insight into the nature of the "structure-property" relation, one has to use several advanced experimental methods for nanocharacterization, including modern approaches making also use of the opportunities at large-scale research facilities, like synchrotron-radiation facilities and x-ray free electron lasers.

The status of cutting-edge spectroscopies for the determination of parameters of the 3D local atomic, electronic, and magnetic structure is presented. One of the methods for extracting the 3D structure parameters is given by an advanced quantitative analysis of X-ray absorption near-edge structure (XANES) spectra that has been developed at the Smart Materials Research Institute of Southern Federal University (http://nano.sfedu). The possibility to extract information on bond angles and bond lengths (with an accuracy up to 1 pm) is demonstrated. This opens new perspectives for XANES as a 3D local-structure probe for any type of material without long-range order in the atomic positions.

Even more possibilities for applications are given by in-situ and in-operando techniques that open up a road for the study of a material not only in its static state, but also during processes involving the material. Time-dependent x-ray spectroscopic methods make it nowadays possible to obtain time resolutions in the picosecond and femtosecond range. The examples of case studies include the analysis of advanced 2D Energy Conversion Materials. The research is supported by joint Russian-Chinese grant was funded by at Russian side by RFBR research project № 18-52-53046.

Density functional theory approach for studying transition metal complexes with redox-active ligands

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Transition metal complexes with redox-active (non-innocent) ligands play a key role in many biologically important enzyme-driven and catalytic reactions and are implemented as the magnetically responsive molecular switches in various molecular electronic and spintronic devices [1]. The proper understanding and interpretation of the specific features of transition metal compounds must be based on the application of methods of modern quantum chemistry, which is the goal of the present report largely addressed to chemists employing quantum chemical calculations for prediction of novel and description of experimentally studied transition metal complexes with redox-active ligands.

Various aspects related to the use of density functional theory (DFT) method for the study of magnetic, geometry and energetic properties of transition metal complexes with redox-active ligands are considered. Particular attention is given to the correct choice of model compounds and methodology of the calculations. The principal strategy employed in the present work for testing selected DFT protocols is based on correlation of results of calculations with the experimental data available for the compounds structurally identical or most similar to those under study.

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References

[1] M.A. Halcrow. Spin-Crossover Materials: Properties and Applications. 564 p. (2013).

Quantum-chemical design of polyfunctional coordination compounds with redox-active ligands comprising biradical linker groups

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The development of fundamentally new types of electronic devices, in which single molecules or electron spins serve as logical elements, represents one of the priority directions of nanosystem industry. The significant efforts of the scientists are aimed at search for the magnetically-active metal complexes capable of performing the functions of molecular switches and spin quantum bits.

We suggest combining in one molecule two paramagnetic metal-containing centers capable of undergoing thermally initiated spin-state switching rearrangements [1] and acene linker group, singlet-triplet transitions of which are driven by photoexcitation [2]. Biradical state of the acene fragment promotes increasing the number of unpaired electrons and also results in the appearance of additional exchange interactions. By means of quantum-chemical calculations the effect of the structure of the acene moiety on the magnetic properties of the dinuclear di-*o*-quinone metal complexes has been studied.

Acknowledgements: This work was financed by the Russian Government grant to support scientific research under the supervision of the leading scientist (Megagrant no. 14.Y26.31.0016).

References

[1] M.A. Halcrow. Spin-Crossover Materials: Properties and Applications. 564 p. (2013).

[2] M. Bendikov, H.M. Duong, K. Starkey, K.N. Houk, E.A. Carter, F. Wudl. Oligoacenes: theoretical prediction of open-shell singlet diradical ground states. J. Amer. Chem. Soc., **126**, 7416-7417 (2004).

The in situ FTIR study of the noble nanoparticles supportedby ceria using CO probing molecules

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FTIR spectroscopy in combination with CO probing molecules was applied to investigate the ceria supported Pd, Au and AuPd NPs synthesized by incipient wetness impregnation and reduced in H_2 flow (mean size 7–11 nm).

DRIFT spectra (fig. 1) were collected using the Bruker Vertex 70 spectrometer equipped by Low Temperature Reaction Chamber (Harrick).

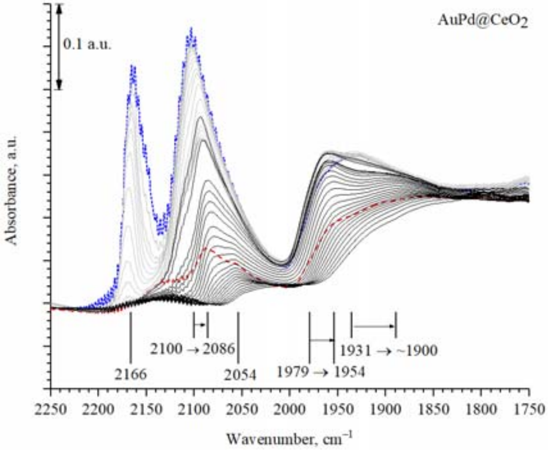

Fig. 1 Absorbance spectra of AuPd@CeO_2: activated at H_2 flow (200 °C, 30 min)samples (red), high CO coverage (blue), outgassing at –140 °C (grey), after further outgassing and heating to 300 °C (black).

It was observed that pure ceria support didn’t form strong bonds with CO at this conditions, whereas Au and Pd containing samples demonstrated chemisorption. Particularly, the adsorption on different Pd faces was distinguished. Analysis of intermediate spectra of AuPd@CeO_2has shown the presence of CO adsorbed both on Au and Pd active centers.

DFT-study of the axial NCX ligands effect on spin-state and geometry in Ru-, Fe- and Co-based quaterpyridine complexes

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In this research geometry, spin-states and geometry of the series of Ru (II), Fe(II/III) and Co(II/III) complexes with 4,4'''-dimethyl-2,2':6'2'':6'',2'''-quaterpyridine-4',4''-dicarboxy ligand and different monodentate NCX- (X=O, S, Se) axial ligands have been theoretically studied by DFT approach with different functionals (TPSSh, OPBE, B2PLYP and B3LYP).

The calculated relative stabilities of HS and LS states depend on the amount of Hartree–Fock exact exchange (C) implemented in the hybrid functional. The dependence of $\Delta E_{HS/LS}$ from C is linear for all studied complexes and the slope has the positive values for Ru based complexes and negative values for Fe- and Co-base complexes. The best match in harmonic vibrational frequencies between the experimental and calculated values has been reached at C=0.15.

For all investigated complexes containing NCX axial ligands its coordination through N atom is more energetically favorable than through S, O or Se atoms. These physical properties were found strongly correlating with the type of binding atom in the CNS ligand (isomerization differs by 4-13 kcal·mol-1). The results of theoretical studies showed that thiocyanato ligands have a greater ligand field strength than isothiocyanato ligands.

From the calculations, it emerges that the LS state is the ground one for Ru(II) and Co(III) complexes regardless the CNS arrangements (with exception of an S-bonded isomer of Fe(III) complex), while for others the HS is characteristic of the ground state. The complexes with N-bonded CNS ligands are energetically preferential. The optical spectra of Fe(II) complex with alternatively bonded CNS strongly depends on the angle between the axial ligands.

Complexes with more covalent character of the metal-ligand bond demonstrate noticeable structural differences when passing between LS and HS states and their ground state more markedly correlates with the amount of HF exact exchange in the DFT functional.

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Applications of machine learning to XANES for palladium nanoparticles

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X-ray absorption near edge structure (XANES) spectroscopy is one of the advanced applications for defining nanocatalysts properties particularly palladium-based catalysts [1]. While modern research facilities allow scientists to obtain experimental data by terabytes per day, the refinement of this data takes more and more time. This fact requires the new processing methods for large amounts of data. One of these methods is a machine learning devoted in this work.

This project presents the current results of the software package development for machine learning based on the extra trees method applied to the palladium nanoparticles spectra in presence of hydrocarbons.

This work was supported by Russian Foundation for Basic Research Grant No. 18-32-00856.

References

[1] A. Bugaev, O. Usoltsev, et al. Palladium carbide and hydride formation in the bulk and at surfase of palladium nanoparticles. J. Phys. Chem. C, 122 (22), 12029-12037 (2018).

Solvothermal synthesis of hybrid material based on UiO-67 and spiropyran molecules

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Spiropyrans (SP) are among the most promising and widely studied classes of photochromic organic compounds. Incorporation of SPs in metal-organic frameworks (MOFs) provides a unique opportunity to tune properties of a polyfunctional hybrid material by the activation irradiation. Photoactive MOFs were applied as adsorbents of gases, elements of molecular electronics and photonics, chemical sensors of metal ions and combustion gases, etc [1]. The aims of the present work are synthesis and detailed diagnostics of a new promising photoactive functional material UiO-67@SP. We suppose that SP molecules coordinate Zr^{4+} ions inside defective cavities. This work was funded by RFBR according to the research project № 18-29-04053.

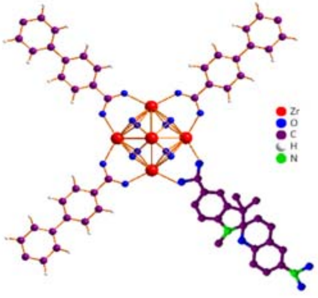

Fig.1. Proposedball-and-stick model of a hybrid UiO-67@SP structure

References

[1] S. Castellanos, A. Goulet-Hanssens, F. Zhao, A. Dikhtiarenko, A. Pustovarenko, S. Hecht, J.Gascon, F. Kapteijn and D. Bléger (2016). Chemistry – A European Journal, 22, 746-752 (2016).

Quantum-chemistry calculations of a spiral-chain phosphorus fluoride

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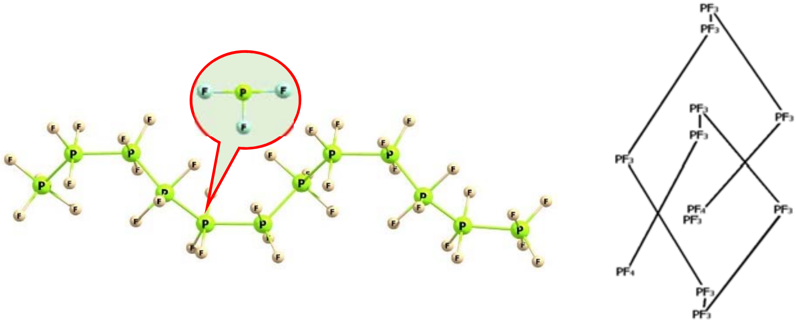
In recent years many important investigations were made in the field of one-dimensional materials. It was offered different inorganic viable chains with novel properties. In this work, the new systems constructed on basis PF_3 moieties are shown (fig.1). Their stability are supported by DFT calculations with B3LYP/6-311+G** theory level.



(a) (b)

Fig.1 Inorganic spiral structure$P_{12}F_{38}$, consist of PF_3 moieties. Side view is (a). Schematic view along the axis of rotationis (b).

Early linear systems were calculated and phonon spectrum pointed out on stability of infinite chain P_nF_{3n}[1].

In the research the spiral series was simulated for P_nF_{3n+2} (n=3-17). All systems are viable and their stability increases with raise of phosphorus atom number.Calculated force constants and the resulting vibrational frequencies showed the last do not have negative values.

This work was supported by Russian Government grant by decree N 220 (agreement N 14.Y26.31.0016).

Reference

[1] S. Zaytsev, D. Steglenko, R. Minyaev. Estimation of stability and properties of extended nonmetallic chains PnX3n+2 (X = F, Cl): materials of XIV youth scien.conf.: achievments and prospects for young researshes, 12-26 april 2018, Roston-on-Don, SSC of RAS publisher, Russia, P-54.

Laboratory-based X-ray microscopy and nano X-ray computed tomography – Technique and applications

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High-resolution nondestructive imaging of materials and structures, including studies of kinetic processes, is a highly ranked request from solid-state physics and advanced materials development, and it is an industrial demand for product development and reliability engineering in several branches including microelectronics, energy storage and lightweight construction. Laboratory X-ray microscopy and nano X-ray computed tomography (XCT) are versatile techniques for nondestructive 3D bulk analysis of materials and for the investigation of complex 3D structures with a spatial resolution of 50 nm and below [1]. Because of their ability to reveal structural characteristics, materials' microstructure and flaws, such as cracks and pores, or local composition and density differences, they are potential techniques for imaging of micro- und nano-structured objects. Examples for high-resolution in-situ X-ray imaging studies will be shown, including studies of kinetic processes in materials: Physical failure analysis in 3D-stacked microchips, kinetic reactions for energy storage and conversion processes, crack initiation and propagation in composites and microchips.

Future developments in high-resolution X-ray microscopy and nano XCT will provide the capability to extend laboratory nano XCT to photon energies > 10 keV. Novel laboratory X-ray sources, e.g. using micro-patterned anodes [2], will reduce the measurement time. Novel focusing optics, e.g. multilayer Laue lenses [3] that substitute state-of-the-art Fresnel zone plates, will enable spatial resolutions down to 10 nm for X-ray microscopy at high photon energies. Further development and better parallelization of alignment, reconstruction and segmentation algorithms, possibly with the help of AI, will improve data quality as well as reduce the time-to-data of the reconstruction and subsequent segmentation steps.

[1] E. Zschech, M. Löffler, P. Krüger, J. Gluch, K. Kutukova, I. Zglobicka, J. Silomon, R. Rosenkranz, Y. Standke, E. Topal, Pract. Metallogr. 55, 539–555 (2018)

[2] W. Yun, B. Stripe, A. Lyon, D. Reynolds, S. Chen, I. Spink, S. Lewis, Synchrotron Radiation Instrumentation Conf. SRI, Brookhaven (2015)

[3] S. Niese, P. Krüger, A. Kubec, S. Braun, J. Patommel, C. Schrör, A. Leson, E. Zschech, Optics Express 22 (2014), 20008-20013

X-ray absorption spectroscopy applications in advanced functional nanomaterials

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Nanostructured materials have fascinating optical, electronic, magnetic, catalytic and chemical properties which make them very promising in the development of new catalysts, sensors, and optoelectronic devices. Understanding their growth processes and the structure-property relation are critical issues for their fundamental science and applications. The X-ray absorption fine structure (XAFS) technique has been applied extensively in nanomaterials fields, thanks to its element-specific feature and powerful probing ability for atomic/electronic structures. We have performed systematic investigations on the structure-performance relationship of a variety of nanostructured materials, ranging from monodisperse nanoparticles, atomically precise nanoclusters [1], magnetic semiconductor nanocrystals, quantum dots, and nanosheets [2, 3]. The importance of time-resolved XAFS technique is also highlighted by in-situ probing the nucleation/growth processes of nanomaterials and identifying reaction intermediates of nanostructured catalysts under operando conditions [4].

References

[1] Y. Y. Li, H. Cheng, T. Yao, Z. H. Sun, W. S. Yan, S. Q. Wei, et al., J. Am. Chem. Soc. 134, 17997 (2012).

[2] W. S. Yan, Q. H. Liu, C. Wang, T. Yao, Z. H. Sun, S. Q. Wei, et al., J. Am. Chem. Soc. 136, 1150 (2014).

[3] H. Tan, W. Hu, W. S. Yan, Z. H. Sun, Q. H. Liu, S. Q. Wei, et al., Small 13 (2017).

[4] L. N. Yang, H. Cheng, Y. Jiang, Z. H. Sun, S. Q. Wei, et al., Nanoscale 7, 14452 (2015).

Reinforcing materials based on AlCuFe quasicrystaline alloys

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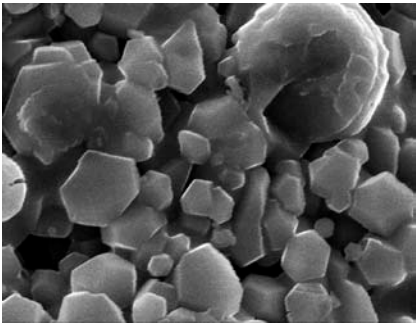

Aluminum alloys are one of the most promising structural materials for mechanical engineering, aviation, construction and other industries. Quasi-crystalline structures based on aluminum alloys Al-Cu-Fe is a new class of materials, which, unlike traditional crystalline structures, are characterized by icosahedral symmetry of short-range order, long-range orientation order, and the absence of translational symmetry inherent in the usual crystalline state [1]. The possibility of using the quasicrystalline phase as reinforcing materials and their other interesting properties stimulates the study of their structure and properties. The *i*-$Al_{65}Cu_{23}Fe_{12}$ quasicrystal was investigated using scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and X-ray absorption near edge structure spectroscopy (XANES). The surface-sensitive XPS technique was used to study the atomic and electronic structure of *i*-$Al_{65}Cu_{23}Fe_{12}$ quasicrystal and structures formed on the surface of the quasicrystal. It was found that The oxidized surface of the icosahedral $Al_{65}Cu_{23}Fe_{12}$ quasicrystal nanoparticles consists of Al_2O_3. The volume structure of the icosahedral $Al_{65}Cu_{23}Fe_{12}$ quasicrystal nanoparticles is made up of icosahedral $Al_{65}Cu_{23}Fe_{12}$ quasicrystal and cubic β-Al(Cu, Fe) phases.

References

[1] J.M. Dubois. Properties and applications of quasicrystals and complex metallic alloys, Chem. Soc. Rev., 41, 6760–6777, (2012).

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