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in 6 volumes**

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Book 6. Satellite symposia:

From Empirical to Predictive Chemistry.

The Periodic Table through Space and Time.

F-Block Elements: Recent Advances and Challenges.

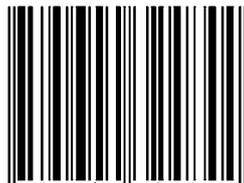
Self-Assembly and Supramolecular Organization.

Elemental Materials for Electrochemical Energy.

Book 6 consists of Plenary, Keynote, Invited lectures, Oral, Poster presentations and Correspondence reports of the symposia «From Empirical to Predictive Chemistry», "The Periodic Table through Space and Time" , "F-Block Elements: Recent Advances and Challenges", "Self-Assembly and Supramolecular Organization", "Elemental Materials for Electrochemical Energy" and index.

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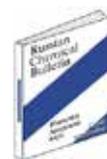
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**PLENARY
LECTURES**

THE STORY OF SINGLE MOLECULES, FROM EARLY HIGH-RESOLUTION SPECTROSCOPY IN SOLIDS, TO SUPER-RESOLUTION NANOSCOPY IN CELLS AND BEYOND

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In the late 1970s and 1980s, many researchers around the world were exploring a novel optical storage concept, frequency domain optical storage, which was based on spectral hole-burning in the zero-phonon lines of impurities in solids at low temperatures. In 1989, experiments aimed at establishing the ultimate limits this optical storage idea led to the first optical detection and spectroscopy of a single molecule in the condensed phase using laser FM spectroscopy. This represented optical exploration of the ultimate limit of one individual molecule at a time, an amount of material equal to (1/Avogadro's Number) of mol. As one might expect from an unexplored new regime, many surprises occurred where single molecules showed both spontaneous changes (blinking due to spectral diffusion) and also light-driven control of emission. These properties were subsequently also observed in 1997 at room temperature with single green fluorescent protein variants, and blinking, or reversible entry into dark states, was found to occur in many situations. In 2006, PALM and related approaches showed that Abbe's optical diffraction limit of ~200 nm can be circumvented to achieve super-resolution fluorescence microscopy, or nanoscopy, with relatively nonperturbative visible light. Essential to imaging with single molecules beyond the diffraction limit are several requirements: single-molecule fluorescence imaging, active control of the emitting concentration, and sequential localization of single fluorophores decorating a structure. Super-resolution microscopy has opened up a new frontier in which biological structures and behavior can be observed in live cells or other materials with resolutions down to 20-40 nm and below. Examples range from protein superstructures in bacteria to bands in axons to details of the shapes of cytoskeletal structures, amyloid fibrils and much more. Current methods development research addresses ways to extract more information from each single molecule such as 3D position and orientation, and to assure not only precision, but also accuracy. Still, it is worth noting that in spite of all the current interest in super-resolution microscopy of extended structures, even in the "conventional" single-molecule tracking regime where the motions of individual biomolecules are recorded in solution or in materials, much can be learned about the dynamics of nanoscale processes when ensemble averaging is removed.

FROM CATENANES AND ROTAXANES TO MOLECULAR MACHINES

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The simplest catenane, a [2] catenane, consists of two interlocking rings. Rotaxanes consist of rings threaded by acyclic fragments (axes). Interlocking ring compounds have attracted much interest in the molecular sciences, first as pure synthetic challenges and, more recently, as components of functional materials. In particular, these compounds appear as perfect precursors to dynamic systems for which motions can be triggered and controlled in a precise manner. This property led to the use of catenanes and rotaxanes as *molecular machine prototypes*.

Subsequently, the research field of artificial molecular machines has experienced a spectacular development, in relation to molecular devices at the nanometric level or mimics of biological motors. In biology, motor proteins are of the utmost importance in a large variety of processes essential to life (ATPase, a rotary motor, or the myosin-actin complex of striated muscles behaving as a linear motor responsible for contraction or elongation). A few recent systems are based on simple or more complex rotaxanes or catenanes acting as switchable systems or molecular machines. Particularly significant examples include a "swinging catenane", "molecular shuttles" as well as multi-rotaxanes reminiscent of muscles or able to act as molecular compressors or switchable receptors. The molecules are set in motion using electrochemical, photonic or chemical signals. Examples will be given which cover the various approaches used for triggering the molecular motions implied in various synthetic molecular machine prototypes. The work of various groups using non interlocking compounds will also be briefly discussed. Potential applications of rotaxanes and molecular machines will also be mentioned.

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J.-P. SAUVAGE, "From Chemical Topology to Molecular Machines", *Angew. Chem. Int. Ed.*, 2017, 56, 11080.

CATALYSIS AND THE PERIODIC TABLE OF ELEMENTS

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Catalytic technologies are currently used in the production of the vast majority of chemicals and materials and about 90% of all contemporary industrial technologies involve catalytic processes. As we have mentioned before, interdisciplinary projects, which interconnect the fields of catalysis, organic synthesis and organometallic chemistry, have quickly and drastically changed the image of the chemical industry [1]. It is important to note that numerous developments made by organic chemists in the field of catalytic technologies find rapid implementation in the industry and facilitate appearance of innovative products.

In this lecture we will touch upon the phenomenon of catalysis in terms of the diversity of catalytic processes, with the emphasis on the unique features of the application of different elements of the Periodic Table in catalytic reactions.

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MATERIALS FOR DEVELOPMENT OF ARCTIC AND COLD TERRITORIES

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The success of the development of cold areas, including the Arctic, largely depends on the availability of materials that can work effectively in hard climatic conditions. The development of cold zones has a long history, but the Arctic materials science (AMS) was formed a few decades in modern form. Now there is an intensive search, synthesis and experimental studies of the arctic materials, but there is virtually no generalizing analysis of the current state of AMS and not formulated trends in its development¹. Domestic AMS significantly behind the indicators of industrial development of the Arctic in the Russian Federation, although to succeed, the trend should be reversed.

The number and variety of materials used in cold climate zones is great: construction, functional, fuel and lubricants and other auxiliary materials of natural and anthropogenic origin and different chemical composition (metal, ceramic, low and high molecular weight, etc.). The specific features and requirements for these materials give reason to allocate AMS in a special section of material sciences. The evolution of AMS has features characteristic of modern materials science: the transition from natural materials to anthropogenic, the chemical and morphological composition and structure, versatility and giving the materials smart elements, etc. The report discusses the climatic factors of the Arctic and the mechanisms of their impact on the properties of materials, formulated requirements for arctic materials necessary for their operation. The classification of arctic materials, taking into account their properties, structure and application in technical devices and constructions is offered. Obtaining Arctic materials are adaptation of existing materials for the Arctic conditions and development of new specifically for Arctic. The report will give examples of the creation of some Arctic materials obtained in domestic scientific organizations. The methods of studying the structure of Arctic materials, their laboratory and nature tests, including the influence of climatic factors, were also discussed. Analysis of the survey of experts and international bibliometric databases revealed research organizations with the greatest competence in certain areas of AMS. The features of interaction between researchers and between scientific structures are evaluated, and proposals to improve the cooperative climate are made.

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SYNCHROTRON RADIATION AND INVESTIGATION OF CATALYTIC SYSTEMS

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Over recent years the progress in development of material science and adjacent fields such as energetics, catalysis, membrane and sensor technologies, elemental base of micro- and nanoelectronics is largely defined by the level of a country's research infrastructure including the sources of synchrotrone radiation and neutrons, in other words, by the presence of "mega-science" plants. We can rely on the international cooperation in conducting such studies assuming the use of the international centers of competence in this field, HZB (known before as BESSY-II) and DESSY in Germany, ESRF in France, Daresbury in Great Britain, centers of synchrotron radiation within the National Laboratories in the USA. Indeed, these options are available and should be used, albeit on a competitive basis; however, the existence of the domestic "mega-science" plants, their regular use and upgrading would not only increase the time for such studies and widen the circle of objects over the technological tasks, but also keep up the research and methodological level of the scholars participating in this international differentiation of labor as well as the technological level of production of non-standard equipment for various purposes.

In my lecture I intend to argue for the importance of using the potential of synchrotron radiation for catalytic studies; I will present not only the forming tendencies but also the latest research results obtained lately while studying the structure of active centers of heterogeneous catalysts in various centers of synchrotron radiation. I will also show the latest results of our experiments on studying the bimetallic Pd-Au catalysts of low-temperature oxidation with CO (the XPS experiments were carried out on the RGBL and ISSS stations of the Berlin source of synchrotron radiation, HCB), the Pt/Al₂O₃ nanocatalysts of the total methane oxidation (studied at the station of the Kurchatov center of synchrotron radiation upgraded for the in-situ XRD and XAFS measurements with our participation), reactions of methane oxidation in the self-oscillation regime on Ni catalyst (studied at the XRD station of the Siberian center of synchrotron radiation in Budker Institute of Nuclear Physics SB RAS).

In conclusion I would analyze the possible directions of development of this approach to the basic research in the field of catalysis, already employed in some countries (Germany, USA, Great Britain, Scandinavian countries), for example by creation of national catalytic hubs with the purpose of coordination of means for conducting the oriented studies including those in the interest of industrial partners as well as the Russian national network of "mega-science" plants planned to be built.

CHEMISTRY OF 2D MATERIALS: FROM 2D MOLECULAR MAGNETS TO HYBRID MOLECULAR/2D HETEROSTRUCTURES

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Graphene and other 2D materials are a hot focus of interest in physics, chemistry and materials science. These materials are almost exclusively based on inorganic lattices and cover a wide range of electronic and magnetic properties: from insulators to superconductors, from diamagnetic to ferromagnetic (FM) and from metallic to non-metallic compositions. Except for the chemical functionalization of the surface of the 2D material, molecules have been scarcely considered in this field. In this talk I will emphasize the role of chemistry in this area paying particular attention to the magnetic properties. In the first part I will show how coordination chemistry can provide examples of molecular 2D magnets that, in contrast to what happens with the inorganic 2D magnets, are chemically stable in open air, keeping their magnetic properties preserved upon functionalizing their surface with different organic molecules.¹ In the second part I propose to create hybrid heterostructures by interfacing a layer of a functional molecular material with a 2D material. The aim is that of tuning the properties of the “all surface” 2D material via an active control of the hybrid interface.² To reach this goal the molecular system of choice will be based on spin-crossover complexes able to switch between the two spin states upon the application of an external stimulus (temperature, light or pressure). This concept will provide an entire new class of stimuli-responsive molecular/2D heterostructures, which may be at the origin of a novel generation of hybrid materials and devices of direct application in highly topical fields like electronics, spintronics and molecular sensing.

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ORIGIN OF ELEMENTS AND CHEMISTRY IN SPACE

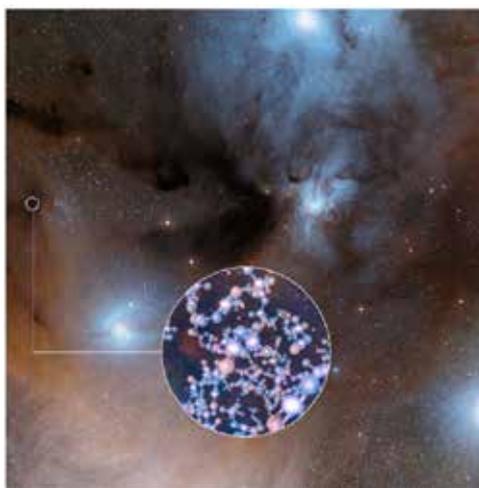
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'We are all stardust'. Most of the elements in the periodic table were formed in space. The simplest species - H, D, He, and Li - were made shortly after the Big Bang in the early Universe, whereas the rest of the elements that make 'us' were produced by nuclear fusion in the interior of stars, gradually enriching the Universe with heavier elements. A brief overview of the production of the main elements that are important for interstellar chemistry will be given.¹

Chemistry starts in the cold and tenuous clouds between the stars. In spite of extremely low temperatures and densities, these clouds contain a surprisingly rich and interesting chemistry, as evidenced by the detection of more than 200 different molecules, from simple to complex¹. Chemistry takes place both in the gas and on the surfaces of interstellar dust grains.^{1,2} New facilities such as ALMA allow us to zoom in on the formation sites of new stars and planets with unprecedented sharpness and sensitivity. Spectral scans of young protoplanetary disks contain tens of thousands of rotational lines³, revealing water and a surprisingly rich variety of organic materials, including simple sugars³, molecules with peptide bonds⁴ and high abundances of deuterated species³. What are the dominant chemical processes at work? How common are they? What material is available to build new exo-cometary and planetary systems?



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NON-CRYSTALLINE NANOSTRUCTURED MATERIALS: THE WAY TO NEW SOLIDS WITH NEW STRUCTURES AND PROPERTIES

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Today's technologies are based primarily on utilizing crystalline materials (e.g. metals, semiconductors or crystalline ceramics). The way to new technologies may be opened by nanostructured materials that are totally or partially non-crystalline. One group of them are nano-glasses. They consist of nanometer-sized glassy regions connected by (nanometer-wide) interfacial regions with atomic and electronic structures that do not exist in melt-cooled glasses. Due to their new atomic/electronic structures, the properties of nano-glass differ from the corresponding properties of melt-cooled glasses. For example, their ductility, their biocompatibility, their catalytic and ferromagnetic properties are changed by up to several orders of magnitude. Moreover, they permit the alloying of components e.g. ionic materials (e.g. SiO) and metallic materials (e.g. PdSi glasses) that are immiscible in the crystalline state. The properties of nano-glasses may be controlled by varying the sizes and/or chemical compositions of the glassy clusters which opens the perspective of a new age of technologies - a "glass age". A second group of nanostructured partially non-crystalline materials with tunable properties are nano-porous metals with electrolyte filled pores. By applying an external voltage between the electrolyte and the nano-porous metal their properties e.g. their superconductivity, magnetic moment, electric resistivity may be varied. Single or multi-atom switchable contacts represent a third group of these materials. They open the way to spontaneously formed single-atom or multi-atom transistors which allow quasi solid state bi-stable switching between quantized conduction levels of $2e^2/h$ or multiples of $2e^2/h$.

THE FUNCTION OF FUNDAMENTAL STUDIES IN DEVELOPMENT OF THE NEW GENERATION MATERIALS

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New generation materials are the basis for development of the competitive civil and special equipment on the world market. The "Strategic directions for the development of materials and technologies of their treatment for the period up to 2030" developed upon the VIAM initiative and approved by the Science & Technology Council of the Military-Industrial Commission of the Russian Federation determine the approaches and implementation phases of fundamental and applied studies in the field of materials science.

The main principles of creation of the new generation materials are materialized on the basis of unity paradigm "material – technology – design". During the development of the new generation materials the multilevel approach is used: material modeling on nano-, micro, meso- and macro-levels, study of mechanisms of elemental samples behavior with results validation for structural elements and goods. Today the development of the new generation materials is impossible without computer modeling of materials and mathematic models of their manufacturing. They allow optimizing the parts and structures production technology by conditions of strain-stress state; evaluate the influence of the initial stock on physical and mechanical properties of the materials; reduce the value of the development of the new materials.

The development of the new generation polymer composite materials (PCM) is the most important direction of growth of the Russian economy. This calls for the new high-strength, high-modulus fillers, foremost – the carbon fiber. It should be noted that nowadays Russia does not possess both the production of intermediate modulus carbon fibers similar to T700 and T800 in their properties and the capacity of the end-to-end cycle of PAN-fiber production, the quality of which predefines the properties of carbon fiber. At the same time the development of PCM branch is in direct dependence on the achievements of the chemical industry. The main task is to develop the components of polymer matrices – oligomers, catalyst systems meeting the high requirements not only to properties, but also to ecological compatibility of production. Under present conditions the technological breakthrough is closely connected with the intense development and wide application of principles of "green chemistry" and molecular design, development of atomic-molecular engineering during the new compounds production. It is necessary to generate the program of manufacturing process management for the highly purified materials for microelectronics, photonics, optoelectronics and biomedicine, as well as to determine the competence center – an industry organization in charge of technologies and production development for chemical compounds of highly purified materials.

The digital and additive technologies play the key part in improvement of the manufacturing process of complex technical systems parts. They allow manufacturing of high-quality parts by means of direct material synthesis ("addition"); it is impossible to create these parts by means of traditional "extracting" technologies, such as welding, mechanical treatment, etc. Additive technologies are rightfully the technologies of 21st century and they have great potential in the realm of energy cost reduction during the various products manufacturing. Thus, it is evident that the intensity index of using of the additive technologies is one of the indicators of industrial and innovative national development.

In general the joint achievements of the Russian Academy of Sciences, state scientific centers and the leading institutes of chemistry and materials science allow creating the basis for the development of the new generation materials. At present it is necessary to expand the scope of application of the scientific knowledge and discoveries and to intensify the innovative activity of scientific facilities and business by means of formation of consortia for implementation of large-scale projects of end-to-end innovative cycle (idea – material – technology – production of innovative products).

PLENARY TALK: XXI MENDELEEV CONGRESS ON GENERAL AND APPLIED CHEMISTRY

Mahaffy P.G.

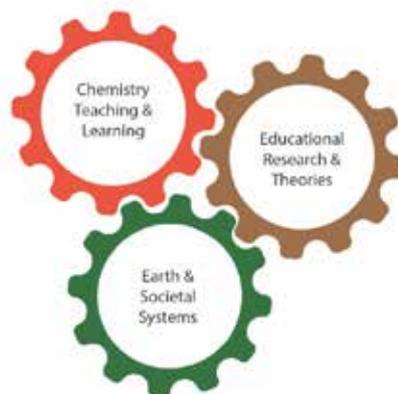
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Title: Systems Thinking to Educate about the Molecular Basis of Sustainability

Abstract: A Systems Thinking in Chemistry Education (STICE) framework has been developed by a global IUPAC project team with the goal of moving learners from fragmented knowledge of chemical reactions and processes toward a more holistic understanding of the field. Systems thinking shows promise in guiding students to see the relevance of their chemistry education for addressing multiple emerging global challenges such as sustainability, alternative energy, planetary boundaries, and the UN Sustainable Development Goals. We will explore progress to date in implementing the IUPAC STICE project and suggest approaches that can be used by chemistry educators to help students develop a deeper understanding of the molecular basis of sustainability.ii To give chemists and educators a concrete example of how systems thinking can be used, we will consider the Haber-Bosch process for the synthesis of ammonia, and the way systems thinking visualization tools can help students move beyond a narrow view of this process to consider chemical and energy inputs, reaction conditions, outputs such as the Ostwald Process leading to ammonium nitrate, and the intended uses of nitrogenous compounds derived from ammonia in agriculture and munitions, as well as unintended consequences resulting from the overuse of reactive nitrogen. Next steps for the IUPAC STICE project will be discussed, including suggestions arising from contributions to a special issue of the Journal of Chemical Education on "Reimagining Chemistry Education: Systems Thinking and Green & Sustainable Chemistry," to be published in late 2019.iii

Abstract graphic (if one can be used):



**Systems Thinking in Chemistry Education
An IUPAC Project**

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THE CHEMICAL ELEMENT: HOW CHEMISTRY IS KEY TO SOLVING OUR GLOBAL CHALLENGES

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Chemistry is a global endeavor that has greatly contributed to improving our quality of life by protecting us against illness and by putting food and clean water on our table.¹ But now, our global challenges are so big that only if we focus all our efforts in solving our most pressing problems we can create a sustainable and better future for all.² From climate change to our dependence on finite natural resources, many of our most global challenges require a technical solution that only better science and technology in general and chemistry in particular can provide.³ During its almost 100 years of existence, IUPAC has created universally accepted chemistry nomenclature and terminology as well as a global platform to discuss and advance some of the most relevant topics on pure and applied chemistry.

Chemistry education is of particular importance. We must train, engage, and inspire the new generation of young chemists able and committed to building a more sustainable future.^{4,5} In order to get there, science education, from primary school to college, needs to be reinvented to put the student at the center of the learning process and provide him or her with the skills needed to become a more complete and creative scientist.

There is still a significant gap between academia and industry that needs to be bridged by bold entrepreneurs able to connect these two worlds and successfully commercialize the new and exciting research carried out in universities. Entrepreneurship is another important part of the equation, taking the discoveries made in the lab to the market place is essential to implementing the solutions we need, and scientists have a key role to play here.⁶

During the presentation some examples and various ideas will be shared to accelerate the discovery and application of chemistry breakthroughs that, hopefully, will ignite a thriving and constructive discussion.

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ELECTROCATALYTIC PRODUCTION OF H₂ FROM WATER WITH F-ELEMENT-BASED MOLECULAR CATALYSTS

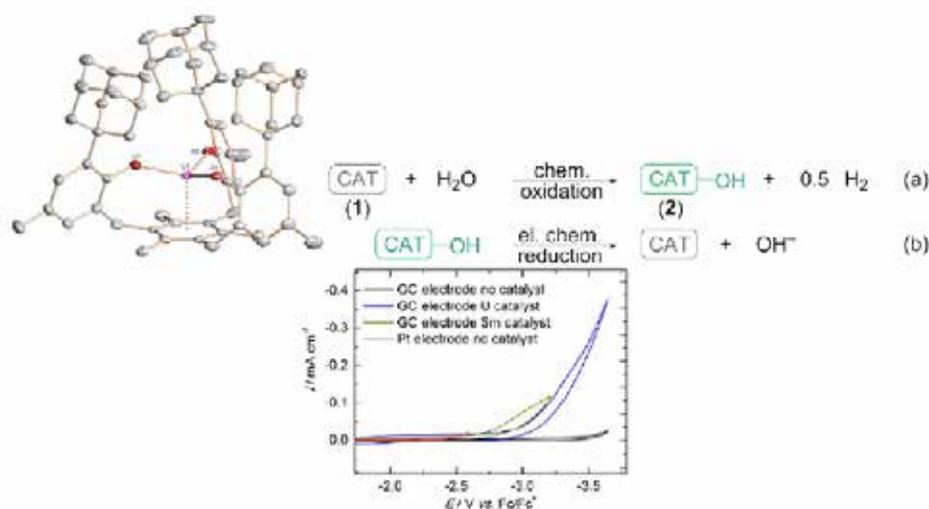
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Research on renewable energies and energy storage, such as H₂ production from H₂O, has become a key challenge for our society. The low efficiency of conventional H₂O electrolysis precludes large-scale applications. Thus, catalysts are desired to make this otherwise convenient strategy more applicable. Due to the high reactivity and oxophilicity of trivalent uranium complexes, as well as the large-scale availability of depleted uranium, uranium complexes are widely discussed as effective and economic catalysts for stable substrates.

In our previous studies of the arene-anchored tris-aryloxy uranium complex [U^{(Ad,Me)ArO}₃mes] (1), unique electrochemical and well-defined synthetic behavior were found, rendering 1 a perfect candidate for electrocatalysis.

Indeed, trivalent uranium coordination complex 1 was found to be the first molecular uranium catalyst for electrocatalytic H₂ production. Utilization of 1 during H₂O electrolysis lowered the overpotential by 0.5 V, increased the steady-state electrolysis current by a factor of 10, and lowered the faradaic resistance by 3 orders of magnitude. Isolation of key intermediates and *in situ* EPR experiments allowed to determine the reaction mechanism of H₂O reduction with low valent U(III). This reactivity is now studied in a series of lanthanide complexes [Ln^{(Ad,Me)ArO}₃mes] (2–Ln), which allows for fine-tuning of overpotential and reactivity of the catalyst by choice of the 4f ion.



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PERIODIC TABLE AFTER 150 YEARS

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One of the fundamental consequences of the modern theory of atomic nuclei (1969) is the prediction of an ‘Islands of Stability’ in the region of hypothetical super heavy elements (SHEs). In a heavy nucleus, going through the large-scale deformation on the way to fission, the motion of single nucleons is coupled with the collective degrees of freedom of the whole system. The most striking effect of this coupling is obtained for the case of fission of the heaviest nuclei, whose existence is defined entirely by the nuclear structure, i.e. by the shell effect.

From this point of view, the synthesis and study of properties of super heavy nuclei (SHN) is a direct way for checking the basic statements of the microscopic nuclear theory. On the nuclide map, SHN outline the border of the heaviest nuclear masses. SHN set the limits of the periodic system of chemical elements. The study of possible existence of SHN in nature offers a way for testing different scenarios of astrophysical nucleosynthesis.

The talk presents results concerning the synthesis and decay properties of the super heavy nuclei from this ‘Stability Islands’ of SHEs obtained in cold and hot fusion reactions. The region of heavy nuclei have expanded and advanced up to mass of 294. New elements filled the 7th row of the Periodic Table of Elements. The results of the first chemical experiments and theoretical predictions about the influence of the "relativistic effect" on the electronic structure of the SH atom are presented.

Super heavy atoms are synthesized today in unit quantities. Theoretical expectations of the chemical properties of the new elements with respect to their light homologues is discussed in connection with the synthesis of elements heavier than 118. A significant increase in the sensitivity of experiments is expected with accelerator complexes of the new generation. At one of them, the “SHE Factory” in JINR (Dubna) the first beam was obtained in the end 2018.

The talk used results of the experiments conducted in 2000-2015 at FLNR (JINR, Dubna) at the U400 heavy ion accelerator in collaboration with researchers from national laboratories and universities: LLNL (Livermore, USA), ORNL (Oak-Ridge, USA), IAR (Dimitrovgrad, Russia), Vanderbilt, Knoxville and Texas A & M Universities (all in USA), as well as data obtained at national nuclear centers: GSI (Darmstadt, Germany), GANIL (Caen, France) and RIKEN (Wako-shi, Japan).

THE PERIODIC TABLE AT 150: METALS, HEALTH AND MEDICINAL APPLICATIONS

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Elements of the Periodic Table have been known since ancient times, even before elements were known and recognized as such. No doubt Gold, Silver and Copper were the first of such metals, and were generally used in jewelry and coins, and in some cases also as weapons (Cu). By the time the Periodic System was tabulated in 1869, one was already aware that some elements and metal-containing compounds were needed for life (like Fe) and others were known to be very toxic, like As, Hg.

Already in the ancient times, some of the elements were used to treat diseases, like colloidal gold. The dosage of many of such metallic elements to humans, to cure or prevent diseases has been a subject of study for many decades. In the last 50 years the usage of metal compounds to diagnose or cure diseases has been rapidly grown.¹ The Periodic Table shown below, has elements that are known to play a role in health of humans bold printed.

Elements needed for live and used in curing and diagnosis

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	Ln	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	An	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Nh	Fl	Mc	Lv	Ts	Og
Lantha noids:		La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actin oids:		Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

In the lecture examples of drugs to cure diseases will be presented, with a focus on treatment of cancers by metal compounds, in particular by certain platinum compounds.^{2,3} The mechanism of action of such compounds will be discussed as well.

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MENDELEEV'S GIFT TO EDUCATION (AND TO ME)

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2019 has been declared the International Year of the Periodic Table in celebration of the 150th anniversary of Dmitri Mendeleev's first publication of his Periodic Table.¹ The purpose of this lecture is to demonstrate that Mendeleev's genius was to create something that anyone can use as a highly flexible framework for expressing their chemical ideas. I shall do this by giving examples of a whole variety of periodic tables ranging from one of the oldest surviving examples of periodic table intended to be shown in a lecture theatre² to the periodic table recently devised specifically by the European Chemical Society (EuChemS) for the IYPT, highlighting some of the elements which are becoming scarce.³ I shall also highlight how the Periodic Table has impacted my own career and research, as well as mentioning our own contribution to the debate about designs of the periodic table.⁴

Acknowledgements: I thank all of my colleagues, collaborators, co-workers as well as our technicians. In particular, I thank Professor Mike George, Brady Haran and Neil Barnes. I also thank the Engineering and Physical Sciences Research Council, The Bill and Melinda Gates Foundation and The Garfield Weston Trust for financial support.

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FROM MATERIALS INNOVATIONS TO NEW SUSTAINABLE BATTERY CHEMISTRIES

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Research's progresses in rechargeable batteries are driven by ever increasing demands for portable electronic devices as well as for powering electric vehicles and providing load-leveling for mass storage of renewable energy. Li-ion batteries are the systems of choice for the aforementioned applications. Therefore, for this to fully happen, new concepts and new sustainable chemistries are sorely needed, and this is what this presentation will address.

Firstly, regarding new concepts, we will show how the discovery of a new Li reaction mechanism that involves the anionic network with the reversible formation of dimers (O-O) represents a transformational approach for creating electrode materials with exacerbated capacities. Towards, higher energy density systems, recent advances on solid state Li batteries will be discussed. Concerning new chemistry, our new findings with the Na-ion chemistry which enlists novel materials/electrolyte designs together with the assembly of 18650 prototypes together with our work on Zn-MnO₂ aqueous systems will be presented. Lastly, an indirect way to enhance simultaneously energy density and sustainability via the use of sensing and self-healing functionalities will be introduced. Through these examples, the importance of materials design will be emphasized together

Altogether, these examples have been selected to show that the future of battery offers new opportunities for materials scientists as long as we are willing to play with the Mendeleev table and explore new risky paths. .

BIOMASS CHEMISTRY: BIOFUELS AND BIOPLASTICS

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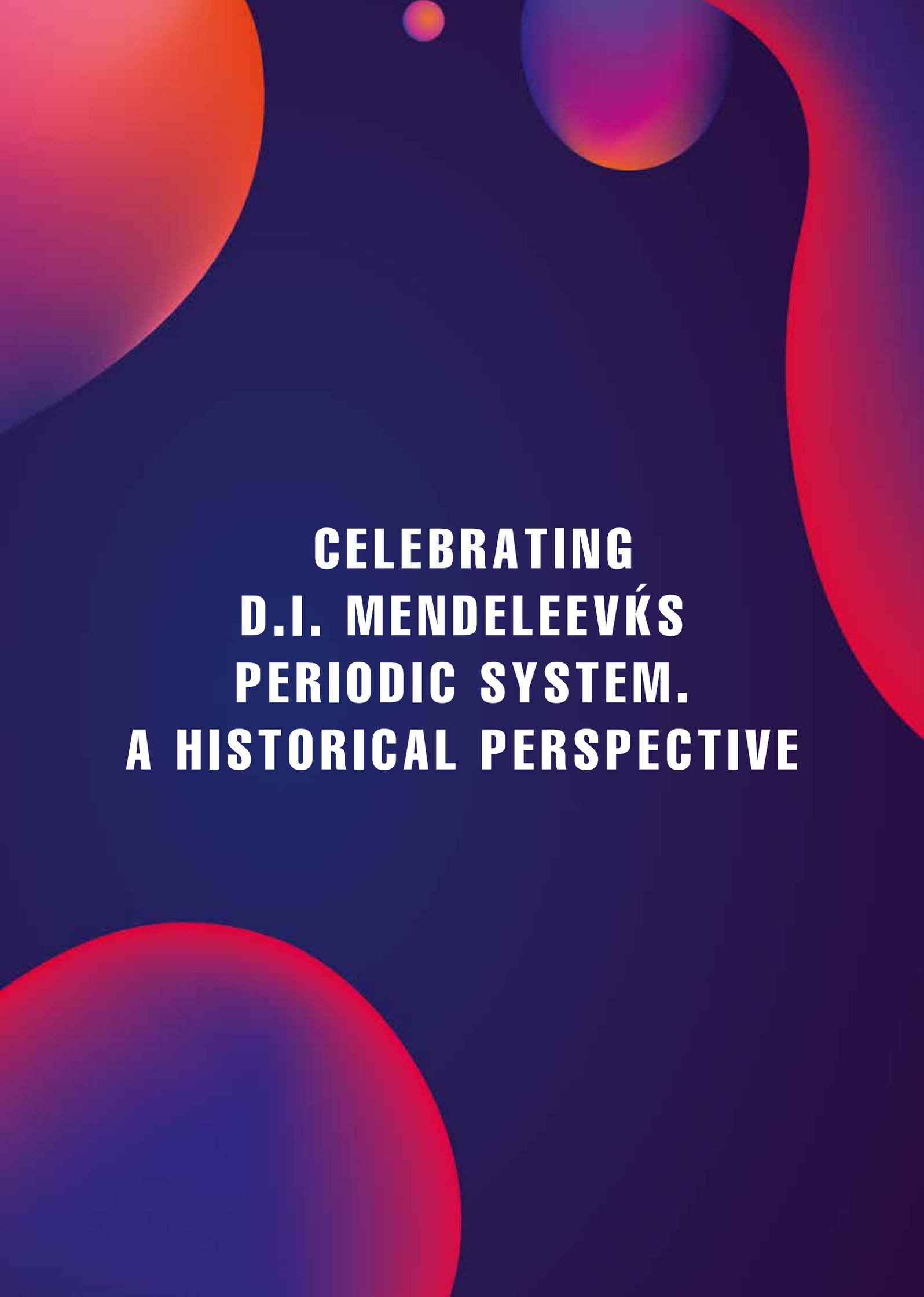
The lecture is devoted to the analysis of the achievements and trends in the renewable raw materials conversion into energy carriers and biomaterials.

The demand for new technologies for producing fuels and polymeric materials is determined by the raw materials sources growing shortage and the need to create fundamentally new large-scale environmentally acceptable methods for chemical industry.

The lecture discusses:

- Trends in the development of biofuels production and use;
- Biomethane and biohydrogen, chemical processes and the basis of technology for biogas production;
- Catalytic ethanol conversion processes;
- New fuels based on bioresources;
- Biotechnological processes for the butanol, acetone, other organic solvents and fuels production;
- Obtaining "bio-oil" and "synthesis oil" by biomass and polymeric materials pyrolysis;
- Biocatalytic synthesis of organic acids and plastics based on them;
- Polyhydroxyalkanoates - natural biodegradable polymers;
- Polyamides based on natural amino acids solid-phase polymerization;
- Bacterial cellulose - biocatalytic synthesis and use;
- Natural rubber - new biotechnological synthesis methods.

The rates of new renewable resource sources development, qualitatively new biofuels and bioplastics properties are considered.



**CELEBRATING
D.I. MENDELEEV'S
PERIODIC SYSTEM.
A HISTORICAL PERSPECTIVE**

MENDELEEV'S NOTION OF CHEMICAL ELEMENT: A KEY ACTOR IN THE CONSTRUCTION OF THE PERIODIC TABLE

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In chemistry textbooks, Mendeleev's periodic classification is often presented as a visionary anticipation of twentieth-century atomic physics. For historians of chemistry it rather looks as a masterpiece in the long quest for a natural classification, which pre-occupied most nineteenth-century chemists-professors.¹

Standard historical accounts emphasize the influence of Mendeleev's pedagogical motivations and of the 1860 Karlsruhe conference that Mendeleev himself pointed out as a major step towards the discovery of the periodic law. They then go on describing Mendeleev's cards game to place the elements in the periodic table.²

This paper outlines the significance of a rather neglected aspect of Mendeleev's approach to the classification of elements: his distinction between simple bodies and elements. Whatever the priority disputes among the discoverers of the periodic system, Mendeleev distinguished himself among his rivals because he was the only one who bothered to provide a clear definition of the entities to order.

This paper will first present Mendeleev's conceptual clarification and emphasize its role in the process of construction of the periodic system. Symmetrically, I will argue that the periodic system helped define the notion of element as the true chemical individual, identified by its atomic weight, and its interactions with other chemical elements, a notion stabilized by the invention of the concept of isotopes in the early twentieth century.

Mendeleev's periodic system thus stands as a major turning point in the long multi-secular history of the notion of element.

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ASTROCHEMISTRY, NEW ELEMENTS, AND MENDELEEV'S PERIODIC TABLE

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Astrochemistry, a science based directly on spectroscopic measurements, emerged at about the same time as the periodic system. From the study of unidentified stellar spectral lines several researchers (e.g. W. Crookes, N. Lockyer, and C. Young) suggested that there might exist in the heavens elements different from those known on the Earth. Among these hypothetical, non-terrestrial elements helium was eventually verified, whereas coronium, nebulium, asterium, geocoronium and others were mistakes. Celestial elements such as helium and coronium were sometimes associated with primeval matter and an evolutionary interpretation of the periodic system, something which Mendeleev was strongly opposed to. Besides, there seemed to be no places in the periodic table for those elements. Mendeleev was well acquainted with chemical spectroscopy but skeptical with regard to the claim of helium as a chemical element. On the other hand, in his late and unorthodox attempt to make place for the ether in his periodic table, he not only accepted helium but also proposed coronium as a new group-zero element with an atomic weight smaller than hydrogen's. The talk will outline the problem of astrochemical elements in the period ca. 1868-1910 and discuss Mendeleev's views in relation to those of contemporary chemists, physicists and astronomers.

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MENDELEEV, MARKOVNIKOV AND THE ZHURNAL RUSSKOGO KHIMICHESKOGO OBSHCHESTVA: CELEBRATING THREE SES- QUICENTENNIALS

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The year 1869 was a banner year for chemistry in Russia. In that year, the newly-founded Russian Chemical Society issued the first volume of its *Zhurnal*, Dmitrii Ivanovich Mendeleev (1834-1907) first disclosed his iconic Periodic System of the Elements, and Vladimir Vasil'evich Markovnikov (1838-1904) disclosed his empirical rule for predicting reaction regiochemistry — the first such paper to do so.

The Russian Chemical Society (now the Mendeleev Russian Chemical Society) was established by members of the Chemistry Division of the 1st Congress of Russian Naturalists and Physicians, in St. Petersburg on January 4, 1868. A year after its founding, the Society began to publish its journal. In the first volume, many eminent Russian chemists published updates of their research in Russian. Among these were Borodin, Butlerov, Engel'gardt and Beilstein. The two stand-out papers, however, were published by Mendeleev¹ and Markovnikov.²

Mendeleev's publication gave us one of the two universally recognized icons of science—the Periodic Table of the Elements (the other is the DNA double helix). Mendeleev's breakthrough came because he was willing to allow the chemistry to be more important than atomic weight as an ordering factor. That same decision also allowed Mendeleev to make his famous predictions of the existence of *eka*-boron (scandium), *eka*-aluminum (gallium) and *eka*-silicon (germanium). Mendeleev's system fairly quickly gained ground, especially after the German language report appeared.³ In 2013, an ACS Citations for Chemical Breakthroughs Award was presented by the ACS Division of the History of Chemistry to St. Petersburg State University for Mendeleev's Table.⁴

Markovnikov's breakthrough publication, which appeared under an older spelling of his name, *Morkovnikov*, was the first to explicitly make a link between the chemical structure of a molecule and its reactivity. Still, it has received much less fanfare than Mendeleev's Table. However, like Mendeleev's paper, it was truly iconic in its way. Prior to Markovnikov's paper, the Structural Theory of Organic Chemistry was static; after Markovnikov's paper, it became dynamic.⁵

In this paper, the lives of these two fascinating chemists and the genesis of their discoveries will be discussed.

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THE PERIODIC TABLE 1969 TO 2019: WHAT HAS CHANGED?

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2019 has been declared the International Year of the Periodic Table (IYPT) in celebration of the 150th anniversary of Dmitri Mendeleev's first publication of his Periodic Table.¹ The IYPT has caused a huge impact all over the world. By contrast, the centenary of the Periodic Table in 1969 was barely noticed in the West. I started my PhD in inorganic chemistry in 1969 and I have no recollection of any celebrations of the centenary in the UK. Indeed, as a schoolboy, my first inorganic chemistry textbook² published in 1962 did not even include a periodic table!

The purpose of this lecture is to give a very personal view of how the Periodic Table has changed in the public's perception over the past fifty years. I do not have a definite explanation for the transformation of the Periodic Table. I merely present a few observations, partly derived from our work in presenting the chemistry of the elements on Youtube.³ My aim is to stimulate the thoughts and discussion of professional historians.

Acknowledgements: I thank all of my colleagues, collaborators, co-workers as well as our technicians. In particular, I thank Professor Mike George, Brady Haran and Neil Barnes. I also thank the Engineering and Physical Sciences Research Council, The Bill and Melinda Gates Foundation and The Garfield Weston Trust for financial support.

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DEVELOPMENT OF D.I.MENDELEEV'S IDEAS ABOUT THE UNIVERSALITY OF THE MASS APPLICABLE TO THE STRUCTURE AND CLASSIFICATION OF ELEMENTARY PARTICLES

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The transition from the model "four-dimensional space-time" to the model "spatial-electromagnetic continuum" leads to the derivation of equations describing the relationship of the spatial parameters of hierarchical structures, the power parameters of the fundamental interactions and the characteristic parameters of the physical vacuum reflecting its properties¹. The physical world is considered in the new model as a spatial-electromagnetic wave continuum and as a set of interconnected oscillators that form hierarchical structures. Substance and physical vacuum are interrelated forms of the continuum and form a single system. Each of these forms has the property of mass. The mass of a physical vacuum is not measured directly by existing devices, as a result of which a false idea of mass absence is created.

D.I. Mendeleev was right, considering the mass as a universal property of the physical world. Having accepted the thesis about the existence of hidden mass², the carrier of which is the physical vacuum, we arrive at an understanding of the internal structure of elementary particles and the construction of a system for their classification, having the character of periodicity. The magnitude of the minimal (unit) latent mass m_0 is 34.75 MeV/c². The union of unit masses into a real particle is determined by the laws of resonance. The relatively high stability of the muon ($3m_0$) is due to the high symmetry of the resulting system of oscillators (an equilateral triangle, at the vertices of which there are carriers of minimal mass, and in the center is an electron or positron). In the case of a nucleon ($27m_0$), one can speak of a three-dimensional resonant stabilization of the system.

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PERIODIC SYSTEM: FROM CHEMISTRY TO OTHER SCIENCES

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Since the discovery of the Periodic system by Mendeleev there are a lot of attempts to develop similar systems in different branches of chemistry, physics, biology, geology etc.¹

The talk will overview these approaches starting from the periodic tables of ions, isotopes, diatomic and triatomic molecules, functional groups and hydrocarbons. In some cases, the idea of periodicity was applied to classes of complex molecules although it was rarely articulated as periodicity principle. Finally, various biological and geological objects were classified as periodic tables for grains, mushrooms, bacteria, flowers, pantopods etc.

Some general criteria for periodic systems are also discussed.

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TO THE HISTORY OF RUSSIAN CONTRIBUTION TO THE PERIODIC SYSTEM

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By creating a Periodic System and formulating a Periodic Law, the Russian scientist D.I. Mendeleev completed the 50-years search for the relationship between the mass of atoms and the properties of the elements. The discoveries of the chemical elements predicted by him that soon followed, confirmed the fundamental importance of his law as the basic law of natural sciences. In this context the priority aspects of L.Meyer's (1870) and D.I.Mendeleev's (1871) tables are considered. Ruthenium entered independently in both tables was the only chemical element discovered to that time in Russia (K.Claus, 1844).

The development of a Periodic System in the 20th century is associated with accumulating experimental material in the field of atomic and nuclear physics. Science successes allowed expanding the boundaries of the Periodic System, first of all, due to the synthesis of new elements – transuranic. The achievements of the works of the group of academician G.N. Flerov (discoveries of the elements with atomic numbers 102-105 in USSR) within struggle of views during the “transferium wars” of the 1960s – 1980s are analyzed.

Synthesis advances of transuranium and superheavy elements with serial numbers 113-118 on the border of the periodic table (Joint Institute for Nuclear Research (JINR) from Dubna, Russia) executed during past 50 years are the indisputable evidence of the validity of the law of periodicity of chemical elements and proof of the triumph of Russian science. At the same time, these results are the culmination of the development of nuclear physics concepts of nuclear stability in the field of superheavy elements. The circumstances of the world recognition and non-recognition of the historical discoveries of Russian scientists are discussed in proposal.

Meanwhile Russian scientists do not stop at this. The discovery of a new area (“islands”) of stability and the fact of the existence of superheavy elements raises questions: where are the boundaries of the Periodic Table? are the properties of superheavy elements similar to their lightweight counterparts? The study of the properties of elements discovered in recent years allows us to make certain judgments on this matter. In the future this will be facilitated by the implementation of the world's first “Factory of Superheavy Elements” organized in Dubna, which will allow Russian researchers to start the realization of syntheses of the elements 119 and 120, already belonging to the 8th period of the Periodic Table.

M.YA. KITTARY'S ACTIVITIES ANALYSIS FROM THE PERSPECTIVE OF THE «UNIVERSITY 3.0» CONCEPT

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The great Russian chemist D.I. Mendeleev wrote in his book “Explanatory Tariff”: “If there can be no modern industry without science, then there can be no modern science without modern industry”¹. Similar goals of university commercialization and building links between industry and academic community are lying in the «University 3.0» development concept. D.I. Mendeleev’s contemporary and colleague, Professor of the Technology Department at Moscow University, M.Ya. Kittary was guided by elements of that concept already in 19th century.

M.Ya. Kittary made a significant impact on popularization of technology as a science and as well on the development of relations with key industrialists of his time. While being a professor at Kazan University, he receives recognition for technological advice; in the beginning of his career, he worked as correspondent at foreign industrial exhibitions, soon after, he organized those in Kazan and Vyatka. Thanks to his relations with industrialists M. Ya. Kittary was invited to head the re-establishment of the Technology Department at Moscow University, liquidated earlier by the Universities Charter of 1835, and the construction of a new technological laboratory. Under his direction, a technological museum was created, - the forerunner of the Polytechnic Museum in Lubyanka Passage. In his estate, he created a school for children of peasants and built an advanced plant for the production of lead whitewash, where management paid attention to the topic of industrial safety, which was unpopular with the owners of production at all times (and still is)^{2,3}.

M.Ya. Kittary has overtaken his time, his work is imbued with the spirit of entrepreneurship and innovation, many of the steps he has taken remain valid today, and can be adapted as successful examples of the commercialization of education and science by the management of modern universities and production⁴.

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JULIUS LOTHAR MEYER (1830-1895) AND THE PERIODIC SYSTEM OF ELEMENTS

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The talk will present the biography of Julius Lothar Meyer who was first studying medicine but then more and more became interested in chemistry. With his good education in physical, analytical and organic chemistry and influenced by the International conference on Chemistry in Karlsruhe 1860 he started to discuss several problems on elements and atoms.

Already in 1864, he published tables of elements. He wanted to find an analogy to the homologous series in organic chemistry and a possibility to understand the regularity in the differences of atomic weights if the elements are ordered with respect to the weights and chemical properties. The development and the integration in one table until 1869 will be explained.

The tables will be compared with the papers of Dmitri I. Mendeleev (1834-1907) under the aspects of how they referred to periodicity, if they predicted new elements, and how they themselves evaluated their own input to the periodic system. Meyer's didactic approach to teach inorganic chemistry on the fundament of the periodic system and several textbooks using Meyer's table will be presented.

Finally, Meyer's role in the chemical community will be discussed. Letters with characterizations of Meyer's will be presented for the first time.

ABOUT HISTORY OF INCORPORATION OF PERIODIC TABLE IN CHEMISTRY STUDIES IN RUSSIA (XIX – BEGINNING OF XX)

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Multiple researches dedicated to the discovery and development of the Periodic Law, cover different stages and aspects of that process. Nevertheless, among that massive amount of publications nothing is said about the way how Mendeleev's understanding of elements' classification and periodicity were integrated into the academic process, as well as how it was reflected in student books at the end of XIX – beginning of XX centuries. Therefore we have done a research right on this topic.

The specific of Russian education in the first part of XIX century was lack of gymnasiums where chemistry was studied as a unique subject (fragments of chemistry knowledge were integrated into physics course). Only starting from 1870 chemistry was included in the nonclassical secondary schools' program created within high school education reform held in the same period. In contrast to gymnasiums such programs were mostly focused on extended study of natural and exact sciences. However, that type of colleges disappeared soon since most of them were closed or redesigned back to gymnasiums by the end of XIX century.

Taking everything in account there is no surprise that there was lack of chemistry high school course books until the beginning of XX century. S.I. Kovalevsky's «Chemistry student's book» was one of the exceptions, it was designed specifically for nonclassical secondary schools, published in 1872 and many times reprinted. That course book was the first among school books as well as among high school student books (except «Principles of Chemistry» by D.I. Mendeleev). The second edition of «Chemistry student's book» published in 1874 included the Periodic Table. At first the Periodic Table was placed at the end of the book as a separate table, but starting from sixth edition it appeared to be in a separate section. This new section described its underlying principles, main advantages, elements predicted by D.I. Mendeleev, etc.

In our research we analyze chemistry course books of other authors that were written for universities and agricultural schools, mining, technology and polytechnic colleges. These are course books by V.U. Richter, A. Almedingen, V.I. Kurilov, A.V. Speranskiy, etc. Periodic law appears in them only in the end of XIX century, but from the very beginning it was followed by comments and description. Interesting fact is that in all the course books the Periodic Table was in the middle of the course - after non-metal and before metal sections.

MENDELEEV: THE PATH TO THE LAW

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1. To understand the history of the discovery of the Periodic Law, it is necessary first of all to find out which concepts and theories Mendeleev adhered to when starting work on the «Attempt at a system of elements based on their atomic weights and chemical similarity» and which he rejected or accepted with reservations and why; how he interpreted and processed information obtained from reading scientific literature.

2. Towards the beginning of his work on the textbook Principles of Chemistry (1867/8) Mendeleev formed a specific conceptual system, which included:

- an abstract notion of chemical element and of atomic weight as its core property that determines the element's chemical energy (as characteristics of the body's potential ability to enter into various chemical transformations) and thus its chemical properties;

- the ideal model of the future classification of elements, built from blocks of type: "alkali metals – intermediate elements «with a less sharp chemical character» – halogens”;

- the realization that properties of simple and complex bodies are the result of the properties of elements that form them.

3. It is important to note that Mendeleev was very critical of atomic theory. The concept of an element corresponded by him with the smallest weight amount of matter of a certain type entering the particles (molecules) of bodies. In addition, an element, in the sense of Mendeleev, potentially contains the whole range of possible forms, properties and states that this “stoichiometric minimum” is capable of detecting and unfolding in certain conditions.

4. With regard to the course of the discovery of the Periodic Law itself, then, according to Mendeleev himself, already considering the totality of elements with atomic weights from 1 to 40 led him to the important conclusion about the periodic nature of the change in the properties of elements as their atomic weights increase.

5. The main difficulty that Mendeleev encountered during the creation of the Periodic System was the lack of clear criteria for combining elements of different classes (in modern terminology, elements of the main and additional subgroups).

After a long search, Mendeleev created a compromise and temporary version of the system, which he called «Attempt at a system of elements based on their atomic weights and chemical similarity» (dated February 17, 1869 in old style). However, the creation of this option was an important step in his work, since now he was confident that:

- atomic weight is one of the most important parameters that determine the fundamental properties of elements;

- the relationship between the properties of elements and their atomic weights is periodicone.

6. Following the temporary, compromise version of the full Periodic System (the “Attempt”), the main issue was chemical criteria to unite elements of different classes of the core and the periphery of the system. Only by solving this problem could the way be opened to the creation of a whole natural classification of elements. Transitional elements clearly displayed analogies to the elements of the first class, although Mn and Cl, Cr and S, V and P, etc. were not full analogues.

By the end of 1869 or the beginning of 1870 Mendeleev understood that the highest forms of oxygen compounds (higher salt-forming oxides and their corresponding hydrates and salts) and their properties are determined not by the «properties of oxygen itself» but by the «state» or nature of the element in the highest oxygen compounds.

This meant that KClO_4 and KMnO_4 are similar not because they have so much oxygen «squeezed into» them that it «over-rides» and disguises the characteristic properties of other elements, not giving them a chance to develop, but because under the influence of four oxygen atoms chlorine and manganese pass into other states, into another «type of movement»; the capacity of chlorine and manganese for transition to similar states is one of their characteristic properties.

7. The immediate history of the discovery of the Periodic Law (excluding the prolonged stage of conceptual and informational preparation completed by the end of 1868), has three periods:

- the composition of the “first attempt” (or, more accurately, of the first attempts) of the system of elements, built upon scheme (2), and the discovery of the periodic character of the dependence of the properties of the elements on their atomic weights, the conceptual core of the Periodic Law (end of 1868–beginning of 1869);

- the creation of the «Attempt» as a temporary, compromise variant of the Periodic Table (February 17, 1869);

- the creation of the Natural system of elements based on the finally worked-out criteria for uniting elements of the first and second classes (finished by November, 1870).

While Mendeleev was searching for the best version of the system, the German chemist Lothar Meyer in March 1870 published an article dated December 1869 and containing a version of the table very similar to Mendeleev's «Natural System». Mendeleev had similar form of system, but ... only in his drafts.

Of course, Lothar Meyer became the strongest competitor of the Russian scientist. Comparing their contributions, one should first of all speak about the main thing: L. Meyer never spoke about the Periodic Law, only about the table or the system of elements. From the very beginning, Mendeleev spoke and wrote precisely about the fundamental law of nature. Meyer's claim (1872)

that the periodic system reflected «no simple law» was to exclude the possibility of making predictions based on the system.

Mendeleev's approach is different: he, in contrast to L. Meyer, considered not only arithmetic patterns in the growth of atomic weights, but also (and, first of all) changes in the properties of elements as their atomic weights increase. In the article “The Natural System of Elements and its Application to the Indication of the Properties of Undiscovered Elements,” (November 1870) Mendeleev described in detail the properties of three unknown elements at that time – the future Gallium, Scandium, and Germanium. All these elements predicted by Mendeleev were discovered during his lifetime.

DMITRY MENDELEEV: AT THE ORIGINS OF THE TOMSK SCIENTIFIC AND EDUCATIONAL CENTER

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D. Mendeleev was not only a great scientist but also an ardent supporter of the development of higher education and science in Russia, an active participant of foundation and formation of the first Siberian University in Asian part of Russia (founded in 1878) and of the first Technical University beyond the Urals – Tomsk Technological Institute (1896). These universities became the base of the Tomsk scientific and educational center. D. Mendeleev was a member of the Commission at the Department of Public Education, which examined the schemes of the future University buildings; he participated in designing of the University Main Building's classrooms and offices. Mendeleev also supported the opening of the Institute of Technology in Tomsk, although he believed that the beginning of higher technical education in Siberia should start with "Special Department of Industrial Knowledge" at Tomsk University. However, at that time, in the world practice, there were no examples of mixing university "pure science" with applied knowledge. When creating the Institute, Dmitry Mendeleev assisted to equip the laboratories with the modern equipment, selected professional scientific personnel.

On the 19th of January 1904 the Academic Council of Tomsk University awarded the outstanding scientist Dmitry Mendeleev with the status of Honorary Member "because of his scientific achievements currently well-known throughout the whole educated world". On the 22nd of January Mendeleev was elected an Honorary Member of the Tomsk Technological Institute. On the 2nd of February 1908, at the special meeting devoted to the first anniversary of the death of the scientist, the Chairman of the Society of Natural Scientists and Doctors at Tomsk University Professor A.A. Kulyabko in particular, said: "Mendeleev is dear to us as our countryman, - the native of Siberia..., he is dear to us as the person who always concerned with a high interest to destinies of the far homeland, and with the high moral authority much promoted the rise of the higher education center in Siberia".

PERIODIC SYSTEM OF GLASS FORMATION

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The periodic law of D. I. Mendeleev is inexhaustible and until now serves as a reference point at strategic planning of important theoretical and practical results. The behavior of atoms of chemical elements when forming vitreous and amorphous film materials shows primary and secondary dependence on a charge of their kernels. It can be shown, using as parameters of glassy ability of elements the limit maintenance of an element in a glassformer P_{lim} and a share of area of a glass formation from all concentration space of system S. The revealed general regularities sharply differ for s-, p-, d- and f-elements. Despite distinctions in techniques of receiving glasses by different authors, secondary frequency is shown in a beautiful mathematical form and is connected with stable electronic configurations $s^0, s^1, s^2, p^0, p^3, d^0, d^5, d^{10}, f^0, f^7$ and f^{14} . Interest is even the fact that in the most unexpected way in periodic system the quartet of the p-elements grouped with each other was allocated: phosphorus, arsenic, sulfur and selenium configurations. These are the only elements capable without the additional alloying impurity to form massive glasses and amorphous films. Their atoms possess external electronic configurations of $s^2p^{3(4)}d^0$ and are capable to form equally successfully as low and high molecular modifications unlike their next elements on periodic system.

All electronic configurations of atoms are modified when forming chemical bonds in the course of formation of the condensed condition of substances. Even empty subtotals with configurations of p^0 and d^0 have fundamental value for formation of physical and chemical properties of substances. Visually it can be shown on the example of s-elements. At combustion of alkaline metals in the atmosphere of oxygen of connection are formed in which there are perokisny bridges increasing the stability with increase of serial number of an alkaline element. With sulfur these elements form polysulfides in which excess of sulfur increases at increase in serial number of an element. The steady glassformation and amorphicity at the expense of p-elements can be characterized electronic and configuration equilibriums.

Thus, secondary frequency of tendency of elements to entry into structure of not crystal substances is shown and the mathematical regularities of secondary frequency connected with features of electron shells of atoms in the isolated and chemically connected states are revealed. The analysis performed allows us to compile a periodic glass formation system for systems with different compositions.

MENDELEYEV MEMORIAL COMPLEX ON THE TERRITORY OF THE VNIIM

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The great Russian scientist D.I. Mendeleev headed the state metrological institution of Russia from 1892 to 1907 and made a great contribution to the development of domestic and world metrology. He founded the school of metrologists, which was further developed at the D.I. Mendeleev Institute for Metrology (VNIIM).

Pupils and associates of D.I. Mendeleev respectfully and warmly venerating the memory of the scientist founded in 1925 the so-called Mendeleev Circle composed of the chairman, Prof. Konovalov, President of the Main Chamber of Weights and Measures, M. N.Mladentsev, A.N. Dobrokhotov, I.I. Kuznetsov, V.A. Muller, A.V. Skvortsov, and the son of a scientist, I.D. Mendeleev.

They celebrated all memorable dates associated with the name of D.I. Mendeleev, and founded the Museum of the Main Chamber, which was opened to visitors in 1928.

To prepare the celebration of the 100th anniversary of D.I. Mendeleev, an organizing committee was created at the Main Chamber (at that time VIMS, now VNIIM). In 1933, an extensive list of events dedicated to the scientist's anniversary and perpetuation of his memory was mapped out. One of the key events was the installation of the mosaic panel "The periodic system of chemical elements of D. I. Mendeleev" on the wall of the building of the Artillery School (now the Suvorov Military School), adjacent to the VNIIM.

The article will describe some circumstances and happenings associated with the accomplishment of this task (from choosing the table layout, artist, decoration and manufacturing techniques to the implementation of the project in 1935). Other monuments and memorial plaques to D.I. Mendeleev, installed on the territory of VNIIM will also be recounted.

THE 120TH ANNIVERSARY OF METROLOGICAL EDUCATION IN RUSSIAN FEDERATION

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In 2019, the Russian Federation celebrates the 120th anniversary of metrological education.

On June 4, 1899, Emperor Nicholas II approved the “Regulations on Weights and Measures” developed by the Russian scientist Dmitry Ivanovich Mendeleev, the founder of Russian metrology.

In accordance with the Provision, the creation of testing institutions and the training of qualified specialists performing verification were envisaged. For the first time in Russian history the foundations for training of specialists in metrology were laid.

This reform initiated by D.I. Mendeleev became the basis for the transition of Russia to the normative and legislatively fixed system of metrology, and also served as the beginning of the national metrological education.

Today the Academy of Rosstandart which is in the system of the Federal Agency for Technical Regulation and Metrology continues the process of specialists in the field of metrology training begun by D.I. Mendeleev. According to the Order of Rosstandart of March 14, 2018 No. 477, the Academy is the organization that provides additional professional education, training and retraining of the personnel of Rosstandart and subordinate organizations in the field of technical regulation, standardization and metrology.

EVOLUTIVE CLASSIFICATION – PORTUGUESE PERSPECTIVE THROUGH TEXTBOOKS AND MATERIAL CULTURE

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In this communication, we will point out the results of the investigation carried out trying to map the acceptance and use of Mendeleev's periodic classification in the Portuguese educative system, from its beginning, confronting with other classifications, and highlighting protagonists and documents evidencing the attention that the subject could receive among us. The research involved the identification of textbooks, programs and graphic presentations used in the secondary and higher education levels in a period that spanned from 1855 and 1976.

Following a traditional French tendency, many textbooks were still relying on the classification between metals, metalloids and nonmetals. Concerning the metals, the Thénard classification was used, based on their affinity with the oxygen; and for the metalloids, the Dumas classification that divided them in four families according to the similarities of the chemical properties[1]. Later, during the 1880s, it is possible to read about Mendeleev's classification in higher-level textbooks and programs, although the secondary school textbooks remained faithful to earlier classifications for some decades more, with some exception by 1906, when the first occurrence found led us to a textbook for advanced high school years. There is what seems to be the first presentation of Mendeleev's classification included as an extra reading for the student, when dealing with the relations between the properties of the different elements and their atomic weights, and the applications of the periodic law [2]. It doesn't seem that the subject was integrated in the official secondary programs before 1938. The periodic table room charts seem to have entered the secondary classroom by the 1960s and the university teaching during the 1930's.

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ILLUSTRATION OF THE PERIODIC LAW THROUGH THE VISUAL LANGUAGE OF THE MUSEUM OF SCIENCE

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Periodic law is one of the fundamental ideas of chemistry, allowing to classify various properties of chemical elements. In the process of creating the new scientific exposition for the Polytechnic Museum, we were faced with the need to develop a way to illustrate the periodic law that could convey its essence to non-specialists, while expressing the modern scientific understanding of the fundamental mechanisms that cause periodic repetition of the properties of chemical elements.

Even though we cannot count on our visitors having even good school-level knowledge in physics and chemistry, we, nevertheless, want to convey to them the most modern and correct understanding of the structure of the atom. Therefore, we have decided to use the solution of the Schrödinger equation for the orbitals of the hydrogen-like atom as the basis for the software generation system of our visualizations of atoms.

To visualize the periodic law, we allow our visitors to observe the process of creating the electronic structure of the atom of any of the 118 elements of the Periodic Table: the electron orbitals are “attached” to the atomic nucleus, up to and including the outer shell, the shape and size of which determine the chemical and physical properties of the selected atom. On the one hand, such a presentation allows to illustrate the periodic law visually, and, on the other, with a small commentary, to present the concept of chemical bonds, clearly illustrating their formation by changing and merging of the outer electron shells of atoms.

COMPOUNDS BY 1869: THE CHEMICAL SPACE FROM WHICH MENDELEEV'S PERIODIC SYSTEM AROSE

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Mendeleev came up with his first attempt to a periodic system by classifying and ordering the known elements around 1869. Order and similarity were based on knowledge of chemical compounds, which constituted the chemical space by around 1868. Despite its importance, very little is known about the size and diversity of this space and even less is known about its influence upon Mendeleev's periodic system. Here we show, by analysing 11,484 substances reported in the scientific literature up to 1869 and stored in the Reaxys®¹ database, that 80% of the space was accounted for by only 12 elements, oxygen and hydrogen being those with most compounds. We found that the space included more than 2,000 combinations of elements, of which 5%, made of organogenic elements, accounted for half of the substances of the space. When we trace the reporting of compounds back in time, we see that while Mendeleev's available space contained a mixture of organic, inorganic and organometallic compounds, after 1830 the organic substances quickly achieved the dominant role. The size and diversity of the space were such that knowledge of oxygen compounds and of some few other organogenic elements sufficed to have a panoramic idea of that space. We finally classified the 60 elements known by 1869 taking into account the resemblance of their combinations. Although we found a unique stable classification, elements are not tied together by strong similarities. In fact, most of the elements and classes of elements share less than 20% of their combinations. Finally, we found that Mendeleev's classification agrees with 43% of the similarities allowed by the chemical space.

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ROLE OF PERIODIC LAW IN FORMATION OF NATURAL SCIENCE WORLD CONCEPTION

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The natural-science world conception is systematized and complete representation on the nature formed as a result of synthesis of experimental and theoretical knowledge at fixed stage of scientific knowledge development [1, 2]. The inalienable attributes of the world scientific conception are an evolutionism, the paradigm shift, and internationalism [1]. The first antique scientific world conception based on ancient Greek philosophical systems enhanced by methodology and formal logic of Aristotle, dominated in mankind minds of nearly two thousand years [3]. The second classical scientific world conception began to form as a result of scientific revolution in astronomy and physics, the main initiators of which became Galileo Galilei, Isaac Newton, and later, Pierre-Simon Laplace. The Mechanism and Determinism of physical processes became a paradigm of classical scientific world conception. Within the frameworks of this conception the main arguments defining the properties and movement of objects was a mass (weight). The scientific revolution in chemistry, which was started by A.L. Lavoisier and was continued by D. Dalton (atomistic theory) came to the logic conclusion as creation of the classical molecular theory and discovery of the Periodic law by D.I. Mendeleev [3]. As a result the chemistry as the science was integrated into the general paradigm of the classical scientific conception of the world.

It is necessary to emphasize that D.I. Mendeleev's Periodic law and Periodic table of chemical elements served one of the main incentive motives of transition to the third nonclassical scientific conception of the world, the paradigm of which consists of special relativity showed that mass is related to energy and vice versa, and the quantum phenomena of a microcosm.

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FROM THE HISTORY OF THE MANOR D.I. MENDELEEV «BOBLOVO»

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Popular modern publications about D.I. Mendeleev are replete with unverified biographical facts that cast doubt on their authenticity.

To a greater extent, this concerns episodes of the life of the great scientist in his manor Boblovo.

Details of Boblovo manor life described by D.I. Mendeleev's relatives, in the author's opinion, are interesting for the general reader.

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PERIODIC SYSTEM OF ELEMENTS: NECHAEV'S METHOD

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It is well known to the community of chemists that there are several dozens of ways (attempts) to classify elements before our great compatriot, D.I. Mendeleev, plunged into this question. The methodological need to prepare a textbook for students, based on a single logical system, was given by D.I. Mendeleev to the formulation of the law, which objectively existed in nature, but unknown to any scientist at that moment in time. This new textbook was «Principles of Chemistry» [1]. Here is this Mendeleev formulation of the law: «the physical and chemical properties of elements, manifested in the properties of simple and complex bodies they form, are periodically dependent (form a periodic function, as they say in mathematics) on their atomic weight» (allocated by D.I. Mendeleev - S.T.) [2, p. 941].

After D.I. Mendeleev realized and built up a system of elements, about which he quite deservedly said that: «It would be more correct to call my system periodic because it follows from the periodic law» [2] and the table was published - the dam of thoughts broke through: today it exists (according to different sources) from 500 to 700 options for the table of elements! Note, the Mendeleev's periodic table of elements!

There are several hundred ways to represent a periodic law both on the plane and in space. We will focus on rather rare versions of the table of elements stored in our small collection. The tables considered below are of historical and chemical, as well as chemical and mathematical interest. We list them in chronological order. For example, the periodic table of elements proposed in Kazan by F.M. Flavitsky in 1887. Interesting are the tables proposed by Lothar Meyer (published in Russia in 1894), J. Thomsen in Denmark in 1895, N.B. Delone in Petersburg in 1898 and V. Crooks in London in 1898, which we demonstrate to our students.

The greatest interest for us is the table of the periodic system of elements proposed by the colonel from artillery Nikolai Pavlovich Nechaev in 1893 [3]. We dealt with Nechaev's table in more detail.

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THE DISCUSSION THAT DIDN'T TAKE PLACE. FRIEDRICH PANETH, LISE MEITNER AND IDA NODDACK AND THE PERIODIC SYSTEM AT THE MENDELEEV CONGRESS 1934

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On the occasion of the centenary of Mendeleev's birth, the Russian Academy of Sciences organized the Mendeleev Congress to which 29 foreign scientists were personally invited. The aim was of course to pay tribute to the Russian chemist, discoverer of the periodic system, but also to showcase scientific and technical progress in the Soviet Union. But beyond commemoration and propaganda, scientific presentations were also looking at current issues, and to contemporary chemists 1934 was indeed an exciting year.

Enrico Fermi had just published his claim to have produced element 93 and 94 in nuclear reactions a few months earlier. The quest for transuranic elements with physical methods had thus started, and these new means of producing elements implied to reassess the definition of element and the understanding of the Periodic system. Fermi's paper also initiated a wealth of experiences and publications in the radiochemical community that eventually led to the discovery of nuclear fission, a proposal made by Ida Noddack as early as 1934 but ignored by Fermi and his colleagues.

In this paper we examine the presentations of Friedrich Paneth, Lise Meitner, Walter Noddack and Ida Noddack on the notion of element, the quest for the missing elements, and the periodic system. In particular the contrast will be drawn between Meitner's and Ida Noddack's use of the Periodic System, and the discussion that didn't take place while the radiochemical community was struggling with the interpretation of experimental results.

EPISTEMOLOGY OF COLOUR IN THE PERIODICAL TABLE, 1920-1970

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Symbolic colour use always played a salient role in the sciences in research and teaching, still however the use of colour in historic diagrams is a lacuna in history of science. To investigate the colour use in diagrams though often enough means to uncover a whole cosmology otherwise not explicit in the diagram.

The periodic table is a salient and iconic example of non-mimetic colour use in science. Famous is Andreas von Antropoff's rectangular table of recurrent rainbow colours (1924); Alcindo Flores-Cabral's (1951) application of colour in his round snail form using the rgb scheme, Mazurs 1967 pine tree system, speaking of warm and cold colors that he attributed to specific groups of elements – an attribution that we can relate back to humoralism and alchemy.

From the first periodic tables in the 19th century on different researchers used different colour regimes. Standardization may play an obvious role in chemistry and its diagrams, all the more impressive is the anarchy in the use of colour in the respective diagrams up to today. This article focuses on periodical tables in chemical journals and text books and explores and compares the development of different colour codes between the 1920s and 1970.

**D.I. MENDELEEV:
"THE PURPOSE OF SCIENCE IS FORESIGHT AND PROFIT"**

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The scientific and methodical work of the MITHT History Museum and some departments of the M.V. Lomonosov Institute of the Fine Chemical Technology on the impact of the D.I. Mendeleev's periodic system on subsequent scientific discoveries and theories is discussed in the report.

The Periodic Law (PL) allowed looking anew at chemistry as a harmonious science by systematizing both the elements and their compounds.

"The Principles of Chemistry" using the PL elements were a smart guide to natural science in general and to chemistry in particular.

The PL allowed foreseeing future discoveries: not only predicting new elements, but also specifying their properties and location in the nature.

The PL changed the world outlook: the atom as a basis of the structure of matter, its inexhaustibility.

The PL allowed applying the methodological approach to the new understanding of natural science: from the particular to the general.

CONTRIBUTION OF PROFESSOR YA.I. MIKHAILENKO IN PROMOTION THE IDEAS OF D.I. MENDELEYEV

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Yakov Mikhaylenko (1864 – 1943) – one of the founders of the first domestic branch of chemical-technological University, for 100 years bearing the name of the great Mendeleev. He is a representative of the old Russian chemical school headed by D. Mendeleev.

His first research he began in the student years while working as a laboratory assistant at the University of Kiev under the guidance of the famous organic chemist S. N. Reformatsky. In 1888-89, after graduating from the University of St. Vladimir in Kiev, he improved his education at St. Petersburg University in the laboratory of organic chemistry led by N. Menshutkin.

From 1924 to the end of his life he headed the Department of General, inorganic and analytical chemistry at the D. Mendeleev Institute of chemical technology. He paid much attention to the theoretical problems of chemistry. His students of the twenties of the last century were the first who attended the course of General and inorganic chemistry, based on modern ideas about the structure of the atom, the electronic theory of redox reactions, the theory of solutions and chemistry of complex compounds. Professor Mikhailenko's books on the Periodic table of elements, published in 1931 and 1940, covered all periodic changes in the properties of atoms with the utmost clarity. In his lectures he used an extended, modernized version of the Bohr-Thomson table, which is essentially a long-period form. One of the first in the USSR Yakov Ivanovich began talking in a training course about artificial radioactivity.

In 1966 the disciples of Professor Ya. I. Mikhailenko prepared and published a textbook "Course of General and Inorganic Chemistry", which was clearly maintained established them sequence and interpretation of educational material.

Ya. I. Mikhaylenko participated in the 1st (1907), 2nd (1912), 3rd (1929) Mendeleev congresses, where he made reports.

CHEMISTRY AND ITS TEACHING AT THE ST. PETERSBURG UNIVERSITY UNTIL MENDELEEV

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In the first decades of the XIX century chemistry was taught as a syncretic field of knowledge, offering encyclopedic information about substances and their transformations. Its development in Russia was stimulated by the needs of industry and went in the direction of applied areas. At the universities of that time there was no division of courses into “general”, organic, inorganic and analytical chemistry. For a long time there was no independent department of chemistry, and the complex of sciences on the structure and transformation of substances was taught in the metropolitan Pedagogical Institute (the forerunner of the university), and then at the university itself “professor of chemistry and technology” A.I. Scherer, invited from the Academy of Sciences. The first comprehensively prepared university chemist was M.F. Solov'ev (1785-1856), who spent three years in Germany and France, preparing for a professorship, studying with S.-F. Hermbstedt, A.F. de Fourcroy and L.J. Thénard. Since 1817, occupying the department of chemistry, Solov'ev has equipped a chemical laboratory, collaborated with scientists of the Academy of Sciences and the Mining Department, participated in writing textbooks ("The Foundations of Pure Chemistry", 1831), developed the Russian chemical nomenclature, ("imenoslovie"), in particular, suggested the name "vodorod".

The pupils of Solov'ev were N.P. Shcheglov, popularizer and publisher of the “Index of Discoveries in Physics, Chemistry, Natural History and Technology” (1824-1831), A. Andreevsky, A. Postels¹. In 1839, Solov'ev gave a course in organic chemistry to A.A. Voskresenskii, which, in turn, created a scientific school of organic chemists at St. Petersburg University². It is known that he was the first teacher D.I. Mendeleev at the Main Pedagogical Institute.

As an academic science, chemistry is formed after the university reforms of 1835 on the basis of the natural science department of the Faculty of Philosophy. In the next 30 years, the process of its differentiation into organic, inorganic, analytical, and technical chemistry is completed; laboratories will be improved, where teachers and students conduct joint research; chemical societies are emerging.

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DETERMINATION OF ELEMENTS BY STRIPPING VOLTAMMETRY AND D.I. MENDELEEV PERIODIC TABLE

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Modern stripping voltammetry (SV) is an electroanalytical method widely used for the determination of metal and non-metal ions and organic compounds in environmental, industrial and biological samples¹⁻⁵. This voltammetry technique is based on preliminary electrochemical or adsorptive accumulation of impurity components onto the working electrode surface followed by stripping of the preconcentrated substance back into the solution by the use of non-modulated (linear, $E_{\text{end}} = E_{\text{init}} \pm Vt$, anodic and cathodic) and modulated (staircase, differential pulse, square-wave, sinusoidal and other) potential sweep.

The electrochemical preconcentration can be achieved in the following ways: 1. Reduction of metal ions into their elements; 2. Formation of an insoluble compound of a determined element with the electrode material, background electrolyte or a reagent added; 3. Adsorption of surfactants or complexes of determined elements on the electrode surface.

Based on investigations on stripping determination of the elements, it was summarized that the particular technique of SV depends on the element position in Mendeleev's Periodic Table¹⁻³.

In this report we provide some details of this dependence. Indeed, over 30 elements of the III-VIII groups of the Periodic Table can be determined by SV including a number of the transition, rare earth and transuranium elements, as well as the elements of the platinum group and non-metals. The cathodic version of SV enables varying parameters of the adsorptive preconcentration step by using the reduction of either a metal ion or a ligand in a complex compound as well as by the use of catalytic processes at the step of the analytical signal registration.

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THE PROBLEM OF "ZERO ELEMENTS" IN THE WORKS OF D.I. MENDELEEV. NEUTRON MATTER AND ITS PLACE IN THE PERIODIC TABLE OF CHEMICAL ELEMENTS

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D.I. Mendeleev was convinced of the existence of elements before hydrogen¹. Elements before hydrogen inevitably fall into the zero group. "This position of argon analogs in the zero group is a strictly logical consequence of the understanding of the periodic law," stated D.I. Mendeleev. He allowed the existence of the elements - X ("newtonia") and Y ("coronia") before hydrogen in the zero group. It should be recalled that Mendeleev had not been mistaken in his predictions of new elements! It should be noted that after D.I. Mendeleev's question about "zero" elements was repeatedly raised by many authors both in the past and in the present centuries, however, for brevity, we only mention the very first and most famous ones: for example, Ernest Rutherford in 1920 and Andreas von Antropov (Andreas von Antropoff) in 1926 as a designation for a hypothetical element with atomic number zero, which he placed at the beginning of the periodic table. A. Antropov was the first to suggest the term "neutronium"². Currently, neutron matter, like neutron stars, is a recognized reality in astro- and nuclear physics. Neutron matter from the standpoint of General chemistry can be classified as chemically simple (i.e., cannot be decomposed into simpler chemical means), then inevitably the question arises about the Element corresponding to it and its place in the Periodic System. Based on the logic of the Periodic Law - (sequence number - electric charge) - the sequence number of neutron matter will correspond to zero, which makes us remember and develop the ideas of Dmitry Ivanovich Mendeleev about the zero group and period³.

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D.I. MENDELEEV' PERIODIC TABLE OF THE CHEMICAL ELEMENTS TODAY END TOMORROW.

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D.I. Mendeleev became on world science as the pioneer of the periodic law and the author of the periodic table of the chemical elements. D.I. Mendeleev proceeded from assumption of near repeatability of properties of the elements through eight, that corresponds the maximal possible valence (oxidation number), an element at least in binary compounds. In this regard the tie to the number 8 remains for many also today (VIII – number of the biggest and forcedly invented group consisting of 3 family of the d-elements and (sub)group of the inert gases).

In 1989 IUPAC recommended for use in science and education version of the table consisting of 18 groups with designations of its numbers in the Arabic numerical instead of the early existed Roman numerical.

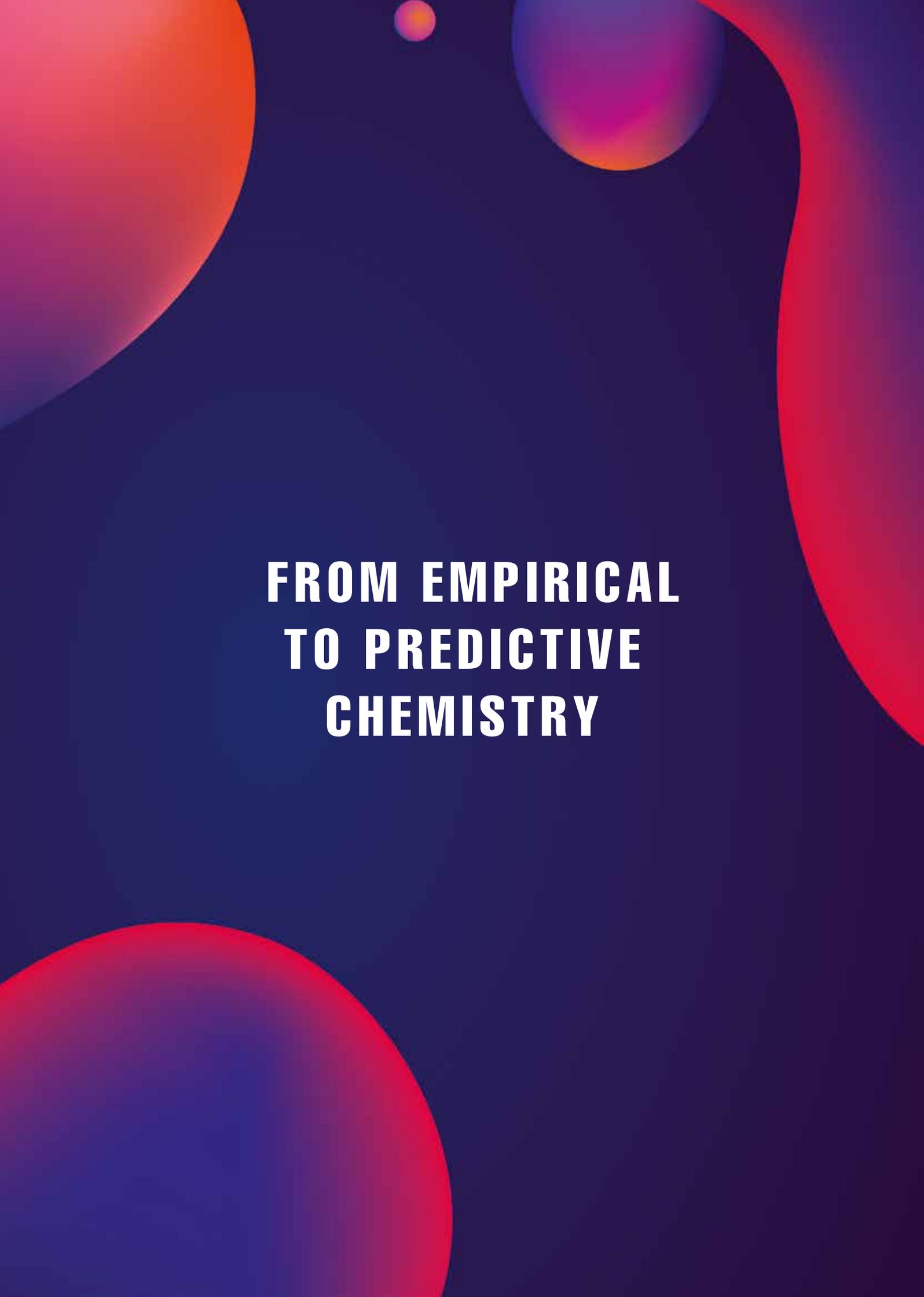
Authors of the article created modern bilingual (Russian and English) and width most information character, table for every element.

The table of the 18 groups will be rather long-living as corresponding to optimal chemical education. It existed in the majority numbers of manuals also earlier at the only feature – with designation the groups number in the Roman. It belongs also to the longest table form with 32 groups including both each lanthanoide and actinoide in their sequences according to their atomic numbers.

From 2016 due to the element 128 detection (Og – oganesson, very short living inert gas) the seventh period of the table became disclosed. Next detect elements will be as eka-Fr and eka-Ra – also more short living radioactive elements, then their predecessors.

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**FROM EMPIRICAL
TO PREDICTIVE
CHEMISTRY**

COMPUTER-AIDED PREDICTION OF BIOLOGICAL ACTIVITY SPECTRA FOR ORGANIC COMPOUNDS: POSSIBILITIES AND LIMITATIONS

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Computer-aided estimation of the biological activity spectra of organic compounds allows selecting among the existing or potentially synthesizable the most promising candidates for synthesis and to determine the priority directions of their experimental testing. Prediction of biological activity using PASS (Prediction of Activity Spectra for Substances) program is based on the analysis of structure-activity relationships for the training set containing more than 1 million compounds with over 8 thousand pharmacological effects, mechanisms of action, specific toxicity, etc.¹ The development of concepts, methods and algorithms of PASS has been going on since the mid-70s of the XX century; for over forty years work has been performed to expand the completeness and improve the accuracy and reliability of predictions.

In 1999, we developed freely available in the Internet the PASS Online program². On this basis, more than 12 different web services have been implemented to date (way2drug.com/projects). The number of users of these web services exceeds 22 thousand from ~ 100 countries of the world. More than 835 thousand predicted biological activity spectra were obtained; over 600 papers with the results of prediction were published. Comparison with web services that predict biological activity profiles, which appeared later, showed that the performance of the PASS exceeded those of the alternative computational tools³.

We will consider in detail the current state, possibilities and limitations of a computer-aided prediction of the biological activity spectra of drug-like compounds.

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APPLICATION OF ARTIFICIAL INTELLIGENCE TO ORGANIC CHEMISTRY: TRENDS AND PERSPECTIVES

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Rapid development of robotic platforms in drugs and materials design stimulates creation of efficient chemoinformatics tools able to plan and to guide synthesis of target molecules. These tools aim to suggest feasible synthetic roots linking target molecule with the available starting materials, to predict a major product of chemical reaction, its thermodynamic and kinetic characteristics and to propose optimal reaction conditions (solvent, catalyst, temperature, etc) leading to reasonable yield. Most of these tasks could be efficiently realized with the help of the Condensed Graph of Reaction (CGR) approach. CGR allows representing a chemical reaction as a sole molecular graph (pseudomolecule). In this presentation, we consider applications of CGR to large reaction database visualization and analysis, to modeling of reaction rate constants of different types of reactions¹⁻⁵, to theoretical assessment of tautomeric equilibrium constants⁶ and to prediction of optimal reaction conditions for selective deprotection reactions⁷. Particular attention will be paid to the application of the Artificial Intelligence methods to *de novo* design of molecules and reactions⁸.

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ANALYSIS OF THE BIOLOGICAL ACTIVITY PROFILES OF ORGANIC COMPOUNDS TAKING INTO ACCOUNT THEIR METABOLISM IN THE HUMAN BODY

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Most drugs may interact with several or even many pharmacological targets, thus possessing the complex profiles of biological activity. Drugs undergo biotransformation in the human body that leads to the formation of one or several metabolites, which may exhibit different profiles of the biological activity. Experimental testing of millions of substances for thousands of biological activities is not feasible; thus, it is necessary to use computational methods to find and optimize new drugs. We have created and continuously develop a dozen public web resources (<http://www.way2drug.com/>), including PASS Online (<http://www.way2drug.com/PASSOnline/>)¹, which currently predicts over 4,000 types of biological activity. We have developed a method for generating the network of the metabolism of xenobiotics in the human body and created a publicly available web resource MetaTox for integral assessment toxicity of xenobiotics (<http://www.way2drug.com/mg/>)²⁻⁴.

The molecular mechanisms of drug action are studied experimentally in vitro on isolated molecular targets. Therefore, the prediction of the biological activity profiles of drug-like organic compounds, taking into account the metabolites formed during their biotransformation in the human body, and the analysis of the associations between the action of the drug and its major metabolites on the multiple molecular targets in the normal and pathological biological processes, are particularly important for both finding and optimization of new drugs, and for their rational use.

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GENERATIVE TOPOGRAPHIC MAPPING OF THE DOCKING CONFORMATIONAL SPACE

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Following previous efforts to render the Conformational Space (CS) of flexible compounds by Generative Topographic Mapping (GTM), this polyvalent mapping technique is here applied to the docking problem. The paradigm of CS mapping “one compound = one CS map” was adapted to the docking-oriented “one active site = one map, accommodating any ligands”. Ligands were docked into the ATP-binding site of CDK2, generating thousands of poses for each ligand with the S4MPLE program. Each pose of each ligand was described by its vector of contacts observed at key protein atoms. Two distinct strategies were pursued: (a) “Contact” maps were built on the basis of the contact fingerprint only, while (b) “Hybrid” maps used a composite descriptor of contact fingerprints concatenated with ISIDA fragment descriptors. Contact maps characterize ligands purely from the perspective of the binding site, with “touched” protein atoms as sole information. Hybrid maps benefit from an additional, geometry-independent description of the ligand providing those contacts. Both approaches were challenged to

(1) Distinguish native from non-native ligand poses, e.g. create RMSD-landscapes “colored” by the conformer ensemble of ligands of known binding modes in order to highlight “native” map zones (poses with RMSD to PDB structures < 2Å). Then, projection of poses of other ligands on such landscapes might serve to predict those falling in native zones as being well-docked.

(2) Distinguish ligands – characterized by their ensemble of conformers – by their potency, e.g. testing the hypotheses whether zones privileged by potent binders are clearly separated from the ones preferred by decoys on the maps.

Hybrid maps were better in both challenges and outperformed the classical energy and individual contact satisfaction scores in discriminating ligands by potency. Moreover, the intuitive visualization and analysis of docking CS may, as already mentioned, have several applications – from highlighting of key contacts to monitoring docking calculation convergence.

THE COMBINED QM/MM AND QTAIM APPROACH REVEALS THE NATURE OF ATOMIC INTERACTIONS IN BIOLOGICAL SYSTEMS

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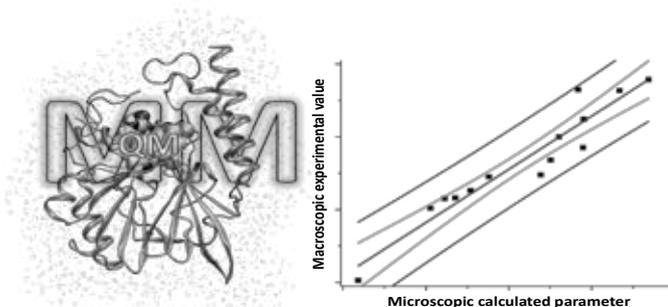
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Recent development of the multiscale molecular modeling tools including combined quantum mechanics/molecular mechanics (QM/MM) method as well as the increase of the performance of the supercomputer facilities has led to the raise of their applications for biological systems. This approach is successful in studies of the mechanisms of the enzymatic reactions as well as for the photochemical processes in proteins. The next step is the Bader's Quantum Theory of Atoms in Molecules (QTAIM) analysis of the wave functions at the stationary points on the potential energy surface obtained at the QM/MM level. This allows to extract additional valuable information. The QTAIM is now widely applied to the small and middle-size molecules, complexes and crystals. Here we discuss its first applications to biological systems. We present the results on an enzymatic reaction and a photochemical process. The first is the mechanisms of the bacterial drug resistance due to the hydrolysis of the antibiotics by the metallo- β -lactamase and we focus on determination of the key interatomic interactions responsible for the catalytic rate constant. The second topic deals with the quantification of the bathochromic and hypsochromic shifts upon π -stacking of the chromophore of the green fluorescent protein.



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PREDICTION OF COMPLEX INTEGRAL QUALITY PARAMETERS IN LIQUIDS USING MACHINE LEARNING AND CHEMICAL SENSOR ARRAYS

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Chemical sensors based on various principles are very attractive tools for fast and inexpensive quantification of chemical composition in liquids. With the development of various machine learning tools and new types of sensors the concept of multisensor systems has gained wide acceptance¹. The idea behind this approach is in application of an array of cross-sensitive chemical sensors in combination with modern multivariate data processing tools. Being applied for analysis of real complex objects such combination offers very unusual analytical capabilities. This presentation will be focused on several most interesting examples of sensor arrays' application. Determination of the bitter taste intensity in chemically diverse active pharmaceutical ingredients (API) using potentiometric multisensor systems and 3wayPLS regression modeling can be performed with satisfactory precision both in terms of human sensory panel and rat panel (Davis Rig "lickometer")¹. The derived model also performed successfully in the blind test of two proprietary APIs with non-disclosed chemical structures. Another example deals with prediction of toxicity of surface waters in terms of *Daphnia magna* bioassay method. The response of specially designed electrochemical sensor array being properly modeled with robust M-regression technique allows prediction of daphnia death rate in aqueous environment². Unlike traditional bioassay which yields the results after 96-hour test, the employment of multisensor system provides the estimates in 3 min only. Several other issues regarding sensor arrays like e.g. analysis of spent nuclear fuel reprocessing technological streams³ and QSPR modeling of active sensor compounds will be discussed.

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SPECIFICITY OF NANOPARTICLES MODELING IN QSAR/QSPR RESEARCHES

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Today, QSAR/QSPR methods have become “de facto” routine tools in the process of creating new drugs, materials, reagents, etc.¹. A set of descriptor systems has been developed for the structural description of molecules, which used in problems of “structure - properties” for organic compounds are mainly. However, the specificity of nanoparticle modeling requires taking into account not only the structure of the molecules forming the nanoparticle, but also the characteristics of the nanoparticle itself as entire object. In addition, well-known 2D descriptor systems, which are used to describe the structure of organic molecules, are not applicable to inorganic compounds. The reason for this is the incorrect description by structural formulas of many inorganic substances in the crystalline state. Thus, it becomes necessary to develop special approaches for modeling various nanoparticles for following QSAR/QSPR analysis.

In this work discusses various molecular modeling methods for nanosystems of various nature, including: combinatorial schemes for describing inorganic nanoparticles (metal oxides)², fragment descriptors of carbon polyhedral (fullerenes), textural (image based) descriptors of various mesophases, mixed descriptors for complex nanoparticles (metal core in an organic shell). For the integral description of nanoparticles as entire object (nano-cluster), the “liquid drop” method³ was used.

The effectiveness of various methods for describing nanoparticles is demonstrated by the successful solution of the “structure of property” problems.

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DATA MINING IN SYNTHETIC CHEMISTRY USING CONDENSED GRAPH OF REACTION

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Due to development of synthetic chemistry toolbox, the rate of reaction data accumulation substantially increased in the last decades. Collection of big data in reaction databases opens a way to apply technologies of chemoinformatics for reaction data handling. However, efficient chemical reactions mining requires useful reaction representation techniques. Among others Condensed Graph of Reaction (CGR) is probably the most universal and versatile, applicable both for reaction modeling, information extraction and analysis. CGR represents reaction as one pseudo-molecular graph with additional bond labels designating bonds that was changed in reaction. CGR explicitly encodes reaction center and using it fragment descriptors of reaction can be calculated. Such property of CGR opens a way to its various applications.

In the presentation we will show how CGR can be applied in different applications of reaction mining:

- Reaction rate prediction based on structure-reactivity approach;
- Prediction of optimal reaction conditions;
- Synthetic route extraction based on reaction networks using desired structure or substructural fragment;
- Extraction of bioisosteric replacements using database of Matched Molecular Pairs with known change in activity;
- Reaction center extraction and statistical analysis of the reaction database diversity and content;
- Analysis of reaction database evolution using reaction space mapping based on Generative Topographic Maps.

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CHEMICAL LIBRARY DESIGN: REVISING THE LIPINSKI RULE

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High-throughput screening (HTS) is a widely used strategy for discovering of new hit compounds. Previously it was used mainly by pharmaceutical companies. However, nowadays it is affordable for academic institutions, especially after launching pan-European initiative EU-OPENSREEN, which should acquire a large collection of small molecules (~ 140 000 compounds). Many different factors are considered during library design: physicochemical parameters, structural filters (reactive/promiscuous/toxic patterns), diversity selection. Lipinski and similar rules is widely and frequently used to select compounds by their physicochemical properties. However, are these properties favorable? The available drug-likeness rules had common issues: a) these rules are too broad and b) they are mainly suitable for selection of drug-like compounds rather than compounds which should be active in intro assays.

In order to derive a more reasonable score to prioritize compound for HTS libraries we developed specially designed models which predict HTS-likeness of compounds based on common physicochemical parameters. The models were trained on a large collection of PubChem data (360 assays and 500 000 compounds) which was split on train and test sets. NCI60 data was used as an additional test set (69 assays and 46 000 compounds).

Models were developed separately for assays with different format (biochemical and cell-based) and target (enzyme, GPCR, etc). In average subsets of selected HTS-like compounds from the PubChem test set was 43-56% of the original size and at the same time hit rate was increased on 20-32%. Similar performance was observed for NCI60 test set. The developed HTS-likeness score outperformed available drug-likeness measures which selected compounds subsets with hit rates lower than baseline hit rates.

Also it was demonstrated that models trained on different assay subsets performed differently. Calculated variable importance also demonstrated that different physicochemical properties important for different assays. Therefore, it would be reasonable to use models trained on assays subsets similar to those which would be used in HTS to create a chemical library. It is possible to use the model trained on all assays if the library will screened in variety of assays.

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MODERN PARADIGM FOR THE DESIGN OF SMALL MOLECULE REGULATORS OF ENERGY HOMEOSTASIS

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Currently, the search for key elements for regulating the body's energy metabolism is an urgent task both in terms of the development of stimulating drugs that increase human endurance under extreme conditions, and the treatment of common metabolic disorders such as diabetes, obesity and cardiovascular diseases. A few decades ago, it was found that AMP-activated protein kinase (AMPK) is one of the most important regulators of energy homeostasis that functions both at the cellular level and at the level of the whole body¹. The basal level of the AMPK activity is significantly reduced in diseases such as diabetes and obesity; under hyperglycemia, the AMPK activity is suppressed in muscles, liver and kidneys. Thus, AMPK is not able to maintain energy homeostasis in many pathological conditions. A decrease in the basal activity of AMPK may cause metabolic syndrome and, therefore, pharmacological activation of AMPK is a promising method for the prevention and treatment of this group of diseases, which will allow if not to eliminate the cause of the metabolic syndrome development, then to overcome its manifestations and prevent the development of such serious complications as diabetes, atherosclerosis and fatal dysfunction of the cardiovascular system.

AMPK is one of the so-called master regulatory proteins and is able to trigger and regulate the intensity of a large cascade of events both in the cell and in the whole body. Selective pharmacological control of this cascade is one of the most complex and attractive tasks of modern science².

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EQUIVALENT ALKANE CARBON NUMBER OF CRUDE OILS: A MODEL BASED ON MACHINE LEARNING

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The concept of equivalent alkane carbon number (EACN) – a number without dimension that reflects the phase behavior of an oil – is commonly considered during surfactant formulation design for enhanced oil recovery (EOR) applications. The EACN determination of an oil consists in experimentally identifying the *n*-alkane matching {brine/surfactant/oil} and {brine/surfactant/*n*-alkane} phase behaviors. For crude oils, it requires days to weeks to reach the thermodynamic equilibrium depending on the nature of the crude oil, *i.e.* whether it is light or heavy.¹ In this context, we used chemoinformatics tools² in order to develop models to predict crude oil EACN.³

We collected 29 crude oil samples originating from around the world. Each of these crude oils has been experimentally analyzed, and we measured property such as EACN, API gravity and fractions of C₂₀ (compounds having less than 20 carbon atoms), saturates, aromatics, resins, and asphaltenes. Evolutionary algorithms have been applied to the so-obtained database to derive models able to predict EACN of a crude oil. This work has shown that the application of such strategy led to a relevant tool for fast and accurate estimations of crude oil EACN values.

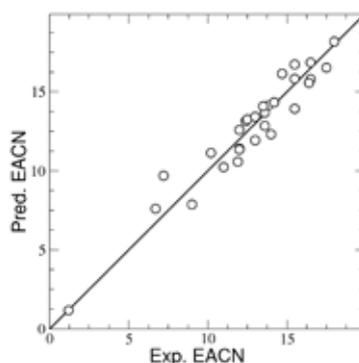


Figure 1. Scatterplots of experimental EACN vs corresponding predicted values

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A VALIDATED DATABASE OF 3D MODELS OF THE RAGE - NF-KB SIGNAL PATHWAY

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The receptor of advanced glycation end products (RAGE) activation has been shown to be one of the significant factors in the development of complications of diabetes mellitus and Alzheimer's disease¹. AGE-RAGE pathway including 14 main signaling chain nodes which lead to the triggering the transcription factor NF-kB².

Validation of 3D models of relevant target proteins to the RAGE – NF-kB signaling chain was performed in several steps. First of all, for each target protein in the IUPHAR / BPS and ChEMBL databases, was found information about highly active reference inhibitors (from 5 to 21 structures). On the second step, using the original Microcosm BioS 18.1.9 system for each reference inhibitor was found one structurally most similar compound that was inactive to a target protein. For all the reference inhibitors and inactive compounds, optimal conformations were constructed. At first, for each of the structures, generates 10 of conformers using the MarvinSketch 17.1.23 program³. All constructed conformers were optimized using the MOPAC2016⁴ program by the semi-empirical PM7 method. Among the optimized conformers, was selected one with the lowest total energy. At the last step for each 3D model has performed an ensemble molecular docking the reference and inactive compounds to the active site of proteins. Docking was fulfilled using AutoDock Vina 1.1.2⁵, with a fivefold repetition for each ligand. The validity metric of a specific 3D model was the difference $\Delta E_{\text{Validations}} = \Delta E_{\text{References}} - \Delta E_{\text{Inactive}}$. For a given target protein, three of the most valid models were selected with the minimum values of $\Delta E_{\text{Validation}}$.

As a result, was created a database of 66 valid 3D models of 22 relevant target-proteins to the RAGE – NF-kB signal pathway was formed.

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SEARCH FOR THE NEW CLASS OF ANTICANCER DRUGS ON THE BASIS OF YB-1 COLD SHOCK DOMAIN INHIBITORS

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Y box binding protein-1 (YB-1) is a cold shock domain (CSD) containing protein. Functionally, YB-1 is DNA and RNA binding protein involved in regulation of several proteins contributing to oncogenesis, metastasis and drug resistance of cancer cells. Inhibition of YB-1 decreases the cell proliferation and migration, and increases sensitivity of cancer cells to drugs. Our work is aimed to search for inhibitors of YB-1 activity by molecular modeling. Binding a small molecule to a site on the surface of CSD of YB-1 near Ser102 is shown to hinder activation of YB-1 and its nuclear translocation, the key process driving malignization. We target the same region and apply ensemble docking to address issues associated with flexibility of the site. Prior to docking, protein conformations retrieved from the NMR-resolved structure of CSD are optimized by using the semiempirical quantum-chemical PM7 method with the COSMO solvent model and assessed by docking of two known YB-1 inhibitors. Four working models are selected for ensemble docking. Virtual screening of Voronezh State University base consisting of around 14000 compounds is then performed by using the SOL docking program. Tens of top compounds ranked by the SOL score are subjected to re-docking with a new approach combining a force field and the PM7 method with COSMO solvent in order to calculate binding energy more accurately and 13 candidates for experimental testing are selected relying upon their binding energies, poses and scores. Of these, two compounds, VGY0018645 and VGY0018615, have discernible cytotoxic effect on HCT-116 cells in the MTT assay. Both compounds contain octahydroquinazolinone fused with triazole as a scaffold. VGY0018615 shows the most potent effect on HCT-116 cells (human colon cancer cell line) with the IC₅₀ being 5 μM. Moreover, VGY0018615 possesses a selective cytotoxicity and does not inhibit viability of human embryonic fibroblasts.

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COMPUTATIONAL PREDICTION OF NEW SUPERHARD MATERIALS WITH OPTIMAL PROPERTIES

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Nowadays one of the most challenging issue is related to development of new superhard materials to replace traditional materials in many fields of science and technology. Traditionally material called superhard if its Vickers hardness is higher than 40 GPa.¹⁻³

We performed a comprehensive computational search for new superhard materials among W-B and Mo-B systems with optimal combination of Vickers hardness and fracture toughness using the global optimization techniques.

New boron-rich compound WB₅ is predicted to be superhard with Vickers hardness of 45 GPa and at the same time it possesses high fracture toughness of ~4 MPa·m^{0.5}.⁴ Newly predicted tungsten and molybdenum boride (WB₅ and MoB₅) are found to be thermodynamically stable in a wide range of temperatures at ambient pressure. Our results suggest that WB₅ and MoB₅ remains a high-performance material even at very high temperatures and can be easily synthesized at large scale according to predicted conditions for synthesis.

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UNRAVELING STRUCTURAL, ORBITAL, AND OPTICAL PROPERTIES OF STRUCTURALLY COMPLEX METALLOCENES

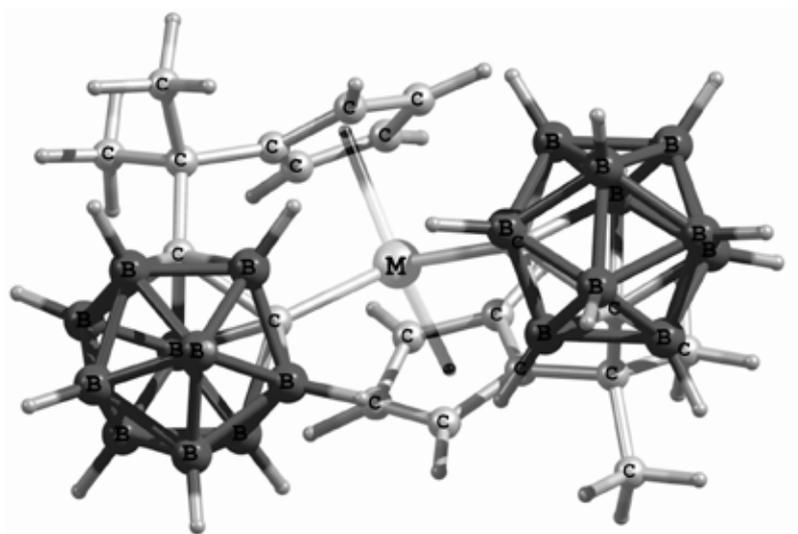
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Group IV bent metallocenes are of particular importance for catalytic polymerization of olefins, activation of small molecules, and as anticancer drugs. The relation between structure and properties of compounds of this family remains a key problem for organometallic chemistry, metal complex catalysis, and molecular photonics. Modeling of geometry and quantities of excited states of non-classical metal complexes is a rather difficult problem. In the present work, the basic geometric and orbital characteristics, electric dipole moment, and optical properties of complex non-classical compounds, d^0 *ansa*-metallocenes with polyhedral carboranyl σ -ligands $M(\eta^5:\eta^1\text{-CpCMe}_2\text{CB}_{10}\text{H}_{10}\text{C})_2$ ($M = \text{Ti, Zr, Hf}$; Cp = cyclopentadienyl), possessing rare emissive ligand-to-metal charge transfer (LMCT) excited states in liquid phase, were simulated using quantum-chemical methods at different levels of theory. Most our computation data are in agreement with the experiment (X-ray, photophysical data). It was revealed that despite the presence of metal-carbon σ -bonds, structurally sophisticated d^0 metallocenes dicarboranyles, in contrast to closely related metallocene dimethyls, possess emissive LMCT excited states with charge transferring from Cp π -ligands to metal, a high molecular dipole moment, and photoluminescent properties, making them similar to metallocene dichlorides which lack the M-C σ -bonds. Electronic excitation spectra of d^0 metal complexes were for the first time simulated (also in solvents), and they almost ideally coincided with experimental data.



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TOOLCHAIN FOR REACTIONS PROCESSING, MODELING AND STORAGE

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Chemical reactions are important objects in chemoinformatics which have been attracting the attention of researchers in last years. Many tasks emerging in chemical synthesis were solved using chemoinformatics technologies. Computer representation of reaction is an important part of modeling workflow, in large extent determining the modeling performance. Among many various methodologies of reaction encoding, the Condensed Graph of Reaction (CGR) approach recently demonstrated its efficiency in structure-reactivity modeling, reaction condition prediction, metabolic reaction products ranking, atom-to-atom mapping error identification, substructure and reaction similarity search. There exist several universal tools that were developed for handling molecular information, both open-source and commercial, such as: OpenEye Toolkits, ChemAxon JChem, Indigo Toolkit, RDKit, CDK, Open Babel, CACTVS. Existing tools provide with relatively weak support of reactions. Only some simple operations for reaction are possible: extraction of reactants and products, some simple operations. To our knowledge, no public tool supporting CGR was developed so far.

Rise in interest to chemical reactions in last two-three years, as well as growing incorporation of Python-based libraries, motivated us to develop native Python based libraries: CGRtools, CIMtools, CGRdb. These libraries fully support operations with reactions. CGRtools is an open-source Python library aimed to handle molecular and reaction information. It is the only one library developed so far which can handle for Condensed Graph of Reaction (CGR) handling. CGRtools supports common structural formats. CIMtools is an open-source Python library which provides the possibility for advanced operations with reaction information, reaction descriptor calculation, structure-reactivity modeling, applicability domain detection. CGRdb is an open-source Python library. CGRdb is postgresql database cartridge, which provides the possibility for reaction storing and searching them in different way.

The approach was developed as part of a project supported by the Ministry of Education of Youth and Sports of the Czech Republic, agreement MSMT-5727 / 2018-2, as well as the Ministry of Higher Education and Science of the Russian Federation, agreement 14.587.21.0049 (unique project identifier RFMEFI58718X0049).

PREDICTIVE POWER OF PUBLIC ANTIVIRAL ACTIVITY DATA

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Data curation is a seminal step for the development of meaningful and predictive models. Large publicly available datasets, such as ChEMBL or PubChem, are usually curated in a semi-automatic manner. Certain specific subsets, such as the subset of antiviral compounds, are additionally sophisticated by the use of NCBI taxonomy and absence of proper assay ontology. For a thorough analysis of antiviral chemical space, additional curation is required. Given the heterogeneity and amount of the assay data, their curation should be performed in an efficient way.

We mapped ChEMBL assays to ICTV (International Committee on Taxonomy of Viruses) taxonomy, thus systematically classifying antiviral activity data points to viral species. The mapping scheme was based on a dictionary matching virus name variants and ICTV taxa. With this approach, a substantial 2.5-fold increase of extracted assays was reached compared to the taxonomy browser of the web interface.¹

This 650K entries subset, called ViralChEMBL, was employed in a study of the antiviral chemical space from the small molecule point of view, providing descriptive statistics of the whole field and the basis for predictive models. Dimensionality reduction approaches allowed to create 2D maps of this dataset, and distance-based prediction showed high effectiveness upon experimental validation.²

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«HYBRID» HETEROCYCLIC SYSTEMS WITH TETRAZOLE AND PYRIMIDINE FRAGMENTS AS POTENTIAL DRUGS FOR TYPE 2 DIABETS TREATMENT

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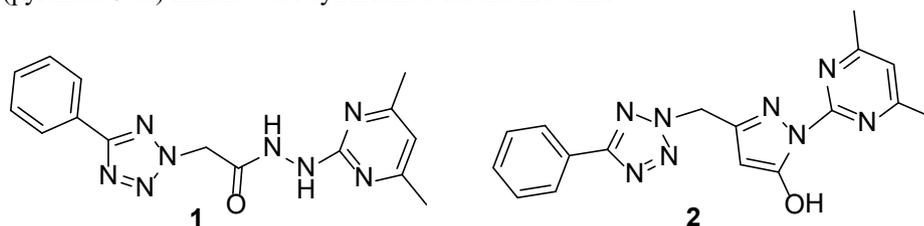
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Binuclear heterocyclic compounds 1 and 2 with 5-phenyltetrazole-2-yl and 4,6-dimethylpyrimidine cycles are separated by linear (hydrazid) and cyclic (pyrazole-5-ol) linkers were synthesized for the first time.



Prediction of Activity Spectra for Substances (PASS) indicated the possibility of using the compound 2 for type 2 diabetes therapies. High binding energy values are obtained by the analysis of docking interaction between substrates 1, 2 and corresponding enzymes. Prediction data have been confirmed by *in vivo* studies of anti-diabetic activity. And now preclinical studies of drug candidates 1 and 2 are being considered.

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CRYSTAL STRUCTURE PREDICTION WITH MACHINE LEARNING POTENTIALS

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Crystal structure prediction consists in searching for atomic structures with lowest energy. Usually theoretical methods of the prediction involve two components: an algorithm sampling the configuration space and a relaxation algorithm which finds local energy minima. Density functional theory (DFT) is typically used as an interatomic interaction model. It offers a sufficient accuracy in reproducing the sophisticated interaction of real atoms in crystals, but is resource intensive that makes crystal structure prediction computationally expensive. Thus, DFT calculation typically takes more than 99.9% of the total CPU time of the prediction.

This work is aimed to accelerate crystal structure prediction by using machine learning interatomic potentials. We propose a methodology for crystal structure prediction, which is based on the evolutionary algorithm USPEX¹ and the Moment Tensor Potentials² (MTPs). Crystal structure prediction is a challenging application for machine learning potentials since we have to predict a structure that is not presented in the training set. To resolve this problem, we involve active learning on-the-fly³. Our methodology allows for an automated construction of an interatomic interaction model from scratch replacing the expensive DFT with a speedup of several orders of magnitude. We tested our methodology on a problem of prediction of carbon allotropes, dense sodium structures and boron allotropes including those which have more than 100 atoms in the primitive cell. All the main allotropes have been reproduced and a new 54-atom structure of boron have been found at very modest computational efforts.

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THE ROLE OF INTERFACIAL LOCATION AND 2D COMPRESSION IN CHARACTERISTIC OF ULTRATHIN FILMS. IS IT POSSIBLE TO PREDICT?

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It is well known for three-dimensional systems that hydrostatic pressure can induce significant changes in electronic subsystem of a separate molecule. The conjugated compounds with labile multielectron systems are quite sensitive to this type actions. Specificity of the physico-chemical state of the Langmuir monolayer is determined by simultaneous effect of mechanical compression and uncompensated force fields of the particles in the surface layer of the subphase that “force” the molecules to orientate in a specific way on the interface. Moreover, such orientation had to cause the appearance of significant asymmetry for molecules which were quite symmetrical in bulk. Consideration of this specificity allows us to show that interfacial location and changes of surface pressure in the monolayer can act as an efficient instrument to control the processes of intermolecular electron transfer at the interface. In the present work the examples of mechanochemical transformations occurring in 2D systems based on sandwich cerium and europium phthalocyaninates upon compression-decompression are demonstrated. Using the methods of UV-Vis reflection-absorption spectroscopy, X-ray photoelectron spectroscopy, spectro-electrochemistry and XSANES spectroscopy it was proved that described transformations are associated with redox-isomerization – intramolecular electron transfer between metal and ligand induced by change of orientation and/or mutual arrangement of discotic molecules upon two-dimensional compression of the monolayer. The possibility of the production of films with set isomeric state of the complex on the solid substrate is demonstrated. The characteristic of such obtained films depend significantly on this state. All the described effects were proved experimentally but for the moment we have no precise thermodynamically correct explanation of these transformations. The possibility to predict such behavior can be much in demand for creation of new smart materials.

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MODELING IN TARGETED SYNTHESIS

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The studies on the modeling of active structures both in the targeted synthesis of biologically active compounds with given properties and in catalysis are considered. The methodology is divided into 3 parts according to the complexity and accuracy of the calculations:

1) Discrete (common), where the total binding energy is the sum of the interactions between functional groups of the ligand and the target.

2) Dynamically optimized – showing the fluctuations of the total energy of the components and allowing for conformational filtering and solvent participation. This method, in addition to modeling kinase inhibitors: PARP¹, Syk² and ABL³, was used to predict the configuration of products of asymmetric synthesis in the presence of an inducer⁴, as well as in calculations of the Suzuki reaction mechanism⁵. Using quantum chemical methods⁶ all possible transition states (TS) in the Diels–Alder reaction catalyzed by SpnF were analyzed and it was established that this reaction preferably proceeds through (6+4)-bis-pericyclic TS rather than (4+2)-TS⁷.

3) In 2019, we found that the accuracy of calculating the binding of a molecule (ligand) to a protein in the framework of the docking approaches is significantly increased if the interaction energy with the active center is normalized to that with the protein surface. To take this effect into account, a ‘over-the-hood docking’, or ‘OTH-docking’, algorithm has been developed, which increases the accuracy of virtual screening by 35–50% ROC AUC.

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NEURAL NETWORK MODELING OF PLEIOTROPIC ACTION OF PHARMACOLOGICAL SUBSTANCES

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Type 2 diabetes mellitus (T2DM) is a multifactorial disease and is caused by numerous metabolic disorders of carbohydrate metabolism. Chronic hyperglycemia leads to the formation of advanced glycation end products, which interact with their specific receptors (RAGE) and, via the RAGE–NF- κ B signaling pathway, generate pro-inflammatory reactions that cause severe complications of T2DM. The relationship between T2DM and Alzheimer's disease was shown. Thus, a directed search for multi-functional multi-target RAGE inhibitors is promising in terms of creating fundamentally new drugs for treating the complications of T2DM.

By the method of artificial multilayer perceptron neural networks, the consensus ensemble models for prediction of the level of RAGE inhibitory activity on the calculated affinity of compounds for significant target proteins of the RAGE–NF- κ B signaling pathway were constructed. The training set included data about the structure and activity level of known RAGE inhibitors from the patented database. The measure of affinity was the binding energy of ligands to bio-target sites, obtained as a result of ensemble docking. Four ensemble models were built, five high significance neural networks in each ensemble, for high-, moderate-, low- and non active RAGE inhibitors, respectively. The final estimate of activity level was obtained as a result of a simple unweighted consensus of five primary predictive estimates, followed by the noncontradiction testing. In cross validation, high accuracy of consensus prediction of the level of RAGE inhibitory activity was shown.

The constructed consensus ensemble neural network model of multi-functional multi-target RAGE inhibitors has been used in the search for new pleiotropic drug substances for the treatment of pathies in diabetes mellitus and Alzheimer's disease.

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CHEMICAL PROTEOMICS IN DISCOVERY OF TARGETS FOR SMALL MOLECULE DRUGS

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Novel potent anticancer agents need to be characterized in terms of their protein target, site of binding, mechanism of action and the cancer cell death pathway. A set of proteomics tools are implemented to provide these characteristics. One tool, Functional Identification of Target by Expression Proteomics (FITeX^P), provides unbiased target identification based on the empirical rule (“central dogma of expression proteomics) that the target proteins shows exceptional regulation in late apoptosis of drug-treated cells. Another popular chemical proteomics tool, thermal proteome profiling (TPP), is based on the empirical observation that thermal stability of target proteins is altered due to interaction with the drug molecule. TPP is a powerful tool, and it can also be used for unbiased determination of the enzyme substrates². Unfortunately, TPP is also extremely instrument-time intensive. To address this challenge, we have developed the Proteome Integral Stability Alteration (PISA³) assay, which reduces the instrument time by one to two orders of magnitude. Concomitantly, these proteomics tools revealed new knowledge of cell death, which may provide help in developing new, efficient anticancer drugs⁴.

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BENCHMARKING OF VARIOUS APPROACHES FOR REACTION CONDITION PREDICTION

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One of the important problems in the development of a synthesis strategy is the selection of optimal reaction conditions that provide the necessary regio-, stereoselectivity, together with a high yield of the target reagent. Using QSPR modeling to solve this problem is complicated by several factors: the reaction can be carried out under several conditions; if a specific reaction is not found in the database, this does not mean that the reaction cannot be carried out under certain conditions in principle; there aren't negative examples in the databases. This problem was solved by changing the general ideology of QSPR modeling: in our case for descriptors encoding the structure of the reaction, it is necessary to arrange the conditions so that at the top of the list there is a condition in which the reaction actually is carried out. Several approaches based on different machine learning methods have been tested: one-class classification - Restricted Boltzmann Machine, OneClass Supporting Vector Machine, two-class classification - Random Forest Classifier, multiclass classification - Artificial Neural Networks, in particular, Multilayer Perceptron. In addition, Autoencoder, Deep Semantic Similarity modeling, and k Nearest Neighbors algorithm were used. A set of approximately 39,000 catalytic hydrogenation reactions, extracted from the Reaxys database, was used for the modeling. Multiclass classification based on Multilayer Perceptron were shown the best results.

This best model was challenged retrospectively (using external dataset preselected from the initial reaction set) and prospectively (using the dataset of reactions published after the training set was downloaded). The model was also subjected to experimental validation. For some compounds possessing several reactive groups, theoretically suggested conditions lead to desirable transformations.

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MOLECULAR-IMPRINTED POLYMERS FOR BENZILMETHYLKETONE, QUANTUM-CHEMICAL STUDY

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Molecular imprinting polymers (MIP) are artificial receptors able to mimic natural recognition entities, such as antibodies¹. The possibility to predict the MIP selectivity and specificity for a target analyte assume the huge potential for used them in various application fields.

Recently a highly sensitive, capacitive MIP based biosensor was developed to monitor trace amounts of an amphetamine and N-formylamphetamine which is intermediate of amphetamine production². It has been shown, that the efficiency of MIP based biosensor depends on the structure of monomers and cross linkers. At the same time the theoretical investigation of the nature of interactions between template molecule and functional monomers is prospective way to improve sensor design and performance, as well as confirming reproducibility and robustness.

In the work the structures of benzyl methyl ketone (template) and compounds with similar structure (amphetamine, N-Formyl-amphetamine and 4-methyl-5-phenylpyrimidine), functional and cross-linker monomers (4-vinylimidazol, itaconic acid, styrene), as well as complexes of template-functional monomers-cross linkers were studied with different ratio of components were studied by B3LYP 6-311G (d,p)/MP2 method. The analysis of the parameters associated with the electronic structure of compounds were performed and the binding energy of the complexes was estimated. The software package FireFly 8.0 was used to calculation.

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REACTIONS MODELING USING CONDENSED GRAPH OF REACTION: FROM DATA TO MODEL

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Nowadays, chemoinformatics have high variety of solutions for molecular characteristics modeling. The opposite situation is for prediction of reaction characteristics that tend to stay challenging. Such characteristics as reaction rate and equilibrium constants are crucial for calculation of reaction yield, conversion, time etc. Taking into account rising interest to reactions and lack of straight-forward modeling schemes for them it was decided to develop workflow for automatic reaction preprocessing and modeling. The designed workflow includes several stages: (i) Condensed Graph of Reaction (CGR)¹ based data curation and analysis, (ii) modeling and validation, (iii) model applicability domain outline.

The first stage are the vital, so it was resulted into standalone CGR based data cleaning procedure. It includes chemical structure standardization, atom-to-atom mapping check, reaction condition verification, duplicates filtering. The workflow was tested on datasets of bimolecular substitution (S_N^2)², elimination (E^2)³, cycloaddition⁴ reactions as well as tautomeric equilibrium constants⁵.

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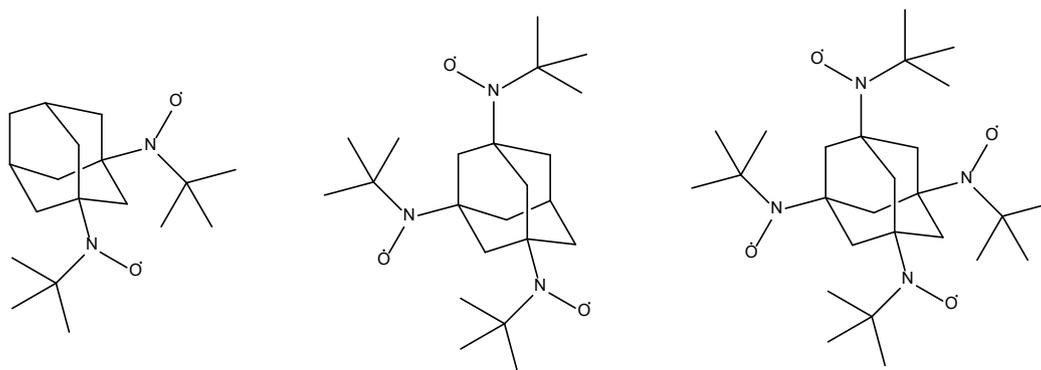
The approach is continued to develop as part of a project supported by the Ministry of Education of Youth and Sports of the Czech Republic, agreement MSMT-5727 / 2018-2, as well as the Ministry of Higher Education and Science of the Russian Federation, agreement 14.587.21.0049 (unique project identifier RFMEFI58718X0049).

QUANTUM CHEMICAL STUDY OF ADAMANTANE MULTIRADICAL DERIVATIVES

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Molecular design of multispin systems is a primary step towards molecule-based organic magnetic materials. A three-dimensional organic skeleton of adamantane seems to be a convenient organic precursor for building exchange-coupled chains and networks. Owing to its compact structure and the availability of relatively active tertiary carbon atoms, the adamantane core makes it possible to create a high concentration of spin-carrying centers in a limited space. Using the DFT methods at the B3LYP/6-311++(2d,2p) level of theory, we have calculated exchange interaction parameters in different staggered conformational states of adamantanes substituted with two, three, and four tert-butylaminoxyl groups.



Both ferromagnetic and antiferromagnetic pairwise interactions are obtained in the studied open-shell systems. The antiferromagnetic interactions prevail in most conformations of the biradical derivative. In the triradical derivative, either both ferromagnetic and antiferromagnetic interactions are equally present, or all the pairwise exchange interactions are ferromagnetic with relatively large exchange-interaction parameters in the range of ca. 3–14 cm⁻¹. Tetrakis(tert-butylaminoxyl)adamantane is characterized by somewhat larger absolute values of exchange interaction parameters (predominantly higher than 20 cm⁻¹), but the sign of the parameter in different conformations can be both positive and negative. Thus, the calculation results show that multispin molecular systems based on the adamantane core are promising building blocks in the design of new organic magnetic materials.

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OXYGEN VACANCIES IN LiMgPO₄: AB INITIO SIMULATION, OPTICAL PROPERTIES

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Recently, LiMgPO₄ doped with RE ions has attracted much attention as a new dosimetric material operating in modes of thermally and optically stimulated luminescence¹⁻². We suggested that oxygen defects may exist in LiMgPO₄ and strongly affect the optical and other properties³. Using the first-principles method, we studied neutral and charged vacancies at three nonequivalent oxygen sites in LiMgPO₄. We have demonstrated that the defect levels are within the band gap and their energy positions explain the observed absorption spectra recorded for the as-prepared LiMgPO₄ as well as for the powder samples additionally treated in argon and oxygen atmospheres.

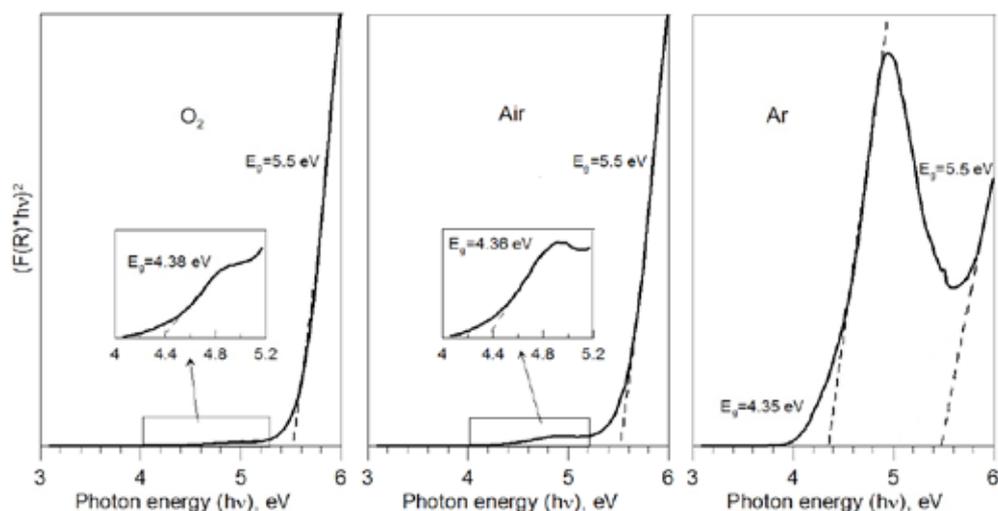


Figure 1. Band gaps in LiMgPO₄ derived from the experimental absorption spectra

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BORN-OPPENHEIMER AND QM/MM MOLECULAR DYNAMICS OF CATIONS BINDING IN SOLUTIONS

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Processes in solutions are hard to be properly studied within the methods of molecular modeling. Particularly entropic contribution is difficult to quantify. The proper method to solve such problems is molecular dynamics (MD). Classic force fields are not reliable enough to study the processes of complex formation in solutions. Another approach relies on the density functional theory (DFT) potentials in MD simulations. The main drawback is the high computational cost and the possible way out is application of GGA functionals with the combined basis sets of the Gaussian functions and plane waves with the pseudopotentials on core electrons. Another way is to perform MD simulations with the combined quantum mechanics / molecular mechanics (QM/MM) potentials. We combined the Firefly program package with the NAMD software and utilized available functionality of both of them to perform MD runs with the QM subsystem of a variable size, i.e. the water molecule is described within DFT approach if it is close enough to the cation or within classical force field if it is distant.

We compare the full-DFT MD simulations and QM/MM MD simulations on two different problems. First, we study the origin of high selectivity of calixarenes to the Cs⁺ and Rb⁺ compared to other alkali metal cations. This problem is important in the fields of solvent extraction and separation as it helps to decrease the amount of radioactive wastes. Another question that we address is the following. We try to understand theoretical background of the observation that the zinc cation is mainly coordinated by cysteines in proteins whereas magnesium cation is usually bound to the alcohol groups of serine and threonine.

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THEORETICAL ESTIMATION OF PHYSICAL PROPERTIES OF IONIC LIQUIDS: HOW FAR CAN WE PREDICT?

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Ionic liquids (IL) have received a great attention due to their green and tunable properties. The negligible vapor pressures allow for their potential use as an alternative for organic volatile solvents. Careful choice of cation / anion combination permits fabrication of ILs with physical and chemical properties well fitted to a specific problem. According to some estimations (Katritzky et al., JCICS, 2002, 42, 225-231), there exist approximately 10^{18} combinations of ions that could lead to useful ionic liquids. Thus, there is a clear necessity to develop predictive computational tools allowing one to design new IL possessing desirable properties. At the same time, numerous theoretical studies of different physical properties of IL lead to the models with poor predictive performance whatever molecular descriptors or machine-learning methods were used. Thus, prediction error (RMSE) found in recent studies was about 38° for melting point, 70 cP for viscosity and 2.5 mS/cm for conductivity. On the other hand, our analysis of experimental data demonstrates that they are strongly affected by following factors: impurities, water absorption, temperature and complexity of solid state structure (glass/crystal variation, polymorphs). Small variation of these factors may lead to significant changes of studied physical properties. This explains high values of inter-laboratory error for melting point, viscosity and conductivity reported in the literature. Thus, further progress in IL modeling depends on the way how these factors are accounted for.

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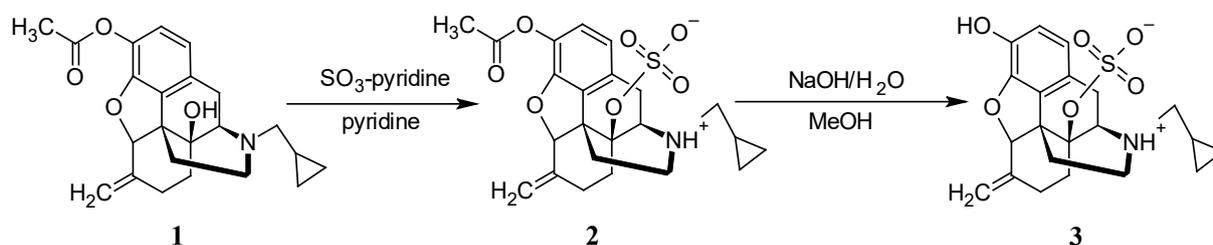
SYNTHESIS AND MODELING OF 14-O-SULFATES OF OPIOID RECEPTOR ANTAGONISTS

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Naloxone, naltrexone and nalmefene are drugs that have increased affinity for the μ - and κ -opioid receptors (OR) and are sufficiently lipophilic for penetration through the blood-brain barrier that leads to their effect on the central nervous system (CNS)¹. It is believed that the products of sulfonation of opioid receptor antagonists for hydroxyl groups in 3 and 14 positions should not be the CNS active due to their ionic structure², such as the selective OR antagonist of the peripheral effect of methylnaltrexone bromide Relistor. However, naltrexone and naloxone 14-O-sulfates showed an ability to act on the CNS with increased affinity for κ -OR³ that presents pharmacological interest due to their simultaneous solubility, CNS activity and high specificity of the binding profile to OR.

We first obtained 14-O-sulfate nalmefene 3 and 3-O-acetylnalmefene-14-O-sulfate 2 from the previously known 3-O-acetylnalmefene 1 for which the distribution parameters were calculated using standard software ACD / Percepta.



Preparation	LogD7.4	LogP	LogPS	LogBB	Ionic form at pH 7,4
naloxone	0,86	1,53	-2,5	0,21	78% protonated / 21% not protonated / 1% betaine
naltrexone	0,71	1,63	-2,59	0,26	87% protonated / 12% not protonated / 1% betaine
nalmefene	1,23	2,42	-2,20	0,44	92% protonated / 06% not protonated / 1% betaine
compound 1	1,53	2,71	-2,00	0,55	93% protonated / 07% not protonated
compound 2	-0,98	1,83	-3,00	-1,68	52% form SO ₃ ⁻ / 48% betaine
compound 3	-1,26	1,27	-3,10	-1,75	93% betaine / 07% in form SO ₃ ⁻

Internal salts of 14-O-nalmefene sulfates 3 and 2 can be considered as prospective opioid receptor antagonists, which provide targeted release of centrally active antagonists.

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VALIDITY AND LIMITATIONS OF ATOM/FRAGMENT-BASED INTERPRETATION OF QSAR MODELS

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Interpretation of QSAR models is useful to understand the complex nature of biological or physicochemical processes. It can be applied to drug and product development to optimise structures of studied compounds. Recently, several approaches have been proposed that have assisted in making QSAR models interpretable. They allow for the calculation of the contributions of single atoms, or arbitrary fragments¹. To the best of our knowledge no comprehensive study of robustness and limitations of these methods has been performed yet. Recent study² was dedicated to investigation of atom contributions only. This work suggested us to perform wider research.

We focused on studying validity and stability/robustness of calculated contributions of atoms/fragments under varying conditions. Particularly, we investigate the influence of the following factors:

- Nature of the dataset and property modelled. Property can be additive or non-additive, transferable or not, etc. Datasets can be homogenous to varying extent.
- Descriptors type, modelling method and model accuracy.
- Fragmentation method and size of fragments.

Additional aim of this work was dataset design, since to investigate all the above factors we needed the data to meet special criteria.

The results demonstrate that the quality of fragment/atom-based interpretation, applied to different datasets/descriptors/modelling and fragmentation methods, is affected by these factors. Therefore, to gain practical use from contributions, the choice of all variables should be made carefully.

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EXTRACTION OF RETROSYNTHETIC RULES FROM REACTION DATABASES

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For the selection of the optimal method of synthesis of any chemical compound retrosynthetic analysis is widely used. But in order to conduct this analysis, it is necessary to find the rules of retrosynthetic transformations. In earlier works, rules were extracted manually, but nowadays there is an interest in automatically extracting rules based on existing reaction databases, which can help to find better ways of synthesis.

The goal of current study was to develop approach for automatic extraction of the retrosynthetic rules. The rule should include information on reaction center, i.e. changes in bonds, atoms and charges, and its environment important for reaction selectivity and performance. In order to describe the environment of the reaction center, the rule includes information about neighboring heteroatoms, three and four membered rings, aromatic cycles, and leaving groups. Since it is important to distinguish intramolecular cyclization reactions from intermolecular reactions, and information about transformations with the formation of cycles was added to the rule.

In the reaction databases, there are multistage reactions with several distinct reaction centers. However, for rule extraction it is necessary that each reaction center is treated separately. A workflow to extract separate reaction centers in multistep reaction centers was implemented.

This approach has been used to extract retrosynthetic rules from Reaxys and USPTO databases. Statistical analysis of rules have been performed. The approach was also used to extract the rules of bioisosteric replacements based on match molecule pairs analysis.

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LECTURE OF HYBRID ORBITALS IN CHEMISTRY USING LINEAR ALGEBRA

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In chemistry, the concept of hybrid orbitals is used to explain or understand the steric structure of organic compounds. In high school of Japan, the hybrid orbitals are introduced as an advanced content in some chemistry textbooks. Usually, students learn hybrid orbitals in subjects of "Physical chemistry" or "Organic chemistry" in university. However, the explanation of the linear combination of atomic orbits describing hybrid orbits is not necessarily clear. I was in charge of a special lecture of "Chemical bond and Crystal structure" held annually in Kanazawa Institute of Technology. In that course, I tried to explain the generation of hybrid orbitals by linear algebra. The first grader of our university has already taken "linear algebra I (compulsory)" in the previous term. If the coefficients of linear combination of atomic orbitals are represented in matrix form, students can understand that the matrices are orthogonal. That is, the hybrid orbitals are the orthogonally transform of atomic orbitals set.

These are clearly understood based on the following two principles.

(a) Atomic orbitals are mutually orthogonal and normalized.

(b) Hybrid orbitals are represented by a linear combination of atomic orbitals. The hybrid orbitals are orthogonal to one another and normalized too. If methane (point group T_d) and ethylene (point group D_{2h}), which are high symmetric, are considered, the coefficient matrix can be easily derived by adding the following condition (c).

(c) The contribution of the s orbital is identical for each hybrid orbitals.

The condition (c) restricts all the components of the first column of the matrix to be equal.

In the lecture, I conducted an exercise to generate coefficient matrix by hand calculation for sp^2 and sp^3 hybrid orbitals. If the students already have knowledge of linear algebra and orthogonal transformation, I believe that they should use it to learn hybrid orbitals. Orthogonality and normalization of orbitals before and after hybridization can be easily understood from the viewpoint of the properties of the orthogonal matrix. Students can understand that the even p orbitals are generated by unitary transformation from other orbital set. They can go to further advanced learning. I felt that using a matrix approaches a more intrinsic understanding of quantum chemistry. In this study, I show the outline.

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BENCHMARKING ANALYSIS OF APPLICABILITY DOMAIN DEFINITIONS CHEMICAL REACTIONS CASE

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One of the OECD principles for model validation requires clearly defining the Applicability Domain (AD) for the QSAR/QSPR models. This is important since the models provide the reliable predictions only for those objects, that are structurally similar to the training set objects used to build the models. Currently, more and more attention is drawn to chemical reactions as objects of QSAR/QSPR modeling. When building quantitative structure-reactivity relationship (QSRR) models and their applicability domains it is necessary to take into account the structures, conditions and types of chemical reactions.

In this study AD definitions extensively used in QSAR/QSPR studies, their modifications and proposed by us for reactions were benchmarked. In the study more than 10 simple AD definitions, 24 combinations of AD and 2 types of consensus AD approaches were compared. Four criteria (coverage, ability to exclude wrong reaction types, ability to improve model performance and to detect outliers) for assessing quality of model with applicability domain were used. Four data sets of reactions were used for benchmarking study. Some applicability domain definitions requires selection of optimal hyperparameters, for doing that we developed especial procedure that includes both internal and external cross-validation of model and applicability domain.

Generally, most applicability domain definition approaches are quite good in ability to exclude wrong reaction type and to improve model's performance. Combination AD approaches with fragment control or reaction type control led to much better model performances than single AD definition approaches. Based on ranking we selected optimal AD definition approaches suitable for reactions.

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STATISTICAL MODELS FOR PREDICTING FUNCTIONALLY RELATED CHARACTERISTICS OF REACTIONS

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Some characteristics of the reactions are functionally related. For example, the equilibrium constant of tautomerism is expressed in terms of the acidities of the corresponding tautomers. Also, the reaction rate constant is related to the value of the pre-exponential factor and the activation energy in the Arrhenius equation. Another example is the reactions occurring through the competing mechanisms of E_2 and S_N2 , when the fraction of the product of one of the reactions in the mixture of products can be expressed in terms of the logarithms of the rate constants of the competing reactions.

For each of the above cases, we proposed a modified ridge regression method, on the basis of which it is possible to build models that have the ability to simultaneously predict several characteristics of the reactions that are functionally related. For each case, we obtained analytical expressions for calculating the regression coefficients. The type of these expressions was determined by the type of functional relationship between the modeled characteristics.

In the case of tautomerism reactions, the proposed approach makes it possible to simultaneously predict the equilibrium constant of tautomerism and acidity of tautomers, and in the case of E_2 and S_N2 reactions, simultaneously predict the fraction of one of the products and the rate constant of competing reactions. The approach based on the Arrhenius equation allows us to build a model for predicting the activation energy without using direct experimental data on it during training models.

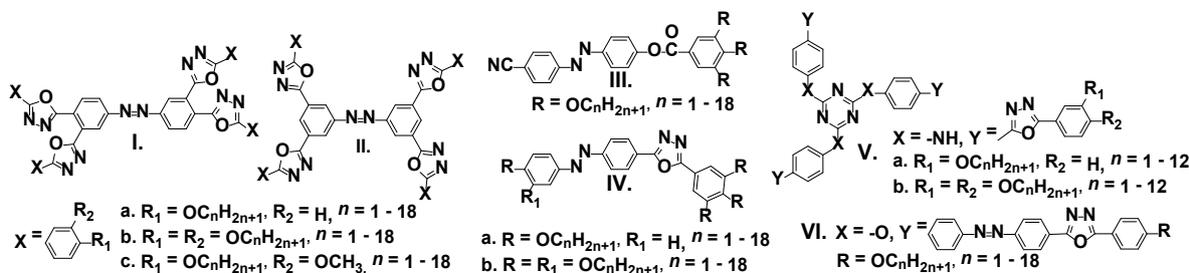
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MODELING OF STAR-SHAPED MOLECULES BASED ON CYANURIC, GALLIC, PHTHALIC AND ISOPHTHALIC ACIDS AND MESOMORPHISM PREDICTION

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In recent years, the interest of researchers lies in the field of creating new liquid crystalline nanomaterials based on heterocyclic star-shaped mesogens (HSM), which can be used in solar cells, light-emitting diodes, sensor devices, etc.¹⁻². The complexity of the synthesis of such compounds possessing a given type of mesomorphism requires a prognostic approach to their creation. Therefore, a search for reliable methods for predicting properties of compound before its synthesis remains relevant. For this purpose, a method for mesomorphism forecast of disk-like compounds using molecular parameters was developed². This method has several advantages over known methods, since it requires low costs machine time with a relatively high predictive ability ($\geq 70\%$) and ease of its use. Later, we attempted to adjust this method for the search of some HSM²⁻³. Developing these first successful results, another new series of HSM based on *o*-phthalic (I), *m*-phthalic (II), gallic (III, IV) and cyanuric (V, VI) acids was studied.



According to the prediction data, the change from *o*-isomers I to *m*-isomers II is accompanied by an increase of the number of possible columnar mesogens almost twice in each homologous series. The replacement of the ester group in non-mesogenic III with an oxadiazole fragment and a more branched hydrophobic periphery (compounds IV) promotes the formation of *Col* mesophases. Among cyanuric acid derivatives, compound Vb shows *Col* phase, VI – *N_d* phase, while Va – both mesophases (*Col* and *N_d*).

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QSAR-MODELING OF SOME THYMIDINE KINASE INHIBITORS OF THE HUMAN HERPES SIMPLEX VIRUS

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The purpose of the work was to establish a “structure-activity” relationship in the series of 5-ethyluridine, N2-guanine and 6-oxo-purine derivatives with a pronounced inhibitory activity against thymidine kinase (TK) of the herpes simplex virus (HSV) of the first and second types of human¹⁻³, and building QSAR models for virtual screening of virtual libraries and databases. Studies were conducted using the GUSAR 2013 program on the basis of two training and two test samples according to the method described in the work⁴. As a result, six statistically significant stable consensus QSAR models for the prediction of the numerical values of IC50 for inhibitors of TK (Table 1). They are applicable for virtual screening and searching for new connections. Additionally, structural descriptors were identified to regulate the activity of TK inhibitors.

Table 1. The statistical characteristics of consensus models M1-M6, where N – number of structures in the TrSet; R^2_{TrSet} – a multiple coefficient of determination calculated for compounds from the TrSet; R^2_{TSet} – a multiple coefficient of determination calculated for compounds from the TSet; Q^2 – a cross-validated R^2 calculated during leave-one-out cross-validation procedure on data of the TrSet; F – Fisher's coefficient; S.D. – standard deviation; V- the number of variables in the final regression equation.

Training set	Models	N	R^2_{TrSet}	R^2_{TSet}	F	S.D.	Q^2	V
QSAR model based on QNA-descriptors								
TrSet1	M1	66	0.875	0.929	55.174	0.579	0.840	7
TrSet2	M4	67	0.905	0.892	86.821	0.556	0.884	6
QSAR model based on MNA-descriptors								
TrSet1	M2	66	0.883	0.896	56.636	0.561	0.856	7
TrSet2	M5	67	0.906	0.872	82.334	0.553	0.887	7
QSAR model based on MNA- and QNA-descriptors								
TrSet1	M3	66	0.901	0.901	65.661	0.519	0.877	7
TrSet2	M6	67	0.916	0.888	82.959	0.525	0.898	7

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QUANTITATIVE RELATIONSHIP "STRUCTURE - ANTIOXIDATIVE ACTIVITY" IN A NEXT OF SOME NATURAL PHENOLS

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The purpose of this work was to establish the relationship "structure-antioxidant activity (AOA)" in a series of some natural phenols. Simulations were performed using the GUSAR 2013 computer program.¹ To describe the relationship "structure-AOA" in this work, we used descriptors of multilevel atomic neighborhoods (MNA) and quantitative atomic neighborhoods (QNA). As a simulated quantitative parameter characterizing the AOA compounds of training samples TrS1 and TrS2, we chose the literature values of the chain-breaking rate constant on the inhibitor in the form of $\lg k$.² In total, six statistically significant QSAR M1-M6 models were built, Table. 1. These models are applicable for virtual screening and searching for new compounds with pronounced antioxidant activity.

Table 1. Statistical characteristics and assessment of accuracy of predictions of the $\lg k$, on the consensus models M1-M6, where N – number of structures in the TrS; R^2_{TrS} - a multiple coefficient of determination calculated for compounds from the TrS; R^2_{TS} - a multiple coefficient of determination calculated for compounds from the TS; Q^2 – a cross-validated R^2 calculated during leave-one-out cross-validation procedure on data of the TrS; F – Fisher's coefficient; S.D. – standard deviation; V- the number of variables in the final regression equation.

Training set	Models	N	R^2_{TrSet}	R^2_{TSet}	F	S.D.	Q^2	V
QSAR models based on QNA descriptors								
TrS1	M1	52	0.891	0.814	–	39.030	0.501	8
TrS2	M4	42	0.877	0.789	0.731	37.212	0.489	6
QSAR models based on MNA descriptors								
TrS1	M2	52	0.939	0.897	–	51.098	0.399	9
TrS2	M5	42	0.926	0.857	0.860	41.623	0.402	7
QSAR models based on QNA and MNA descriptors								
TrS1	M3	52	0.935	0.887	–	53.122	0.405	8
TrS2	M6	59	0.930	0.876	0.885	49.964	0.385	7

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**THE PERIODIC TABLE
THROUGH SPACE
AND TIME**

THE CHEMICAL PECULIARITIES OF MULTIPLE STELLAR POPULATIONS IN GLOBULAR CLUSTERS – CONSTRAINTS FROM/FOR NUCLEAR ASTROPHYSICS

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I will review the chemical characteristics of the multiple stellar populations observed in globular clusters, and discuss the various scenarios that have been developed to explain their origin. I will focus on the (many) current theoretical issues and open questions.

THE PERIODIC TABLE AND THE ASSEMBLY HISTORY OF THE MILKY WAY

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In this Keynote talk I will first present the state of the art of our understanding of the MW assembly and formation available thanks to astrometry, spectroscopy and asteroseismology. In particular, I will illustrate how important is the feedback between Galactic Archaeology and Stellar physics (and nucleosynthesis) especially now in the Gaia era, with some important conclusions on the origin of the chemical elements. Because most stars carry in their outer envelopes the chemical composition inherited at birth, I will also show that it is possible to map the star formation history in different parts of the Milky Way by measuring, for stars of different ages, a large array of chemical elements covering different nucleosynthetic sites. This goal which seemed to be challenged upon the discovery that stars can move away from their birth places (via a process named radial migration), seems to be still reachable once detailed multi-dimensional chemical analysis and precise ages are combined.

BIG BANG NUCLEOSYNTHESIS

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Big bang nucleosynthesis (BBN) is one of the three observational evidences for the big bang model. In the standard BBN model, the thermodynamic conditions can be calculated exactly, given the baryonic density of the universe. Hence, it is possible to accurately calculate the abundances of the “light elements” (^4He , D, ^3He and ^7Li) produced during BBN. There is indeed a good agreement between ^4He , D and ^3He primordial abundances, either deduced from observation or from BBN calculations. In particular, precision on primordial abundances, deduced from observations, have now reached the percent level for ^4He and deuterium. To achieve the same level of precision in BBN predictions, the involved nuclear [1,2] and particle [3] physics need to be thoroughly investigated. (A state of the art code, including the, presently, most elaborate microphysics as recently been made freely available [3]). On the contrary, there is a tantalizing discrepancy of a factor of ≈ 3 between the primordial ^7Li abundance deduced from observations of halo stars, and the BBN calculations. Solutions to this problem have been proposed, involving stellar physics, non-standard BBN models, or nuclear physics, but none is fully satisfactory [1]. Beyond these light elements, thanks to an extensive network of reactions, it is possible to predict the minute abundances of isotopes of B, Be, C, N and O [2,3], seeds of the first stars. In spite of this lithium problem, BBN remains a valuable tool to probe the physics of the early universe, as it is, when we look back in time, the last milestone of known laboratory physics. It can hence be used to test deviations from standard theories.

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UNRAVELLING DUST NUCLEATION IN ASTROPHYSICAL MEDIA

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Over 200 molecules and 15 dust species have been detected in the interstellar medium (ISM), stellar winds, exoplanets, supernovae, active galactic nuclei etc. One of the most fundamental questions in astrochemistry deals with the phase transition from simple molecules to larger gas-phase clusters and eventually dust grains. The winds of evolved stars are the best laboratories to answer this pivotal question due to their rich chemistry and relatively simple dynamical structure.

In these stellar winds, a large variety of chemical reactions occur, including unimolecular, 2- and 3-body reactions, cluster growth and grain formation. However, current models simplify dust formation, which starts as a microscopic phase transition called nucleation. Various nucleation theories exist, yet all assume chemical equilibrium, growth restricted by monomers, and commonly use macroscopic properties for a microscopic process. Such simplifications for initial dust formation can have large repercussions on the type, amount, and formation time of dust. By abandoning equilibrium assumptions, discarding growth restrictions, and using ab-initio quantum mechanical properties, we have constructed and investigated an improved nucleation theory in stellar wind conditions for four dust candidates, TiO_2 , MgO , SiO and Al_2O_3 . To obtain the quantum mechanical properties, we have performed density functional theory (DFT) calculations, including a vibrational analysis, to determine the Gibbs free energy for all nucleating species.

We report the viability of these four candidates as first dust precursors and reveal implications of simplified nucleation theories. Assuming the monomers are present, we show that Al_2O_3 is the favoured precursor due to its rapid growth at the highest temperatures and as such is the only species that potentially can explain the detection of large transparent dust grain in the close vicinity of some AGB stars. However, when considering an initially atomic chemical mixture, only TiO_2 -clusters form but at considerably lower temperature. Still, we believe Al_2O_3 to be the prime candidate due to substantial physical evidence in presolar grains, observations of dust around evolved stars at high temperatures, and its ability to form at high temperatures. We expect the missing link to be insufficient quantitative data of gas-phase reactions with Al atoms or Al-containing molecules.

We show how the recently awarded ALMA Large Program ATOMIUM (113 hr) will allow elucidating the dominant chemical pathways in these winds, as such forming an observational testbed for constraining chemical kinetics modelling including pinpointing some of these missing reaction pathways. Some of these missing pathways are currently investigated, both using laboratory experiments and the Rice-Ramsperger-Kassel-Markus (RRKM) theory to derive their reaction rates. We report on the newly obtained reaction rate coefficients and the impact thereof in chemical kinetics wind modelling and the impact thereof on ISM modelling.

THE BUILD-UP OF CHEMICAL ELEMENTS THROUGH COSMIC TIME: OBSERVATIONS IN THE LOCAL UNIVERSE

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Three minutes after the Big Bang the Universe had an extremely simple chemical composition: three elements, H, He and traces of Li, which comprise only five isotopes 1H , 2H , 3He , 4He , 7Li . From this primordial simplicity the Universe evolved to the present-day chemical complexity as the result of the nucleosynthesis occurring mainly in stars, but also in the Inter Stellar Medium (ISM). Thanks to their long lifetimes, in fact larger than the age of the Universe itself, old low mass stars in the Galaxy and Local Group galaxies, provide us an uncontaminated sample of the chemical composition of the gas clouds out of which they were formed. This allows us to trace the build-up of the abundances (concentrations) of chemical elements in the Galaxy and Local Group galaxies. I will review the observational knowledge we have on this build-up of elements, and some of their isotopes in the local Universe.

INGREDIENTS FOR SOLAR-LIKE SYSTEMS

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Comet 67P/Churyumov-Gerasimenko (67P/C-G) has been studied with unique in-situ measurements by various instruments aboard the Rosetta spacecraft, which have shown that the comet has a rich molecular inventory¹. The currently available data on 67P/C-G is one of the best probes of the innate protosolar disk that evolved into our modern day Solar System. Similar chemical richness extends beyond the Earth and our Solar System as attested by countless observations towards high- and some low-mass protostars. One of the best-studied low-mass systems is IRAS 16293-2422, which is thought to be analogous to the earlier phases of our Solar System and has been surveyed with ALMA within an unprecedentedly wide spectral range at high spectral and spatial resolutions (Protostellar Interferometric Line Survey; PILS)². The cometary data from Rosetta and the protostellar observations from ALMA will be used in this talk to draw comparisons between 67P/C-G and IRAS 16293-2422 to go after the origins of the chemical content of our Solar System³. The observational results will be substantiated with theoretical physicochemical models of the formation of Solar-like systems⁴. The talk will highlight the evidence that suggests that the volatile composition of cometsimals and planetesimals is set in the pre- and protostellar phases of evolution.

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BINARY STARS AS FOSSILS OF PAST NUCLEOSYNTHESIS

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Low- and intermediate-mass stars (LIMS, with $0.8 < M < 8M$) dominate the stellar populations in our Galaxy. During their ascent of the thermally-pulsing asymptotic giant branch (TP-AGB) phase, LIMS are the site of a rich nucleosynthesis, forging mainly carbon and roughly half of the elements heavier than iron through the so-called s-process. Ejecting these elements at the end of their life, they play a major role in the chemical evolution of the Galaxy.

Some specific families of LIMS are exclusively found among binary systems and the mass transfer between the stellar components can have a dramatic impact on the surface chemical composition through the exchange of nuclearly-processed material between the stellar components¹. Besides, such polluted (extrinsic) stars constitute precious fossils, as they can keep track, sometimes during billions of years, of a past nucleosynthesis.

For example, extrinsic S, barium, CH and CEMP-s stars are all members of binary systems and have been polluted by a former TP-AGB (which has now turned into an undetected white dwarf). These objects bear the imprint of s-process nucleosynthesis at different metallicities (CEMP stars being the most metal-poor).

We review the different families of such extrinsic stars, several of them still being ill-understood, and of the various nucleosynthesis diagnostics that can be derived from their abundance profiles. In particular, the role of key elements like niobium², technetium³ and lead⁴ is developed.

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HEAVY ELEMENT NUCLEOSYNTHESIS IN LOW AND INTERMEDIATE- MASS STARS

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The chemical evolution of the Universe is governed by the nucleosynthesis contribution from stars, which in turn is determined primarily by the initial stellar mass. Stars with initial masses less than 10 solar masses are common inhabitants of galaxies in the Universe and contribute toward chemical evolution and dust production. These low and intermediate-mass stars experience their richest phase of element production at the end of their lives, when they are evolved red giant stars. Theoretical predictions suggest that these low and intermediate-mass stars are important element factories for carbon, nitrogen, fluorine and elements heavier than iron that are synthesized by the slow neutron capture process (the s-process) [e.g., 1]. In this talk I review the latest theoretical predictions and show that while the qualitative picture of the s-process is well known, there are major uncertainties that affect stellar yields and our understanding of the chemical evolution in galaxies. I will discuss some of these uncertainties and also highlight areas where progress has been made.

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THE ORIGIN OF ELEMENTS AND THEIR EVOLUTION IN GALAXIES

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At the beginning of the Universe, the Big Bang, only light elements such as hydrogen, helium, and lithium are formed. Elements heavier than carbon are formed only in stars and are distributed into the cosmos when the stars die. Among them, so-called alpha elements (O, Mg, Si, S, and Ca) are produced by core-collapse supernova explosions of massive stars, while iron-peak elements are produced predominantly by Type Ia supernovae - thermonuclear explosions of binary star systems^{1,2}. Elements heavier than iron are formed by neutron-capture processes, two extreme cases of which are the slow neutron-capture process in low-mass stars and the rapid neutron-capture process in a binary of compact objects (neutron stars and black holes)³, which have been recently detected as gravitational wave sources. Individual elemental abundances have been well measured in the atmosphere of nearby stars, and from such observations it is possible to test the origin of these elements. We find that stellar rotation and/or magnetic fields are important in producing the observed abundance of heavy iron-peak elements (such as zinc) and some neutron-capture elements^{2,3}. With future astronomical telescopes, it will also be possible to map elemental abundances over a range of cosmic times from nearby to distant galaxies, and I will also present computer simulations on the evolution of elements^{4,5}.

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MASSIVE STARS: EVOLUTION, EXPLOSION AND NUCLEOSYNTHESIS

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Massive stars, by which we mean those stars evolving through all the stable nuclear burning stages and eventually exploding as core collapse supernovae, play a fundamental role in the evolution of the Universe. In particular, a good knowledge of their evolution is required in order to shed light on many topical subjects like the chemical evolution of the Universe, the UV outputs of the first stars, the properties of the Galactic and the Magellanic Clouds Wolf-Rayet stars, the origin of the Extremely Metal Poor stars, the final fate of massive stars and how they explode as core collapse supernovae of different types, the nature of the progenitors of the long Gamma Ray Bursts, the nature of the sources of gravitational waves. In this talk I will review our current understanding of the life and death of massive stars, their contribution to the chemical evolution of the Universe and the nature of their remnants as a function of the initial mass, metallicity and rotation velocity.

NLTE SPECTROSCOPY OF METAL-POOR STARS

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We review the abundance results obtained using high-resolution spectroscopic datasets, homogeneous and accurate atmospheric parameters, and the non-local thermodynamic equilibrium (NLTE) line formation for up to 17 chemical species, from Li to Eu, in two samples of the galactic stars, that is, halo cool giants and nearby FGK-dwarfs, uniformly distributed over the $-3.7 < [\text{Fe}/\text{H}] < +0.2$ metallicity range. The use of the NLTE element abundances gives increased credit to the interpretation of the data in the context of the galactic chemical evolution. We find that, at $[\text{Fe}/\text{H}] \leq -0.9$ both nearby and distant stars reveal a similar plateau at $[\alpha/\text{Fe}] \approx 0.3$ for each of the α -process elements: Mg, Si, Ca, and Ti, and the knee occurs at common $[\text{Fe}/\text{H}] \sim -0.9$ [1]. This provides a firm evidence for a common chemical history of different volumes in the Galaxy. As determined only for the nearby stars, the knee at the same metallicity is observed for $[\text{O}/\text{Fe}]$, and, at the lower metallicity, we obtain an upward trend of $[\text{O}/\text{Fe}]$ with decreasing $[\text{Fe}/\text{H}]$ [2]. NLTE leads to a substantial reduction of the spread in the Na/Mg abundance ratios at given metallicity, resulting in nearly constant $[\text{Na}/\text{Mg}] = -0.5$ to -0.6 in the $[\text{Fe}/\text{H}] < -1$ stars. Our NLTE element abundances confirm an existence of the dichotomy in the $[\text{Sr}/\text{Ba}]$ versus $[\text{Ba}/\text{H}]$ diagram found earlier from the LTE analysis of the $[\text{Ba}/\text{H}] < -3$ stars and indicative of two different nucleosynthesis channels for Sr at the earliest evolution stages of the Galaxy. We extended our approach to the very metal-poor ($[\text{Fe}/\text{H}] < -2$) giants in the dwarf spheroidal galaxies (dSphs) orbiting the Milky Way. For most elemental ratios, the classical dSphs Sculptor, Ursa Minor, Sextans, and Fornax reveal trends with metallicity, which are very similar or indistinguishable from the corresponding trends in the Milky Way [3].

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SUPERNOVA EXPLOSIONS OF FIRST STARS AND THEIR NUCLEOSYNTHESIS

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I present supernova models of first stars in the big bang universe and their nucleosynthesis. The nucleosynthesis yields are compared with the abundance patterns of extremely metal-poor (EMP) stars. These EMP stars show peculiar abundance patterns such as very high ratios of (C,N,O)/Fe and Zn/Fe, which suggest that first supernovae that produced such abundance ratios were jet-induced very high energy explosions (hypernovae).

ASTROCHEMISTRY TOWARDS SEEDS OF LIFE

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It is generally accepted that origin of life was the result of chemical evolution of organic molecules on the primordial Earth. Thus, an important issue in astrobiology is where prebiotic organic molecules are formed, terrestrial or extraterrestrial. After the famous Urey-Miller's experiment, many researchers believed that the primary formation site of prebiotic organic molecules was the surface of Earth under reducing atmosphere.

Recent modelling of the Earth's early atmosphere suggests more neutral conditions which preclude the formation of significant amount of prebiotic organic molecules. The situation, in turn, lead people to consider another possibility: delivery of extraterrestrial prebiotic organic molecules through comets, asteroids, meteorites, and interplanetary dust particles (the exogenous delivery hypothesis). One research suggested that extraterrestrial organic compounds may be more abundant by three orders of magnitude than their terrestrial formation¹. It is likely that a combination of these sources contributed to the building blocks of life on the early Earth. What is certain is that once life emerged on the primordial Earth, it was capable to adapt quickly to the surrounding environment for its survival through finding shelter from the UV photons and energy source. This continuing process led to complex metabolic life and even our own existence.

I will talk on recent progress regarding prebiotic organic molecules in space, which may be brought to the early Earth. If the exogenous delivery hypothesis works, similar process would occur even in other extrasolar Earth-like planets.

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NUCLEOSYNTHESIS OF HEAVY ELEMENTS IN EXTREMELY NEUTRON-RICH ENVIRONMENTS

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The first registration of neutron stars merger process and simultaneous registration of the r-elements¹ have confirmed our understanding that the main scenario of the r-process is connected with the jets appeared during neutron stars merger in close binaries rather than with supernova explosion².

As it was shown for the first time in numerical calculations of the r-process in neutron star merger (NSM)³ scenario, fission in such a scenario of the main r-process leads⁴ to fission cycling and formation of heavy r-elements from the second peak at abundance curve till uranium and thorium.

The models of NSM scenario are known³ since 1999 and they create the conditions for production of heavy nuclei in the r-process nucleosynthesis up to thorium and uranium. Besides the main branch of nucleosynthesis of heavy nuclei the other weak branch can exist⁵, in which chemical elements beyond uranium up to superheavy ones can be formed.

Under very high neutron environment the nucleosynthesis region lies close to the neutron stability boundary and the r-process can not overcome the region of spontaneous fission due to very high fission-induced rates. The calculation have done for different conditions and nuclear input and it was turn out that superheavy elements can be formed but only with $Z < 106$. Their abundance by the end of the r-process is compatible with uranium abundance, but their lifetimes are rather short and they decay quickly.

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ON THE IMPACT OF STELLAR ROTATION ON THE CHEMICAL EVOLUTION OF THE MILKY WAY THIN AND THICK DISKS

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I will present an overview of recent work concerning a new generation of stellar yields of massive stars with mass loss and rotation (Limongi and Chieffi 2018) and their impact on the chemical evolution of the solar neighborhood (Prantzos et al. 2018) and of the Milky Way thin and thick disks (Prantzos et al. 2017, Prantzos et al. 2019, in preparation) .

ELEMENTAL ABUNDANCES FROM MASSIVE STARS: THE PRESENT-DAY CHEMICAL COMPOSITION OF THE LOCAL MILKY WAY

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Massive stars in the range ~8-20 solar masses are ideal tracers for present-day chemical abundances, i.e. the current endpoint of more than 13 Gyrs of galactochemical evolution. They can be employed to study the spatial distribution of heavy elements throughout the Milky Way - and other galaxies - because typically they stay close to their birth places within their short lifetimes.

An overview is given which elements of the period table are accessible in their spectra throughout the main-sequence to the supergiant evolutionary stages, and a summary of our standing to analyse these spectra through non-LTE techniques. Application to a sample of OB-type main-sequence stars and BA-type supergiants in the local Milky Way has allowed a cosmic abundance standard to be established that is complementary to the solar abundance reference. Further emphasis is given on the promises that spectroscopy beyond the classical optical wavelength range offers to extend our knowledge of the heavy element content in massive stars.

NEUTRON STAR MERGERS AND THE ORIGIN OF HEAVY ELEMENTS

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The origin of the heaviest elements formed via "rapid neutron capture" or "r-process" has puzzled astrophysicists for decades. These elements constitute about half of the elements heavier than iron. While the basic nuclear mechanisms were understood a long time ago, the actual astrophysical production site has remained elusive. This situation changed on August 17, 2017: a gravitational wave signal from a merging neutron star binary was detected, closely followed by a short gamma-ray burst and week-long transients across the electromagnetic spectrum. The electromagnetic emission is consistent with the expectations from a few percent of a solar mass of freshly produced r-process elements, thereby underlining that neutron star mergers are (at least) a major cosmic production site. In this talk I will give an overview over recent developments with a particular focus on heavy element formation.

SUPRATHERMAL ATOMS AND MOLECULES IN ASTROCHEMISTRY

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The review presents the kinetic Monte-Carlo method for studying the role of suprathermal (hot) particles in astrochemistry at the molecular level of the description. Various modifications of the kinetic Monte-Carlo method aimed to investigate the kinetics and transport of suprathermal particles in the gas and dust envelopes surrounding astrophysical objects such as prestellar and protostellar cores of molecular clouds, planets, their icy moons and comets in the Solar and extrasolar planetary systems are discussed. In astrochemical applications of this approach, the important role of the suprathermal particle fraction is shown, whose presence: (a) leads to the changes of the local chemical composition, since non-equilibrium rate coefficients of chemical reactions (especially with high activation energies) between suprathermal particles and the surrounding gas are much higher than ones for chemical reactions at thermal energies¹; (b) causes non-thermal emissions in the gas and dust envelope; (c) enhances the chemical exchange between the gas and dust fractions of the envelope; (d) leads to the formation of extended hot coronae of the planets in the Solar and extrasolar systems, causes the increase of non-thermal atmospheric losses, thereby determining the evolution of the planetary atmosphere on astronomical time scales²; (e) increases the chemical complexity of the gas and dust envelopes³.

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CARBON AND NITROGEN AS PROBES OF MIXING PROCESSES IN GIANT STARS

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Carbon, nitrogen, and oxygen are among the first elements to form in the nucleosynthesis chain and comprise most of the mass of elements heavier than helium. These elements play important roles in stellar interior as sources of opacity and energy production through the CNO cycle, and thus affect the star's lifetime, its position in the Hertzsprung-Russell diagramme, and its heavy-element yields. Carbon and its isotopes as well as nitrogen give a comprehensive information on material mixing during stellar evolution. An overview of the ongoing work^{1,2,3,etc.} on CNO abundances in Galactic open cluster and field stars in the context of stellar evolution modeling^{4,5, etc.} will be presented.

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We acknowledge support by the European Social Fund via the Lithuanian Science Council grant No. 09.3.3-LMT-K-712-01-0103. This research uses the Gaia-ESO Survey data products from observations made with ESO Telescopes at the La Silla Paranal Observatory under programme ID 188.B-3002 and 193.B-0936. These data products have been processed by the Cambridge Astronomy Survey Unit (CASU) at the Institute of Astronomy, University of Cambridge, and by the FLAMES/UVES reduction team at INAF/Osservatorio Astrofisico di Arcetri. These data have been obtained from the Gaia-ESO Survey Data Archive, prepared and hosted by the Wide Field Astronomy Unit, Institute for Astronomy, University of Edinburgh, which is funded by the UK Science and Technology Facilities Council.

COMPLEX ORGANIC MOLECULES AS COMPANIONS OF FORMING STARS

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During last decades, almost two hundred molecular species have been detected in the interstellar medium. Among those species, the majority are the polyatomic carbon-bearing molecules¹. Many of those molecules also contain oxygen and nitrogen. As of today, such organic molecules are detected at every stage of the evolution of a low-mass protostar, from pre-stellar cores to evolved hot cores and protoplanetary disks². There are relatively simple species (such as formaldehyde and methanol) and complex pre-biotic molecules needed to synthesize amino acids (formamide, acetic acid, ethylene glycol, aminoacetonitrile) among the detected organic molecules. Such a developed chemical composition in the harsh conditions of interstellar medium is supported by a complex combination of physical and chemical processes which take place both in gas phase and on the dust grain surfaces^{3,4,5,6}. While some of those processes are relatively well studied, the others are not fully understood so far.

In my talk, I will review our current understanding of physical and chemical mechanisms that lead to the formation of complex organic and prebiotic species at different stages of star formation. I will show that most likely the scenarios of the formation of organic molecules differ from each other at every stage of the development of a protostar. They may or may not include chemical reactions in the gas phase, but at each scenario, chemistry on interstellar dust grains should play a pivotal role.

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THE LITHIUM-RICH GIANTS AND THEIR ORIGINS

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About 1% of giant stars^{1,2} have anomalously high lithium abundances in their atmospheres, conflicting directly with the prediction of standard stellar evolution models³. This finding makes the production and evolution of lithium in the Universe intriguing, not only in the sense of Big Bang nucleosynthesis^{4,5} or the interstellar medium⁶, but also for the evolution of stars. Decades of effort have been put into explaining why such objects exist, yet the origins of lithium-rich giants are still being debated. LAMOST has obtained over 10 million spectra in its seven years survey, and have found thousands of lithium-rich giants. Combing those spectra with data from other observations is making us approaching the origins of lithium-rich giants, which will eventually push our understanding to this element and its evolution in our Galaxy a big step forward.

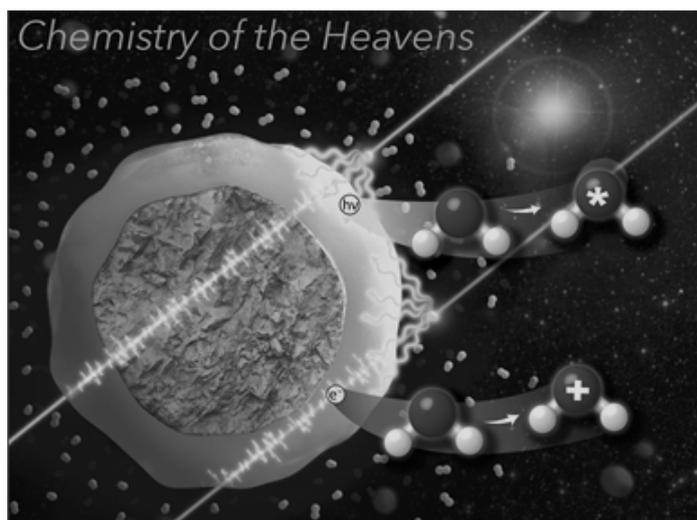
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COSMIC CHEMISTRY: PHOTOCHEMISTRY VS. RADIATION CHEMISTRY

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Energetic processing via photochemistry and radiation chemistry of cosmic ices is thought to be the dominant mechanism for the cosmic synthesis of prebiotic molecules.¹ Radiation chemistry is defined as the “study of the chemical changes produced by the absorption of radiation of sufficiently high energy to produce ionization.” Ionizing radiation in cosmic chemistry includes high-energy particles (e.g., cosmic rays) and high-energy photons (e.g., UV and X-rays). In contrast, photochemistry is defined as photon-induced electronic excitation not involving ionization. Because most previous astrochemical studies have used light sources that produce > 10 eV photons which can initiate both photochemistry and radiation chemistry, discerning the role of photochemistry vs. radiation chemistry in astrochemistry is challenging. By using a source whose photon energy does not exceed 8 eV, we have studied ammonia and methanol cosmic ice reactions attributable solely to photochemistry. We will compare and contrast these photochemistry results to those obtained in the same ultrahigh vacuum chamber with 1 keV electrons which initiate radiation chemistry in cosmic ice analogs.

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NUCLEOSYNTHESIS REFLECTED IN LIGHT CURVES OF TYPE II SUPERNOVAE

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Classical supernovae of type II-P display a clear plateau in their light curves in V band of the spectrum and in redder filters. At the same time, they show a fast linear decline in U band which is very well reproduced in models with non-gray radiative transfer¹⁻². This behavior is naturally explained by the role of metals (mostly iron) in the opacity in ultraviolet. One may expect that in stars of first generations with zero metallicity the behavior should be different. Indeed, the models of supernovae born from zero-metal stars produce the light curves in U without fast decline, i.e. very similar to those in V and redder filters³.

We perform a systematic study of U and \underline{V} light curves for a set of presupernova models with metallicity growing as the result of cosmic nucleosynthesis. The resulting templates may be used for estimates of metallicity for the environment of distant supernovae. In cases, when the metallicity is known from other indicators, those templates may be used for estimates of photometric cosmological redshifts.

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I-PROCESS HEAVY ELEMENT NUCLEOSYNTHESIS

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The cosmic production of elements heavier than iron occurs predominantly via neutron capture processes. Depending on the competition between the neutron capture and beta decay time scales, the neutron captures are either slow or rapid with respect to the beta decay; with the slow (s-process) characterised by low neutron densities ($n \sim 10^{7-11} \text{cm}^{-3}$) whilst the rapid (r-process) is characterised by very high neutron densities ($n > 10^{20} \text{cm}^{-3}$). These two processes produce quite distinct abundance patterns. However, recent observations of heavy element distributions in some of the oldest stars in the Universe demonstrate the limits of this simplified picture: some stars appear to require a process with neutron densities in between that of the s- and r-processes, with $n \sim 10^{15} \text{cm}^{-3}$, dubbed the intermediate (i) process¹. From a theoretical perspective, i-process conditions are being uncovered in a range of stellar sites for example: low-mass asymptotic giant branch (AGB) stars, super-AGB stars and massive stars.

We present calculations of i-process nucleosynthesis within dredge-out events of super-AGB stars. These stars reside in the mass range $\sim 8-10$ times the mass of the Sun, and bridge the divide between low-mass stars that end lives as white dwarfs and massive stars that die after undergoing violent supernovae explosions. The refining of this mass boundary has important implications for the energetics and chemical enrichment of galaxies.

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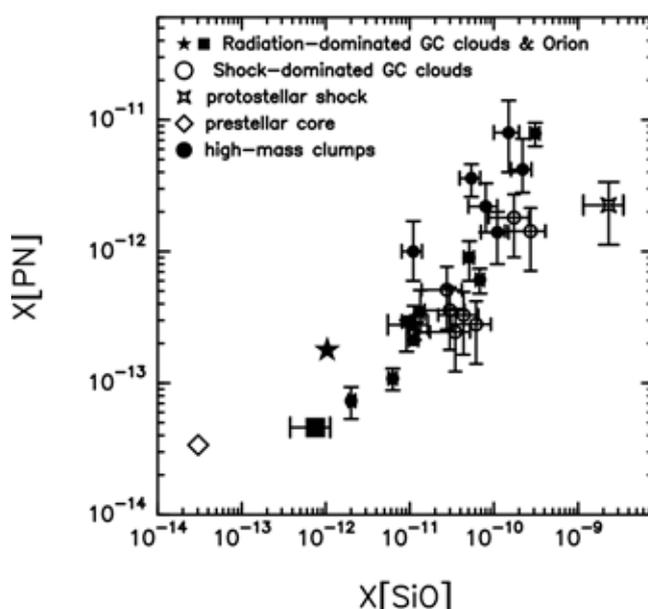
INVESTIGATING THE INTERSTELLAR CHEMISTRY OF PHOSPHORUS, THE MISSING PRE-BIOTIC ELEMENT

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Phosphorus is a crucial element for the development of life as we know it¹, but because of its low cosmic abundance, until recently its interstellar chemistry was almost totally unknown. Since 2016, the star formation group at Arcetri has made a fundamental contribution to our understanding of the astrochemical processes that involve this element in the star-forming regions of the Galaxy, paving the way for a growing number of studies on this pre-biotic element that had been “forgotten” up to now. Among the most important results, we have achieved the first detection of the PO molecule², the basic bond of phosphates, in two star-forming regions, W51 and W3(OH). Another crucial result was the tight relation between PN - the P-bearing molecule detected first in the interstellar medium and with the highest number of detections in star-forming regions so far - and SiO, a well-known shock tracer^{3,4}. Based on an unprecedented statistics, we have demonstrated that the abundances of SiO and PN, X[SiO] and X[PN], are strongly correlated in a variety of interstellar environments (Fig. 1), indicating a similar production process.



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LITHIUM: A JOURNEY THROUGH THE MILKY WAY

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The chemical evolution of lithium in our Galaxy, the Milky Way, is still a matter of debate. Indeed, lithium is severely depleted in stellar interiors, while synthesized during the Big Bang, and at some specific stages of stellar evolution.^{1,2,3} As a consequence, lithium abundances in stellar photospheres are not representative of the ISM in which they formed, making chemical evolution of lithium hard to constrain. In this talk, I will discuss on what has been done in the literature in terms of measurement of lithium abundances in FGK stars, thanks to high-resolution spectroscopy.^{4,5,6} Also, I will show that Galactic Chemical Evolution models of lithium are crucial when trying to understand the lithium history of the Milky Way.^{7,8} Finally, I will present latest results, especially on the puzzling decrease of ISM lithium at super-solar metallicities.⁹

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AN ASSESSMENT OF THE ORIGIN OF THE ELEMENTS THROUGH HIGH-RESOLUTION STELLAR ABUNDANCES

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The chemical elements provide a wealth of information both on Earth and in remote stars. We use their chemical composition to gain information on past long gone generation of stars as well as galaxy formation and evolution.

Through high-resolution spectra of various populations of stars we can use galactic archeology to uncover the highest level of detail of what the Milky Way looked like several billions of years ago as well as how massive and energetic some of the first supernovae were.

Here I will present new abundance results from high-resolution PEPSI spectra covering numerous elements from the lighter alpha elements to the more massive neutron-capture elements such as Ba, Nd, Sm, Eu or even Th.

Almost complete abundance patterns will allow for an assessment of the nature of past generations of, e.g., AGB stars and supernovae. However, stellar abundances derived under the 1D, LTE assumption will likely lead to a different view than 1D, NLTE abundances which I will discuss. Moreover, I will show a detailed comparison to yield predictions of metal-poor stars from various Galactic components such as the discs or halo and comment on the nucleosynthetic origin of the elements.

THE ELUSIVE ORIGIN OF NITROGEN IN PLANETARY SYSTEMS

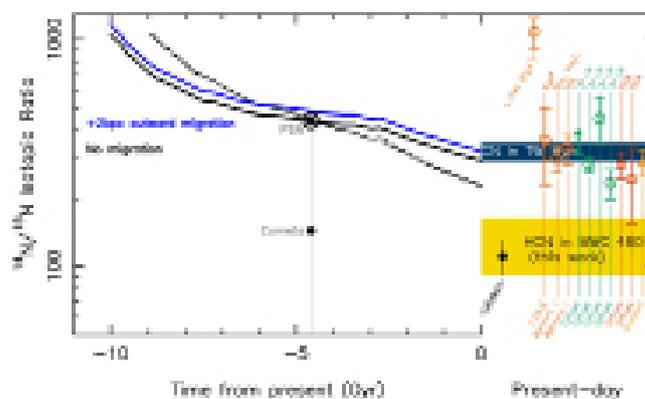
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The composition of the protosolar nebula (PSN) determines that of the planets that form within. Understanding in which form and abundances chemical elements originate in analogs of the PSN is a cornerstone of a comprehensive knowledge of the building of planetary systems in general. Among the most abundant atoms, nitrogen is certainly the most problematic [1]. As for other elements, the history of the various carriers of nitrogen, from prestellar cores, to protostars, and protoplanetary disks, is studied through isotopic ratio [2]. Yet, the elemental isotopic ratio of nitrogen in the solar neighborhood is not well constrained, precluding any attempt to accurately quantify the amount of fractionation in present-day star-forming regions in the Sun's vicinity and therefore to follow the isotopic reservoirs. However, recent progress in spectral line analysis, focusing on direct isotopic ratios measurements in prestellar cores and protoplanetary disks, suggests that the present-day $^{14}\text{N}/^{15}\text{N}$ elemental isotopic ratio in nearby star-forming regions is ~ 330 [3,4,5]. This ratio is also in very good agreement with Galactic Chemical Evolution model predictions [6]. These results will also be discussed in the context of new ESA/Rosetta results obtained in our group.



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COSMIC EVOLUTION OF R-PROCESS ELEMENTS: IMPACT OF NEUTRON STAR MERGER AND SUPERNOVA

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The afterglow of optical and near-infrared emissions from neutron star merger (NSM) GW170817/SSS17a was observed in addition to GW and GRB. No specific r-process element was identified, but the total energy release is consistent with theoretical prediction of radiative decays of r-process nuclei. Although NSM is a possible explanation for the solar-system r-process elements, it could not contribute to the early Galaxy. Supernova (SN) is still a viable candidate because it explains the “universality” of the observed elemental r-process abundance pattern found in metal-poor stars.^{1,2}

The essential difference between SN and NSM is the emergent event rate as a function of cosmic time. SN can explode in a few Mys from the early Galaxy, while binary neutron stars rarely merge at the rate of 0.1-1% of SN rate, and their coalescence delays by ~100 My due to too slow GW radiation. Therefore, NSM could not contribute remarkably to the early Galaxy.³ We carry out numerical N-body SPH simulations by taking account of hydrodynamic evolution of gas, stars and DM, coupled with evolutionary cycle of star formation, explosion and ejection of materials into space.³⁻⁵

We find that the “isotopic” abundance pattern of the r-process elements manifests clear cosmic evolution due to the different contribution in time from SN and NSM.⁴ The “isotopic” abundance pattern is different in the early Galaxy from the solar-system pattern due to very small contribution from NSM r-process, still satisfying the “universality”.^{1,4} We conclude that the solar-system elements consist of both SN and NSM r-process contributions as a consequence of cosmic evolution such that the SNe contributed from the early Galaxy to enrich r-process elements, while the NSMs have arrived later. We propose several observational tests for our theoretical prediction.^{4,5}

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CHEMICAL COMPOSITION OF COSMIC RAYS AS A KEY TO REVEALING THEIR SOURCES

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For most elements, the isotopic ratios seen in cosmic rays (CRs) are similar to those in the solar wind. The most important exception to this is $^{22}\text{Ne}/^{20}\text{Ne}$ where the CR value is ~ 5 times that of the solar wind¹. Such a difference in chemical composition can shed light on the sources where Galactic CRs are born and accelerated. According to most recent models of nucleosynthesis, a large amount of ^{22}Ne is generated in Wolf-Rayet (WR) stars²⁻³. In the winds of carbon sequence of WR stars, i.e., WC stars, the isotopic ratio $^{22}\text{Ne}/^{20}\text{Ne}$ can be much larger than in the solar wind. Here, we consider CRs produced by ^{22}Ne -enriched WR winds in young massive star clusters assuming the acceleration occurs from an ensemble of shock waves from the massive stars' winds. We present the results of modeling of the chemical composition of CRs from young massive star clusters for different sets of the cluster parameters. The fraction of Galactic CRs from such sources, needed to provide the observed neon isotopic ratio, is discussed.

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ESTIMATES OF THE EXTINCTION LAW AND METALLICITY FOR THE GALACTIC BULGE STARS

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Based on the VVV/ESO infrared sky survey data, we investigate properties of red clump giants (RCG) of the bulge of the Galaxy. It allows us to obtain estimates of the extinction law and metallicity for stars in the central regions of the Galaxy. We show that the extinction law significantly differs from the standard one everywhere and moreover noticeably variable along the bulge. According to our estimates, this variability is also characteristic for the metallicity of RCGs inside the galactic bulge and other some parts seems to be higher than generally accepted values.¹

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SIMULATIONS OF MERGED H/H₂ AND C⁺/C/CO TRANSITIONS IN THE ORION BAR

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Birth of each massive star is accompanied by active interaction with a parental molecular cloud. Theory predicts that a shock wave should precede an ionization front expanding around the star. However, it is not easy to prove a movement of a compressing wave with observational data around real young massive stars. High-resolution ALMA images (spatial resolution is 1 arcsec) towards the Orion Bar photodissociation region (PDR) reveal no discernible offset between the peak of H₂ emission in the PDR and the ¹³CO(3–2) and HCO⁺(4–3) emission in the molecular cloud. We make simulations of a molecular cloud irradiated by strong ultraviolet radiation using the chemo-dynamical model MARION^{1,2} to show that the observational view of the PDR, namely, no resolved offset between the ¹³CO(3–2) and HCO⁺(4–3) peaks, merged dissociation fronts of H₂ and CO, bright HCO⁺(4–3) emission, can only be explained by the ongoing propagation of the dissociation fronts through the molecular cloud. While the merging of the fronts can be reproduced in constant-pressure model, it predicts no bright HCO⁺(4–3) emission due to insufficient heating. The dynamical model fits not only HCO⁺ abundance and line emission but also reproduces abundances of several PDR tracers such as C, C⁺, CH, CH⁺ and CO⁺. We conclude that modeling of various ionized, atomic and molecular gas tracers complemented by high-resolution observational maps of different lines are needed to confine physical conditions in the Orion Bar.

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PROBING THE PERIODIC TABLE IN THE OUTER HALO

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Globular clusters are amongst the oldest objects in our Galaxy. In particular those clusters at large Galactocentric radii bear important information on the build-up of chemical elements in the early Universe. While some of the outer halo clusters are younger than their inner halo counterparts and might be accreted from satellite galaxies, others appear, chemically speaking, to be coeval with the inner, in-situ halo component. In this talk I will present our endeavours to chemically characterize elements from carbon to europium in these most remote stellar systems and highlight some of the most striking similarities and differences.

INVESTIGATING THE IRON 6.4 KEV EMISSION LINE ORIGIN IN MOLECULAR CLOUDS OF THE GALACTIC CENTER REGION

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The neutral iron emission line at 6.4 keV is the valuable spectral diagnostic instrument for X-ray astronomy. The non-thermal Fe K α 6.4 keV line results from the interaction between low-ionized medium and external hard X-ray emission or low-energy cosmic rays.

Variable X-ray emission was observed in the molecular clouds near the Galactic Center and characterized by the power law spectrum ($\Gamma \sim 2$) with the iron 6.4 keV emission line. This Fe K α line emission can be explained by two main hypotheses. The first approach implies an irradiation of the molecular cloud by an external X-ray source. The past flaring activity of the supermassive black hole Sgr A* considered as a possible external source with the sufficient X-ray luminosity. Variations of the emission line, which were observed in the Galactic Center molecular clouds, trace the propagation of illuminating fronts, presumably induced by past flaring activities of Sgr A*.

Alternatively, a fluorescent emission of the molecular cloud can be a result of a bombardment by low-energy cosmic ray particles. This scenario requires a stationary level of the non-thermal emission.

Presumably a combination of both hypotheses is responsible for the non-thermal emission of the molecular cloud near the Arches stellar cluster located in the Galactic Center region. Recent NuSTAR and XMM–Newton observations of the molecular cloud around the Arches stellar cluster demonstrate a dramatic change both in the morphology and intensity of its non-thermal X-ray emission, similar to that observed in many molecular clouds of the Central Molecular Zone at the Galactic Center. We present results of a long NuSTAR observation of the Arches complex in 2016, taken a year after the previous XMM+NuSTAR observations which revealed a strong decline in the cloud emission. The 2016 NuSTAR observation shows that both the non-thermal continuum emission and the Fe K α 6.4 keV line flux are consistent with the level measured in 2015. We discussed both scenarios: the non-thermal emission reached a stationary level in 2016 or continue to decrease.

INHOMOGENEOUS PRIMORDIAL MAGNETIC FIELD AND ITS IMPACT ON BIG BANG NUCLEOSYNTHESIS

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There is a long-standing cosmic Lithium Problem in the standard Big Bang Nucleosynthesis (BBN) model that the predicted primordial ${}^7\text{Li}$ abundance is 4 times higher than the observational constraint from Pop.II stars.

The effect of primordial magnetic field (PMF) on BBN has been studied in literature¹, where a constant scale-invariant PMF strength during the BBN epoch was assumed, which virtually did not solve the Lithium Problem. Theoretically, the length scale of the PMF fluctuations inside the co-moving horizon scale in its energy density can survive during the BBN epoch². It is therefore realistic to assume that the PMF was in the inhomogeneous distribution which satisfies extrapolated observational constraints from CMB anisotropies. We have recently studied the effects from such inhomogeneous PMF on the BBN³: The primordial baryons are in local equilibrium at the same temperature and obey Maxwellian distribution. Globally, however, due to the existence of a fluctuating PMF energy density, radiation energy density becomes inhomogeneous as the radiation temperature does.

In this talk, we will extensively show our recent new results so that the inhomogeneous PMF eventually leads to a non-Maxwellian baryonic energy distribution function and eventually affects strongly the primordial ${}^7\text{Li}$ abundance⁴ to solve the cosmic Lithium Problem. Moreover, we find that our extended multi-zone BBN calculation results in the same effect as the BBN model with an inhomogeneous PMF would make. In this extended calculation, the multi-zone inhomogeneous PMF is encoded into nuclear reaction network code. This code can be used in the future studies of BBN under the various circumstances that the cosmological plasma evolution could make including fluctuations and magneto-hydrodynamical processes in the early Universe.

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INTEGRAL VIEW OF THE PRODUCTION OF ELEMENTS IN THE SPACE

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INTEGRAL is the astrophysical observatory successively worked in the orbit since 2002 and dedicated to the study of the Universe in gamma rays. We review the most important results of the observatory starting from the systematic sky survey in the 67.9 and 78.4 keV nuclear de-excitation lines of titanium-44 (^{44}Ti), detections of several supernova remnants in these lines, and ending with the contribution of INTEGRAL to the detection of the electromagnetic signal from binary neutron stars merging and estimations of the heavy elements production.

NUCLEOSYNTHESIS IN NEARBY NOVAE

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The Universe is richly populated with elements beyond hydrogen and helium, partially thanks to violent stellar explosions¹. While novae may be less violent than the more spectacular supernovae, they more than make up for this by being far more numerous.

In my talk I will use many thousands of densely time-sampled spectra taken by the Global Jet Watch observatories to demonstrate that evolving novae, especially in the days following detonation, have many interesting properties. Our observations of two recent Milky Way novae, Nova Sagittarii V5668 and ASASSN-18fv (Nova Carinae 2018), span more than 1000 days, reveal dramatic activity on short timescales (hours) exhibited by several chemical elements, most notably oxygen, nitrogen and hydrogen – the building blocks for life. The datasets span many distinct spectroscopic phases, including a spectacular dust dip of Nova V5668 Sagittarii², during which epoch there are significant changes in line profiles. I will discuss the role played by novae in the enrichment of the interstellar medium, and how these datasets refine our modern understanding of classical novae.

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ELEMENTAL ABUNDANCES IN THE HOT INTRA-CLUSTER MEDIUM

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Since the first complete theories of stellar nucleosynthesis in the 1950's, it is well established that chemical elements heavier than helium are almost entirely the result of thermonuclear processes in stars at various stages of their lifetimes. The diffuse and hot intra-cluster medium (ICM), glowing in X-ray and detected in the deep gravitational potential well of galaxy clusters, is rich in metals. This means that the heavy elements, synthesised by billions of supernovae over cosmic times, are present even at the largest scales of the Universe. The distribution of these elements in the ICM is determined by a number of physical processes, which mix and transfer elements ejected by supernovae^{1,2}. In this talk we will discuss the possible role of diffusion in shaping ICM abundance profiles. In particular, the element diffusion can potentially lead to significant changes in the He abundance, accurate knowledge of which is important for interpretation of X-ray and SZ data of galaxy clusters, namely, calculation of angular distance, gas masses and metal abundance diagnostics. We estimate possible diffusion effects by calculating a simple element sedimentation model with no magnetic fields. Based on calculations with such a model for a set of parameters typical of a cool-core clusters we discuss possible observational signatures and biases in X-ray derived quantities of galaxy clusters caused by diffusion^{3,4}.

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ASTROCHEMICAL MODELLING OF C/O RATIO IN PROTOPLANETARY DISKS

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Volatile chemical species in protoplanetary disks are either gaseous or make up icy mantles of dust grains. Many volatiles contain carbon and oxygen which results in redistribution of these elements between gas and ice phases. Carbon-to-oxygen (C/O) ratio in gas and ice phases in disks varies depending on which species are frozen-out in given physical conditions. The distribution of C/O ratio in the disk along with the mechanism and location of planet formation might affect the chemical composition of atmospheres of forming planets.¹

We use astrochemical modelling with ANDES code² to calculate 2D distribution of chemical species and resulting C/O ratio in gas and ice phases for a set of protoplanetary disk models. We explore different disk masses and radii, types of central star, and initial elemental abundances. We indicate the regions of the disk where C/O ratio in gas or ice significantly differs from the initial elemental C/O ratio, especially where it exceeds unity, and analyse the effect of disk parameters.

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ROLES OF ${}^7\text{Be}(n, p){}^7\text{Li}$ RESONANCES IN BIG BANG NUCLEOSYNTHESIS WITH TIME-DEPENDENT QUARK MASS

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The standard Big Bang nucleosynthesis (BBN) model predicts primordial abundances of hydrogen, helium and lithium which are in reasonable agreement with astronomical observations except for ${}^7\text{Li}$.

Recent precise reanalysis of Lyman-alpha forests along the line-of-sight toward high red-shift quasar Q1243+307 has placed tighter observational constraint on the primordial abundance of deuterium¹. Comparing this observational result with the theoretical prediction allows us to explore possible beyond-standard physics². In particular, the BBN is sensitive to quark mass variations because they change nuclear binding energies. The effect of the quark mass variations on the BBN has been studied in literature^{3,4,5}, but it was the case ignoring the roles of the ${}^7\text{Be}(n, p){}^7\text{Li}$ resonant reaction which is known to affect the primordial abundance of ${}^7\text{Be}$. In this talk, we report for the first time that this reaction significantly decreases the abundance of the $A=7$ nuclear systems when the quark mass variation is negative⁶. This is because the resonance at $E=0.33$ MeV is found to contribute strongly to the reaction rates at the BBN temperature.

We also report that the ${}^7\text{Li}$ abundance significantly decreases if the quark mass is larger than the present value, although this is the conclusion assuming that the resonance energies are independent of the quark mass variation. In order to prove this solution, more careful theoretical studies of the binding energies of the excited states are desirable⁶.

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CHEMICAL EVOLUTION IN C-TYPE SHOCK WAVES

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A magnetohydrodynamic model of a steady non-dissociative (C-type) shock wave in a dense molecular cloud is presented. A complete gas–grain chemical network is taken into account: the gas-phase chemistry, the adsorption of gas species on dust grains, various desorption mechanisms, the grain surface chemistry, the ion neutralization on dust grains, the sputtering of grain mantles.¹

The focus of the report is on the chemical processing of gas material and ice mantles of dust grains by the shock wave. At high shock speeds, molecules ejected from ice mantles are effectively destroyed in hot gas, and their survival time is low. These results imply that strict constraints must be put on the physical parameters for the shock regions where large astronomical molecules are observed – shock velocity and gas density must be low enough to allow molecules survive in the hot shocked gas.

After a passage of high-speed C-type shock, a gas layer of high abundance of atomic hydrogen appears in the cooling postshock gas that triggers formation of large organic species. The efficient methanol production on the surface of dust grains in the cool postshock gas may be one of the reasons of high abundance of methanol ice observed toward some young stellar objects.²⁻³ Gas-phase methanol is re-formed via reactive desorption mechanism. The efficiency of reactive desorption is a key parameter that determines the gas-phase abundance of methanol and other complex species that are produced via it.

These results are important for interpretation of observations of molecular emission in protostellar outflows and supernova remnants.

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LANTHANIDES IN STELLAR ATMOSPHERES

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Lanthanides or the rare-earth elements (REE) constitute a compact group of 15 elements from the 6th period of Mendeleev's table. All REEs but Pm have stable isotopes and are observed in solar and stellar atmospheres. Cosmic/solar REE abundances are low which makes their analysis in stellar spectra difficult, often even impossible. However there is a group of middle Main Sequence stars, magnetic chemically peculiar (Ap) stars, which reveal prominent REE overabundances in their atmospheres. The lines of the REEs probe the unique properties of Ap stars: pulsations, element separation, surface chemical inhomogeneity.

ISOMERIC CARBON-CONTAINING COMPOUNDS OF INTERSTELLAR MEDIUM: STRUCTURE, ENERGY, AND POLARIZABILITY

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About 100 carbon-containing molecules have been currently detected in interstellar and circumstellar environments, and this list includes isomeric substances. In most cases, the minimum energy principle is able to explain the ratio of abundances of the isomeric compounds¹ but in some cases is not. To solve the questions unanswered within the energetic approach, we use the dipole polarizability as it is often correlates with the stability of organic compounds.² As we found,³ in general both energy and polarizability provide the consistent estimates for the ratio of the isomers (e.g., the isomers having generic formulae CHO, CHN, C₃H, C₃H₂, CHNO, C₂H₃N, C₂H₆O, etc.). In the case of the C₄H₃N isomers, the most abundant isomer (cyanoallene) is not the most stable but the least polarizable that is in a good agreement with relevant experimental study. We assume that the predictive efficiency of polarizability is due to its relevance to the molecules' response to the external electric fields, i.e., more polarizable molecules are more responsive, more reactive, and, hence, less abundant. Further, we have analyzed the polarizabilities of polycyclic aromatic hydrocarbons, fullerene hydrides (fulleranes), polyynes, and their derivatives with respect to their possible detection under interstellar conditions.

Fullerenes are intriguing molecular species detected in interstellar and circumstellar environments.⁴ They have the largest molecular size among the other interstellar molecules and there is a gap between the sizes of C₆₀/C₇₀ and typical interstellar organic molecules (having up to 13 atoms). Formation of fullerenes under circumstellar and laboratory conditions in the aspect of their kinetic,⁵ thermodynamic⁶ and structural⁷ properties are discussed.

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HOW THE PERIODIC TABLE TRAVELS FROM GALAXIES TO VOIDS

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Elements heavier than helium are born in stars which normally are concentrated in galaxies. Some part of this matter is buried forever in low mass stars but substantial amount of heavy elements is expelled into the interstellar medium (ISM) by stellar explosions and stellar wind. This is a common scheme of chemical enrichment of the ISM and circumgalactic space. The scheme does not explain existence of some detectable amount of heavy elements in voids which are believed to be most empty regions of the Universe. Since the elements could not be born there we need to explain how these are transported into intergalactic medium (IGM) and much further away, into voids. In other words, having in mind the title of the symposium our question of interest can be formulated as follows: how the Periodic Table travels through Space from the place of birth into the deepest regions of the Universe and how long Time it takes.

The major mechanisms of loss of heavy elements from galaxies and expulsion those into the IGM are: (1) galactic wind and (2) the expulsion of dust by stellar radiation pressure from galaxies. We compare both mechanism and argue that the latter one is apparently underestimated. After being expelled out of galaxies heavy elements are transported to the rest of the Universe. Observations show presence of heavy elements even in huge (10 – 100 Mpc) voids at redshifts $z \geq 3$. Nor galactic wind neither dust expulsion that we observe in our epoch are capable to bring matter so far. The problems we are facing are: how heavy elements have been transported so far away, when and how fast was this transportation, whether dust survives there, etc.

Here we briefly review recent progress on the topics mentioned above. We confirm that galaxy – IGM mass exchange processes (wind and dust outflows) play an important role in chemical evolution of galaxies and IGM. We argue that presence of heavy elements in voids is intriguing evidence of still poorly understood but powerful dynamical processes acting efficiently at early stages of evolution of the Universe. We briefly discuss these processes.

TOMOGRAPHY OF HIGH MASS X-RAY BINARY PULSARS IN THE FLUORESCENT 6.4 keV IRON LINE

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Many compact X-ray sources appear as a parts of binary systems, while other companion is a regular star. High-mass X-ray binary pulsars consists of a neutron star and a massive regular star. High mass pulsar systems can be separated by the type of the mass-transfer processes into three different groups: accretion from a circumstellar envelope, accretion from a strong wind and a Roche lobe overflow, in which case an accretion disk is formed. Spectra of X-ray pulsars are usually modelled as an absorbed hard powerlaw continuum plus a number of emission and absorption features. The powerlaw continuum is likely a Comptonized photons from the neutron star. The most often evident feature in spectra of X-ray binary pulsars is the fluorescent Fe K-alpha line.

Significant fraction of X-rays emitted by a pulsar is absorbed in a relatively cold plasma. Such plasma may be found in the photospheres of an optical companion, at the outer radii of an accretion disk, in a stellar wind, in gas streams within the system, etc. At a typical temperature of cold plasma ($T \sim 10^4$ K) the atoms of heavy elements (S, Ar, Fe, Ni) are in rather low stages of ionization with filled K- and L-shells. X-ray photons are absorbed mainly due to photoeffect on K-electrons. The radiative transition from the occupied L-shell following the ejection of K-shell electron produces a K-alpha photon.

The relative amplitude of a regular variations in the K-alpha equivalent line width over the spin and orbital periods is insensitive to chemical composition and is determined by the mass ratio of the binary components and the degree of Roche-lobe filling by the regular star. The absolute amplitude of the variations allows one to estimate the chemical composition of the star.

We discuss the dependence of the Fe K-alpha line parameters on the high-mass X-ray binary system parameters, the line formation regions and the heavy elements abundances, also we trace the line profile variability over the spin and orbital phases.

CHEMICAL COMPOSITION OF ANCIENT STARS AS A KEY TO NUCLEOSYNTHESIS IN THE FIRST STARS

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We present accurate stellar parameters and chemical abundances for ancient stars, formed after a small number of nucleosynthesis episodes. Our stellar sample contains seventeen ultra metal-poor (UMP, $[\text{Fe}/\text{H}] < -4$) stars in the Milky Way (MW) halo stars and six metal-poor stars (MP, $[\text{Fe}/\text{H}] < -1.6$) in Coma Berenices ultra-faint dwarf galaxy (UFD) and Segue 1 system. To determine effective temperature and surface gravity we rely on photometry, isochrones, distances, and ionization balance for up to three elements (Ca, Fe, and Ti), and fitting the wings of the Balmer lines. Our spectroscopic method is based on accurate line-formation calculation taking into account deviations from the local thermodynamic equilibrium. Our results for stars in Coma Berenices and Segue 1 take advantage on employing new photometric observations in the visible and infra-red bands obtained with the 2.5-m telescope of the SAI MSU Caucasian observatory. Using this data, we found effective temperatures from different colours to be consistent within 20 K for each star. Coma Berenices S1, S2, and S3 stars are enhanced in alpha-elements. However, different elements in a given star and the same element in different stars show various $[\alpha/\text{Fe}]$ abundance ratios. For example, $[\text{Mg}/\text{Fe}] = 0.15, 0.92, \text{ and } 0.79$ in S1, S2, and S3, respectively, while stars with $-3.5 < [\text{Fe}/\text{H}] < -2$ in the other dwarf galaxies and the MW halo show a typical ratio $[\text{Mg}/\text{Fe}]$ of 0.3 dex. We found a very similar $[\text{Na}/\text{Mg}]$ of -1.2 in the three stars, while a typical for MP stars value is $[\text{Na}/\text{Mg}] = -0.6$. Such peculiar element abundance properties argue for a small number of nucleosynthesis episodes contributed to chemical composition of these stars. For three stars in Segue 1, we derived similar $[\text{Ca}, \text{Mg}, \text{Ti}/\text{Fe}]$ ratios of 0.5 dex, while their $[\text{Fe}/\text{H}]$ takes different values from -1.6 to -2.4. This result argues for absence of Fe enrichment from SNeIa and short star formation history. We compared our abundances with those from Mashonkina et al. 2017 derived with the same method for stars in seven dwarf spheroidal galaxies. Our Sr and Ba abundances in three stars in Coma Berenices confirm the main result of Mashonkina et al. 2017 about different nucleosynthesis channels for Sr production in UF and classical dwarf galaxies.

Reference: Mashonkina L., Jablonka P., Sitnova T., et al. *Astron. Astrophys.* 2017, 608, A89.

LAUNCHING OF HOT GAS OUTFLOW BY DISC-WIDE SUPERNOVA EXPLOSIONS

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Galactic gas outflows are driven by stellar feedback with dominant contribution from supernovae (SN) explosions. The question of whether the energy deposited by SNe initiates a large scale outflow or gas circulation on smaller scales – between discs and intermediate haloes, depends on SN rate and their distribution in space and time. We consider circulation of gas and metals driven by disc-wide unclustered SNe with galactic star formation rate in the range corresponding to mid-to-high star formation observed in galaxies. We show that such disc-wide SN explosion regime can form circulation of warm ($T \sim 10^4$ K) and cold ($T < 10^3$ K) phases within a few gas scale heights, and elevation of hot ($T > 10^5$ K) gas at higher ($z > 1$ kpc) heights. Metals are found to follow circulation of hot phase, and because of inefficient mixing their major part is ejected from the disk. We estimate the metallicity and line-emissivity of such hot metal-enriched outflow, and discuss observational manifestations of such outflows in optical and X-ray bands.

LIGHT NUCLEAR CLUSTERS IN SUPERNOVA MATTER

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We explore the appearance of light nuclear clusters at high densities of collapsing stellar cores. Special attention¹ is paid to the unstable isotope ${}^4\text{H}$, which was not included in previous studies. We have found that for light nuclei it is important to use the exact information about its properties (values of spins and energies of known excited states) to obtain a reliable EoS.

In addition, we consider² the exotic possibility of the existence of a dineutron and tetraneutron in these conditions. We explore the influence of nuclear parameters, binding energy first, on their abundances. We find that at some conditions dineutron can be as abundant as light hydrogen and helium isotopes.

Our main conclusion is that thermodynamic quantities are only weakly sensitive to the light clusters effect. The change in pressure and hence the direct change in collapse dynamics will be minor. But the change in neutrino heating and neutronization processes can be significant.

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NONTHERMAL ANTINEUTRINOS OF BIG BANG NUCLEOSYNTHESIS

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At the epoch of Big Bang nucleosynthesis (BBN)¹ there were two nuclear β -unstable species: neutrons and nuclei of tritium. Decays of these elements resulted in existing of the nonthermal antineutrino background in the Universe.

The information about temporal evolution of the abundances of light nuclei and the value of baryon-to-photon ratio during the era of BBN have been imprinted on the energy spectra of this antineutrino background presented for the first time in the paper².

The particle number density of these antineutrinos is smaller than the average concentration of nucleons in the Universe, which is nine orders of magnitude less than the concentration of the relic neutrinos of the CvB, but the average energy of the nonthermal antineutrinos is one-two orders of magnitude more than that of the relic neutrinos. For this reason the nonthermal antineutrinos of BBN hypothetically can serve as a one of direct sources of the information about progression of the nuclear processes during the BBN.

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A SURVEY OF DEUTERATED MOLECULES IN REGIONS OF HIGH MASS STAR FORMATION

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The effect of deuterium fractionation in interstellar clouds is rather well known. So far it has been observationally investigated mainly in cold low-mass cores where the enhancement of the abundance of deuterated molecules is very strong. Studies of deuteration in high-mass star-forming regions (HMSF) are much more limited¹. Usually deuteration is expected to be weak in warm clouds.

In 2017-2018 we performed with the 20-m Onsala radio telescope a survey of about 60 massive cores in the DCN, DNC, DCO⁺, N₂D⁺ J=1-0 and ortho-NH₂D (1_{1,1}-1_{0,1}) lines in the 3-4 mm band. This study continues our investigations of the chemical differentiation in high-mass star-forming regions². The sample includes warm cores associated with H II regions, masers and luminous IR sources as well as several cores in infrared dark clouds. The detection rate was quite high for DCN, DNC, DCO⁺ and NH₂D, while N₂D⁺ was detected only in a few sources.

The gas temperature for our sample is in the range from ~ 15 K to ~ 50 K. We found in particular that the DCN and NH₂D relative abundances are nearly constant in this temperature range while the DNC and DCO⁺ abundances drop with increasing temperature.

Several sources have been mapped in these lines but in most cases only a single position was observed. Significant variations of the deuteration fraction across some sources are seen. Physical parameters of the sources are estimated.

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WHAT ELEMENTS CAN BE USED TO CHECK THE STELLAR PULSATIONS?

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There exists the strong radiation stratification in the expanding stellar atmospheres (stellar winds) of early type stars. The ions with higher ionization potential (C III, N III, O IV, Si III, etc.) are disposed closer to the stellar photosphere. Studying of the line profiles variations (lpvs) at the short time scales (hours) allows to investigate the non-radial photospheres pulsations. Perturbations of the velocity field in the photosphere caused by pulsations can be propagated in the stellar wind. An analysis of lpvs of C, N, O, Si and other elements allows studying how the velocity field perturbations travel in the wind. We present the results of the wavelet analysis of lpvs for C, N, O, Si, He, and Balmer lines in spectra of OB stars. It is shown that the disturbances of the velocity field in the stellar wind can be traced up to several stellar radii. However the frequencies of regular variations of the line profiles formed in the stellar wind can be changed.

DESORPTION OF COMPLEX MOLECULES FROM DUST GRAINS IN ORION BAR PDR

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Complex molecules and their precursors such as formaldehyde, methanol and many more are observed in highly UV-irradiated gas in the Orion Bar which is a template of a highly-irradiated photodissociation region in astrochemical studies. Origin of these molecules in the gas phase of the PDR is a matter of debate. We study how the molecules desorb from dust grains formed deep inside of parent molecular cloud and appear in the PDR due to gas and dust drift away from young massive stars illuminating the Bar. MARION^{1,2} model with updated chemical module which now contains extended chemical network and surface reactions is used to simulate chemistry in the PDR. We show that abundances of methanol and its precursors HCO and H₂CO in the PDR can be fitted within an order of magnitude even without the surface reactions. However, more accurate chemical model is required to fit spatial distribution of H₂CO and CH₃OH in the PDR and dependence of their abundances on gas density and temperature.

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DEUTERATED ISOTOPOLOGUES OF WATER AND OTHER ASTROBIOLOGICALLY IMPORTANT SPECIES IN REGIONS OF STAR FORMATION

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Since observational technologies allow astronomers to get detailed molecular spectra, the presence of isotopologues in space is being discovered. As deuterium came into play the measurements of D/H ratio became an important issue for astrobiology, especially if it comes to water ices on comets, planets¹ and satellites². Knowing the ratio helps to understand evolution of water on surfaces of the objects and their past. Still in search for relevant answers to questions about history taking the very origins of deuterating into account is important. First deuterated species appear in cold dense clouds in the regions of star formation.

We conducted numerical calculations starting with atomic compound of the region and simulated chemical evolution there. Our study^{3,4} shows that for some of the deuterium-bearing species evolution differs from the one for main isotopologues, and ratios of abundances of isotopologues on each step do vary and may differ from global isotope ratio.

Since significant part of the molecules produced on earlier stages of star formation survive impetuous processes of later ones, considering the primary stage of evolution (cold dense cores) is important for studies of deuterium bearing species on later stages (from protoplanetary disks to planets). Here we present the results for water and some other astrobiologically important species.

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CARBON, NITROGEN AND OXYGEN IN AFG SUPERGIANTS: THE N/C VS N/O RELATION AS AN INDICATOR OF THE STAR'S EVOLUTION

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The N/C vs N/O relation is known to be a sensitive indicator of stellar evolution⁴. Basing on our recent NLTE analysis of the oxygen abundances for about 50 AFG supergiants and bright giants and our earlier NLTE determinations of the N and C abundances for many stars from the same sample^{2,3}, we constructed the [N/C] vs [N/O] relation for these stars. A correlation between these values is found to be pronounced; the observed [N/C] increase from 0 to 1.5 dex is accompanied by the [N/O] increase from 0 to 0.8 dex.

We compared the observed [N/C] vs [N/O] relation with theoretical predictions for stellar models with rotation¹. There is a good agreement between the observed and theoretical relations. It was found that the [N/C] and [N/O] increment is strongly dependent on the initial rotational velocity V_0 . For stars with low [N/C] and [N/O] values the theory predicts the low velocities $V_0 < 100$ km/s, whereas for some stars with the most enhanced [N/C] and [N/O] values (they are likely at the end of the First Dredge-Up) one may suggest the velocities V_0 about 200-300 km/s.

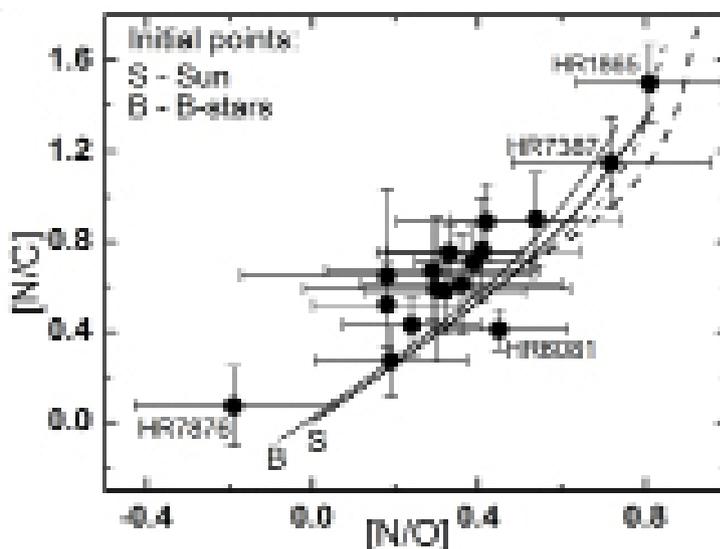


Figure 1. Comparison of the observed [N/C] vs [N/O] relation with the theoretical relations computed for stellar models with rotation¹.

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GALACTIC EVOLUTION OF COPPER IN THE LIGHT OF NLTE COMPUTATIONS

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With the help of new data on the photoionization cross-sections and oscillator strengths for the copper atom¹ we created a quantum-mechanical atomic model in order to calculate the atomic level populations for the stellar atmospheres, where we suppose that condition of the local thermodynamical equilibrium (LTE) is not valid. Using the stellar spectra in visual and far UV range we showed that our NLTE atomic model allows one to describe the copper line profiles much better than in the LTE case.

We determined NLTE copper abundance in 14 metal deficient stars.^{2,3} It was showed that NLTE approximation eliminates the copper overdeficiency compared to iron abundance at regime of lower metallicities: the mean [Cu/Fe] is about -0.2 dex for metallicity range from [Fe/H] = -1.5 to -3.5. Another important conclusion: the relative-to-iron copper abundance is almost independent of the metallicity. According to these important results, we can conclude that copper behaves as a primary element at the low metallicities, and this fact requires a substantial revision of the theory that determines the rate of its formation during explosive nucleosynthesis in the supernovae of second type.

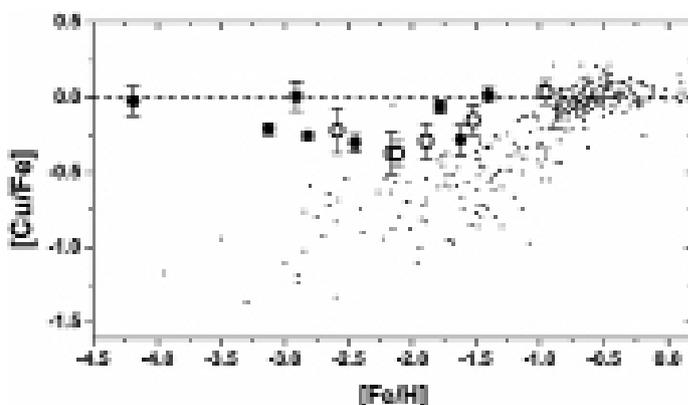


Figure 1. The Galactic evolution of Cu. Filled symbols are the NLTE results². Open symbols are the NLTE results³. Points are data from previous LTE studies.

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EXTREMELY METAL-POOR STARS IN DWARF GALAXIES

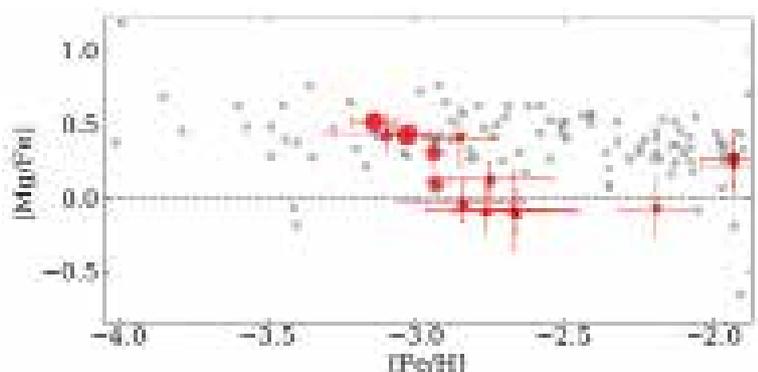
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We present the high-resolution spectroscopic study of some of the most metal-poor stars known in two dwarf spheroidal galaxies (dSph) of the Local Group. Two stars in the dSph Sextans, with metallicities down to $[\text{Fe}/\text{H}] = -3.1$ (i.e. chemical elements heavier than helium about 1000 times less abundant than in the Sun), and two stars in the dSph Fornax, with metallicities down to $[\text{Fe}/\text{H}] = -2.8$ (in prep.).

Extremely metal-poor stars (EMPS) are actively sought in the Milky Way and beyond, because these oldest observable stars carry the imprint of the first stages of galaxy formation. So far, only in the Milky Way it has been possible to analyse these rare targets in sufficient detail to guide our understanding of the physics of star formation, supernovae, the early build-up of galaxies and the epoch of reionization.¹ While the existing samples remain too small in dwarf galaxies (with at most 10 stars with $[\text{Fe}/\text{H}] < -2.5$ known per dSph), the existing spectroscopic surveys have shed substantial light on their evolution. We carry out a detailed analysis of the chemical abundances of the α -element group (Mg, Si, Ca, Ti), iron-peak (Sc, Cr, Fe, Co, Ni, Mn, Zn) and neutron-capture elements (Y, Ba, Sr, Eu). We draw comparisons with the Milky Way Halo and other dSphs stellar populations to show the similarities, and the differences, in their conditions of formation.



While the halo of the Milky Way (small circles) presents a mean over-abundance of magnesium of about +0.4 dex at low metallicity¹, the dSph Sextans (large symbols) has higher dispersion, from solar² ($[\text{Mg}/\text{Fe}] = 0.0$) to halo ($[\text{Mg}/\text{Fe}] = +0.4$) Mg abundances.

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HERBIG Ae/Be STARS: SPECTROSCOPIC SIGNATURES OF MAGNETOSPHERIC ACCRETION

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Models of magnetically driven accretion and outflows reproduce many observational properties of T Tauri stars. Corresponding picture is not established for the more massive Herbig Ae/Be stars. Nevertheless, we can indicate some spectroscopic signatures observed in several Herbig Ae/Be stars, which evidence that accretion flows in their envelopes are guided from the circumstellar disk to the stellar surface inside a magnetosphere. The first case is HD101412 with the magnetic axis orthogonal to the rotation axis. The parameters of HeI 10830 Å and Pa-gamma IR lines in the spectrum of HD 101412 which are formed near the accretion region of the Herbig star are cyclically variable with the period equal to half rotation period of the star. The profiles of these lines are modulated by the stellar rotation, when both magnetic poles pass near the line of sight twice during the rotation period. The next case is HD 259431. The object demonstrates variability of the HeI 5876 Å and H-beta line profiles with a period equal to the expected rotation period of the star. Moreover, the red absorption component of the HeI 5876 Å line becomes strongly extended up to +400 km/s during a period. This can be possible only if the magnetospheric character of accretion takes place. And, at last, the third case is HD 37806. In this object we observe a fast variability (during a night) of the HeI 5876 line in the form of standing intensity waves in the region of the red absorption component. We can prove that this phenomenon can be observed only if the local accretion flows are rotating rigidly with the magnetic field of the star inside the magnetosphere.

ABUNDANCES IN ATMOSPHERES OF Ap-STARS: HD 188041 (V1291 AqL), HD 111133 (EP VIR), HD 118022 (78 VIR), HD 204411 AND HD 110066 (AX CVn).

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A comparative analysis of the average chemical abundance in the atmospheres of magnetic Ap stars is presented. HD 188041, HD 111133, HD 118022, and HD 110066 are located in the middle part of the Main Sequence on the Hertzsprung-Russell diagram, building up a compact group of stars with similar strengths of surface magnetic field ~3–4 kGs. HD 204411 is an evolved Ap star with small magnetic field which does not exceed 1 kGs. The element abundances were determined using the lines of different ionization stages: neutral/first ions (C to Ba) and first/second ions for lanthanides (La to Yb). Atmospheric abundances of HD 111133, HD 188041, HD 118022 and HD 110066 are similar within the errors of the determination, and the abundance patterns correspond to the generally observed anomalies in Ap-stars. There is deficiency of light elements of carbon, nitrogen and oxygen (CNO), practically solar Na and Mg abundance, 1-2 dex overabundance of the iron peak elements, and a large excess of the lanthanides (rare-earth elements).

In evolved star HD 204411, the iron peak elements show smaller anomalies, and the lanthanide abundances decrease up to solar values.

MEASUREMENT OF MAGNETIC FIELDS OF STARS WITH SLD METHOD

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We present a method of Spectral Line Deconvolution (SLD), a superior analogue of the commonly used method of Least-Squares Deconvolution (LSD) originally developed by Donati¹ for stellar spectra with low S/N-ratio. The two fundamental assumptions of the LSD technique are: 1) all spectral line profiles have similar shape and scale according to their central depth, and 2) stellar spectrum is represented as a linear sum of the said individual profiles. However, neither of these two assumptions are met in real stellar spectra, hence we propose the method that overcomes both of them. We extend the classical line mask utilized by the original LSD method from a set of delta functions to a set of individual theoretical profiles predicted by the radiative transfer theory (pre-computed with the SynthV² code in this particular case). Contrary to the LSD method that finds an average line profile, the SLD technique is based on a convolution of a priori un-known function with the said individual theoretical profiles. The best fit SLD function is found through minimization of the difference between the observed and modelled spectrum, where the latter is built taking individual spectral line contributions into account.

The SLD method can be applied to determination of the Zeeman shifts in polarization spectra. The idea is to divide spectral lines into groups according to their sensitivity to magnetic field strength and to find the shifts of SLD-functions for each group.

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CHEMICAL EVOLUTION OF THE GALACTIC DISC

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The binned oxygen and iron distribution, derived using new, most accurate data of abundances from Cepheids, demonstrates wiggling radial pattern with different gradients in various ranges of the Galactic radius, in particular, a plateau-like structure within $7 < 9$ kpc. This feature in the radial abundance patterns of oxygen^{1,2} and iron³ we associate with the combined effects of corotation resonance and turbulent diffusion of heavy elements. In addition, oxygen is mainly produced by core-collapse supernovae (CC SNe) (their progenitors are massive stars with very short lifetimes) which are concentrated within spiral arms. Iron is produced by CC SNe and Ia SNe, which have two sub-populations: prompt (short-lived sub-population) that concentrates in spiral arms and tardy (long-lived SNeIa sub-population) that do not concentrate in arms.

To explain radial distributions of iron and oxygen in the Galactic disc, we undertake a statistical analysis of the radial abundance distributions in the Galactic disk within a theoretical framework for Galactic chemical evolution which incorporates the influence of spiral arms. Our approach allows us to estimate the mean masses of oxygen and iron ejected per each type of supernovae event and constrain the relevant SNe progenitor models.

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ANALYSIS OF STELLAR SPECTRA: SLD VS LSD

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As demonstrated in the original paper¹, the classical Least Squares Deconvolution (LSD) method² is an extremely useful tool for the analysis of stellar spectra. However, its application to real stellar spectra is often limited due to the two fundamental assumptions this method makes, namely 1) all spectral line profiles have identical shape, and 2) all lines in the stellar spectrum add up linearly. Neither of these two assumptions often holds in real stars leading to a dilemma whether discrepancies between the observed and model LSD spectra are due to the imperfections of the method or are physical in nature, hence intrinsic to the star.

Here we propose a strong modification to the original method of LSD by turning it into the method of Spectral Line Deconvolution (SLD). Instead of searching for the average line profile as LSD does, we search for a function $X(\nu)$ that is being convolved with the pre-computed individual line profiles gives the best representation of the observed spectrum of the star:

$$R_{\lambda} = \sum_i a_i P_i(\nu) X(\nu)$$

where R_{λ} stands for the normalized flux at wavelength λ , P is the convolved line profile, and a_i are set of pre-computed, wavelength-dependent coefficients accounting for non-linear addition of individual profiles forming a blend.

This way, the SLD approach is no longer subject to any of the two limitations of the original LSD method.

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APPLICATION OF THE PROBABILITY CURRENT METHOD TO NUCLEAR DYNAMICAL CALCULATIONS IN COLLISIONS WITH HYDROGEN

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Consideration of inelastic collisional processes, especially in case of collisions with hydrogen atoms and ions, is very important for non-local thermodynamic equilibrium (non-LTE) modeling of stellar spectra. Data on the rate coefficients for inelastic processes in hydrogen collisions are calculated within the Born-Oppenheimer formalism using the probability current method^{1, 3} for nuclear dynamical treatment. This method is applied when ab initio electronic structure calculations do not provide data for nonadiabatic coupling matrix elements. In this case, a transition probability in all nonadiabatic regions is calculated using the Landau-Zener model and the probability of an inelastic process is calculated using the probability current method. The proposed method shows good agreement with data, obtained by different methods, including ab initio nuclear dynamics calculations. The probability current method is applied to investigations of collisions in LiH², CaH³, CaH⁺⁴, OH⁵ quasimolecules.

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INELASTIC PROCESSES IN COLLISIONS WITH HYDROGEN

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Calculations of rate coefficients for inelastic processes in collisions of different chemical elements with hydrogen are performed within the framework of Born-Oppenheimer formalism that treats collisional problem in two steps: electronic structure and nuclear dynamics. Several approaches with different level of simplification on both stages are proposed. The strict approach includes ab initio calculations for electronic structure and the reprojection method for solving coupled channel equations¹, it was applied to MgH and CaH. When the ab initio calculations don't provide data for nonadiabatic couplings nonadiabatic nuclear dynamics can be treated within the Landau-Zener model using the probability current method (applied to CsH, LiH, CaH, CaH⁺, OH) or analytical multichannel formulas (applied to CaH, OH). In the absence of ab initio calculations the model semi-empirical approach based on the asymptotic method for electronic structure calculations can be used combined with the multichannel Landau-Zener nuclear dynamics treatment² (applied to AlH, SiH, MnH, BaH, BaH⁺, KH, RbH, LiH⁺). Analysis of the obtained data lead us to the formulation of the simplified model approach, that expresses a rate coefficient of a partial process via the reduced rate coefficient depending only on the binding energies of the electron in the states involved in the process³⁻⁴ (applied to FeH, FeH⁺).

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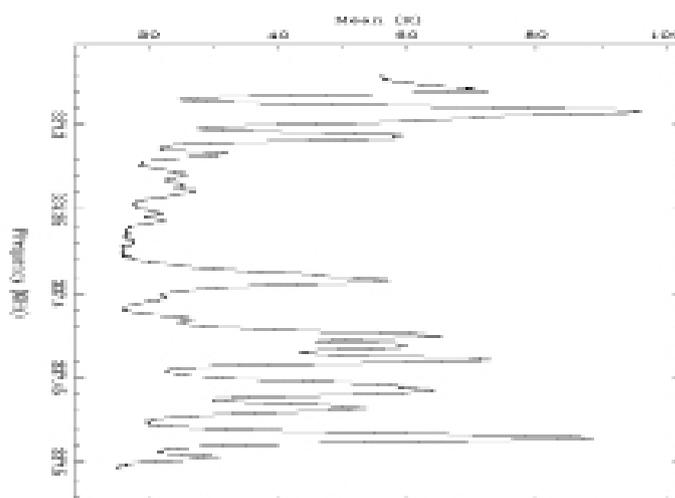
CHEMICAL COMPLEXITY IN THE S255IR REGION OF HIGH-MASS STAR FORMATION

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Molecular spectral lines represent the main source of information about physical conditions and processes in star-forming regions. Understanding the chain of chemical reactions, which lead to formation of these molecules, is a separate important task. The molecular content is especially rich in the hot core environments in regions of high mass star formation. Here we present the results of our investigation of the object S255IR-SMA1, which represents a disk around the massive YSO, showing signs of episodic accretion. We observed it with the SMA¹ and recently with ALMA², which provides an unprecedented sensitivity. A part of the ALMA data is shown in the Figure.



Dozens of the spectral lines of various molecules, including complex ones are detected. We discuss their spatial distribution and abundances.

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**F-BLOCK ELEMENTS:
RECENT ADVANCES
AND CHALLENGES**

LANTHANIDE METALLOCENES: FROM SINGLE-MOLECULE MAGNETS TO NITRIC OXIDE REDUCTASE MIMICS

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Single-molecule magnets (SMMs) are metal-organic compounds that display magnetic hysteresis below a blocking temperature, T_B .¹ Such materials have been proposed for numerous device applications, including as qubits in quantum computers.² We have interests in metallocene SMMs based on dysprosium, and, over the years, we have reported a few examples of such materials.³

Our work has shown that $[Cp]^-$ ligands provide a strong axial crystal field that enhances the magnetic anisotropy of Dy^{3+} , leading us to propose that a cation of the type $[Cp_2Dy]^+$ should be an interesting synthetic target.⁴ Recently, we described the properties of $[(\eta^5-Cp^*)Dy(\eta^5-C_5^tPr_5)][B(C_6F_5)_4]$ ($[1][B(C_6F_5)_4]$), which has $T_B = 80$ K, making it the first (and, so far, only) SMM to display hysteresis above the boiling point of liquid nitrogen (Figure 1).⁵

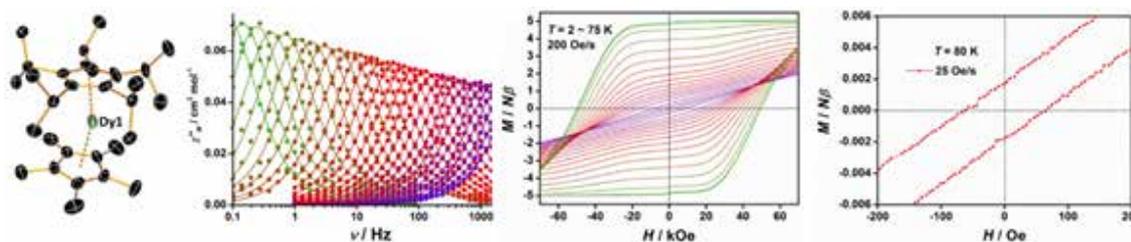


Fig. 1 Molecular structure of 1, and frequency-dependence of the out-of-phase susceptibility, magnetic hysteresis at 2-75 K (sweep rate of 200 Oe s^{-1}) and at 80 K (sweep rate of 25 Oe s^{-1}) for $[1][B(C_6F_5)_4]$.

Having established the design principles required to optimize the SMM properties of dysprosium sandwich complexes, we now turn our attention to alternative ligand environments. Recent finding on SMMs containing cyclobutadienyl ligands, $[Cb]^{2-}$ will be described,⁶ as will a 'bio-inspired' synthetic route to SMMs that resembles the chemistry of flavo-diiron nitric oxide reductase (FNOR).⁷

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F-ELEMENT REACTIVITY: WHAT CAN THEORY DO ?

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In this presentation, we will focus on the performance of an efficient interplay between experience and theory to elucidate the reactivity of f-element catalyzed reactions. In this lecture, the limit of the DFT approach but also the importance of the definition of reaction mechanism will be addressed. Several examples of reactivity involving rare-earth complexes and actinide complexes will be described especially in the field of small molecule activations. A particular interest will be devoted to redox type chemistry but also to non-redox or industrial-type reactivity. The importance of multireference groundstate molecules, especially in the case of cerium or uranium, will be emphasized.

LANTHANIDES COMPLEXES CONTAINING TTFS LIGANDS : SINGLE MOLECULE MAGNET BEHAVIOUR AND LUMINESCENCE

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Lanthanide-based complexes have greatly contributed to the development of molecular magnetism in the last decade and more particularly in the branch of single molecule magnets (SMMs) 1. The main reasons are their large magnetic moments associated to their intrinsic large magnetic anisotropy.

We will present an introduction to the molecular building blocks used as well as Ln luminescence and SMMs. Then we will focus on TTF (tetrathiafulvalene)-based lanthanide mononuclear and polynuclear complexes showing luminescence through TTF antenna effect, SMM properties and combination of both SMM, luminescence, redox activity, memory effect in diluted frozen solution³⁻⁵ and finally, the recent finding of Redox- and Hydro- magnetic switches⁶.

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SUMMARY AND HIGHLIGHTS OF THE ASGARD PROJECT

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The ASGARD project (Advanced for Generation IV reactors: Reprocessing and Dissolution) started in January 2012 and finished in 2016. The aims were originally multi-dimensional with the overall focus on the recyclability of novel nuclear fuels.

At the end of the project 27 papers in peer reviewed journals were published and it is expected that the real number will be the double. Using the travel fund in an appropriate way allowed 4 young scientists to spend more than 1 month at another partner laboratory, funded 23 young scientists to visit conferences and meetings presenting their achievements as well as the organisation of 3 dedicated summer/winter schools having about 15 participants

In the oxide domain the recyclability of the inert matrix fuels based on MgO or Mo was investigated and it was clear that it is possible to both dissolve the fuels in a good way but also to pre-treat the dissolution liquor in a way that it can be fed into the already existing reprocessing process. It was shown that fabrication of pure 50/50 (Pu,Am)O₂ was possible. In the nitride domain it was shown that the pivotal cost for production of ¹⁵N can be reduced significantly but is still a bit high for competitive fuel production. UN production technique was optimised to obtain a total control of e.g. oxygen impurities and controlling porosity obtaining a 99.88% dense pellet. A significant achievement was also the production of pure PuN by using both nitriding from oxides and by sol-gel route. It is unsure if this kind of material was ever produced by these means before. In the carbide domain the alleged pyrophoricity of carbide material was investigated showing that by controlling oxygen and water access even fine power can be handled safely. The parameters for ignition of both power and pellets were determined thus increasing the safety of this kind of fuel handling significantly. A new sol-gel technique based on microwave gelation was also developed. By this ground breaking invention the industrial applicability of the sol-gel technique for production of any fuel precursor from solution was increased significantly. Now there is no need for washing, drying etc the microspheres and also the production of contaminated oils is prevented.

ACTINIDE NANOPARTICLES- FORMATION ROUTES AND PROPERTIES

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Earlier it have been demonstrated that Pu(IV) forms oxide-like nanoparticles at the mineral/water interface as well as in the aqueous solution. Here we demonstrate the results of plutonium nanoparticles studies under simulated geological repository conditions - formation routes and properties. Initially Pu was taken in various redox forms and the kinetics of redox transformations and nanoparticle formation was traced at various pH/Eh values. HR-TEM, SAED, XRD, PDF, HERFD at L3 and M5-edges, XES and EXAFS spectroscopy were applied to characterize the precipitates.

It was established that crystalline 2-3 nm PuO₂-like nanoparticles are formed under the steady state conditions independently on the initial oxidation state. According to the spectroscopic studies the presence of other oxidation states, e.g. Pu(III) or Pu(V) has not been detected. In case of Pu(VI) the formation of such PuO₂-like nanoparticles proceed through slow formation of Pu(V) intermediate phase that result in significant solubility increase.

MOLECULAR CHALCOGENIDE COMPLEXES OF LANTHANIDES

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Solid phases based on chalcogenides (Q = S, Se, Te) of rare-earth metals (Ln) are well-known as widespread versatile inorganic materials revealing unique luminescent, magnetic, thermoelectric properties. In contrast, the molecular chalcogenide complexes of Ln are far less common and are often considered as ‘unconventional’ compounds because of the combination of highly ionic metals and highly covalent ligands. Interest to the Ln chalcogenide complexes mainly caused by a possibility to use them as molecular precursors of functional solids with unusual compositions and structural motifs. In this respect, the compounds of more variable compositions, namely homo- and heterometallic polychalcogenide complexes, are of particular interest. The report is based on our recent results in the field of synthetic chemistry of the compounds with Ln–Q bonds: functionalized chalcogenolates, homometallic Ln polychalcogenides, and mixed d-f-metal chalcogenides (see Fig. 1, for examples). Details of the chemistry and structural features of the novel Ln–Q compounds as well as their chemical and physical properties are the matter of the discussion.

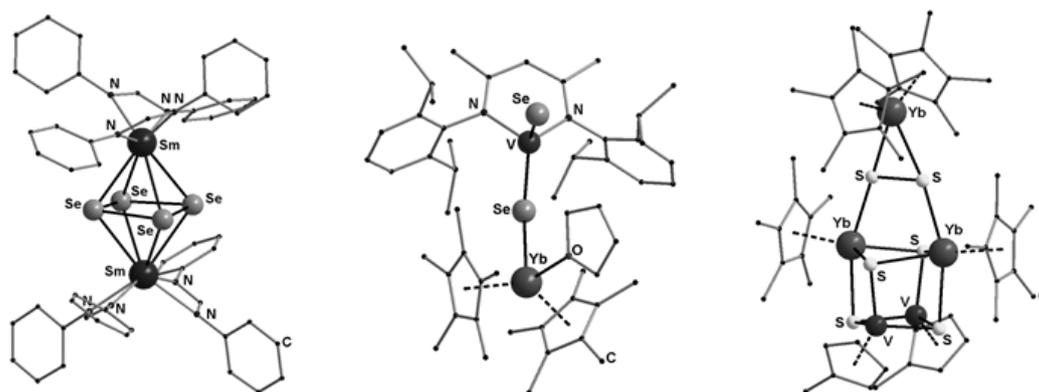


Fig. 1. Molecular structures of the compounds (left to right): $[\{(\text{DippForm})_2\text{Sm}\}_2(\mu, \eta^4\text{-}\eta^4\text{-cyclo-Se}_4)]$, $[\text{Cp}^*_2\text{Yb}(\mu\text{-Se})\text{V}(=\text{Se})(\text{DippNacnac})]$, $[(\text{CpMeV})_2(\text{Cp}^*\text{Yb})_2(\text{Cp}^*\text{Yb})(\mu_3\text{-S})_4(\mu\text{-S}_2)]$. All H atoms are omitted for clarity

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LANTHANIDE IONS-BASED MAGNETIC MOLECULAR MATERIALS: TOWARD MULTIFUNCTIONALITY

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Molecular magnetic materials based on lanthanide ions have emerged as a family of magnetic materials with flexible molecular architectures and fascinating physics promising for future technological applications in different fields including data storage, sensors and quantum computing. They attract a great deal of attention during several decades due to the presence of a strong coupling between the spin and orbital angular moments leading to a huge anisotropy and a large magnetic moment. On the other hand, Ln³⁺ ions often exhibit interesting long-lived luminescence, which may be combined with the magnetic properties in order to design multifunctional molecular magnets. This overview presents recent advances in this field of research focusing on molecular magnets with extended structure¹ and Single-Molecule Magnets (SMM),² and demonstrating the possibility to design magneto-luminescent materials.^{1,3}

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MULTIFUNCTIONAL SINGLE-MOLECULE MAGNETS: SLOW RELAXATION, LUMINESCENCE AND ABOVE ROOM-TEMPERATURE FERROELECTRICITY

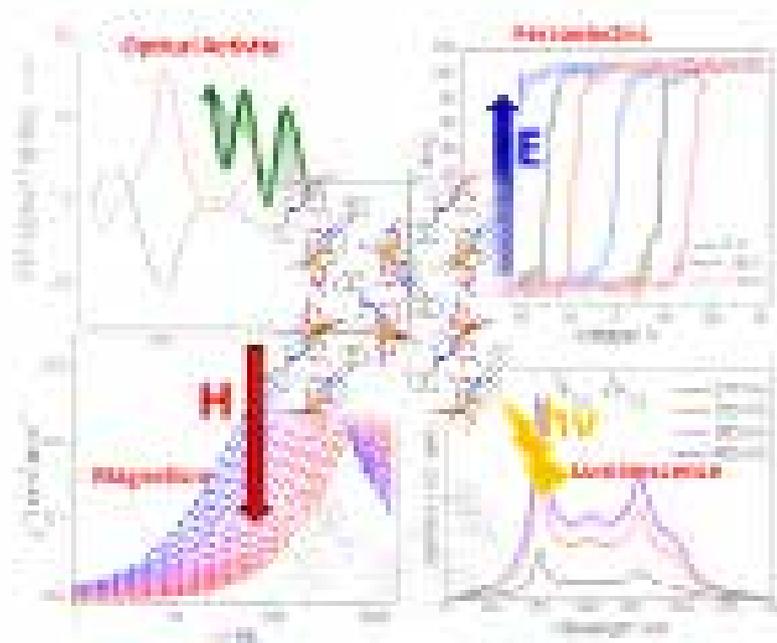
Long J.,^a Ivanov M. S.,^b Khomchenko V. A.,^b Mamontova E.,^a Rouquette J.,^a
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Coordination chemistry of lanthanide ions allows the tailored design of multifunctional ferroelectric molecule-based materials where the properties are gathered into a single molecular system. We investigate here, by using luminescent and magnetically anisotropic lanthanides ions assembled with an enantiopure antenna ligand, the synthesis of high temperature ferroelectric complexes having a high degree of functionality, combining Single-Molecule Magnet behavior, optical activity and lanthanide luminescence.¹⁻² Remarkably, these molecular systems behave as ferroelectrics up to a temperature above 180 K of the Curie temperature of BaTiO₃, making it the highest temperature working molecular ferroelectric yet reported.³ Remarkably, investigation of the magnetoelectrical coupling at room temperature confirms their great potential as magnetoelectrical material.



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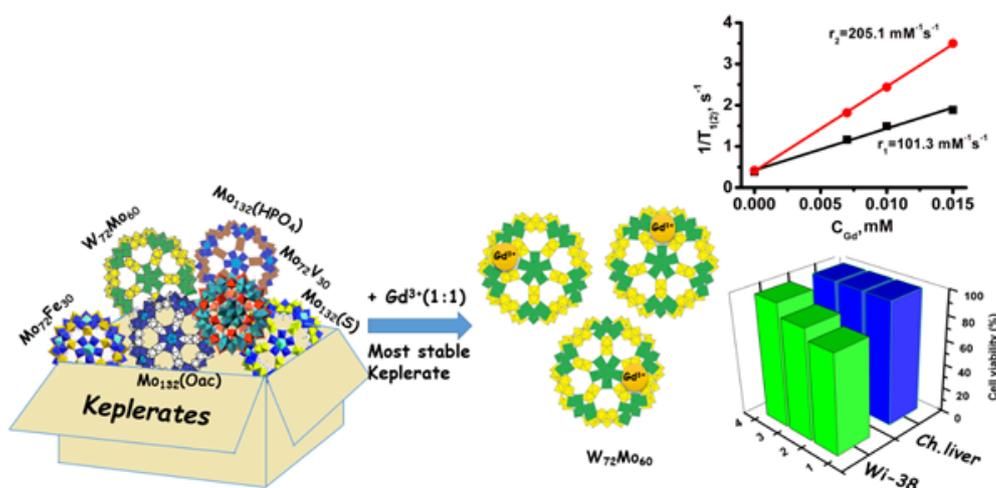
GADOLINIUM COMPLEXES WITH NANOSIZED INORGANIC POLYANIONS AS CONVENIENT BASIS FOR MRI CONTRASTING AGENTS

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The present work introduces structure optimization of keplerate anions in order to achieve a gain in tight binding of Gd³⁺ ions, stability to oxidative degradation of keplerate units and high magnetic relaxivity of Gd³⁺ ions.



The impact of keplerates structure on the magnetic relaxivity and stability of their complexes with Gd³⁺ ions is guided by the size of the external pores and structure of pentagons. Thus, keplerate W₇₂Mo₆₀ is the optimal ligand from the viewpoint of the above mentioned requirements. High magnetic relaxivity of the molecular gadolinium complexes with the keplerate (r_1 and r_2 are 101.3 and 205.1 mM⁻¹s⁻¹), high stability in the buffer solutions of bovine serum albumin, low cytotoxicity makes the molecular gadolinium complexes of W₇₂Mo₆₀ a promising basis for further development of CAs in MRI.

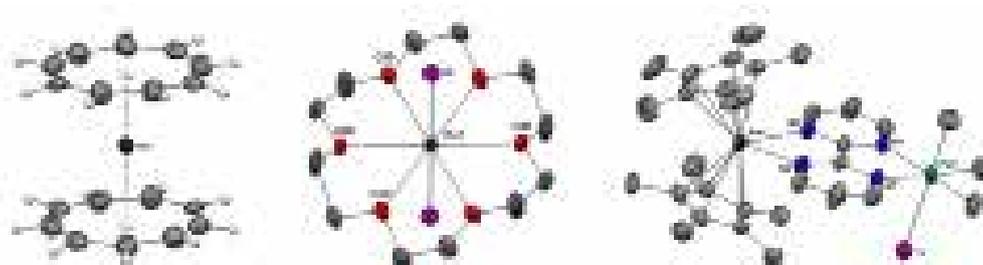
Acknowledgements. We thank RSF (grant no 17-13-01013) for financial support

ORGANOMETALLIC CHEMISTRY OF LANTHANIDES: OXIDATION STATES IN TROMPE L'OEIL AND MAGNETIC SANDWICHES

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Organolanthanide complexes are a class of organometallic compounds that have been developed since the seminal work of Wilkinson in the 1950's¹ and that now concern most of the rare earths in their trivalent and divalent states.² Depending of their oxidation state, the applications for such compounds are numerous because of their optical and magnetic properties³ but also for single electron transfer reactivity.⁴ However, the establishment of a clear cut electronic structure is often difficult because of the propensity of the surrounding ligands to behave as redox non-innocent ligands. This electronic picture is however extremely important in order to better understand and manipulate their physical properties and reactivity. We will present a short overview of our methodology for the synthesis of original organolanthanide complexes as well as their deep study using multiple spectroscopic and theoretical tools. The presentation will highlight recent coordination studies on divalent sandwich complexes with the cyclononatetraenyl (Cnt) ligand (Fig 1. left),⁵ on the coordination chemistry of divalent thulium (Fig 1. center)^{6,7} and on heterometallic complexes of organolanthanides and transition metals (Fig 1. right).⁸



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MULTIMODAL CHEMICAL IMAGING INVESTIGATION OF NP AND PU INTERACTIONS WITH OPALINUS CLAY AND PYRITE COMPOSITES

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Argillaceous rocks are considered as potential host rock for the construction of high-level nuclear waste repositories. The migration of long-lived and radiotoxic waste constituents like ²³⁷Np and ²³⁹Pu in the rock is governed by sorption and diffusion. To determine reactive transport mechanisms for Np and Pu in a natural sedimentary rock (Opalinus Clay (OPA), Switzerland), the diffusion of Np(V) and Pu(V) in intact OPA cylinders was studied by X-ray fluorescence (μ -XRF), X-ray absorption spectroscopy (μ -XANES) and X-ray diffraction (μ -XRD) at the microXAS beamline (Swiss Light Source). These measurements showed that Np and Pu undergo a redox transformation during their diffusion inside the OPA rock. In addition, an enhanced immobilization of Np and Pu in spatial correlation with pyrite composites of sub-millimeter size was found.¹⁻²

Several 50–100 μ m sized pyrite particles of different morphologies were isolated from OPA and contacted with Np(V) and Pu(VI) solutions under environmentally-relevant conditions. Selected particles were measured by multimodal, three-dimensional chemical tomography (CT) at the microXAS beamline. Structural information was obtained through absorption coefficient contrast measurements, elemental information through μ -XRF-CT and mineral phase information through μ -XRD-CT. These CT measurements showed that sub- μ m-sized pyrite crystallites combine to a structure of framboidal morphology with its interspace cemented by calcite. In addition, a spatial correlation of Np and Pu with the cementing phase as the retaining phase has been observed. These experiments illustrate the benefit of synchrotron-based multimodal chemical imaging techniques for investigating the chemical reactivity of actinides and other heavy metals in natural systems.

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PATTERNS OF DIVALENT EUROPIUM ORDERING IN THE SOLID STATE

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Europium stands out of the lanthanide family owing to its propensity for forming compounds in a divalent state. The pronounced stability of Eu^{2+} is explained by its $4f^7$ electronic configuration with a half-filled shell and gives rise to quite a number of compounds exhibiting various important properties including spin fluctuation, magnetic order, and Kondo behavior. In many solid state compounds, Eu^{2+} cations can interact through conduction charge carriers or further couple to the second magnetic system built by transition metal cations ultimately leading to unexpected magnetic properties.

In this paper, we discuss several families of compounds containing divalent europium. They range from simple and complex derivatives of the BaAl_4 structure type to structural analogs of layered LaOFeAs superconductor to clathrates and related compounds. Within each family, the interaction of seemingly localized $4f^7$ electrons through an appropriate itinerant system evokes spin ordering rendering ferromagnetic or antiferromagnetic ground state depending on the details of the crystal structure.¹⁻³ The interplay of magnetic ordering and thermoelectric or magnetocaloric properties will also be presented

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RARE- AND ALKALINE-EARTH COMPLEXES - UNIVERSAL CATALYSTS FOR C-P, C-N, C-S AND C-C BONDS FORMATION

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Alkyl and amido rare-earth metal complexes (in both +3 and +2 oxidation states) are of great interest due to their unique reactivity in stoichiometric reactions, ability to activate normally inert sp^3 - and sp^2 -hybrid CH bonds as well as due to the powerful catalytic potential in a wide range of transformations of unsaturated substrates.

New classes of alkyl and amido rare-earth metal complexes were synthesized. Elaborated ligand systems proved to be able to allow for stabilization of highly reactive complexes providing steric and coordination saturation of the sphere of the metal ion and preventing Schlenk-type equilibria. New alkyl Ln(III), Ln(II) and Ca(II) complexes containing diphenylmethanide and benzhydryl fragments with pendant NMe₂ groups demonstrated extraordinary thermal stability, while maintaining the highest reactivity characteristic for M–C bonds.

The synthesized alkyl and amido Ln(III), Ln(II) and Ca(II) complexes proved to be efficient universal and selective catalysts for intermolecular hydroamination, hydrophosphination and hydrothiolation of alkenes and acetylenes, as well as for intermolecular styrene hydroarylation and hydrobenzylation, atom-economic methods of formation of C-P, C-N, C-S and C-C bonds. It is shown that the activity and selectivity of metal complexes in intermolecular hydrofunctionalization of multiple C-C bonds is strongly affected by both the nature of the central metal atom and by the ancillary ligand.

MODELLING HIGH RESOLUTION XANES OF ACTINIDE-BASED MATERIALS

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X-ray Absorption Near-Edge Structure (XANES) is an invaluable tool in material science, allowing to probe the oxidation state and the local electronic structure of a selected atomic species. Despite XANES conceals a wealth of information on the local geometry and electronic structure of the absorber, it is less exploited than the Extended X-ray Absorption Fine Structure (EXAFS) because of the more complex analysis. Nowadays the availability of *ab initio* codes and the use of high resolution (HR) XANES boosted the interpretation of XANES. HR XANES is particularly advantageous to study actinide systems. We systematically used *ab initio* simulations to reproduce the L₃ edge of HR XANES of different actinide-based materials and obtained valuable information on the local environment and the electronic structure of the system studied.

The analysis of ThO₂ small nanoparticles revealed that a post-feature of the Th L₃ edge XANES is very sensitivity to the more exposed cations at the surface.

The simulations of numerous structure containing U⁵⁺ and/or U⁶⁺ in different local coordinations reveals that the uranyl and the uranate geometries give well distinct features in the first 30 eV of L₃ edge XANES. HR XANES can therefore help detecting the presence of U⁵⁺ in mixed systems.

Because XANES in the hard X-ray regime allows to measure samples in their realistic conditions, intermediate products formed in the synthesis of nanomaterials can also be measured. We exploited the post-edge region of Pu L₃ edge HR XANES to determine the intermediate phase formed during synthesis of PuO₂ nanoparticles. The simulations of several structure containing Pu show very divers post edge features that can be compared to the data to exclude/confirm which phases are possibly formed.

The cases presented illustrate that HR XANES supported by *ab initio* simulations have great potential for the investigation of actinide-based materials.

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CONFORMATIONAL ANALYSIS OF N-HETEROCYCLIC PHOSPHINE OXIDES

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Phosphine oxide extractants are promising ligands used in the extraction of rare-earth and transuranic elements. In this work extraction properties towards Am(III) and Eu(III) of pyridine-based phosphine oxides were investigated.

It was shown (Table 1) that pyridinephosphine oxides with non-bulk substituents (L1, L4-8) have high distribution coefficients D, but extractants L2-3 and L9 in which the substituents R1 and R2 are bulky - the distribution coefficients are extremely small.

Name	R1	R2	D(Am)	D(Eu)	SF(Am/Eu)
L1	phenyl	phenyl	1,38	0,37	4
L2	phenyl	tert-butyl	0,05	0,06	1
L3	tert-butyl	tert-butyl	0,001	0,001	1
L4	phenyl	3,5-dimethylphenyl	91	5	18
L5	3,5-dimethylphenyl	3,5-dimethylphenyl	317	11	28
L6	2-ethylphenyl	2-ethylphenyl	4	1,2	3
L7	phenyl	octyl	19	6	3
L8	octyl	octyl	0,19	0,87	5
L9	cyclohexyl	cyclohexyl	>0,001	>0,001	N/A

Table 1. Extraction properties of the investigated extractants

This tendency is explained by the fact that during the formation of a complex, extractant molecules need to take a different conformation, and the lower the energy of such a rearrangement (preorganization energy), the higher will be the distribution coefficients with respect to actinides and lanthanides. To confirm this hypothesis, a conformational analysis of ligands was performed using quantum chemical modeling methods. Different approaches were used to solve this problem, which showed a high correlation with experimental data.

The solvent extraction experiments reported study was funded by RFBR according to the research project № 18-33-00616.

STUDYING OF PLUTONIUM NANOPARTICLES WITH VARIOUS SYNCHROTRON METHODS

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Plutonium is one of the most significant elements among actinides due to its high radiotoxicity and long period of high-decay. The migration of plutonium in the environment is a challenging and global problem. Plutonium migrates at scale of kilometers from previously contaminated sites in the form of intrinsic colloids or “pseudocolloids”.¹⁻² In the last few years it was found that so called “colloidal Pu(IV) polymers” actually represents as aggregates of PuO₂ nanoparticles with size ~ 2 nm.³⁻⁵ The revealing of the mechanism of these particles formation (including the consideration of different factors which may have an influence), as well as their characterization is a key to understanding the conditions for long-term storages for the nuclear waste.

With the combination of different laboratory and synchrotron techniques it was found that small (2 nm) nanoparticles are formed from Pu(III), Pu(IV), Pu(V) aqueous solutions at pH 8-12, with the crystal structure close to PuO₂, and with only Pu(IV) oxidation state present. Any other Pu-O contributions except Pu(IV)-O (in oxide) were not revealed.

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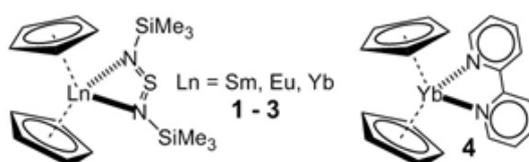
QUANTITATIVE PREDICTION OF THE MAGNETIC PROPERTIES OF LANTHANIDE COMPLEXES – A DREAM OR A REALITY

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



This report will present and discuss results of the high-level *ab initio* calculations with non-perturbative account of spin-orbit coupling at the SA-CASSCF/CASPT2/SO-RASSI level for the comprehensively studied lanthanide complexes with non-innocent ligands (1 – 4).^{2,3} In agreement with experiment, calculations predict for 3 and 4 unusual temperature dependences of magnetic susceptibility with a maximum at ~300 K, which is caused by the population of the lowest energy pseudo-singlet and pseudo-triplet states. The splitting of these states is unexpectedly large and not typical of lanthanides, and is determined by the isotropic and asymmetric exchange interactions between the Yb(III) and the radical anion of the ligand ($J \sim -250 \text{ cm}^{-1}$, $D \sim -60 \text{ cm}^{-1}$). Thus, high-level calculations correctly predict the energy splitting due to the exchange interaction, however, none of the calculations with a large number of relativistic basis sets could reproduce a mixed valence state for the Yb cation of complex 4.³

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THE ROLE OF STRUCTURAL PREORGANIZATION AND BONDING NATURE OF 4,7-DICHLORO-1,10-PHENANTHROLINE-2,9-DICARBOXYLIC ACID DERIVATIVES IN AN(III)/LN(III) SEPARATION: EXPERIMENTAL AND THEORETICAL STUDY

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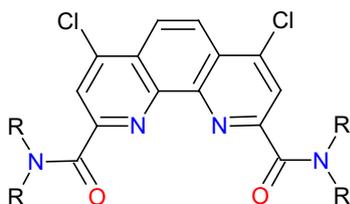
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The separation of minor actinides and lanthanides is the difficult task, since these elements have very similar chemical properties - the same stable oxidation state in solutions (+3), close ionic radii and similar electronic shells structure. To solve this problem, the most suitable method for the industrial reprocessing is liquid-liquid extraction.

We have investigated the extraction properties of four 4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamides towards Am(III) and lanthanides(III). The observed efficiency and selectivity towards americium in the presence of lanthanides is determined by the type of substituent in the amide nitrogen atom. Extractants possessing only aliphatic substituents, have moderate selectivity in relation to the americium – SF(Am/Ln) ≈ 10 and allow for the separation of americium and lanthanides at the stage of extraction, when the content of nitric acid 4 mol/l. The presence of aryl substituents increases the efficiency of extraction and "switches" selectivity – lanthanum and cerium are extracted better than americium in the studied range of nitric acid concentrations.



4,7-dichloro-1,10-phenanthroline-2,9-dicarboxamides

We have used various techniques (HR-ESI-MS, XAS, DFT calculations) to establish the composition and structure of the complexes and it has been shown that the steric aspects of the complement formation affect selectivity in this case more than electronic effects.

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DEVELOPMENT OF Gd AND Nd-LOADING LIQUID SCINTILLATORS

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Gd is introduced into a liquid organic scintillator (LS) to increase the re-gistration efficiency of reactor antineutrinos due to the high neutron capture cross section of the ^{157}Gd and ^{155}Gd isotopes.

Nd is used in LS to search for a neutrino-free mode in double beta decay reactions on the ^{150}Nd isotope¹.

Since Gd and Nd belong to the same group of f-elements, the technique developed for introducing gadolinium into LS² is also suitable in the case of creating Nd-LS.

Compounds of f-elements, intended for introduction into LS, must be coordination-saturated and remain stable for a long period of time during which the scintillator works. In addition, they must be well dissolved in LS and not degrade much of its characteristics: transparency and light yield. For these purposes, the complexes of carboxylates² and beta-diketonates³ are well suited. But if we compare their light yield (Fig. 1), it can be seen that in the case of using carboxylate (3,5,5-trimethylhexanoate), the light yield is significantly higher than in the case of using beta-diketonates.

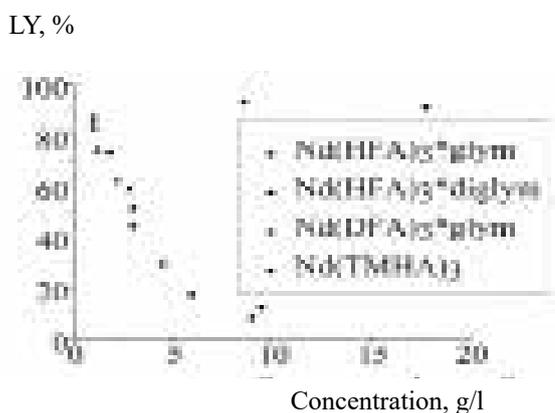


Fig.1 Scintillator light yield (LY%) as a function of Nd concentration

In the case of the creation of Nd-LS, high demands are placed on the level of radioactive background of the scintillator, therefore, it is necessary to remove U, Th from neodymium compounds and solvent.

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SORPTION OF F-ELEMENTS ONTO NANO-SIZED H-TITANATES

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The development of nuclear energy results in increasing discharge of radionuclides in natural environments due to accidents in nuclear power or reprocessing plants. Among different products, actinides and lanthanides are formed in spent nuclear fuel (SNF) and radioactive waste (RW). These elements can be released into the natural water and soil environment. Therefore, it is very important to develop materials and methods for their effective removal from wastewater and groundwater.

Different techniques of An and Ln extraction from water solutions have been developed using inorganic sorbents, organic/polymer sorbents, and different types of chromatography. Recently nanosized Na,H-titanates attracted attention due to their properties. In this work we have investigated the sorption of trivalent f-elements (europium and americium), onto nano-sized H-titanates with different structures.

An efficient An/Ln sorption of about 100% is observed at pH higher than 4. The typical pH range of the trivalent metal cations sorption edge on different oxide surfaces is within 2–6. Thus, H-titanates demonstrate very strong binding with trivalent actinides and lanthanides. The investigated samples of H-titanates demonstrate total reversibility of An/Ln sorption. This is again typical for the sorption by formation of inner-sphere complexes with surface hydroxyl groups. Fitting of the sorption isotherms with the Langmuir equation allows to obtain values for the maximum sorption capacity of the investigated samples.

Investigated H-titanates of different nanostructures demonstrate fast and efficient sorption of trivalent lanthanides from aqueous solutions. The sorption of An/Ln is strongly dependent on pH values, but almost independent on structure of H-titanates. These results, along with low solubility of H-titanates and previous data reported in literature, show that these materials have a high potential for the decontamination of polluted wastewater and groundwater.

This work was supported by Russian Science Foundation (project 14-13-01279).

THE FATE OF NANOSIZED THORIA IN AN AQUEOUS ENVIRONMENT: FORMATION, SOLUBILITY, AND AGING PROCESSES

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Thorium dioxide (thoria, ThO₂) is an interesting object to study in light of the development of thorium nuclear fuel cycle and as model systems for studying actinide migration in the environment. According to the literature sources, ThO₂ could exist in both X-ray amorphous and well-defined crystalline phase. Despite the large body of experimental results on X-ray amorphous thoria solubility, the property and the structure of ThO₂ colloids are still under discussion. Therefore, the present study is aimed to synthesis ThO₂ by chemical precipitation and to investigate the relationship between synthesis conditions, ThO₂ particles crystallinity, its size, and structural-related properties.

At the present study, ThO₂ samples were prepared by mixing aqueous solutions of Th(NO₃)₄ · 5H₂O (10⁻⁴ - 1 M) and aqueous ammonia or NaOH of different concentrations. As-prepared samples were characterized immediately after synthesis procedure and after various temperature treatments: gentle drying on air, hydrothermal processing or high-temperature annealing. Structure features and phase composition of the samples were investigated by XRD, PDF analysis, HRTEM, TGA/MS, Raman spectroscopy and EXAFS techniques. The solubility experiments in pH range 2 – 7 for crystalline ThO₂ nanoparticles (NPs) of different size in aqueous solutions were also conducted.

It was found, that crystalline ThO₂ NPs of around 2.5 nm size are formed under selected precipitation condition even at room temperature. The choice of precipitant and its concentration affect the phase composition and NPs size. By carefully adjusting heat treatment conditions (time, temperature and the composition of the medium) of as-prepared samples, the size of ThO₂ NPs can be increased up to 34 nm. The dependence of the unit cell on the particle size was discovered for the first time: ThO₂ unit cell shows a tendency to expand (around 1% from bulk) with decreasing particle size from 34 to 2.5 nm.

This work was supported by the Russian Foundation for Basic Research (project 18-33-20129).

F-ELEMENTS FOR ADVANCED LUMINESCENT MATERIALS

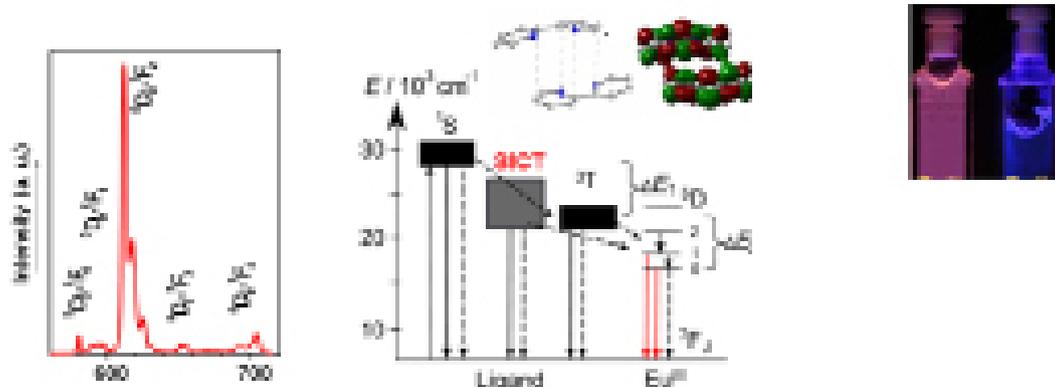
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The luminescence of f-elements is widely used owing to its narrow bands and high quantum yield as well as relatively long-lived excited states. The introduction of these elements into self-assembling molecular architectures leads to the obtaining such advanced luminescent materials as room temperature liquid crystals, nanoparticles, OLEDs, polymers etc.



Scheme 1. General view of energy transfer process in $\text{Eu}(\text{NO}_3)_3(\text{bp})_2$

The luminescence properties of lanthanide β -diketonates containing the 2,2-paracyclophane derivatives, 2-benzoylpyridines (bp) and polyphenylsubstituted cyclopentadienyl complexes have been analyzed (Ln= Nd, Eu, Tb, Er, Yb, Gd), as well as polymers based on ionic liquids. All complexes are luminescent at room temperature and some have high quantum yield up to 80%. New aspects for design of lanthanide complexes containing π and σ -type ligands with desired luminescence properties have been proposed.¹⁻³

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COORDINATION POLYHEDRA ANSEN IN CRYSTAL STRUCTURES

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Selenium tendency to participate in homoatomic interactions is an important feature of its stereochemistry that also affects the properties of compounds. It has been noted that the wide spectrum of interatomic Se–Se contacts in crystal structures makes it difficult or impossible to clearly determine the true charges of atoms^{1,2}. Using the example of compounds containing more than 4000 crystallographically nonequivalent AnO_n coordination polyhedra, it was shown^{3,4} that the parameters of Voronoi–Dirichlet (VD) polyhedra allows to clearly distinguish the valence state of An atoms in the structures of crystals.

The structures of 177 compounds containing 250 AnSe_n coordination polyhedra (An – Th, U, Np, Pu, Am or Cm) are analyzed using VD polyhedra. It is shown that the parameters of VD polyhedra allows to determine the valence state of An atoms. It is established that selenides contains An(II), An(III), An(IV) and An(V) atoms bonding from 6 to 10 selenium atoms. The dependence of the multiplicity of the Se–Se covalent bond on its length is revealed through the parameters of VD polyhedra.

There were two types of selenium atoms in the structures of the considered compounds. Most of these (647 out of 708) can be considered as Se²⁻ ions; the other 61 – Se⁻ ions. The volume of VD polyhedra of Se²⁻ and Se⁻ ions coincide within the limits of σ . We may assume that the approximate constancy of VD polyhedra volume is due to the stable 8-electron valence shells in all cases. The main difference between Se²⁻ and Se⁻ ions is that the former creates this shell through a combination of heteroatomic chemical bonds only, while Se⁻ ions also (apart from Se–An bonds) form homoatomic covalent Se–Se bonds. The crystal chemical role of Se²⁻ and Se⁻ ions is discussed.

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A UNIFIED CHEMICAL MODEL FOR EXTRACTION AND PARTITIONING OF *f*-ELEMENTS BY TRIBUTYL PHOSPHATE AND ITS SOLUTIONS IN PARAFFINS FROM NITRATE MEDIA

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A model for simulation of RE (and Y), actinides in various oxidation state and nitric acid extraction by TBP with respect to its dilution has been developed in application to optimization of radiochemical processes. It covers the wide range of the component concentration in neutral and acidic media including the presence of salting-out agents up to complete solvent loading.

100% TBP is taken as a basic state. In this case the plots of concentration constant dependence from TBP concentration in paraffins and other diluents (5-100% vol.) were found to be rays outgoing from the same common point. The model is based on the idea about the simultaneous running of a number of parallel reactions for one and the same component including complex formation and non-stoichiometric weak interactions in aqueous and solvent phases of the "open" system with unlimited number of the components without activity coefficients. The change in the number of components does not lead to the change in the values of chemical equilibrium constants and/or parameters of weak interactions.

The set of equilibrium constants for each component is calculated using the least squares method and Microsoft Excel Solver by minimizing the deviation between experimental and calculated distribution coefficient in logarithmic scale. The error in distribution coefficient calculation is <10%.

The proposed model simulates the distribution of nitric acid (0.05-10 mol/L), water, RE and actinides in various oxidation states and other fission products and nuclear materials such as Tc, Zr and Hf as well as component interaction with each other, with anions and their possible hydrolysis and polymerization at weak acidity with respect to component content.

In the case of RE and trivalent actinides extraction the following interactions were taken into consideration: formation of trisolvate $\text{Ln}(\text{NO}_3)_3(\text{TBP})_3$ and tetrasolvate $\text{Ln}(\text{NO}_3)_3(\text{TBP})_4$ (the latter in reaction with TBP dimer), extraction of hydrated solvate and of complex acid as well as the salting-out by various nitrate salts including self salting-out effect caused by apparent Ln^{3+} hydration in aqueous phase.

The proposed equations could be used in the software for simulation of steady-state and transitional regimes of counter-current extraction processes in the units of complicated structure.

STUDY OF THORIUM (IV) HYDROXO COMPLEXES DESTRUCTION KINETICS IN AQUEOUS SOLUTION

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It is known that Th(IV) cations hydrolyze in aqueous solution with formation of different hydrolytic species: mononuclear – $\text{Th}(\text{OH})_n^{(4-n)+}$, polynuclear – $\text{Th}_p(\text{OH})_q^{(4p-q)+}$ hydroxo complexes, pseudocolloid and colloid particles. Therefore kinetics study of Th(IV) hydrolytic reactions is complicated by simultaneous presence of various metal ion forms possessing common chemical and physical properties. As a result there is a problem to obtain correlation between analytical signal and specific hydroxo complex concentration.

Our kinetics study of Th(IV) hydroxo complexes destruction was performed by spectrophotometry of Th(IV)–arsenazo-III complex. This complex is formed with hydrated cation $\text{Th}(\text{H}_2\text{O})_n^{4+}$ only. That's why we can determine selectively the concentration of Th^{4+} -cation in solution, containing various Th(IV) species.

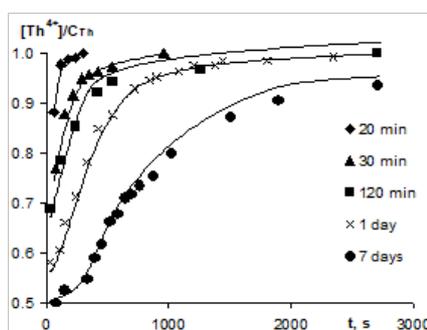


Figure 1. Influence of solution “aging” time on Th(IV) polynuclear hydroxo complexes destruction.
 $C_{\text{Th}} = 1 \cdot 10^{-5} - 1 \cdot 10^{-3} \text{ M}$; pH 2,0 – 5,0.

It was shown that the observed change in optical density correlate to Th(IV) polynuclear hydroxo complexes destruction. Though the reaction kinetics is not elementary, it can be closely approximated by the following equation:

$$v = -\frac{d[\text{Th}_{\text{poly}}]}{dt} = k_{\text{cat}}[\text{Th}_{\text{poly}}][\text{H}^+]$$

The obtained results indicates, that metal-ion hydrolysis is a multi step reaction, and the reaction end cannot be always determined by such indirect features such as constant solution pH value.

BEHAVIOUR OF CeO₂ NANOPARTICLES IN WATER AND BIOLOGICAL FLUIDS

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Among a large number of promising applications, applying of CeO₂ nanoparticles in biomedicine is the newest and intensively developing one. There are a lot of studies demonstrating its antioxidant activity. There is also a lot of information in the literature about the regularities of CeO₂ formation in aqueous solutions. However, the processes occurring with the solid phase over time in water and especially in biological solutions, as well as their relationship to particle size, morphology and chemical prehistory remain unknown. Previously it was believed that the potential use of cerium dioxide in living cells is also promoted by low solubility of cerium oxide. Nevertheless, according to the latest data, the solubility of cerium dioxide in nanodisperse state in several orders of magnitude higher than expected¹.

On the basis of numerous researches on the toxicity of cerium dioxide, it could be established that the most suitable ceria form for the use in biological media are particles of less than 10 nm obtained by low-temperature synthesis routes. At present work we studied three samples of CeO₂ nanoparticles with size 2, 5 and 8 nm that were obtained by chemical precipitation technique.

The behavior of CeO₂ including solubility behavior, phase and morphology transformation, colloidal stability in isotonic solution, phosphate buffer solutions, hydrogen carbonate solutions and simulated interstitial fluid. The kinetic of the processes as well of influence of the temperature were studied.

The most significant changes, compared to the behavior of CeO₂ in aqueous solution, were found in systems containing phosphate anion. In this case substantial transformation of solid phase to the CePO₄ was observed. This process has a dramatic effect on solubility values, namely, it leads to a decrease of cerium concentration in the solution. Thermodynamic modeling of the CeO₂ behavior in different solutions was done in the work.

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QUANTUM-CHEMICAL MODELING OF PLUTONIUM HELATION BY DIAMIDES IN SOLUTIONS

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The increase of the efficiency of spent nuclear fuel processing is important for the increase of output from natural raw materials and for the decrease of final waste amount. The experimental investigations on sorption properties of the new type of diamide molecules $C_8N_2H_{10}O_2(CH_3)_2$ (dimethylbicyclicdiamide – DMDA) with bicyclic structure showed that their efficiency in the extraction of uranium and plutonium from solutions was higher than that of the known $C_3N_2H_2O_2(CH_3)_4$ (tetramethyl-malonamide - TMMA) molecules with acyclic structure. The suggested in experimental work explanation of this effect due to more “optimal” positions of the two oxygen atoms in DMDA in comparison with TMMA is very doubtful because the structure of TMMA is more flexible and could be easily transformed by the interaction with actinide.

In the present work, the theoretical study on the formation of plutonium complexes with the two types of diamide molecules was carried out using *ab initio* methods DMol3 and RDV. The results of gaze phase modeling showed that the simple interaction of actinide ion with organic ligands can not explain the considerable difference in sorption affinity of acyclic and bicyclic molecules. For the simulation on the role of solution, the “implicit” and “explicit” approaches were used: the former is based on the COSMO potential and the latter is based on the direct inclusion of several water molecules, NO_3^- , Cl^- and H^+ ions into the system under investigation. For the estimation of “net interaction energy” between Pu^{Z+} and organic ligand (E_{Pu-L}) in $PuL(H_2O)_{40}A_{16}$ and $PuO_2L(H_2O)_{40}A_{16}$ systems ($A = HNO_3, HCl$) we used the method based on the calculations on energies of the three model systems (E_{r1}, E_{r2}, E_{r3}), where the interactions between certain components were consecutively excluded: $E_{Pu-L} = \frac{1}{2} (E_{opt} - E_{r1} - E_{r2} + E_{r3})$. The obtained results showed that in both models of solution, the weakening of actinide interaction with TMMA molecule due to the interaction with water molecules and NO_3^- or Cl^- ions was larger than that with DMDA. Moreover, in all investigated systems, Pu -TMMA and PuO_2 -TMMA complexes transformed from bidentate to monodentate type while the complexes with bicyclic ligand kept their bidentate structure.

The reported study was funded by RFBR according to the research project № 19-03-00735.

THEORETICAL AND EXPERIMENTAL INVESTIGATION OF RADIATION STABILITY OF ORGANIC EXTRAGENTS: TBP, TOPO AND VARIOUS N,O-DONOR LIGANDS

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During the operation of nuclear reactors spent nuclear fuel (SNF) is formed and should be recycled. Different ways of recycling include liquid-liquid extraction steps to separate valuable components from the SNF. But influence of radiolysis on extractants should be considered because of high radioactivity level of processed compounds. However, experiments to study molecules degradation due to radiation are not always possible in laboratories or industry and usually they spend a lot of time. So, creating a theoretical model to predict radiolytic behavior of molecules is a very important task.

The main aim of this work is theoretical and experimental investigation of radiolytic degradation of different molecules. Five solutions of di-(2-ethylhexyl)-phosphoric acid (D2EHPA), tributyl phosphate (TBP), trioctylphosphine oxide (TOPO), dibenzo-16-crown-6, 2,6-bis(biphenylphosphoroso)pyridine (2,6-BBP) in CHCl₃ were irradiated by Co-60 gamma-rays with an average dose rate of 2.5 Gy/min. After irradiation products of radiolysis were detected by GC-MS. Theoretical part of the work includes quantum chemistry calculation to study mechanism of radiolysis. The calculations were made by DFT (D3-B3LYP, def2-TZVPD) level of theory.

Fukui indexes and condensed dual descriptor were calculated and reactivity of compounds was estimated. Also steric availability of atoms in molecules to attacking particles was investigated by solvent-accessible surface area (SASA) model. These two theoretical approaches were combined to develop the radiation stability determination model.

The solvent extraction experiments reported study was funded by RFBR according to the research project № 18-33-20179.

OXIDATION PROCESS IN ORGANIC SCINTILLATORS IN PRESENCE OF GD-SALTS

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Linear alkylbenzene (LAB) is a base solvent for creating of Gd-loading liquid organic scintillator, in which the transparency of the hydrocarbon solvent used is particularly important. The transparency is primarily affected by the oxidation products of alkylbenzene¹, therefore it is important to analyze them. To this end, experiments were carried out on the liquid-phase oxidation of cumene, a model hydrocarbon whose structure is close to the LAB structure.

Since organic compounds can be oxidized in air, the oxidation process was carried out under non-catalytic conditions and under the action of a Gd-containing catalyst. Air oxygen was chosen as the oxidizing agent; the process temperature was 120; the process was carried out in a batch reactor.

According to the data of spectroscopic analysis in the catalytic and noncatalytic processes, an accumulation of hydroperoxides (HP) is observed - intermediate products of the process, whose concentration decreases with time, which leads to the formation of the main products - acetophenone and dimethylphenylcarbinol. This data is also confirmed by the chromatographic analysis, as well as by the generally accepted laws governing the oxidation of alkylaromatics².

Comparison of non-catalytic and catalytic oxidation allowed to speak about the general trend of the course, consisting in the expenditure of the initial hydrocarbon and the accumulation of products. However, it should be noted that during the oxidation of cumene under the action of Gd salt, its oxidation rate is higher than the oxidation without a catalyst under similar conditions. For a more complete evaluation of the process, it is necessary to carry out the oxidation with atmospheric oxygen for a longer time.

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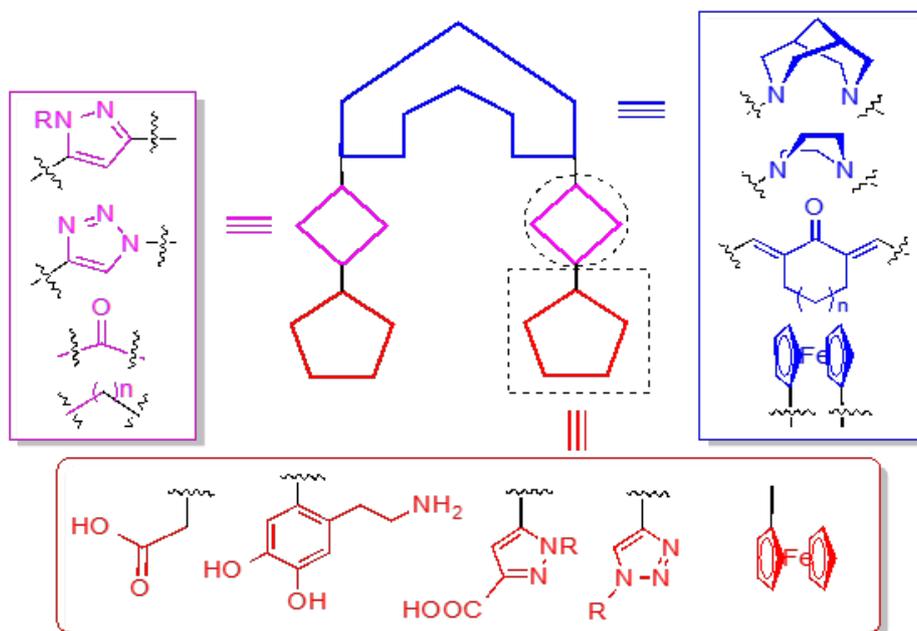
This work was supported by Russian Science Foundation (grant no.17-12-01331)

MULTIFUNCTIONAL MOLECULES FOR DIVERSE APPLICATIONS

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Our lab works on the design of multifunctional molecules which could be prepared by modular approach. We apply standard methods of organic synthesis using available starting compounds; also we explore our reach experience in the work with such building blocks as bispidines, pyrazoles, triazoles, ferrocenes, dienones etc (Scheme).



The examples of the properties and structures studied include: luminescence of lanthanide complexes,¹ radiopharmaceuticals,² asymmetric catalysis,³ photolabile and macrocyclic receptors,⁴ supramolecular polymers.⁵ Some of our new molecules could be used as models for studying the stereoelectronic effects.⁶

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NANOCRYSTALLINE GADOLINIUM ORTHOFERRITE AS A PROMISING DUAL-MODAL CONTRAST AGENT FOR MAGNETIC RESONANCE IMAGING

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Dual-modal T_1 - T_2 contrast agents for magnetic resonance imaging (MRI) may facilitate improved diagnosis and sharpen anatomic information in the magnetic resonance image.^{1,2} Nanocrystalline gadolinium orthoferrite ($GdFeO_3$) seems to be a promising dual-modal MRI contrast agent because it contains gadolinium in form of Gd^{3+} , which is involved in T_1 -contrast agents, and iron in form of $[FeO_6]$, which is involved in T_2 -contrast agents.

The synthesis was carried out by the reverse co-precipitation of gadolinium and iron(III) hydroxides followed by heat treatment of the co-precipitated hydroxides in the air.³ The co-precipitated hydroxides were investigated by X-ray diffraction (XRD) and simultaneous thermogravimetry and differential thermal analysis (TG-DTA). After the heat treatment of co-precipitated hydroxides at 750°C for 4 hours in the air, the as-synthesized product was investigated by XRD for phase identification and crystallite size estimation.

According to the XRD measurements, the co-precipitated hydroxides were amorphous. The X-ray phase analysis of the as-synthesized product obtained after heat treatment revealed that it was mainly composed of $GdFeO_3$ with a small amount of $Gd_3Fe_5O_{12}$, which is thermodynamically more stable.⁴ The crystallite size was approximately 30 nm as calculated by Scherrer's formula.

The activity of the obtained nanocrystalline $GdFeO_3$ as a dual-modal contrast agent is to be evaluated by measuring relaxation times T_1 and T_2 .

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SOME FEATURES OF STABILIZATION OF THE VALENCE FORMS OF SMALL MASSES OF NEPTUNIUM AND PLUTONIUM IN SOLUTIONS

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The stabilization of the valence forms of neptunium and plutonium in nitric acid and hydrochloric acid solutions using various reagents was studied.

When determining in samples of solutions, micro-, nano- and picogram masses of neptunium and plutonium carry out a selective extraction of these elements in the Np(IV) and Pu(IV) forms. To stabilize Np(IV), iron(II) sulfamate is added to the solution. Plutonium is reduced to Pu(III). When determining the impurity of neptunium in plutonium, the quantitative stabilization of Np(IV) and Pu(III) is achieved by treating the sample with a mixture of iron(II) sulfamate and ascorbic acid.

For quantitative stabilization of Pu(IV), a sequence of operations is used: Pu(IV,VI) → Pu(III) → Pu(IV). The best is the use of iron(II) sulfamate and ascorbic acid as a reducing agent, potassium bromate and sodium nitrite as an oxidizing agent. Neptunium goes into the pentavalent state.

During the oxidation of Pu(III) in the flow of eluent (1 M HNO₃), the effectiveness of oxidizing agents decreases in the series: NH₄VO₃ > KBrO₃ > KMnO₄ > K₂Cr₂O₇.

With the sequential treatment of a nitric acid solution with iron(II) sulfamate and iron(III) nitrate, the simultaneous stabilization of neptunium and plutonium in oxidation state +4 is observed. However, this technique is sensitive to the composition of the solution and may give irreproducible results.

When processing samples of solutions containing ultra-small amounts of plutonium with a mixture of concentrated nitric acid and hydrogen peroxide when heated, full stabilization of Pu(IV) is not achieved.

When determining the impurities of neptunium and plutonium in uranium solutions, it is necessary to consider the possibility of photochemical reactions with the formation of the impurity of tetravalent uranium. The resulting U(IV) recovers Pu(IV) to Pu(III).

When analyzing solutions with an unknown prehistory, it is necessary to carry out their preliminary processing to destroy the polymer forms of the elements.

HIGH TEMPERATURE INTERACTION BETWEEN MoO₃ AND CsI, IN HIGHLY HUMIDIFIED AIR

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In the event of a nuclear accident, one of the more worrying fission product is iodine. Especially, considering that iodine in the body accumulates in the thyroids and with its high specific activity could subject a person to a considerable dose. Therefore, it is important to have an accurate estimate of the release of iodine during an accident.

It has been indicated that molybdenum is capable, under oxidizing conditions, to affect the iodine source term. This occurs through the interaction with cesium iodide and formation of different types of cesium molybdates. Previously it has been observed that when molybdenum trioxide is present together with cesium iodide in a steamy argon atmosphere at high temperature, molybdenum reacts with the cesium part and consequently releases gaseous iodine. This would mean an increase in the iodine source term. However, a question that remains is what happens in a steamy air atmosphere at a high temperature (e.g. an air ingress scenario) when molybdenum and cesium iodide are present.

In this work, molybdenum trioxide (later also: molybdenum metal, molybdenum dioxide) was heated to 1470 K where it was subjected to a flow (1.5 l/min) of air saturated with water and an additive. This was achieved using an atomizer, which was filled with water and dissolved cesium iodide (the additive). This allowed the air to become saturated (100% RH, measured without the additive) and transport the cesium iodide to the heated zone. Afterward, the flow was cooled down rapidly to room temperature, by extending the tube far outside the tube, where aerosols are collected on a filter and gaseous species (mainly iodide) in sodium hydroxide traps.

The preliminary findings are that cesium molybdate does form under highly humid air at high temperature. However, in these conditions, the speciation that remains at room temperature is a mixture of different molybdenum oxides and cesium molybdates (not only Cs₂MoO₄). Thus, it could be possible that a variety of cesium molybdates.

LIQUID EXTRACTION AND EXTRACTION CHROMATOGRAPHY AM (III), CM (III), LANTHANIDES (III) DIAMID OF PHENANTHROLINDICARBONIC ACID: EFFECT OF A SALTING-OUT AGENT AND ANION TYPE

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One of the main problems of nuclear energy is the management of high-level waste. One approach to solving this problem is the concept of "fractionation and transmutation" the implementation of which will lead to a reduction in total activity in the long term. However, for realization this concept it is necessary to separate the actinides (An(III)) and the lanthanides (Ln(III)), what is a difficult task, since the physicochemical properties of the two groups of elements are very similar. The most acceptable method in chemical technology for this is liquid extraction. In the case of laboratory tests extraction chromatography can be used.

Previously it was found that the diamides of phenanthrolinecarboxylic acids have good extraction properties with respect to An(III) and Ln(III), and also show selectivity for separating the pairs Am(III)/Eu(III) and Am(III)/Cm(III). One of the representatives of this class of compound (ligand, L) is the object of study of this work.

The purpose of this work is to establish the effect on the extraction ability of the ligand (both in solvent extraction and in extraction chromatography) of the various components of the system: type of a salting-out and type of anion.

Methanitrobenzotrifluoride was used as solvent. The ligand concentrations were changed in the range of 0.001 - 0.1 M. Extraction was performed from aqueous media containing 3 M solutions of inorganic (HNO_3 , HCl, HClO_4) and organic (CH_3COOH , HCOOH) acids or salts – lithium, sodium, potassium and ammonium nitrates. The highest values of distribution coefficients and selectivity of separation are obtained in solutions of inorganic acids.

In this work we investigated the properties of solid phase extractants (SPE) based on a polystyrene-divinylbenzene matrix and hydrophobized silica gel, on which the extractant was fixed non-covalently. Sorption experiments were performed from nitric and perchloric acids of various concentrations. For SPE the same distribution and selectivity coefficients were obtained as in the case of liquid-liquid extraction. It is established that the "fixing" of the ligand on the polymer matrix does not affect the quality of the extraction ability.

The solvent extraction experiments reported study was funded by RFBR according to the research project № 18-33-00616

EXTRACTION BEHAVIOUR OF CALIX - AND THIALICALIXARENES TOWARDS ^{137}Cs AND ^{241}Am BEFORE AND AFTER IRRADIATION

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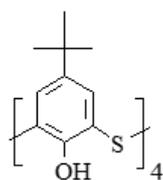
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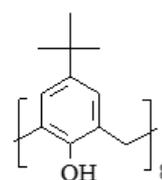
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Potential applicability of two functionalized calixarenes, *p*-*tert*-butyl-thiacalix[4]arene TCA and *p*-*tert*-butyl-calix[8]arene TB8, for extraction systems creation was studied as a solution of the technological problem of accumulated high-level alkaline waste processing.



p-*tert*-butyl-thiacalix[4]arene TCA



p-*tert*-butyl-calix[8]arene TB8

One of the conditions of extractant applicability in industry is its radiolytic stability. In this regard, in addition to testing the extraction efficiency of these compounds with towards ^{137}Cs and ^{241}Am , a study of their stability under the γ -irradiation in the range from 20 to 80 kGy was performed.

It was found that both studied calixarenes have low extraction efficiency towards ^{137}Cs (DCs ~ 0.1). Comparison of the results of ^{241}Am extraction before and after irradiation together with the data of mass spectrometric analysis indicates the nonlinearity of the change in the extraction efficiency. For TCA, this can be due to the formation in the system under the action of radiolysis of the calixarene cycle disclosure products, also extracting ^{241}Am . In the case of TB8, at constant distribution ratios of ^{241}Am , mass spectrometric analysis indicates the formation of numerous forms of attachment of organic diluent molecules to the extractant molecule in the solution.

TREATMENT OF MODEL DECONTAMINATION SOLUTIONS CONTAINING PLUTONIUM AND AMERICIUM

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Operation and decommissioning of nuclear and radiation facilities lead to the formation of liquid radioactive waste (LRW), including solutions used in the decontamination.¹ The purpose of this work was to determine the effective method for decontamination solutions treatment using the data on the radionuclide speciation.

Model decontamination solutions were prepared by mixing organic reagents, synthetic surfactant and sodium carbonate, solution pH ranged 8–9. Σ Pu and ^{241}Am were added to the solution with a total α -activity of $\sim 500 \text{ Bq/dm}^3$. The study was carried out with model solutions both freshly prepared and aged for a few years.

To determine the forms of radionuclides in solutions, methods of ion exchange, coagulation and ultrafiltration were used. The results obtained by ultrafiltration showed that in the model solutions Pu and, in part, Am are found in LRW in the form of hydrophobic particles with a size of 1–25 nm, consisting mainly of oxide and hydrolysis forms of metal ions.² The presence of surfactants and organic reagents significantly increases the stability of these particles, that excludes treatment by coagulation. In aged for a few years solutions a bottom sediment was formed, chemical oxygen demand and the total α -activity reduced nearly 10 times comparing to freshly prepared. It was found that radionuclides in solutions form only soluble low-molecular species, being the complexes with organic reagents. Destructing of organic components was one of the ways to increase the efficiency of treatment methods for solutions. For removing of organic agents, oxidation by hydrogen peroxide, potassium permanganate and ozone were considered and permanganate oxidation showed the best efficiency.

Based on the results of the conducted research, the speciation of Pu and Am radionuclides in LRW was obtained. It was shown that the long-term aging of solutions may cause the sedimentation of radionuclides and organic reagents up to 90% and the state of radionuclides changes with aging from predominantly colloidal species to soluble complexes with organic reagents. Experiments showed the possible effective combination of permanganate oxidation and coagulation methods for LRW treatment. The feature of this method is that the products of manganese reduction form good collectors for Pu and Am radionuclides.

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MAGNETORESISTANCE OF LOW TEMPERATURE HCP PHASE OF ELEMENTARY YTTERBIUM

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There are not many works dedicated to measuring resistance of ytterbium (Yb) at low temperatures, and information on the magneto-resistance of Yb is presented only in one work¹, where a large magneto-resistance is reported at $T = 1.8\text{K}$ and insignificant at $T = 300\text{K}$. In the temperature range 150–350K there is a martensitic transition from the hcp to fcc structure, which should be reflected in the dependences of the $\rho(T)$ and $\rho(H)$ of this metal.

In this work, we investigated the dependences $\rho(T)$ in the interval (2-400K) and $\rho(H)$ (up to 140kOe) of Yb samples similar to those used in study².

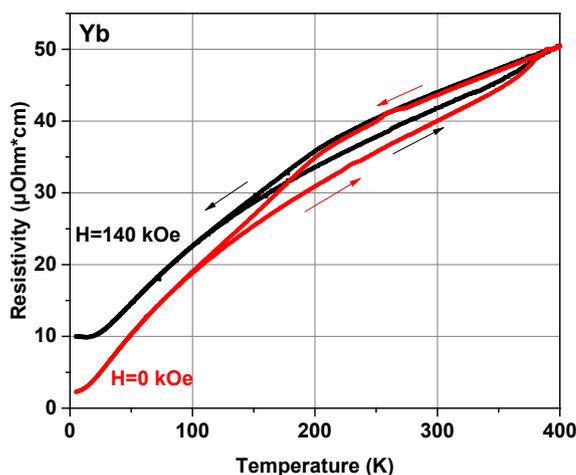


Figure 1. Temperature dependences of ρ of polycrystalline ytterbium for $H=0$ and 140kOe

Figure 1 shows the hysteresis of the $\rho(T)$ dependence associated with the structural transition and significant (up to 440% at 5K) magneto-resistance in the low-temperature hcp phase, which decreases with increasing temperature and becomes much smaller (about 0.1-1%) during the transition to Yb fcc phase at 350K.

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RARE EARTH METALS – INNOVATION ASPECT OF THE MODERN INDUSTRY

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For the first time rare earth metals in various minerals in the form of mixtures of oxides were found and were called "yttrium earth" and "cerium earth". The first of the rare earth metals was found black mineral ytterbite in 1787 in Sweden by K. Arrhenius. After 7 years open by K. Arrhenius the specific sample of the new mineral were studied by Finnish chemist Y. Gadolin. Mineral ytterbite was later renamed gadolinite after the Finnish scientist Gadolin Y.

Table 1. Discovery of rare earth metals²

№	Обозначение	Name	Etymology
1	Er	Erbium	the name from the site Ytterby (Sweden), 1843
2	Tm	Thulium	from the ancient Greek name of Northern Europe, 1879
3	Yb	Ytterbium	the name from the site Ytterby (Sweden), 1878
4	Lu	Lutetium	from the Roman name of Paris-Lutetia, 1907

Table 2. Rare-earth metals (REM)¹

Cerium - group LnCe					Yttrium - group LnY										
lightweight LnCe					Samarium-group (middle) LnSm						Erbium-group (heavy)				
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Th	Dy	Ho	Er	Tm	Yb	Lu	Y
lanthanum	Cerium praseodym		neodymium	promethium	samarium	europium	gadolinium	thulium	dysprosium	holmium	erbium	thulium	ytterbium	lutetium	yttrium

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Grant of President of Russian Federation, project MK-14.Z56.17.424 "Intensification of foam concentration of rare-earth elements in the processing of multicomponent industrial solutions."

QUANTITATIVE CORRELATION OF XPS STRUCTURE PARAMETERS WITH CERIUM IONIC COMPOSITION (Ce^{3+} AND Ce^{4+}) IN CeO_{2-x}

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Cerium dioxide is known as a non-radioactive structural surrogate of UO_2 and PuO_2 . The studies of influence of ionic irradiation in the wide energy range on CeO_2 structure have been carried out. Fission fragments damage effects on CeO_2 , as it takes place with UO_2 in reactors, have been studied thoroughly. The main difficulties arise with determination of cerium ionic composition (Ce^{3+} and Ce^{4+}). This work developed a technique of determination of cerium ionic composition on the basis of the XPS spectral structure parameters.

XPS spectra of single-crystalline CeO_2 film (250 nm) on the silicon substrate and polycrystalline pellets were measured in the binding energy range 0 to 1250 eV. Non-irradiated samples were shown to contain mostly Ce^{4+} ions with a small admixture of Ce^{3+} on the surface formed under the air or X-ray influence. The core-electron XPS structure of CeO_2 reflects a complex final state with holes resulted from the photoemission. Thus, for the Ce 3d electrons the final state consists of three states: $\text{Ce } 3d^94f^0$ – ground final state (882.3 and 900.9 eV); $\text{Ce } 3d^94f^1\text{VMO}^{-1}$ – charge transfer satellites with $\Delta E_{\text{sat1}}(\text{Ce } 3d_{5/2}) = 6.8$ eV; $\text{Ce } 3d^95p^54f^0\text{np}^1$ – shake-up satellites with $\Delta E_{\text{sat2}}(\text{Ce } 3d_{5/2}) = 16.0$ eV characterizing weakly screened holes in the Ce 5p quasiatomic shell. These final states shows up in the XPS spectra of all core electron shells. Spectra interpretation involved a technique of quantitative evaluation of the ionic composition based on the intensity of the reliably identified high-energy feature at 916.6 eV (sat_2 at the Ce $3d_{3/2}$ component). This technique showed for the non-radiated film AP1 the presence of Ce^{3+} ions (AP1: 96% Ce^{4+} and 4% Ce^{3+}). $^{129}\text{Xe}^{23+}$ -irradiation (92 MeV, fluence 4.8×10^{15} ions/cm²) leads to the increase of Ce^{3+} content on the surface (AP2g: 78% Ce^{4+} and 22% Ce^{3+}), (AP5g: 75% Ce^{4+} and 25% Ce^{3+}). Ce^{3+} concentration grows significantly as the film thickness decrease and film fragmentation (AP3g: 26% Ce^{4+} and 74% Ce^{3+}).

The work was supported by the RFBR grant 17-03-00277a.

CHEMICAL BOND NATURE IN CeO₂

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Cerium dioxide CeO₂ is important in catalysis, widely used in the studies as a non-active structural surrogate of radioactive materials (UO₂ and PuO₂) and can be used as matrix for spent nuclear fuel disposal.

This work studied the chemical bond on the basis of the X-ray photoelectron spectroscopy structure of valence electrons of CeO₂ in the binding energy range from 0 to ~50 eV. The analysis took into account the core-electron spectral structure and results of the relativistic discrete variation electronic structure calculation of the CeO₈¹²⁻ (D_{4h}) cluster reflecting Ce close environment in CeO₂. Comparison of the valence and the core electron spectral structures yielded that formation of the inner and the outer valence molecular orbitals (MO) make a more significant contribution to the valence electron spectra than the many-body processes. It was found that the Ce 4f electrons participate directly in the chemical bond formation in CeO₂ partially losing their f-nature, and are located mostly within the outer valence band. The Ce 5p atomic orbitals (AO) participate in formation of not only inner valence MOs, but also in formation of the outer valence MOs. The Ce 5p_{1/2,3/2} and the O 2s AOs take the most part in the inner valence MO formation, and the Ce 5s electrons participate weakly in the chemical bond formation. Despite the crystal field theory, the covalence effects in CeO₂ are high due to a strong overlapping of not only the Ce 5d AO, but also the Ce 5p and Ce 4f AOs with ligand orbitals. This makes the chemical bond more covalent. The composition and the sequent order of the molecular orbitals in the binding energy range 0 – ~50 eV was established. A quantitative scheme of the molecular orbitals for CeO₂ was built. This scheme is fundamental also for the interpretation of other X-ray spectra of CeO₂. Evaluations yielded that the inner valence MO electrons weakened by 36.5 % the chemical bond formed by the outer valence MO electrons.

The work was supported by the RFBR grant 17-03-00277a.

CHEMICAL BOND NATURE IN UO_2

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This work analyzed the valence XPS spectra of the single-crystalline UO_2 (111) film on the YSZ (yttria-stabilised zirconia) (111) substrate in order to study the chemical bond nature (ionic, covalent) in UO_2 . The core electron spectral structure and the relativistic discrete variation (RDV) calculation results for the UO_8 (D_{4h}), $\text{U}_{13}\text{O}_{56}$ and $\text{U}_{63}\text{O}_{216}$ clusters were taken into account.

A bar graph of the theoretical XPS of the outer (0 - ~15 eV; OVMO) and inner (~15 - ~35 eV; IVMO) valence molecular orbitals. The graph shows the degree of participation of the U 5f and U 6p electrons in the chemical bond in UO_2 . A satisfactory agreement was reached between the calculated and experimental XPS spectra of UO_2 single crystalline thin film cleaned with Ar^+ ions for 60 seconds. The effective charge $Q_{\text{U}^{n+}}$ in UO_2 was found to be $+1.1e^-$, which differs from that $Q_{\text{U}^{4+}} = +4$ for U^{4+} ion. Unlike the crystal field theory results, the covalence effects in UO_2 are significant due to the strong U 6p and U 5f overlapping besides the U 6d AO overlapping with ligand orbitals. This results in the strong covalent nature of the chemical bond in UO_2 . The MO structure related with the U 6d, 7s and 7p AOs does not change significantly compared to other actinide dioxides. These AOs together with those containing the O 2s and O 2p ones make a "rigid skeleton" of the band where the An 5f containing MOs float with the changing of the atomic number Z. MO compositions and sequent order in the binding energy range from 0 to ~35 eV in UO_2 were determined. A quantitative MO scheme for UO_2 was built. This scheme allows understanding the XPS structure and chemical bond nature in UO_2 and can be used for interpretation of other X-ray spectra of this dioxide. The contribution of the MO electrons to the chemical bond covalence component was evaluated on the basis of the bond population values. It was found that the IVMO electrons weaken the chemical bond formed by the OVMO electrons by 32% (UO_8) and by 25% ($\text{U}_{63}\text{O}_{216}$).

The work was supported by the RFBR grant 17-03-00277a.

FORMS OF URANIUM IN “HOT” PARTICLES

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Accidents on nuclear power plants (Chernobyl) and nuclear tests (Semipalatinsk) cause uranium (in UO_{2+x}) and its fission products spreading in the environment in many different forms. The most interesting forms are high radioactive fuel particles, so called “hot” particles. Unlike the other forms of uranium, in the environment “hot” particles are more kinetic stable, that depends on the temperature of expose. The establishing of forms of uranium in the environment is rather controversial issue¹.

In our work Chernobyl soils and soils from Semipalatinsk nuclear polygon were analyzed by digital and alpha-track radiography, XRD and XAFS and methods of local microanalysis (SEM-EDX). Using these methods elemental composition, structure, valent state, stoichiometric composition, and as a result, the migration behavior can be established.

Digital radiography with Imaging Plate was used for search of “hot” particles. Two dozens of “hot” particles were found. The proportion of “hot” particles are different in Chernobyl and Semipalatinsk. The percentage of “hot” particles in Chernobyl soils were from parts of percent to ten percent particles are massive and have different activity, in Semipalatinsk it is over the dozen percent, particles are small and have common small activity.

Alpha-track radiography established that “hot” particles content alpha-emitters and the energy of alpha-particles. Measured energy was 5,6; 5,2; 4,9 MeV in Chernobyl particles.

For establishing the elemental composition of “hot” particles SEM EDX was used. Morphology of “hot” particles was established. The content of uranium and zirconium was found.

For further analysis methods XAFS is to be used to establish the valent state and surrounding of uranium in UO_{2+x} . The “x” parameter depends on the conditions of burning and explosions. It is already established that uranium sublattice keeps the fluorite structure up to $x=0,33$ while the oxygen sublattice change its properties². The future plan of research is to establish the structure of oxygen sublattice in UO_{2+x} in Chernobyl and Semipalatinsk “hot” particles to predict its migration and for nuclear forensics.

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BIPYRIDYL-ETHYLENE AS A NEUTRAL LIGAND OR A COUNTER CATION IN URANYL CROTONATE COMPOUNDS

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Crystal structures of $[\text{UO}_2(\text{crt})_2(\text{bpe})_2]$ (I) and $(\text{H}_2\text{bpe})_2(\text{OH})_2[\text{UO}_2(\text{crt})_3]_2[\text{UO}_2(\text{crt})_2(\text{H}_2\text{O})_2]$ (II), where crt = crotonate ion $\text{C}_3\text{H}_5\text{COO}^-$ and bpe = 1,2-bis(4-pyridyl)ethylene $\text{C}_{12}\text{H}_{10}\text{N}_2$, were solved via single crystal X-ray diffraction analysis and characterized via FTIR spectroscopy. Both compounds represent 3D conjugated systems due to the prevalence of unsaturated aromatic moieties, double C=C bonds and carboxylate anions.



The pyridine rings in the mentioned compounds (together with crotonate ions) show parallel-displaced and inclined arrangements, while T-shaped arrangements are not observed. As known, such types of arrangement of aromatic rings as well as the presence of crotonate ions give rise to lots of C–H... π and C–H...N interactions.

Analysis of all available to date uranyl compounds with bpe molecules/cations in the CSD¹ by means of Voronoi–Dirichlet tessellation reveals that the arrangement of bpe is topologically equal in most of them. This is consistent with the mechanism of crystal growth which implies such a packing of bulky species, when the overlap of their outer electron shells is minimal.

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**POLYMORPHIC TRANSITIONS IN PRASEODYMIUM HALIDE
COMPLEXES OF ACETYLUREA**Savinkina E.V.,^a Grigoriev M.S.,^b Golubev D.V.^a^aLomonosov Institute of Fine Chemical Technologies, RTU MIREA, Moscow, 117571, Vernadskogo 86, RUSSIA
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Crystal structures of praseodymium chloride and bromide complexes with acetylurea (AcUr) were studied by X-ray diffraction at 293 and 100 K. Crystals of $[\text{Pr}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{X}_3$ ($\text{X} = \text{Cl}, \text{Br}$) at room temperature are isostructural to the crystals of $[\text{Sm}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Cl}_3$ and $[\text{La}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3$, respectively; it is noteworthy that crystal structure of the bromide complex differs significantly from the earlier reported structure of the praseodymium complex of the same composition¹. On lowering temperature down to 100 K, crystal structures of both compounds change (table 1). According to the DSC data, polymorphic transition for $[\text{Pr}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3$ begins at ~208 K. On cooling, similar crystal lattices of the complexes distort due to changes of relative arrangement of complex cations and anions. In addition, angles between mean planes of acetylurea ligands slightly vary. Transformation in the crystal structures are reflected in the IR spectra of the compounds. Quantum chemical calculations confirm possibility of several conformations for the complex compounds.

Compound	$[\text{Pr}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Cl}_3$		$[\text{Pr}(\text{AcUr})_2(\text{H}_2\text{O})_5]\text{Br}_3$	
Temperature, K	100(2)	293(2)	100(2)	293(2)
Crystal system	triclinic	monoclinic		
Space group	$P1$	$C2$	$P2_1$	$C2$
a (Å)	7.4918(6)	18.0498(7)	7.4972(2)	18.3895(5)
b (Å)	7.5397(6)	7.4766(3)	31.1736(9)	7.8206(2)
c (Å)	9.6561(8)	7.6502(3)	16.8265(6)	7.6444(2)
α (°)	109.750(3)	90	90	90
β (°)	112.000(3)	113.904(2)	91.7410(10)	113.398(2)
γ (°)	93.545(3)	90	90	90
Volume (Å ³)	464.74(7)	943.85(7)	3930.8(2)	1008.99(5)
Z	1	2	8	2

Table 1. Unit cell parameters of the complex compounds

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THE NEW U(VI) COMPLEXES WITH METHACRYLATE IONS AS LIGANDS

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In recent decades the transition metal carboxylate complexes are extensively studied. Despite the perspective for the use of new materials based on unsaturated transition metal carboxylates in catalysis and separation and gas storage, the structural data for uranyl ones were limited in scientific literature until recent time.¹ We have synthesized some new U(VI) complexes including methacrylate ions as ligands with different organic cations with compositions $(\text{NH}_2)_2\text{CNH}_2[\text{UO}_2(\text{macr})_3]$ (I), $(\text{NHPH})_2\text{CNH}_2[\text{UO}_2(\text{macr})_3] \cdot 0.5\text{C}_2\text{H}_5\text{OH}$ (II), $\text{PhCH}_2\text{N}(\text{CH}_3)_3[\text{UO}_2(\text{macr})_3]$ (III) and $\text{PhCH}_2\text{N}(\text{C}_2\text{H}_5)_3[\text{UO}_2(\text{macr})_3]$ (IV), where $\text{macr} = \text{C}_3\text{H}_5\text{COO}^-$.

Synthesis of new methacrylate-containing uranyl complexes is hampered by the predisposition of methacrylic acid to rapid and irreversible polymerization, manifested in the turbidity of an aqueous solution and the subsequent formation of a gel-like product. Therefore, the synthesis was carried out in the black painted vessels. Compounds I–IV were crystallized by isothermal evaporation of aqueous or aqueous-alcoholic solutions. The portion of UO_3 was dissolved in methacrylic acid solution followed by the portions of organic compounds.

The crystallographic parameters of I–IV were obtained through X-Ray analysis. The definition of coordination numbers was carried out using the method of intersecting spheres.² In all cases the uranium atoms coordination polyhedra are hexagonal bipyramids UO_8 , where six atoms of oxygen in equatorial plane belong to three bidentate cyclic (type of coordination B^{01}) methacrylate ions. The type of coordination is indicated according to the nomenclature in ref.³ In structures I–IV uranium containing units are 0D complexes with composition $[\text{UO}_2(\text{macr})_3]^-$ and crystallochemical formula AB^{01}_3 , where $\text{A} = \text{UO}_2^{2+}$, $\text{B}^{01} = \text{macr}$. The 0D complexes form framework through noncovalent interactions with different organic cations.

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OXIDIZED AMERICIUM SEPARATION IN UNEX-T PROCESS

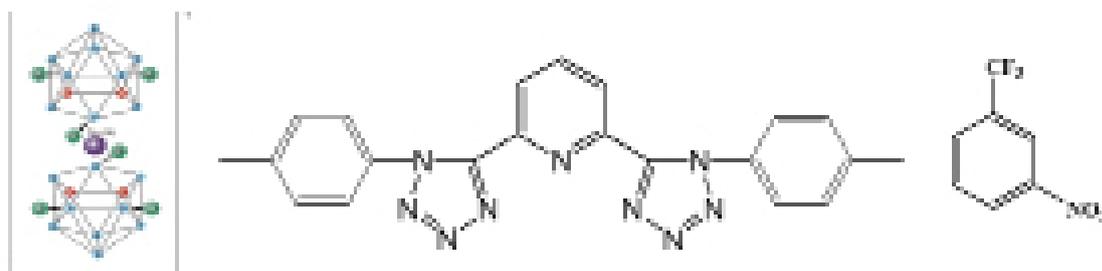
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The UNiversal solvent EXtraction (UNEX-T) process developed at the Khlopin Radium Institute permits the separation of cesium, strontium and trans-plutonium elements from acidic radioactive wastes in one extraction cycle. The use of one extraction cycle instead of 2-3 cycles drastically decreases the cost of waste treatment. The UNEX-T solvent is comprised of three active components: chlorinated cobalt dicarbollide and bis-tetrazolylpyridine, dissolved in a polar diluent – m-nitrobenzotrifluoride.

The extractability of radionuclides in 1 M nitric acid in UNEX-T process decreases in the range: Am(III) \approx Cs > Pu(III) > Sr(II) > Pu(IV) > Pu(VI) > Eu(III) > U(VI) > Np(V) with separation factors of Am/Eu \approx 100 and Am/Np > 2000. Among the stable HLW components Pd, Ni and Co extract remarkably. At the dynamic test of UNEX-T process with simulated HLW the separation factor 36 between americium and rare-earth elements was achieved.



We found that the oxidized forms of americium (+5, +6) are not extracted with UNEX-T solvent, which allows us to separate americium from curium. Ozone, sodium persulfate, sodium perxenate, silver (+2) nitrate and copper periodate (+3) were tested as americium oxidants. The most effective oxidizing agents were sodium perxenate and copper periodate (+3): the separation factor between curium and oxidized americium during the extraction with UNEX-T solvent reached 1,000.

DETERMINATION OF CHARGE AND STRUCTURE OF THORIUM (IV) POLYNUCLEAR HYDROXOCOMPLEXES

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It is established that hydrolysis of cations in solution proceeds in two stages – formation of mononuclear hydroxocomplexes and formation of polynuclear hydroxocomplexes. The formation of polynuclear hydroxocomplexes proceeds always through the first stage – dimerization, however, this scheme also does not correspond to real equilibria in solution, as it will be shown in this work.

We have developed methodological approach that allows direct experimental determination of the composition of polynuclear hydroxocomplexes. This approach involves three necessary steps: determination of the polymerization degree,¹ determination of hydroxogroups quantity in polynuclear hydroxocomplex, determination of polynuclear hydroxocomplex charge.²

So, applying the above three methods we studied formation of polynuclear hydroxocomplexes of iron (III) and thorium (IV). According to our data, obtained by all of the methods at the early stages of polymerization, the following species form in solution: $\text{Fe}_2(\text{OH})_{5,2-5,8}^{+0.2-0.8}$ and $\text{Th}_2(\text{OH})_{7,8}^{0.2+}$. These results change principally the existing in the literature conception of the mechanism of cations polymerization in solution according to which the species that form at the first stage of hydrolysis have high positive charge the value of which depends on the charge of a cation hydrolysed.

Kinetics of the polymerization process usually is a much longer process than formation of mononuclear hydroxocomplexes. Usually, it can take days, sometimes weeks and even longer.

Particularly interesting for solution of a number of practical tasks, the data on hydrolysis of cations in the systems with more than one cation are. Joint research of our laboratory and Swedish University of Agricultural Sciences (Uppsala) have been studied hydrolysis in Fe(III)-Th(IV) system. A heteronuclear hydrolysis complex with the composition $[\text{Th}_2\text{Fe}_2(\mu^2\text{-OH})_8(\text{H}_2\text{O})_{12}]^{6+}$ was proposed to form in solution.³

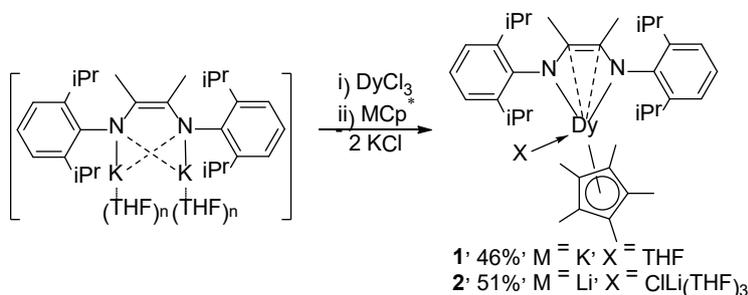
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SINGLE-MOLECULE MAGNETS BASED ON Dy^{3+} HALF-SANDWICH COMPLEXESTrifonov A.A.,^{a,b} Tolpygin A.O.^{a,b}^aG.A. Razuvaev Institute of Organometallic Chemistry, RAS,
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Coordination complexes exhibiting slow relaxation of their magnetization associated with magnetic bistability show tremendous potentialities for information storage or spin-based computing.¹ Single-molecule magnets (SMM) have been greatly enhanced by taking advantage of the fascinating properties of lanthanide ions.² Lanthanide ions such as Dy^{3+} exhibiting oblate electronic density are efficiently stabilized by axial crystal-field that maximizes the splitting of the m_j levels, while minimizing the Quantum Tunneling of the Magnetization (QTM).³

Aiming at synthesis of new SMM we propose in current investigation to associate bulky DAD-type ligands that are known to generate short Dy–N distances with rigid Cp* moiety in order to design heteroleptic half-sandwich dysprosium complexes.⁴



Heteroleptic Dy^{3+} complexes 1 and 2 based on DAD and Cp* ligands which differ by the nature of an additional coordinated species (THF vs. Cl^-) exhibit distinct slow relaxation of the magnetization dynamics caused by slight changes in the Dy–N distances and Cp*–Dy–DAD angles. Thanks to the great tunability of both, DAD and Cp ligands, extension to other heteroleptic complexes exhibiting shorter Dy–N distances and greater bite angles may be viewed as a promising route to enhance the magnetic relaxation properties in lanthanide SMM.⁴

The authors thank the Russian Science Foundation (grant 17-73-30036).References

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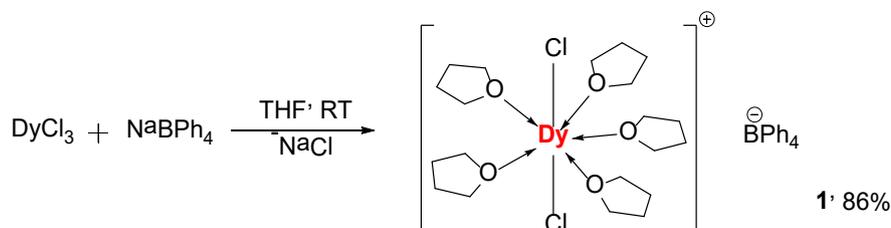
SINGLE-MOLECULE MAGNET BEHAVIOUR IN A Dy(III) PENTAGONAL BIPYRAMIDAL COMPLEX WITH QUASI-LINEAR Cl–Dy–Cl SEQUENCE

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The ability of a coordination complex to present bistable magnetic states continues to attract attention of chemists and physicists since the discovery of this phenomenon nearly thirty years ago.^{1,2} In this sense, the field of Single-Molecule Magnets (SMMs) has taken an upturn with the use of lanthanide ions to design highly magnetically anisotropic complexes exhibiting exceptional performances, making such molecular systems potential candidates for applications in datastorage, spintronics or quantum computing. In lanthanide SMMs, the slow relaxation of magnetization is directly correlated to the lanthanide crystal-field generated by the surrounding ligands that favours the creation of an anisotropic barrier, Δ , opposing two antiparallel directions of the magnetic moment ($\pm mJ$).



We report the synthesis and magnetic investigation of a dysprosium pentagonal bipyramidal complex $[\text{Dy}(\text{THF})_5\text{Cl}_2][\text{BPh}_4]$ (**1**) exhibiting a linear Cl–Dy–Cl sequence suitable for providing a coordination environment allowing a zero-field slow relaxation of the magnetization. Besides, the complex also shows dual luminescence originating from $[\text{BPh}_4]^-$ and Dy^{3+} .³

The authors thank the Russian Science Foundation (grant 17-73-30036).

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MAGNETIC AND LUMINESCENCE PROPERTIES OF LN(III) COMPLEXES COORDINATED BY TRIS(PYRAZOLYL)METHANE LIGAND

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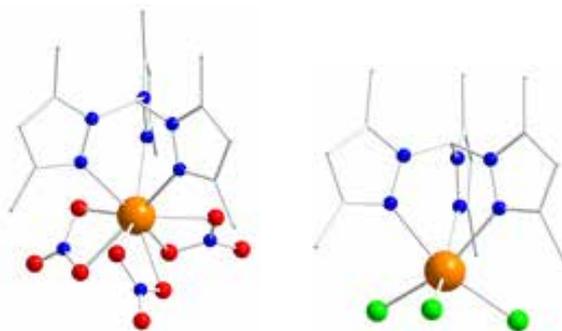
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Lanthanide Single-Molecule Magnets (SMM) captivate due to their possible applications in data storage, spintronics or quantum computing. In such coordination complexes, a slow relaxation of the magnetization originates from the appearance of an energy barrier that opposes two directions of the magnetization. The foundation of such remarkable property lies in the synergistic combination between the intrinsic nature of the Ln ion through its angular dependence of the 4f electronic density (oblate vs. prolate) with the crystal-field generated by the surrounding ligands. In this sense, mononuclear Ln SMM with tremendous magnetic properties represent a challenge for synthetic chemists in order to design optimized complexes with appropriate symmetry and coordination sphere in order to maximize the magnetic anisotropy of the $\pm m_j$ states. N-containing ligands, which are easily incorporate in the complexation with Ln ions due to their hard Lewis acidity, are suitable candidates for synthesis of complexes of these metals.

Herein we report synthesis, structure and investigation of magnetic and luminescence properties of a series of Ln(III) complexes of the general formula $[\text{Ln}(\text{Tpm})\text{X}_3]$ coordinated by Tpm ligand (tris(3,5-dimethyl-pyrazolyl)methane; Ln = Tb, Dy, Er, Yb; $\text{X}^- = \text{NO}_3^-, \text{Cl}^-$).¹ The observation of a field-induced slow relaxation of magnetization of these derivatives is highly dependent on the anion's nature. NO_3^- moieties appear to be suitable to stabilize the oblate electronic density of Dy^{3+} , while Cl^- generate an equatorial crystal-field allowing the slow relaxation of the prolate Er^{3+} ions. More over Tpm ligand was found to be suitable coordination environment for Eu, Tb and Dy luminescence sensebilization.



The authors thank the Russian Science Foundation (grant 17-73-30036).

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Ln AND An CHEMISTRY UNDER ADVANCED SEPARATION PROCESS CONDITIONS-ALSEP

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Solvent extraction systems that combine neutral and acidic extractants have been investigated to provide a single process solvent for separating the minor actinide elements from acidic high-level liquid waste, including their separation from the trivalent lanthanides. This approach of combining extractants is referred to as the Actinide-Lanthanide SEparation (ALSEP) process.

The process was successfully demonstrated on a lab scale using both genuine used nuclear fuel PUREX raffinate and a simulant solution.. The multi-stage process demonstration was run using a simulant solution spiked with

Am-241, Cm-244 and Pm-147. A bank of 1.25-cm centrifugal contactors was produced by 3D printing. The MA were completely separated from the lanthanides: less than 0.5 milligram/Liter of total Ln reported in the MA product while no actinides were detected in the Ln product.. The measured separation factors (SF) for the Pm/MA (worst case scenario) are in the range of 17 to 24, close to the equilibrium values. Overall decontamination factors over 1000 were accomplished for the MA/Ln separation. The process performance was successfully validated with the dissolved used fuel raffinate solution after U, Np and Pu removal in a hot-cell environment in a batch regime.

The Ln and An speciation in the ALSEP organic and aqueous phases will be discussed in detail.

MIGRATION FEATURES OF CERTAIN LONG-LIVED RADIONUCLIDES IN LAKE ECOSYSTEMS OF EURT IN A DISTANT POST-ACCIDENT PERIOD

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It has been more than 60 years since the radiation incident on the "Mayak", which corresponds to at least two half-lives of the main long-lived radionuclides (^{90}Sr and ^{137}Cs). In fact these radionuclides are already built into natural ecosystems and the assessment of the radiological situation should take into account their behaviour in different ecosystem environments. The purpose of the research is to identify migration features of ^{90}Sr and ^{137}Cs on components of lake ecosystems of EURT in a distant post-accident period. The migration of long-lived radionuclides in lake waters is characterized by a multiplicity of water purification. Conditioned to radioactive decay, the multiplicity of the purification is no more than 3 and has nothing to do with migration. Physical and chemical precipitation and biological absorption for certain lakes in the central areas of EURT is up to 500-800 times for ^{90}Sr and up to 1300 times for ^{137}Cs . The main depot of ^{90}Sr and ^{137}Cs in a lake ecosystem is bottom sediments. The first meter of bottom sediments in many lakes of middle and far areas of EURT is represented by olive sapropel. This is the reason of a relatively slow migration of ^{90}Sr and ^{137}Cs by profile: inert sapropel with foliaceous-free minerals allowed radionuclides to penetrate no deeper than 35-45 cm below the accident layer. At high sediment formation rate (from 2 to 5-6 mm per year) including compaction over the accident layer, there have been accumulated up to 25-30 cm of silt in certain lakes. The accumulated silt gets radionuclides from the water and hydrobionts as a result of the cycle (migration) of all the substances in the lake ecosystem. The schedule of radioactivity changes on the profile of bottom sediments shows increase in the values from the surface precipitation to the accident layer. Then exponential reduction is noticed to about 60 cm to zero. The silt is still deeper, it doesn't experience any technogenic impact.

Thus modern migration of long-lived radionuclides in lake ecosystems of EURT is characterized by integration of ^{90}Sr and ^{137}Cs into natural environments and processes. Migration speed depends on physical, chemical and physiological interaction of natural ecosystems components with radionuclides.

DEGRADATION OF NATURAL URANIUM CONTAINING MICROMINERAL PHASES: IMPLICATIONS TO CONTAMINANTS TRANSPORT AT ABANDONED MINING SITES

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In this work a combination of multiple synchrotron and laboratory based micro-techniques is utilized to unveil the speciation, heterogeneities and degradation of uranium (U) micro-mineral phases accumulated on rock outcrop from natural U deposit area. The investigated system is sampled from the abandoned Krunkelbach U mine in Southern Germany with 2-3 km surrounding area which represents a natural analogue site with an unique accumulation of U minerals suitable for investigations of potential mobilization-immobilization processes expected in a real spent nuclear fuel repository. A specific feature of the site is the occurrence of more than forty secondary U minerals, from uraninite and mixed U oxy-hydroxides to uranyl silicates, representing a wide scale of U ore weathering events.¹ Available data on the age of the secondary U mineralization indicates that oxidizing processes at the site started some 340,000 years ago and continues up to date. Several phases close to $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_{2-x}(\text{AsO}_4)_x \cdot 8\text{H}_2\text{O}$ are identified on $1 \times 2 \text{ mm}^2$ area with presumably older, more evenly distributed uranyl silicate and uranyl tungstate mineralization. Based on a multi-technique investigation $10\text{-}200 \mu\text{m}$ $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_{2-x}(\text{AsO}_4)_x \cdot 8\text{H}_2\text{O}$ particles with widely varying arsenic-phosphorus (As-P) content are analyzed. The evidences of a degradation on some zones of selected crystals are found which are associated with higher As content. This observation can be apparently attributed to different degradation properties of the mixed As-P phases depending on As-P ratio and originate from drastically different solubility properties of $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and $\text{Cu}(\text{UO}_2)_2(\text{AsO}_4)_2 \cdot 8\text{H}_2\text{O}$ species. The conditions for preferential formation of As rich $\text{Cu}(\text{UO}_2)_2(\text{XO}_4)_2 \cdot 8\text{H}_2\text{O}$ [X=As, P] phases and its possible role on U transport in environment under oxidizing conditions are discussed.²

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THE STRUCTURE OF TETRACHLOROURANILATE COMPLEXES WITH BENZYLTRIMETHYLAMMONIUM OR BENZYLTRIETHYLAMMONIUMRogaleva E.F.,^a Serezhkina L.B.,^a Grigoriev M.S.^b^a Samara National Research University, Moskovskoe shosse 34, Samara, 443086, Russia,
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In this study, the structures of two new compounds were investigated: $(C_{10}H_{16}N)_2[UO_2Cl_4]$ (I) and $(C_{13}H_{22}N)_2[UO_2(NO_3)Cl_2]$ (II), where $C_{10}H_{16}N^+$ – benzyltrimethylammonium, $C_{13}H_{22}N^+$ – benzyltriethylammonium.

Crystals I and II were investigated using the method of XRD analysis. Coordination numbers of all atoms in the structure are defined with the method of intersecting spheres. It is determined that coordination polyhedron (CP) of uranium atom in the structure I is tetragonal bipyramid UO_2Cl_4 . The main structural units of crystals I are tetrachlorouranilate particles $[UO_2Cl_4]^{2-}$, those are referred to crystallochemical group AM_1^4 , where $A = UO_2^{2+}$, $M^1 = Cl^-$. Coordination types are written according to the paper in ref. ² The particles are linked into the framework due to the system of hydrogen bonds with outer-sphere benzyltrimethylammonium cation.

According to the obtained data two crystallographically nonequivalent uranium atoms are contained in the structure II. CP of the uranium atoms are tetragonal bipyramids UO_2Cl_4 (U1) and hexagonal bipyramids UO_6Cl_2 (U2). Four chlorine atoms are in the equatorial plane of U1 atom CP (coordination type M^1). The equatorial plane of U2 atom CP contains four oxygen atoms, which belong to two bidentate-cyclically coordinated nitrate-ions (coordination type B^{01}), and two chlorine atoms (coordination type M^1). The main structural units of crystals II are the particles $[UO_2Cl_4]^{2-}$, those are referred to crystallochemical group AM_1^4 , where $A = UO_2^{2+}$, $M^1 = Cl^-$, and $[UO_2(NO_3)_2Cl_2]^{2-}$, which belong to crystallochemical group $AB01_2M_1^2$, where $A = UO_2^{2+}$, $B01 = NO_3^-$, $M^1 = Cl^-$. The particles are linked into the framework due to the system of hydrogen bonds with outer-sphere benzyltriethylammonium cation. Results of FTIR spectroscopic study are well conformed with XRD analysis data.

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SYNTHESIS AND STRUCTURES OF NEW MIXED LIGAND URANYL COMPLEXES

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The crucial role of uranium in the nuclear industry and its specific crystallochemical properties excite the interest of many scientific groups to the chemistry of this element, especially to its coordination compounds. The carboxylate complexes of uranium are explored intensively for several decades.¹ The structures of mixed ligand acetate-another anion complexes also exist in structural databases. However, the data about mixed ligand uranyl compounds with halogenated analogues of acetic acid are absent in literature.

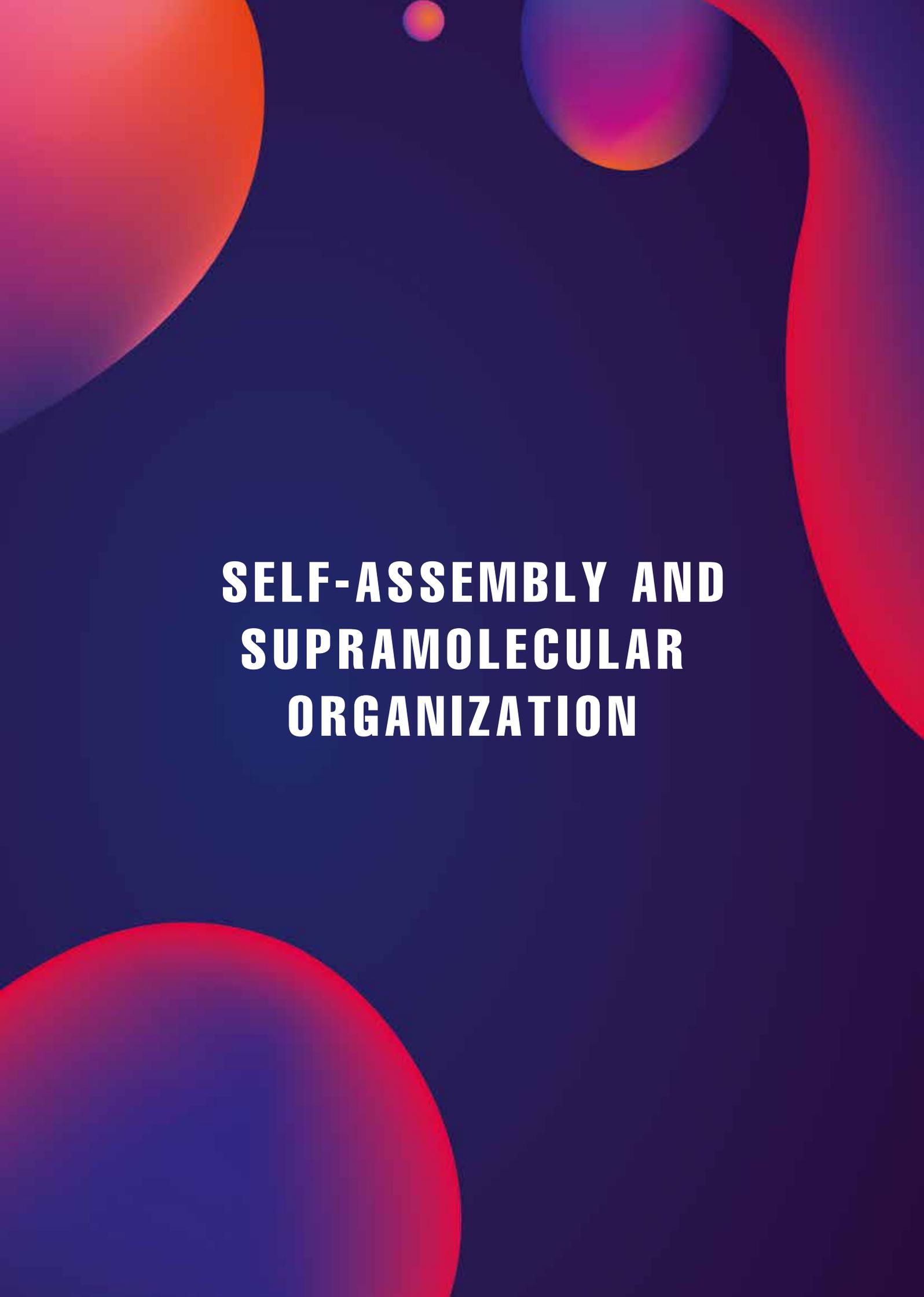
The crystal structures of complexes $(C_4H_{12}N)_2[UO_2Br_3tca]$ (I) and $Cs[UO_2(dca)_2mca]$ (II) (where $tca = CCl_3COO^-$, $dca = CHCl_2COO^-$, $mca = CH_2ClCOO^-$), obtained as yellow crystals after a few days of isothermal evaporation of the reaction mixtures at ambient conditions, are determined with the method of X-Ray diffraction analysis.

In the structure I the only uranium atom has CN = 7 and the coordination polyhedron in the form of pentagonal bipyramid, while in the structure II the only atom of uranium has CN = 8 and forms the coordination polyhedron in the form of a hexagonal bipyramid. The Voronoi-Dirichlet polyhedra, dual to coordination polyhedra, of U atoms are pentagonal and hexagonal prisms, respectively.

In the synthesized compound I the uranyl ion coordinates one trichloroacetate-ion and three bromide-ions and forms complex units $[UO_2Br_3tca]^-$ (coordination mode of trichloroacetate-ion B⁰¹⁻⁴),² meanwhile in the structure II one monochloroacetate- and two dichloroacetate-ions are coordinated to uranyl ion. Thus, the main structural units in II are $[UO_2(dca)_2mca]^-$ (coordination types of monochloroacetate- and two dichloroacetate-ions B⁰¹⁻⁴).²

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**SELF-ASSEMBLY AND
SUPRAMOLECULAR
ORGANIZATION**

METAL-ORGANIC FRAMEWORKS BASED ON PERFLUORINATED LIGANDS

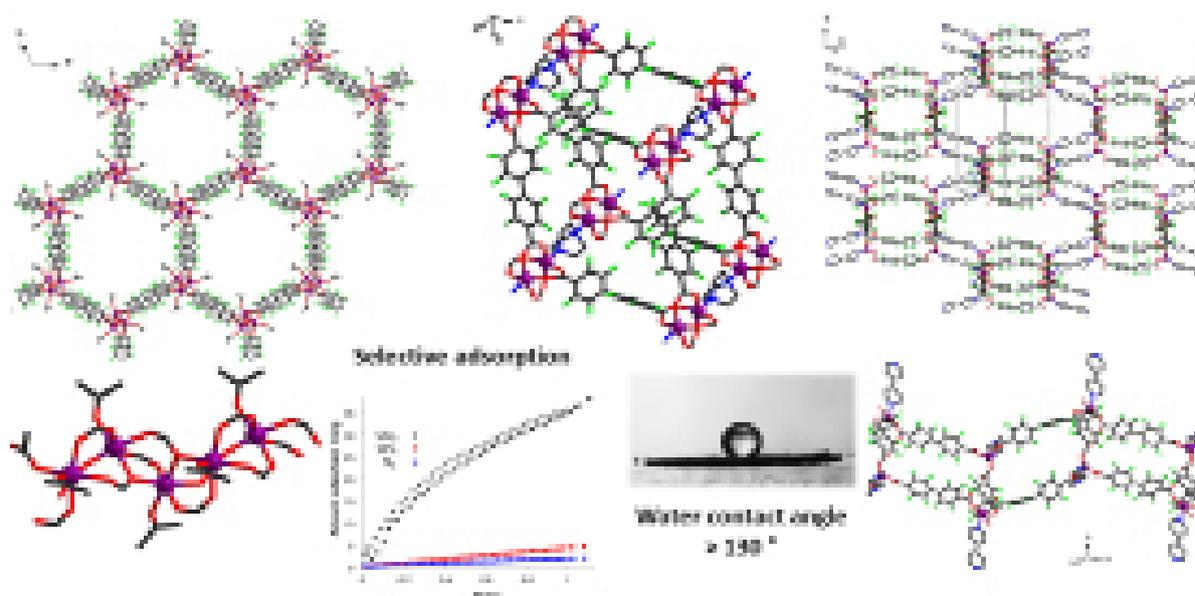
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Metal-organic frameworks (MOFs) have attracted much attention due to their high specific surface area, pore volumes and the feasibility of functionalization of the internal surface. Application of perfluorinated carboxylates, e.g. octafluoro-4,4'-biphenyldicarboxylate (oFBPDC)²⁻, is a promising approach to get novel MOFs with interesting surface properties, including hydrophobicity and selectivity of adsorption.

The conditions for the synthesis of perfluorinated MOFs are different from those for non-fluorinated material. New 1D, 2D and 3D coordination polymers were obtained, and crystal structures were determined by single crystal X-ray diffraction.^{1,2}



One of them, doubly interpenetrated [Zn₂(dabco)(oFBPDC)₂], is a permanently porous solid with the BET surface area of 441 m²/g. In addition, it shows IAST selectivity factors of 11.3 and 4.9 for the separation of gas binary mixtures CO₂/N₂ and CO₂/CH₄, respectively. The value of water contact angle (136°) and the shapes of water and C₆-hydrocarbon vapour adsorption curves confirm hydrophobic nature of this material.

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IRON CAGE COMPLEXES AS LIGANDS IN METALLOSUPRAMOLECULAR CHEMISTRY

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The lecture summarizes work on the utilization of iron cage complexes ('clathrochelates') as metalloligands in supramolecular chemistry and materials science.¹ Different molecular architectures are described, including coordination cages with unusual gyro-bifastigium or square orthobicupola-like structures.²⁻⁵ Metalloligands containing multiple clathrochelate complexes are particularly well suited to build large metal-ligand assemblies (> 3 nm) with minimal synthetic efforts. Clathrochelates complexes have also been investigated in the context of materials chemistry. For example, we have prepared polymeric networks with permanent porosity, and we have incorporated clathrochelate metalloligands in metal-organic frameworks.

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MOLECULAR PROTONICS AND SUPRAMOLECULAR CHEMISTRY, PHYSICS AND BIOPHYSICS

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The process of proton transfer in gaseous and liquid media for more than a hundred years has been discussed as the main one during the structure formation involving water. This is the initial step in the mechanism of hydrogen bonding in chemical systems. The proton transfer rates are very high and constitute the subject of molecular protonics in chemistry¹. It is of fundamental importance in the bioenergetics, directing the transport processes and the synthesis of ATP.

In our works, proton transfer in aqueous solutions, including the media of a living organism, is taken into account in order to substantiate an effective mechanism of association. Such a mechanism is connected with a known high affinity for a proton in a water molecule, which leads to the formation of polyatomic Rydberg molecules^{2,3}. We have shown that association in biosolution can be regulated by an exposure to microwave radiation^{4,5}. A natural source of such radiation has always been the terrestrial ionosphere with solar-geomagnetic disturbances, and in recent decades the anthropogenic component of electromagnetic noise has continuously increased.

The supramolecular physics of over-molecular structures describes processes developing outside the molecule in whose evolution to complex forms (associates, clusters) microwave radiation of external origin absorbed by excited Rydberg components of this molecular complex takes part. Due to increasing value of orbital momentum of Rydberg electron stability of the complex grows because probability for forming a stable neutral associate becomes higher since the electron more seldom penetrates into the ion core^{4,5}.

Estimated approbation was carried out on a comparison with the known measurements in droplet medium of the condensation-cluster haze of the troposphere⁵. An explanation is given of the anomalous behavior of the characteristics of high dilution bio-solutions⁶, including under electromagnetic shielding conditions, as well as the effect of a magnetic storm on humans^{4,5}.

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INTERPLAY BETWEEN LIPID STRUCTURE AND MEMBRANE RESISTANCE TO PORE FORMATION

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The lipid matrix of cell membranes forms a natural barrier between the cell and its organelles and the outer environment. The basis of this barrier function are amphiphilic properties of lipid molecules. By forming a bilayer with the central hydrophobic core, they ensure the almost complete absence of passive fluxes through the cell membrane for ions and polar molecules. The appearance of ion-conductive defects – pores – in the lipid bilayer disrupts normal cellular homeostasis that can lead to cell death.

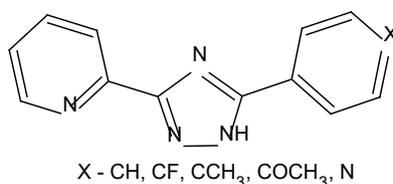
Cell membranes contain hundreds of different lipids, the structure of which, in many ways, determines the stability of the lipid matrix to the appearance of conductive defects. Unique properties in ensuring the stability of membranes are possessed by archaeal lipids, the structure of which allows these organisms to survive under extreme conditions. Archaeal lipid hydrocarbon tails are predominantly fully saturated isoprenoid chains and sometimes contain cyclopropane and/or cyclohexane rings. In our work, we studied the process of pore formation in bilayer lipid membranes formed by both ordinary eukaryotic lipids and lipids containing in their structure elements characteristic of archaea using the electroporation method. These results were compared with the computational experiment conducted by the methods of molecular dynamics. In addition, we proposed a theoretical model of the pore formation process, based on the theory of elasticity of liquid crystals, adapted to lipid membranes. We have shown that branched lipid tails have a great influence on the probability of pore formation and the kinetics of their growth.

THE IMPACT OF SUPRAMOLECULAR EFFECTS ON LUMINESCENCE OF ZINC COMPLEXES OF PYRIDYLTRIAZOLES

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Recently, the design of organic–inorganic hybrid complexes based on coordinate bonds and multiple weak non-covalent forces have become a research field of rapid expansion in coordination chemistry and crystal engineering. In the focus of our research is the role of intermolecular effects in a crystal on the luminescent properties of coordination compounds. In this report, we describe the interesting emissive behavior of Zinc complexes of pyridyltriazoles (L), displaying bright fluorescence and excitation dependent chromic properties.



The title complexes ZnLCl₂ were obtained by reaction of the corresponding ligands with ZnCl₂ in acetonitrile. The zinc complexes were characterized by elemental analysis, IR-, ¹H-NMR spectroscopy and mass spectrometry. Additionally, to confirm the phase purity and stability of complexes, the original samples were characterized by PXRD. The features of the crystal packaging were determined by X-rays studies. General molecular structure of title complexes are the same and the main differences are in the intermolecular interactions (H-bonds, π-π-interactions).

Upon excitation at 350 nm complexes demonstrate strong emission in blue region. The most interesting results were obtained by studying the photoluminescence of solid samples upon different excitations. When the wavelength of excitation light increases from 360 to 430 nm, the emission maximum also gradually shifts to red-region. Visually, the excitation shift is accompanied by a shift of the color of the emitting of complexes from blue to greenish yellow. Detail TD-DFT analysis of emission origin indicate that red-shifted bands is results of molecular dimers luminescence. Upon the gradual decreasing of excitation energy the molecular fluorescence becomes weaker, while the red-shifted emission of molecular dimers increases. These properties, make title complexes a versatile luminochromic material despite its simple structure.

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SELF-ASSEMBLY OF METAL ORGANIC FRAMEWORKS ON 2D SOLID TEMPLATES

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Substrate-mediated self-assembly is a new strategy which exploits surface effects for tailoring solid surfaces with well-defined supramolecular and hybrid assemblies presenting various functionalities. Herein, we discuss several examples enlightening the application of this concept to the fabrication of stable surface-attached metal organic frameworks (SURMOFs) as films on planar solid supports as well as on dispersed solid particles. We showed that SURMOFs can be assembled from variously substituted zinc porphyrins or PDI derivatives as linkers on surfaces, decorated with graphene oxide (GO). (Fig. 1a) Another new approach was used to fabricate catalytically active supramolecular hybrids on colloidal templates. We describe two types of the SURMOF-based catalysts: (i) the porphyrin-based SURMOF/GO composites obtained in the Pickering emulsions, and (ii) a synergetic catalyst assembled from ZnTCPP and zinc acetate on the particles of layered europium hydroxochloride as anion-exchange 2D template. (Fig. 1b) We showed how to apply a combination of methods including MALDI-TOF spectroscopy for understanding the origin of synergetic effects and the mechanisms of catalysis in these solid-associated supramolecular hybrids.

We believe that our strategies provide a basis for new types of self-assembled coordination structures on solid matrices suitable for their integration with modern planar technologies in chemical sensing, optics, molecular electronics and catalysis.

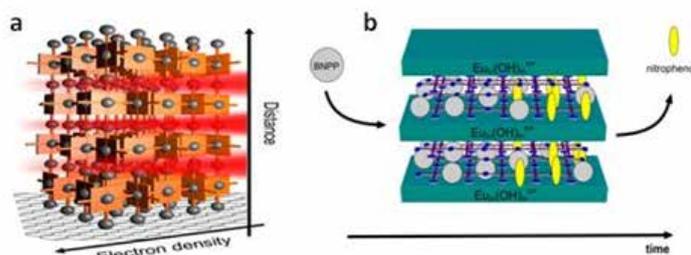


Figure 1. Schematically illustrated (a) structure and distribution of electron density in the SURMOF on the GO-decorated surface and (b) mechanism of the hydrolysis of BNPP catalyzed by the SURMOF-hybrid in acidic solution.

The work was supported by RFBR (grant 18-29-04026-MK) and the Ministry of Science and High Education RF.

COORDINATION COMPLEXES OF METAL PHTHALOCYANINES WITH DIFFERENT PROPERTIES

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Large series of coordination complexes of metal phthalocyanines with different functional ligands was obtained. It is shown that such coordination provides new properties of the compounds.

Complex $[(\text{Bu}_4\text{N}^+)_2\{\text{Sn}^{\text{II}}(\text{Pc}^{3-})\}(\text{cis-indigo-}N,N\text{-}^2\text{-Cp}^*\text{Ir}^{\text{III}})]^{-}; \cdot 0.5(\text{H}_2\text{Indigo})$ contains two functional ligands coordinated to an Ir^{III} center (Fig. 1a). Due to an effective π - π interaction between two ligands, thermally activated charge transfer from $[\text{Sn}^{\text{II}}(\text{Pc}^{3-})]^{-}$ to (cis-indigo- N, N)²⁻ is observed.¹ Coordination complexes of titanium(IV) and indium(III) phthalocyanines with organic dyes indigo, thioindigo and squarylium dye III have been also developed.

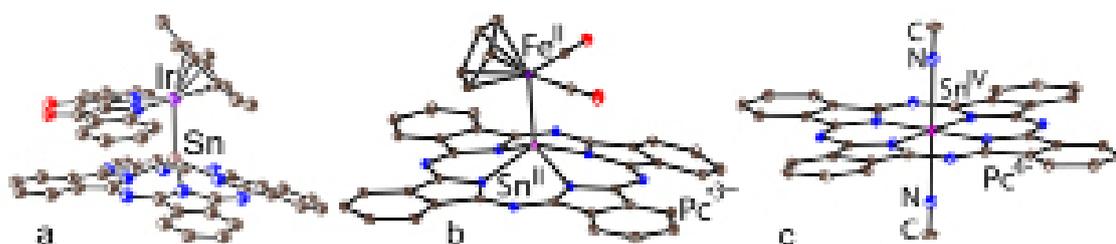


Figure 1. Molecular structures of: (a) $[(\text{cis-indigo-}N,N\text{-}^2\text{-}\{\text{Sn}^{\text{II}}(\text{Pc}^{3-})\})(\text{Cp}^*\text{Ir}^{\text{III}})]^{-}; \cdot 1$ (b) $\{\text{CpFe}^{\text{I}}(\text{CO})_2\text{Sn}^{\text{II}}(\text{Pc}^{3-})\}^0; \cdot 2$ (c) $\{\text{Sn}^{\text{IV}}(\text{CN})_2(\text{Pc}^{4-})\}^{2-}$.

Metal fragments are coordinated to $\text{Sn}^{\text{II}}(\text{Mac}^{2-})$ in series of $\{\text{CpFe}^{\text{I}}(\text{CO})_2[\text{Sn}^{\text{II}}(\text{Mac}^{3-})]\}$ complexes (Fig. 1b). Intramolecular charge transfer from $\text{CpFe}^{\text{I}}(\text{CO})_2$ to the macrocycles is observed and these complexes manifest strong antiferromagnetic coupling of spins with J/k_B up to -110 K.²

Coordination induced charge transfer from Sn^{II} to the macrocycles is observed in the $\{\text{Sn}^{\text{IV}}(\text{L})_2(\text{Pc}^{4-})\}^{2-}$ dianions where $\text{L} = \text{CN}, \text{OCN}^-, \text{Im}^-$ (Fig. 1c for $\text{L} = \text{CN}$). It is shown the effect of cationic surrounding on the orientation of CN ligand and the geometry of tetraanionic macrocycle.

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FROM TRADITIONAL TO SUPRAMOLECULAR CHEMISTRY: CONFORMATIONAL ANALYSIS AND TAUTOMERIC FORMS OF THE SUPRAMOLECULAR SYNTHONS

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Supramolecular chemistry as a field of science emerged as a generalization of traditional chemistry. At the same time, some concepts were naturally adapted with the same or similar meaning. One of the successful examples of such borrowing is the concept of supramolecular synthon — the structural part of the supramolecule formed by a predictable synthetic operation with the formation of intermolecular noncovalent bonds. This concept is widespread in crystal chemistry and crystal engineering, where supramolecular synthons mean associates that are repeated in crystals of compounds with similar functional groups. Typically, the description of the synthon indicates only its dimension (dimer, chain, layer or framework), as well as the type and number of intermolecular bonds in it but does not consider the geometric characteristics. This work is devoted to the generalization of two concepts of traditional chemistry: conformation and tautomeric form — when considering supramolecular synthons of different dimensions in crystals. The possibility of such a generalization is shown by the example of molecular crystals of organic compounds with hydrogen bonds of different strengths.

The study was supported by the Russian Science Foundation (project 19-13-00238).

CRYOGENIC FLUORESCENCE NANOSCOPY OF SINGLE MOLECULES IN SOLID MATRIXES

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Spectroscopy and microscopy of single molecules (SM) in solid matrices¹ is a research direction that has become by now one of the most topical issues in physics, physical chemistry, biophysics and related sciences. Detection of SM fluorescence images can give also their all three spatial coordinates with a subdiffraction (nm) accuracy from the analysis of the point spread function and its modification using the adaptive optics elements. With a large number of SMs this technique (nanoscopy) allows one to reconstruct the structure of the material with *nm*-spatial resolution.

The possibilities of nanoscopy are expanded qualitatively with the detection of spectral (physical/chemical) characteristics of probe emitters. In these experiments, nanoscopy acquires extra "spectral coordinates", which are individual spectral characteristics of nanoprobe, thus makes it possible to carry out a kind of "spectral nanotomography". Especially informative are the zero-phonon spectral lines (ZPL) of single impurity organic molecules (SM), which are reachable at low temperatures. ZPLs are extremely sensitive to static and dynamic local fields as well as guest-host interactions.²

This talk reviews the main possibilities of techniques for detection of SMs at cryogenic conditions³, temporal and spectral characteristics of SMs in different environments⁴. It is shown how the unique ZPL properties can become the basis for a new technique of "multicolor" far-field optical nanodiagnostics of solids and nanostructures, where the reconstruction of the image is carried out by registering the ZPL-fluorescence images and the coordinates for a large number of probe SMs. We also demonstrate a novel approach for mapping the effective local value of the refractive index in solid films and the analysis of related local-field enhancement effects⁵.

The presented studies were supported by DFG, DAAD, RFBR and the Program of the Russian Academy of Sciences №5.

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SELF-ASSEMBLY OF NANOCARBON BOWLS UPON MULTI-ELECTRON ACQUISITION

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Bowl-shaped polycyclic aromatic hydrocarbons (PAHs), also called fullerene fragments and carbon bowls, represent a unique class of π -ligands with both convex and concave faces open and accessible. Corannulene ($C_{20}H_{10}$), mapping a one-third of the C_{60} -fullerene surface, has been broadly used as a key model for structure-property correlation studies of nonplanar aromatic surfaces using a variety of theoretical and experimental methods. This has revealed a very rich redox chemistry of corannulene that can serve as an excellent reservoir for stepwise acquisition of four electrons.¹ Moreover, upon multi-electron charging corannulene demonstrates unique supramolecular chemistry unmatched by planar PAHs.^{2,3} As carbon bowls with different depth, symmetry and sizes become available, this has opened a new broad area of nanocarbon chemistry for investigation. A direct comparison of corannulene with larger carbon-rich bowls will be provided, revealing the effect of framework topology on electronic properties, reduction limits and self-assembly patterns of novel nonplanar PAHs. Supramolecular and host/guest chemistry of new nanocarbon materials such as carbon belts⁴ and wires,⁵ as well as fragments of nanographenes with controlled molecular compositions will also be discussed.

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BODIPYRRINE CONJUGATES WITH AMINOACIDS AND STEROID HORMONES

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In recent years, due to the growing interest in visualization of biological processes in real time (bioimaging), a considerable number of molecular structures have been created that meet the requirements for the implementation of these tasks. The most popular imaging agents today are bodipyrrins (Bodipy), which, unlike coumarin, fluorescein, rhodamine, cyanine and squaraine dyes, are characterized by high chemo- and photo-stability, determined by the kinetic and thermodynamic stability of the boron-containing coordination unit. In this regard, Bodipy attract the attention of researchers in many countries, and the synthetic possibilities of their functionalization, and, accordingly, the “tweaking” of their reactivity and spectral-luminescent characteristics allow you to create connections for specific purposes. Bodipy conjugates with a number of steroid hormones, cholesterol and other biomolecules are currently synthesized; all of them have found application in biology, mainly as selective dyes of cellular organelles. The report presents the results of recent studies by the authors, which are devoted to the chemical modification of Bodipy for the development of methods for non-invasive diagnostics of saliva hormones and the preparation of Bodipy conjugates with various amino acids and steroid hormones. The modeling of structures proposed for synthesis was performed using quantum chemistry methods. The compounds obtained are characterized by the most important physicochemical methods. Reactions testing substances for sensory activity were studied using fluorescence spectroscopy. Detailed results are presented in the report.

The presented results were obtained as a result of the work performed under the RFBR grants (grants No. 18-43-370035 and 18-33-20218).

AGGREGATION WORK AND EQUILIBRIUM DISTRIBUTION OF SELF-ASSEMBLED MICELLES WITH SOLUBILIZATE

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Establishing the relation between the molecular structure of the amphiphiles and their self-assembling thermodynamic and kinetic behavior still stays the actual problem of soft matter physics and chemistry.¹ In this report, we focus on development of an analytical predictive thermodynamic model for aggregative equilibrium of self-assembled nonionic spherical micelles in presence of molecules of hydrophobic solubilizate. Previous thermodynamic models for micellar systems with solubilizates had been considered on the basis of the Tanford model in². However, it should be noted that there is still a need in analytical models for direct nano- and microemulsions, for which the methods of well-developed nucleation and aggregation theory can be successfully applied. The basic part of such models is establishing a minimal work of formation a nonionic micelle as a function of the aggregation number of surfactant molecules and the number of solubilizate molecules in the micellar core. This minimal work determines an aggregative equilibrium distribution. In past,^{3,4} two appropriate analytical models had been elaborated for minimal work of formation of spherical surfactant aggregates as a function of the surfactant aggregation number which were called the 'droplet' and 'quasi-droplet' models of spherical micelles. Here the droplet model for pure micelles is extended to include the dependence on the number of solubilizate molecules in the spherical micellar core. This dependence is present through the size of the micellar core, the hydrophobic contribution due to incorporated solubilizate molecules, through concentration and surface tension contributions and the free energy contribution of the electric double layer of the micellar crown. Depending on parameters of surfactant and solubilizate, the resulting model describes the stable and unstable states for the corresponding emulsion and can be directly incorporated in the kinetic analysis of processes in micellar solutions.⁵

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SELF-ASSEMBLING OF TAPERED DENDRONS ON THE BASIS OF 2,3,4- AND 3,4,5-TRIS(DODECYLOXY)BENZENESULFONIC ACID

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Supramolecular chemistry offers the possibility to design functional materials of highly complex structure by exploiting the self-assembling abilities of the matter. Instead of forcing the required molecular arrangement and macroscopic morphologies by macroscopic techniques, chemical synthesis is used to design molecular shapes and mutual interactions allowing for the spontaneous formation of the desired structures and functionalities (“bottom up” approach). Recently a new class of “cunitic” molecules, 2,3,4- and 3,4,5-tris(alkoxy)benzenesulfonates, became of paramount interest due to an unique richness of their phase behaviour. Such compounds are important examples of self-assembling systems which are extremely sensitive to the state of the environment, because even a slight modification of the shape of a molecule, caused by a change in the functional of its free energy, may significantly alter the shapes of its supramolecular aggregates.

Our investigation of the structure and phase behaviour of alkali 2,3,4- and 3,4,5-tris(dodecyloxy)benzenesulfonate revealed that variation of the volume ratio of the organic anion to the inorganic cation leads to systematic changes in material temperature behaviour. Mesophases of different types and dimensionalities were discovered: 1D (smectic bilayers), 2D (ordered and disordered columnar phases), and 3D (crystalline hexagonal, micellar plastic crystals, low-temperature cubic phase). Phase sequences were represented in the phase diagram, associating the cation size with the temperature behaviour of the material. Cylinders of their ordered columnar mesophase include in their structure central coaxial channels. They are formed by the ordering of focal parts of dendrons. With increasing temperature, thermal motion of the molecules leads to the closing of the central cylinder channel. Such effect may open a way for the creation of ion-selective membranes with temperature controlled channels. The inner structure of the columns in ordered and disordered mesophases, as well as temperature of phase transitions, are delicate functions of the chemical structure of dendrons. This allows fine tuning of the structures as well as to exploit the properties to create new kinds of functional materials such as ion-selective membranes.

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SELF-ASSEMBLY OF SILVER COMPLEXES WITH POLYOXOMETALATES

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Polyoxometalates (POM) form a unique field of research at the edge of coordination and supramolecular chemistry. The main feature of this class of compounds is structural versatility producing an infinite possibilities for the synthesis and modification of such compounds. This aspect gives an opportunities to tune the structure in order to get an applications in catalysis, material science, biology or spintronics.

The main synthetic strategy to prepare as POM itself as POM complexes with different heterometals is the self-assembly. In the context of the supramolecular chemistry methods, POM offer many advantages (stability, uniform charge distribution over a large surface, the ability to form large number of hydrogen bonds, etc.) for the assembly into hierarchically ordered materials through both strong ionic or covalent and weak non-specific and specific interactions. Study of the self-assembly using new building blocks based on POM shall open access to unknown complex structures with interesting chemical, electrochemical, optical, magnetic, contrast, catalytic, etc. properties. In this field preparation of Ag^+ complexes with POM is very attractive for their potential applications in non-linear optical materials, molecular wires, organic light-emitting diodes (OLEDs) and photo-luminescent materials. Recent progress has proved that POM-based silver compounds have antibacterial properties, which are mainly ascribed to the Ag component.

In this research a set of new POM complexes with Ag^+ and $\text{Ag}(\text{C}_2\text{R})$ derivatives has been prepared and characterized by different techniques, their luminescent properties have been studied.

This work was supported by RFBR (grant number 18-33-20067).

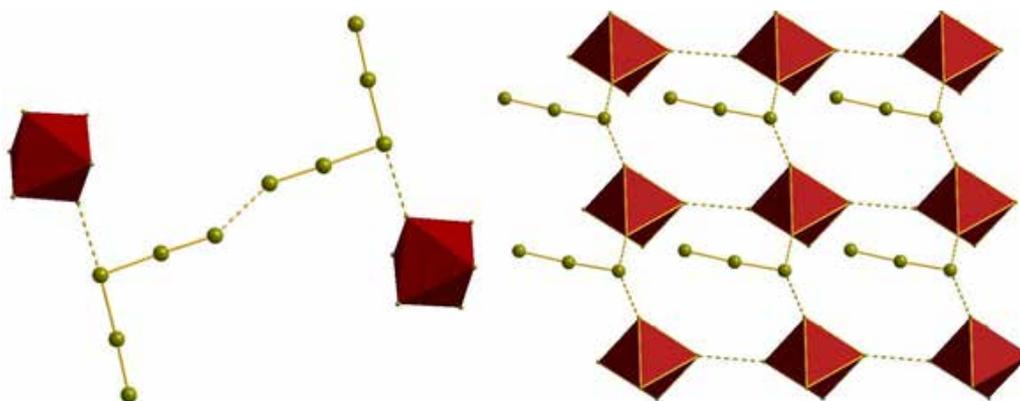
HALOGEN-RICH COMPLEXES OF SB, BI AND TE: HALOGEN BONDING-ASSISTED FORMATION OF EXTENDED SUPRAMOLECULAR FRAMEWORKS

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Halide complexes of p-block elements attract an interest due to their optical properties and possible applications in photovoltaics. During our studies of bromobismuthates (III), we have found that reactions of general scheme “[BiBr₆]³⁻ + Br₂ + (cation)Br_x” in HBr solutions may result in anionic polybromide Bi(III) complexes where {Br₂} units are connected with bromide ligands of Bi(III) coordination sphere via halogen bonding, yielding in {Br_x}_y-type polymeric ligands. In some cases, there also form tribromide {Br₃}⁻ ligands coordinated to bismuth atoms. The structure of anionic part strongly depends on the nature of cation used in reaction. Mixed-halide complexes – polybromide-chlorobismuthates and polyiodide-bromobismuthates – may be obtained by similar straightforward synthetic approach. Related polybromide- or polyiodide-bromotellurates (IV) can be obtained as well; in all cases, those consist of mononuclear [TeBr₆]²⁻ and {X₂} (X = Br, I) dihalogen building blocks. For antimony, similar reactions in presence of Br₂ proceed in more sophisticated way, usually resulting in formation of bromoantimonates (V), sometimes accompanied by polybromide units (Figure 1).



In presence of I₂, there form polyiodo-bromoantimonates (III), revealing several additional structural types, including those where Sb atom is 5-coordinated (pyramidal environment).

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LYSOZYME-SURFACTANT SELF-ORGANIZATION AT THE AQUEOUS-AIR AND AQUEOUS-XYLENE INTERFACES

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Lysozyme is a globular antimicrobial enzyme that forms part of the innate immune system of animals. Being a component of the mucous membranes, lysozyme contacts with substances, including drugs, that enter the body. In present work we investigated the coadsorption and complex formation of lysozyme with ionic (SDS, DTAB, Myramistin) and non-ionic surfactants (Brij-35, pluronic P123, L121 and F127) at the aqueous-air and aqueous-organic liquid interfaces as a model of cellular membrane.

To determine the amount of lysozyme and surfactant in the composite adsorption layer at the liquid-liquid interface we used liquid scintillation spectrometry of tritium as scintillation phase method and tritium labeled compounds, that were obtained by means of tritium thermal activation method. In the adsorption experiment tritium label was included either in protein or in the surfactant molecule. Such approach allowed to measure surface concentration of one the compound on the background of the other.

The decrease of protein concentration at the aqueous-xylene interface was observed in presence of the surfactants. Interaction parameters were calculated from adsorption isotherms for protein and surfactant in the mixed adsorption layer and interfacial tension isotherms. On the basis of the values of the adsorption parameters the composition of the adsorption layer at the aqueous air interface was calculated.

The mixed adsorption layers formed on the aqueous-air interface were subjected to atomic tritium bombardment and tritium distribution in the protein amino acids residues were analyzed. Based on the supposition about the availability of amino acids residues to the interaction with atomic tritium the structure of the adsorption layer was suggested.

This work was supported by Russian Foundation for Basic Research (grant # 18-33-20147)

SYNTHESIS OF HYDROPHOBIC OIL SORBENT BASED ON CALCIUM MONOSILICATE

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In this work a complex approach for synthesis of hydrophobic oil sorbents based on highly water-repellant template (polymer latex) is presented. Our approach is based on combination of two methods of “wet” synthesis of inorganic materials. In that case, sol-gel technology ensures formation of inorganic basis of the material, the framework in the form of amorphous calcium silicate (xonotlite) and template synthesis allows introducing into its volume the waterproofing admixture in the form of template, which is the colloid solution – dispersion of micelles of “core-shell” type of exact size and spherical shape (Fig. 1).

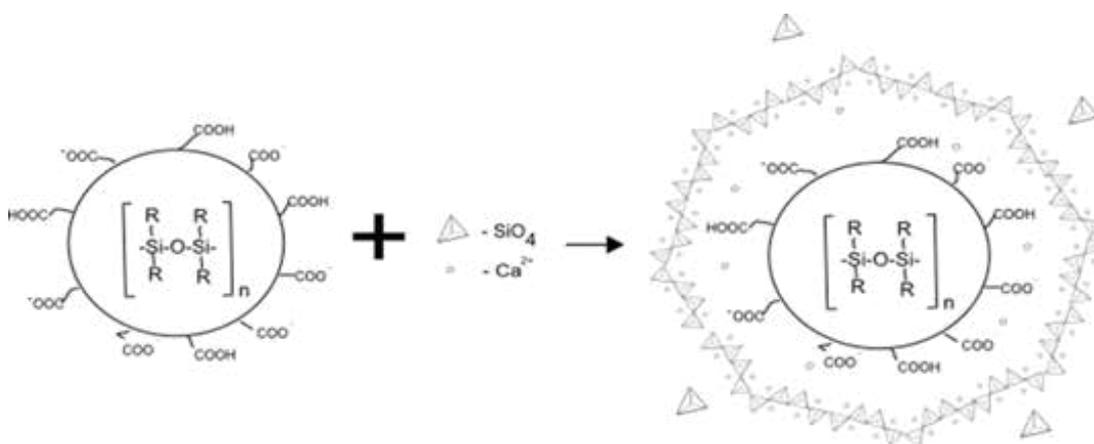


Figure 1. General scheme of synthesis of hydrophobic sorbent based on calcium monosilicate, containing polymer latex.

The work assessed the physicochemical properties of the resulting hydrophobic oil sorbent. It was established that the sorbent structure is characterized by the presence of micro- and nano scale porosity (the specific surface area is 130 m²/g). The degree of hydrophobicity of the sorbent was measured, it was shown that it's wetting angle (or contact angle) with water is 132.9 °, which it classifies as hydrophobic.

Suggested approach will ensure fabrication of silicate sorbents for oil products removal and their efficiency will be determined mainly by their hydrophobic properties.

The work was supported by the Russian Foundation for Basic Research, project № 19-03-00119

RATIONAL DESIGN, STRUCTURE AND CHARACTERIZATION OF A NEW NICKEL(II) PORPHYRYNYLPHOSPHONATE METAL-ORGANIC FRAMEWORK

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Development of the efficient approaches towards new metal-organic frameworks (MOFs) with promising proton-conducting properties is a great challenge of the modern science for the creation of novel functional materials. Porphyrinylphosphonates as an organic moiety of MOFs are of particular interest owing to their thermal and chemical stability along with the high tendency of the phosphonate groups to bind various metal cations. Previously we reported an original pathway towards new porous MOF based on nickel(II) *para*-phosphonatophenylporphyrinate (IPCE-1Ni), possessing a high value of proton conductivity of $1.55 \times 10^{-3} \text{ S cm}^{-1}$ at 75 °C and 80% RH.¹

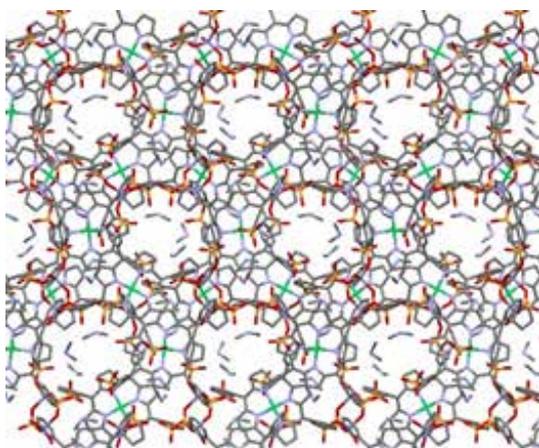


Fig. 1. Fragment of the crystal structure of IPCE-2Ni.

Here we report on the design, structure and characterization of a new MOF based on *meta*-substituted nickel(II) porphyrinylphosphonate, $[\text{Zn}_3(\text{Ni-H}_6\text{TPPP})(\text{Ni-H}_3\text{TPPP})(\text{Ni-H}_2\text{TPPP}) \cdot 7(\text{CH}_3)_2\text{NH}_2 \cdot \text{DMF} \cdot 6\text{H}_2\text{O}]$, IPCE-2Ni. The binding of partly deprotonated phosphonate moieties of porphyrin molecules with zinc cations resulted in formation of a new unique 3D structure with 1D open channels along with the *b* axis, which have a smaller diameter in comparison with IPCE-1Ni and, therefore, could effect on proton-conductive properties of this material. Dimethylammonium cations are trapped in the channels of lattice and compensate a charge of the framework. The structure determination and the chemical composition of IPCE-2Ni were proved based on the data of elemental and TGA analysis, X-ray photoelectron spectroscopy, single-crystal and powder X-ray diffractions. This work was supported by the Russian Foundation for Basic Research (Grant №18-29-04036 mk).

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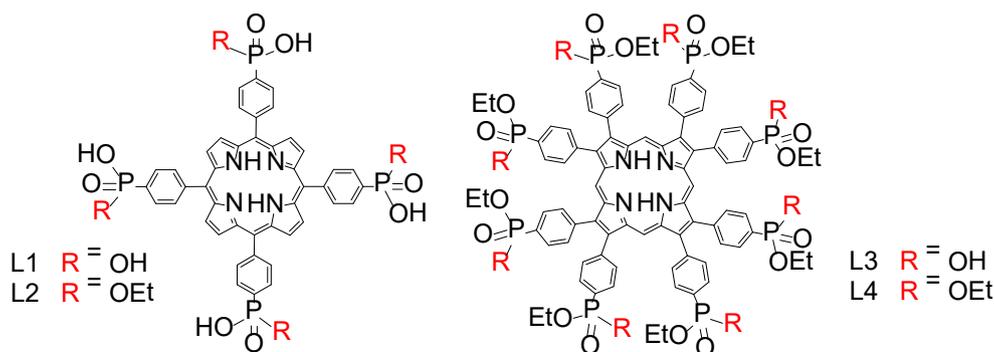
NANOSTRUCTURED OPTICAL SENSORS OF VARIOUS TYPES BASED ON TETRA- AND OCTA-SUBSTITUTED PORPHYRYL PHOSPHONATES

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Porphyrins are promising compounds for the development of sensors for detection trace amounts of toxic metal cations in aqueous environments. In this work, the effect of the composition and number of receptor groups on the analytical characteristics of ligands for binding of toxic metals cations in aqueous solutions and in organized ultrathin films on liquid and solid substrates was studied.



Colorimetric and fluorescent sensors, as well as polymer films selective for copper and lead cations in aqueous solutions based on water-soluble tetrasubstituted porphyrin (L1) were created. Polymer films of porphyrin L1 in a composition with agarose are capable of detecting copper cations in aqueous solutions up to 10^{-9} M, which are almost 2 decimal orders lower than the MPC of copper cations in drinking water (1.6×10^{-7} M). Increasing the number of peripheral receptor groups from four to eight (porphyrin L3) allowed one to create a fluorescent sensor for determination of copper cations in aqueous solutions with absolute selectivity. For a monolayer of octa-substituted porphyrin L4 on the surface of deionized water, a reversible switching of the optical characteristics in the “compression-expansion” cycles was detected, which is explained by the change in the film's aggregation state. Nanostructured thin-film sensors on the surface of a liquid or solid substrate for determination of copper cations in aqueous solutions were created based on organized planar systems of porphyrins (L2 and L4).

This work was carried out in the frame of the International Associated French–Russian Laboratory of Macrocyclic Systems and Related Materials (LAMREM) of CNRS-RAS. The authors thank Russian Foundation for Basic Research for financial support (project № 17-53-16018).

CRYSTAL STRUCTURES, OPTICAL AND MAGNETIC PROPERTIES OF RADICAL ANION SALTS BASED ON METAL PHTHALOCYANINES

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Metal phthalocyanines (MPcs) are promising components for the development of conducting and magnetic compounds. Generally such compounds are obtained by oxidation of MPcs. Essentially less attention was paid to reduced MPcs because of their air sensitivity.

We have developed a method of the reduction of MPcs and obtained a series of salts with radical anions of $\{M(\text{Pc}^{\cdot-})\}^-$, where $M = \text{Cu}^{\text{II}}, \text{Ni}^{\text{II}}, \text{H}_2, \text{Sn}^{\text{II}}, \text{Pb}^{\text{II}}, \text{Ti}^{\text{IV}}\text{O}, \text{V}^{\text{IV}}\text{O}, \text{Al}^{\text{III}}\text{R}, \text{Ga}^{\text{III}}\text{R}, \text{In}^{\text{III}}\text{Br}$ and $\text{Sn}^{\text{IV}}\text{Cl}_2$ as single crystals.^{1,2} Radical anions of MPcs have $S = 1/2$ spin state, whereas those with Cu^{II} and V^{IV} additionally containing paramagnetic Cu^{II} and $\text{V}^{\text{IV}}\text{O}$ metals have two $S = 1/2$ spins with relatively weak intramolecular magnetic coupling.^{1,2} Depending on axial substituents, $\{M(\text{Pc}^{\cdot-})\}^-$ can have isolated (no substituents), dimeric (one substituent) or layered (two substituents) arrangements. Magnetic properties of the salts with the $[\{\text{M}^{\text{IV}}\text{O}(\text{Pc}^{\cdot-})\}^-]_2$ dimers (Fig. 1a) are defined by the size of the counter cations. Bulkier cations provide larger shift of the $\text{Pc}^{\cdot-}$ macrocycles in the dimers and weaken magnetic coupling of spins from very strong ($J/k_B = -256$ K) to nearly the absence of such coupling. Transition from one- to two-dimensional layers enhances magnetic coupling of spins in the salts with the $[\text{Sn}^{\text{IV}}\text{Cl}_2(\text{Pc}^{\cdot-})]^-$ radical anions (Fig. 1b). This work was supported by RSF Grant №. 17-13-01215.

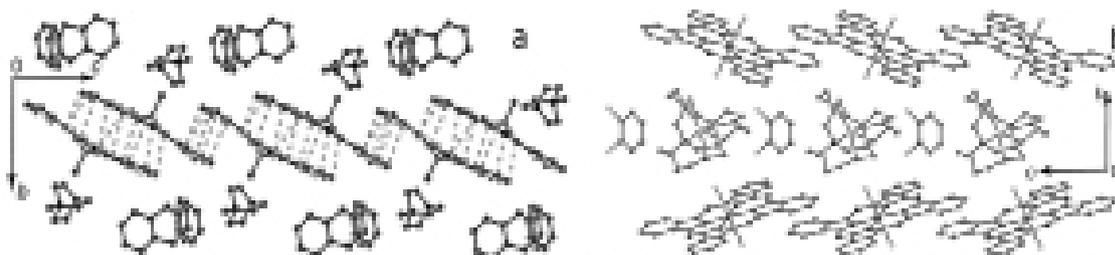


Figure 1. View along the: (a) layers composed of the $[\{\text{Ti}^{\text{IV}}\text{O}(\text{Pc}^{\cdot-})\}^-]_2$ dimers; (b) layers from the $[\text{Sn}^{\text{IV}}\text{Cl}_2(\text{Pc}^{\cdot-})]^-$ radical anions

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METAL-ORGANIC COORDINATION POLYMERS BASED ON RHENIUM CLUSTERS AND RARE-EARTH METAL CATIONS

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Synthesis and investigation of coordination polymers and metal-organic frameworks are of the most intensively developed areas of modern inorganic chemistry. These compounds provide a unique opportunity to utilize the properties of metal-based building blocks forming crystalline solids with various extended structures. In recent years, octahedral rhenium clusters $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-3-}$ (Q = S, Se, Te) were intensively investigated as building units for construction of luminescent coordination polymers and liquid crystals.¹ Similar to the mononuclear cyanometallates, they readily form polymeric compounds with *d*- and *f*-block metals.

We have found that $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-3-}$ clusters form a metal-organic frameworks (MOFs) with lanthanide cations in the presence of multidentate organic ligands. Particularly, reactions in aqueous solution between $[\text{Re}_6\text{Se}_8(\text{CN})_6]^{4-}$ anions, lanthanide cations and furan-2,5-dicarboxylate (*fdc*), thiophene-2,5-dicarboxylate (*tdc*) or selenophene-2,5-dicarboxylate (*sdc*) led to formation of MOFs with a common formula $[\{\text{Ln}(\text{H}_2\text{O})_3\}_2(\text{L})\text{Re}_6\text{Se}_8(\text{CN})_6] \cdot n\text{H}_2\text{O}$ (L = *fdc*, *tdc* or *sdc*).² These compounds display permanent porosity, good CO_2/N_2 selectivity, red luminescence and ability to be reversibly oxidized in solid state. On the other hand, reactions in hydrothermal conditions between $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ anions and lanthanide cations in the presence of isonicotinate led to crystallization of framework polymers containing cubane polynuclear oxo-clusters $\{\text{Ln}_4(\mu_3\text{-OH})_4\}^{8+}$. In all cases, the rhenium clusters act as metal-lolinkers bonding the polymeric chains composed of lanthanide cations and organic moieties. Moreover, cluster fragments act as structure-forming functional building blocks stabilizing the resulting frameworks.

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IDEAS OF SUPRAMOLECULAR ORGANIZATION AS A BASIS FOR STRUCTURAL DESCRIPTIONS OF SOME LIQUIDS

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As a rule, supramolecular organization in liquids is illustrated by formation of large but rather compact groups of molecules such as various micelles¹ that lead to heterogeneity of solutions. However, there are experimental reasons for the assumption that presence of one or more components may result in similarity of extensive structural elements in macroscopically homogeneous liquids (microheterogeneity at molecular level in these liquids is often subject to discussion). It was proposed to name these structural elements as supramolecular motifs². In my opinion, the most structurally determined of them is so-called "water" motif in aqueous solutions with low molar concentrations of non-charged organic compounds (this motif is a framework of water molecules connected by cooperative hydrogen bonds). The analysis of concentration dependences of molar compressibility may be used for its revealing².

Comparison of various supramolecular motifs formed due to hydrogen bonds and aggregations of halogen contacts will be presented in the report on the basis of experimental data and molecular dynamics simulations.

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COMMON FEATURES OF HALOFORM–METAL HALOGEN BONDING

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Halogen bonding (XB) being analog of much more studied hydrogen bonding is actively investigated as a tool for supramolecular chemistry, crystal engineering, and catalysis. Most of XB studies involve organic species, but utilization of organometallic compounds as XB acceptors is interesting for the design of new materials.

In this report, we generalize our results [1–3] about unique R–X⋯M metal-involving halogen bonding (Fig. 1), which was found in a large series of single-crystal XRD characterized adducts, containing halide dialkylcyanamide complexes trans-[MX₂(NCNR₂)₂] (M = Pd, X = Cl, R₂ = Me; M = Pt, X = Cl, Br, I, R₂ = Me₂, Et₂, (CH₂)₄, (CH₂)₅) and halomethanes taken as XB donors.

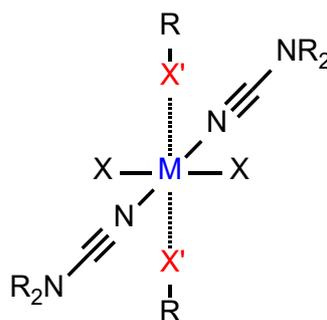


Fig. 1 Common features of the R–X⋯M XBs

We believe our observations may be useful for the mechanism of the haloalkanes oxidative addition to platinum and palladium centers, which is important step for C–C cross-coupling (Suzuki, Heck, Sonogashira, etc.).

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NONLINEAR OPTICAL PROPERTIES OF METAL FREE AND NICKEL BINUCLEAR PHTHALOCYANINES

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Considerable efforts have been dedicated to the synthesis of novel phthalocyanines (Pcs), with the aim of improving their functional properties. Monomeric and low symmetry Pcs have been largely studied with the aim of optimising their second order nonlinear optical (NLO) properties for applications in practical area such as telecommunication systems, high speed electro-optic switching, data processing and optical limiting¹⁻³. This work employs the open and closed Z-scan aperture technique to comparatively study the nonlinear optical (NLO) properties of nickel and metal free 4-tert-butylphenoxy phthalocyanine, biphenyl bridged bis-4-tert-butylphenoxy phthalocyanine and naphthalene bridged bis-4-tert-butylphenoxy phthalocyanine, see Figure 1.

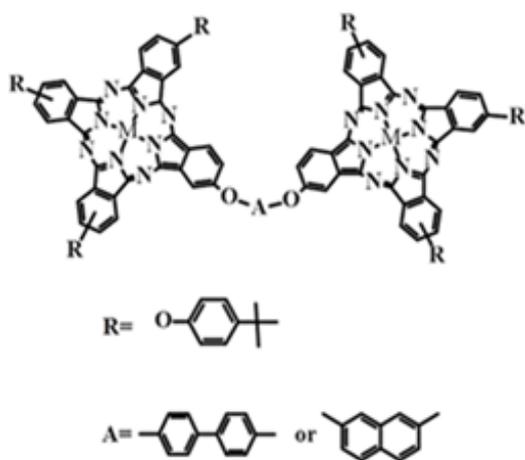


Figure 1: Binuclear phthalocyanine

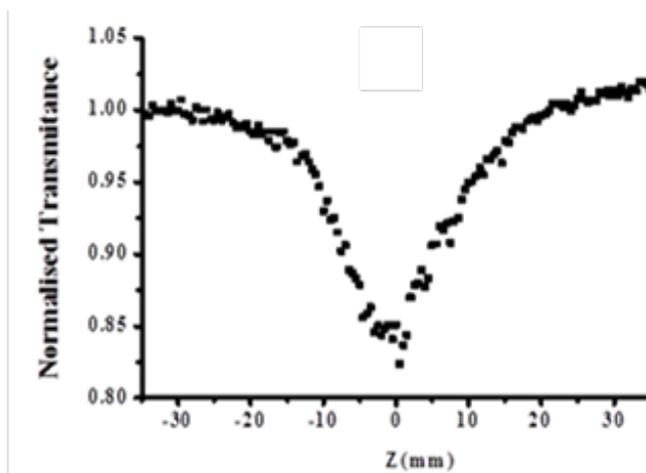


Figure 2: Open aperture Z-scan trace

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DIPYRRINCOORDINATIONCOMPOUNDS: MECHANISMS FOR THE FINE TUNING OF SPECTRAL CHARACTERISTICS

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Molecular sensorics is one of the most promising and dynamically developing area in modern chemistry. The main requirement in the design of new molecular sensors is the possibility of implementing various mechanisms of the sensor response to changes in the nature of the molecular environment. In this regard, the fluorescent molecular sensor has a significant advantage due to the wide variety of possibilities for customizable and selective changes in the properties of sensors. Among organic luminophores that act as sensors, it is worth to highlight the coordination compounds of dipyrrens, which, combining good spectral characteristics, the possibility of synthetic modification of the dipyrren core and a wide variety of mechanisms for controlling optical properties, are currently used as components of optical converters, therapeutic agents, analytical sensors of cations, anions and small molecules.

The report highlights the results of the authorsteam on the design and synthesis of structures based on complexes of dipyrrens with boron (BODIPY), as well as fundamentally new complexes of dipyrrens with phosphorus (PODIPY). A comparative analysis of approaches to the synthesis and isolation of compounds. The spectral and photophysical characteristics of the studied complexes are examined in detail under the variation of the nature of the molecular environment, temperature, viscosity, and the concentration of compounds in solution. The influence of the central atom, manifestation of the effects of fluorescent molecular rotors by the compounds, the ability to control the aggregation equilibrium in the solution for fine-tune of the spectral properties, as well as the practical application of the compounds under study as sensors of biological molecules and environmental parameters are discussed.

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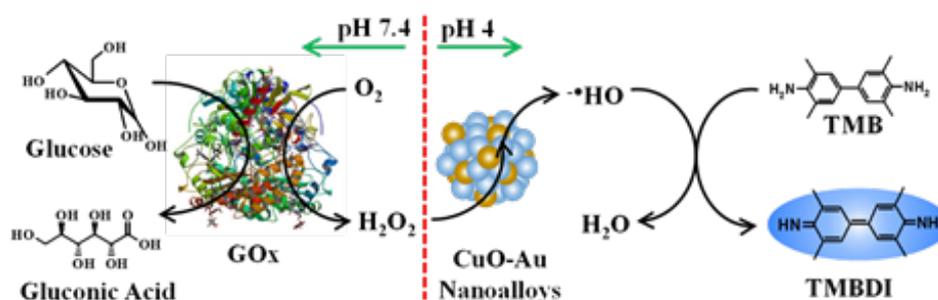
NANOMATERIALS AS ENZYME MIMETICS THEIR PREPARATION AND COLORIMETRIC DETECTION OF DISEASE BIOMARKERS

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Nanomaterials have at least one dimension between 1 – 100 nm and they possess intrinsic peroxidase-like properties [1-3]. As artificial enzymes, nanomaterials overcome various natural and synthetic enzyme limitations (such as biological enzymes inherent instability in extreme environmental conditions). Metallic nanomaterials, on the other hand, have high efficiency as artificial nanoenzymes and this is attributed to low cost of preparation, stable to biodegradation, and are less prone to environmental denaturation [3]. Nanomaterials can withstand extreme pH conditions and temperatures that affects natural enzymes [4, 5]. Several nanomaterials have been prepared and investigated their enzymatic properties. The prepared nanoenzymes consist of metal oxides and bimetallic nanoparticles (as alloys) for the colorimetric detection of disease biomarkers such anti-P53 antibodies for lung cancer diagnosis and glucose for diabetic monitoring. The synthesized nanomaterials are based on copper oxide-gold nanoalloys (for glucose detection) and silica nanoparticles gold-palladium nanoparticles for the detection of anti-P53 antibodies (lung cancer biomarker). Scheme 1 shows the use of copper oxide-gold nanoalloys for the detection of glucose using glucose oxidase (GOx) enzyme. These systems provide both qualitative and quantitative analytical capability and can be used in determining the analytical parameters such as analyte concentrations so that timeous medical interventions can be undertaken. The presentation will cover the synthesis, characterization and enzyme mimetic studies of various nanomaterials and their use in the detection of glucose and anti-P53 antibodies.



Scheme 1: Enzymatic detection of glucose using GOx based on the CuO-Au nanoalloys. The colorimetric assay utilized TMBDI (3,5,3',5'-tetramethylbenzidinediimine) as coloured product.

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STRUCTURAL ANALYSIS OF LAYERED PORPHYRIN-BASED SURMOFS

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Porphyrin-based metal–organic frameworks deposited on surfaces (SURMOFs) are a new class of planar materials with promising properties for applications in chemical sensing, catalysis, and organic optoelectronics. Herein, we studied a series of the SURMOFs assembled from four types of *meso*-carboxyphenyl/pyridyl-substituted porphyrins and zinc acetate on graphene oxide template monolayers via layer-by-layer deposition. The layered structures of the obtained thin films can be hardly described by a common XRD techniques, since they are well textured, *e.g.* all crystallites usually have similar orientation. Applying the D'yakonov method,¹ which has been previously used for the extraction of self-convolution of electron density in clay minerals, allows to analyze the experimental diffraction patterns of the SURMOFs: maxima of the calculated function correspond to the distribution of an electronic density (Fig. 1)²

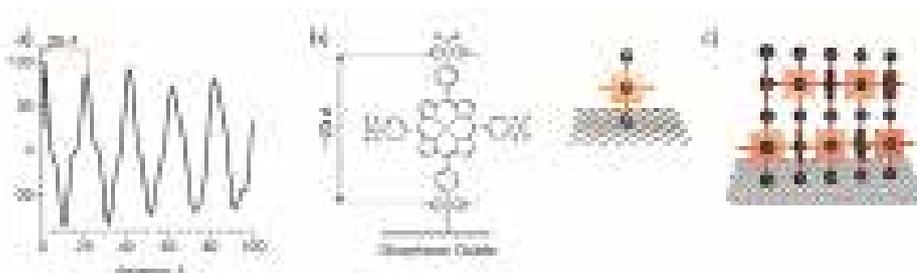


Fig. 1 Electronic density distribution (a), linear dimension of the organic linker (b) and proposed packing of the obtained SURMOF (c) based on Zn(II) *meso*-tetrapyrrolylporphyrin and Zn(OAc)₂

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ISOCYANIDES AND THEIR COORDINATION COMPAUNDS AS DONORS AND ACCEPTORS OF NONCOVALENT INTERACTIONS

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Noncovalent interactions play an important role in biological, chemical and physical processes due to the ability to control the molecular and supramolecular structure of various systems, starting from the dimerization of water molecules and ending with the protein folding and the formation of the DNA double helix. Currently, the control of the properties of the molecules and the molecular systems by noncovalent interactions is widely applied in biochemistry, medical chemistry, catalysis, material science, crystal engineering, polymer chemistry, etc.

Despite the more expanding range of potential donors and acceptors of noncovalent interactions, there are almost no examples reported of noncovalent interactions involving such class of compounds as isocyanides. In this work, the ability of free and metal-coordinated isocyanides to act as donors and acceptors of various noncovalent interactions was studied, what affects the solubility, supramolecular structure, and conformational stability of the studied compounds.¹⁻³

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(THIA)CALIX[4]ARENES AS VERSATILE MOLECULAR BUILDING BLOCKS FOR DESIGN OF COORDINATION COMPOUNDS OF VARIOUS DIMENSIONALITIES IN THE CRYSTALLINE PHASE

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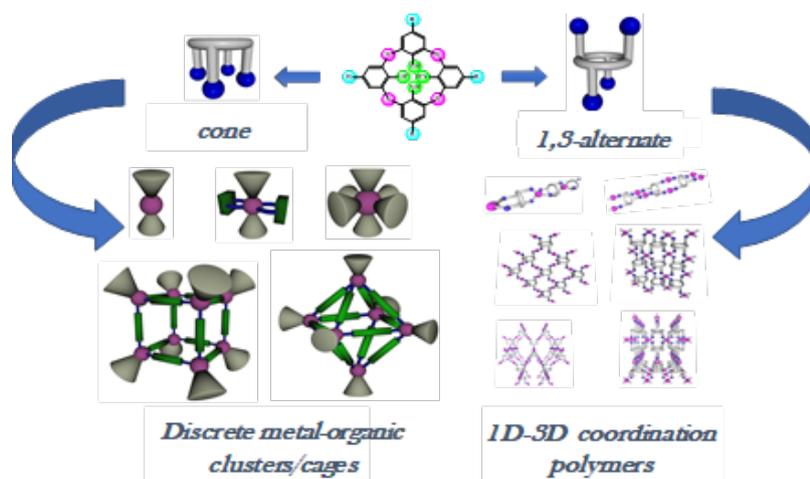
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(Thia)calix[4]arenes present versatile molecular platform extremely adopted for generation of various crystal state supramolecular assemblies. Being fixed in two symmetrical conformations (*cone* or *1,3-alternate*), they can be involved in formation of either discrete cluster-like coordination compounds (cages) or extended coordination polymers while coordinating with metal cations [1-3] (Scheme 1). Controlling on the self-assembly of these compounds by the rational design of (thia)calix[4]arene platform in the crystalline phase in combination of used organic co-ligands may lead to creation of new functional materials which can exhibit attractive physical properties (molecular magnets, photocatalytic activity, etc.) [4].

Here we report the new metal clusters and coordination polymers obtained as a result of the interaction of (thia)calix[4]arenes in *cone* and *1,3-alternate* stereoisomeric forms with *d* and *f* metal cations.



Scheme 1.

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SUPRAMOLECULAR AGGREGATION OF SUBSTITUTED NAPHTHALOCYANINES

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Naphthalocyanines (Nc) attract special attention as π -extended phthalocyanine (Pc) derivatives with absorbance in the near IR range, which affords their application as materials for optoelectronics, nonlinear optics, etc. However, Ncs also possess high tendency to aggregation, which leads to low solubility in organic solvents as well as loss of photochemical activity.

In this work the approach towards the novel type of tetra(15-crown-5)substituted Ncs was developed (Fig.1). It was shown that aggregation of 1H₂, 1Mg and 1Zn, solubility and photostability of these compounds can be controlled by temperature variation or fine-tuned by the supramolecular approach, that leads to soluble cofacial dimers. Interaction of Ncs with potassium salts with further removal of K⁺ ions by [2.2.2]cryptand leads to monomeric forms of crown-Ncs which were found to generate singlet oxygen but this process is also responsible for their fast photodegradation¹.

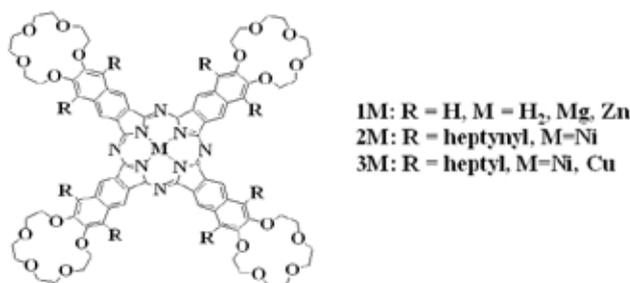


Figure1.

To increase the photostability of Nc, the Ni(II) and Cu(II) complexes with heptyl- and heptynyl-substituted ligands were obtained. The introduction of these substituents into Nc's molecule also leads to increase of their solubility. The investigation of supramolecular assembling of such complexes has shown that more conformationally labile substituents (heptyl- in 2Ni) strongly prevent the formation of cofacial dimers.

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This work was supported by the Russian Foundation for Basic Research (grant #18-33-00887-mol_a).

SILVER NANOPARTICLES STABILIZED BY SORBITAN OLEATE AND CONDUCTIVE COATINGS BASED ON THEM

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Concentrated hydrosols and organosols of silver are one of the main objects in such a field as printing electronics. According to experts, the printing method for electronic components obtaining seems to be more profitable on a large scale. At the moment, many formulas of ink for printed electronics have been developed. But all of them have some disadvantages: low stability, high temperature or incompleteness of the stabilizer decomposition, low metal content. The problems described require a comprehensive solution. Often, improving one of the ink characteristics has a negative effect on the other characteristics.

Despite the obvious shortcomings compared to hydrosols, organosols have several useful advantages. They are often more stable and tolerant to the usage of various organic solvents. In addition, in the case of organosols, electrophoresis can be used to concentrate the nanoparticles without side processes of electrolysis and aggregation. It is important that the stabilizer used (for example, surfactant) was ionic. Otherwise, the nanoparticles will have no diffuse part of the electrical double layer and their zeta potential will be zero. But ionic surfactants often contain difficult-to-remove components, usually sodium and sulfur. It was shown in this work that even with the usage of non-ionic surfactant Span 80 (sorbitan monooleate), the zeta potential of the resulting silver nanoparticles with a hydrodynamic diameter of 15-30 nm can reach very high values (up to 22 mV according to phase analysis light scattering). It is also possible to obtain stable concentrated organosols with a metal content of about 0.5 M using non-aqueous electrophoresis. Mirror-like coatings with high conductivity can be obtained by their thermolysis (2 hours, 200-250 ° C). This is due to the fact that Span 80 has a low thermal decomposition temperature and significant volatility at relatively low temperatures.

This work was financially supported by the Russian Foundation for Basic Research, project code 18-33-00064 mol_a.

NEW CROWN-SUBSTITUTED HETEROLEPTIC DOUBLE-DECKER PHTHALO-OXANTHRENOCYANINATE Tb(III) COMPLEXES

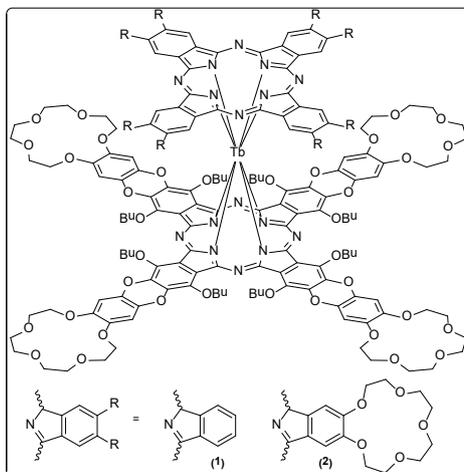
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Single Molecular Magnets (SMMs) are very promising compounds for application in molecular memory storage. These systems are continuously being improved in order to achieve higher energy barriers to magnetic relaxation, and higher magnetic blocking temperatures.

Here we present new crown-substituted double-decker Tb(III) phthaloxanthrenocyaninate complexes 1 and 2, which provide the ability to form supramolecular ensembles in presence of potassium cations, moreover their properties can be triggered by protonation of *meso*-N-atoms in oxanthrenocyanine ligands¹, which can affect their SMM properties.



Both complexes were synthesized from corresponding La(III) bisphthalocyaninates (LaPc_2 or $\text{La}[(15\text{C}5)_4\text{Pc}]_2$) and tetra-15-crown-5-octabutoxy-oxanthrenocyanine with $\text{Tb}(\text{acac})_3$ in chloronaphthalene. Q-bands of these complexes are shifted bathochromically in comparison with homoleptic Tb(III) bis-phthalocyaninates.

It is anticipated that in the presence of potassium ions the complex 1 forms supramolecular dimers, while complex 2 forms supramolecular 1D polymers which might exhibit enhanced SMM properties.²

This work was supported by the Russian Science Foundation (Grant 18-73-10174).

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KNOWLEDGE BASE FOR THE DESIGN OF COORDINATION COMPOUNDS WITH OXO LIGANDS

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Metal-Organic Frameworks (MOFs) are a subclass of coordination compounds. MOF materials can be used for storage and separation of gases, catalysis, manufacturing of sensors, etc. Therefore, thorough control of the composition, structure and properties of MOFs is necessary. Developing of principles of MOF assembly from structural building units (SBUs)¹ can be one of the approaches to find solution of this problem. Coordination compounds are constructed from SBUs, such as ligands, metal ions or clusters, and outer-sphere particles. To predict the topology of a MOF structure and design of new coordination compounds or MOFs with specified properties, it was interesting to create a reliable knowledge base of the SBU descriptors.

Using the program package ToposPro², we collected a set various descriptors of coordination compounds, ligands or metal centers, such as chemical composition, topological type, charge, coordination number, coordination mode, coordination figure. Beyond that, we used this set for machine classification of ligands and search patterns. To reduce diversity, we examined complexes with ligands that contain only carbon, hydrogen, and oxygen atoms in their composition. In addition, all ligands should form coordination sigma bonds with metal atoms through oxygen atoms. Erroneous, incomplete and disordered structures were not considered. To improve the data quality, we checked the charge balance for all the crystal structures.

7690 structural studies, 6171 crystal structures, and 1279 ligands that differ in chemical composition or molecular graph satisfy the conditions above. The algorithm of angular fingerprints³ was used to determine the shape of the coordination figure of ligands and metal atoms in the underlying net. As a result of the work done, for the first time, the SBUs were classified according to the shape of the coordination figure. As well as some patterns of assembly of the coordination compounds from the SBUs are studied, and the most significant features to predict the topology are highlighted among the SBU descriptors.

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THE ROLE OF THE SURFACE FORCES OF THE SECOND KIND IN THE FORMATION OF REVERSE MICROEMULSIONS

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A reverse microemulsion is a thermodynamically stable macroscopically homogeneous dispersion of a polar liquid in a non-polar one with a densely packed surfactant monolayer at the boundary between them. The dominant viewpoint on the mechanism of formation of such dispersions is based on the assumption that their free energy is determined mainly by the surface integral of some local-curvature dependent interfacial free energy over the boundary between the liquids. However, we have shown^{1,2} that any correct explanation of the thermodynamic stability of reverse microemulsions must consider the so-called surface forces of the second kind, introduced by B.V. Derjaguin to account for disjoining pressure in thin films.

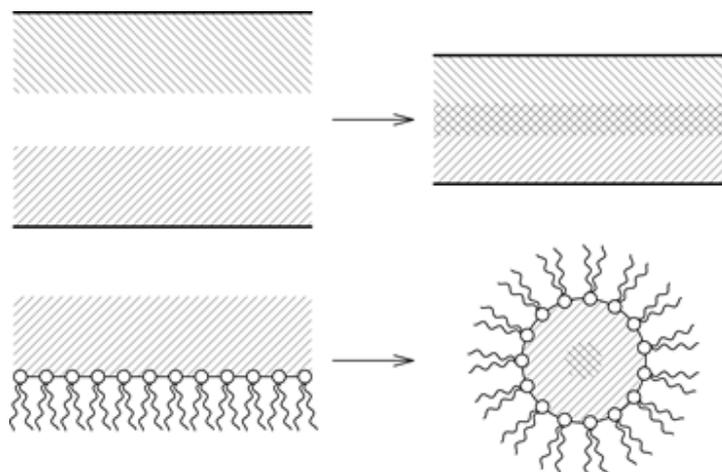


Figure 1. Illustration of the boundary-layer overlap introduced by Derjaguin (top) and of the origin of the surface forces of the second kind in a reverse microemulsion droplet (bottom).

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SELF-ASSEMBLY AND SUPRAMOLECULAR CHEMISTRY OF POLYNUCLEAR RARE-EARTH CARBOXYLATES

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Coordination compounds of rare-earth compounds (REE) are extensively studied and employed for volatile and soluble precursors for inorganic REE-based materials, as emitting layers in OLEDs, as magnetic recording materials. Metal-Organic Frameworks (MOFs) attract a great deal of attention. Their development is limited by the absence of REE-based rigid Secondary Building Units because of structural flexibility of their compounds. During the last 5–7 years, the frameworks with polynuclear nodes $\text{Ln}_4(\text{OH})_4$, $\text{Ln}_6(\text{OH})_8$ or Ln_6O_8 of REE hydroxo/oxo carboxylates have been emerging in the literature. Up to now, only polynuclear hydroxonitrates of REE containing an octahedral core $\text{O}@\text{Ln}_6(\text{OH})_8$ with an oxide anion inside have been studied in detail. These compounds, however, easily disassemble themselves in solution because nitrate anions are weakly coordinated by REE ions and practically do not participate in the stabilization of the octahedral core. In order to organize the flexible REE compound into desired structures and to improve their stability we apply supramolecular chemistry approaches. Namely, hydrophobic interactions, H-bonds and specific packing effects were revealed and designed to promote self-assembly of polynuclear REE carboxylates. A series of isolated molecules (0D), coordination polymers (1D, 2D) and MOF (3D) structures based on $\{\text{Ln}_2(\text{Carb})_{2,4}\}$, $\{\text{Ln}_4(\text{OH})_{2,4}\}$ and $\{\text{Ln}_6(\text{OH})_8\}$ species were synthesized and characterized. Stability of species was studied by DFT simulations with further electron density distribution analysis. Local and non-local structure transformations were studied by means of X-ray diffraction and Pair Distribution Function.

XRD experiments were performed using the facilities of X-ray Structural Center of the A. N. Nesmeyanov Institute of Organoelement Compounds (Moscow, Russia) and XRD1 beamline of Elettra Synchrotron. The quantum chemical calculations were performed using the facilities of the Supercomputing Center of the Moscow State University. This work was financially supported by Russian Science Foundation (grant No 19-73-00277).

THERMODYNAMICS OF INTERACTIONS OF CROWN ETHERS AND CYCLODEXTRINS WITH BIOLOGICALLY IMPORTANT MOLECULES

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Studies on the complexing properties of synthetic macrocycles such as crown ethers and cyclodextrins are of considerable importance for applications and make it possible to simulate molecular recognition processes occurring in biological systems. Low solubility and low bioavailability of some biological molecules make their application difficult. In order to increase the solubility of poorly soluble compounds in water, a complex formation with cyclodextrins and crown ethers can be applied. It is assumed that targeted selection of the solvent will allow creating optimal conditions for selective complexation and solubilization by macrocycles.

Our finding on the effect of H₂O-EtOH, H₂O-DMSO and H₂O-Me₂CO solvents on the enthalpy and entropy of molecular complexations of 18-crown-6 with glycine, D,L-alanine, L-phenylalanine and glycyl-glycyl-glycine on the stability of the resulting complexes and the literature data for related systems were analyzed. The ratios between the thermodynamic parameters of complex formation reactions and the reactant solvation were applied to reveal the key factors that are crucial for the increasing stability of the complexes and the increasing exothermicity of the processes under study in water- organic solvents.

Unlike molecular complexes of crown-ethers with amino acids and peptides, the additions of ethanol to water up to X (EtOH) = 0.20 mol. fr., leads to an decrease in the stability of the molecular complexes between quercetin (QCT) and hydroxypropyl-β-cyclodextrin (HPβ-CD), and benzoic acid (BA) with β-cyclodextrin (β-CD). For the [QCT HPβ-CD] and [BA β-CD] complex formation reactions there are an increase in the exothermicity and a decrease in the entropic contribution to the reaction's Gibbs energy changes. Probably in H₂O-EtOH solvent with 0.2 and more molar fraction of EtOH the replacement of a "guest" in the cavity of CD by molecules of EtOH is presented. In consequence the complexes does not form.

The calorimetric measurements reported in this work were carried out at the Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology (ISUCT) using the equipment of the Centre for Collective Use of ISUCT.

This work was funded by RFBR and VAST according to the research project №19-53-54004.

PLATINUM(II) AND PALLADIUM(II) COMPLEXES WITH ELECTRON-DEFICIENT *MESO*-(DIETHOXYPHOSPHORYL)PORPHYRINS: TUNING OF PHOTOPHYSICAL PROPERTIES BY VARYING PERIPHERAL SUBSTITUENTS

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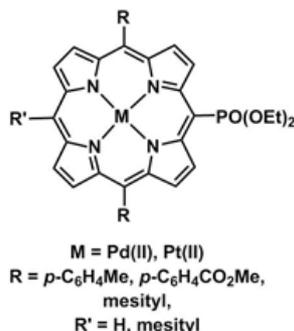
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The photophysical properties (UV-vis, luminescence and excitation spectra, phosphorescence quantum yields (ϕ_{em}) and lifetimes (τ) of electron-deficient Pt(II) and Pd(II) *meso*-(diethoxyphosphoryl)porphyrins and corresponding reference complexes with non-phosphorylated porphyrins were investigated.



The complexes under investigation emit at 298K in the near-IR region (670–770 nm). It was shown that incorporation of phosphoryl group at the *meso* positions of the porphyrin ring results in bathochromic shifts of the absorption (~15 nm) and the emission (~25–30 nm) bands of complexes compared to those of the parent A₂-type porphyrins. The ϕ_{em} for the Pd(II) *meso*-phosphorylated porphyrins lie in the range of 3.4 to 5.8%, with τ of 633 to 858 μ s; Pt(II) complexes exhibit ϕ_{em} in the range of 9.2 to 11%, with τ of 56 to 69 μ s in deoxygenated toluene solutions at 298K. The obtained values are consistent with those known for the most photostable Pt(II) and Pd(II) porphyrinates (PtF₂₀TPP and PdF₂₀TPP) reported so far.^{1,2} The investigation of photostability of complexes together with obtained photophysical data demonstrates the prospect of their studies for the development of molecular oxygen sensors.

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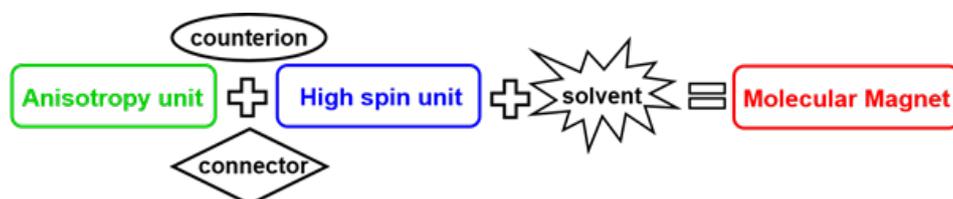
This work was supported by the Russian Foundation for Basic Research, grant number 18-33-00734 mol_a and performed in the framework of French-Russian laboratory – LIA LAMREM.

SELF-ASSEMBLING AND MOLECULAR MAGNETISM

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Molecular magnetism is a relatively recently developed research area that targets the design, the synthesis and the investigation of the magnetic properties of molecular materials. It is actually extended to every magnetic material that can be obtained by using molecular approaches.¹ Not long ago the efforts of the scientists were concentrated on elaboration of low dimensional nanomagnets. Single molecule magnets (SMMs) and singlechain magnets (SCMs) have attracted considerable attention due to low-temperature magnetic hysteresis and fascinating quantum effects, assuming their application in the high-density information storage devices, spintronics and quantum computing.² Magnetic behavior of such quantum objects is determined by an energy barrier U that has to be surmount to reverse magnetization. The value of U for SMM depends on the uniaxial anisotropy energy and total spin of the molecule.³ The first contribution is usually provided by magnetically anisotropic transition metal complex exchange-coupled with a high spin molecule. The target material is obtained in solution by a self-assembly of starting coordination compounds:



In our report, we will analyze the main factors affecting the composition, structure and dimensionality of molecular magnets upon their supramolecular assembling in solution.⁴⁻⁶

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OXIDES AND IODIDES AS STARTING MATERIALS FOR OBTAINING ORIGINAL MOLYBDEN AND TUNGSTEN CLUSTER COMPLEXES

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Recently, it was reported that tungsten trioxide is a new simple precursor for the synthesis of tungsten cluster compounds with a new type of cluster units. The CCN^{3-} (a fully deprotonated form of acetonitrile) was implemented in the tetrahedral tungsten cluster complex of $[\{\text{W}_6\text{O}_2(\text{CCN})_4\}(\text{CN})_{16}]^{10-}$ (I) as a μ_3 -bridging ligand coordinated to the W_3 faces of the W_6 metal cluster. The CCN^{3-} anion formed from cyanide ion in a one-step reaction between WO_3 and KCN under relatively mild conditions (450 °C). A similar cluster complex $[\{\text{W}_6\text{O}_2\text{As}_4\}(\text{CN})_{16}]^{10-}$ (II) with μ_3 - As^{3-} instead of μ_3 - CCN^{3-} was synthesized by an analogous reaction between WO_3 , As and KCN¹.

Further studies have shown that molybdenum trioxide, as expected for a close relative of tungsten, is also able to form a similar tetrahedral complex $[\{\text{Mo}_6\text{O}_2(\mu_3\text{-CCN})_4\}(\text{CN})_{16}]^{10-}$ (III), but the reaction with arsenic results in the only mixed ligand complexes with disordered μ_3 -($\text{As}^{3-}/\text{-CCN}^{3-}$) ligands.

The result of the interaction of MoI_2 with KCN was quite unusual. At 450 °C, a potassium salt with the anion $[\{\text{Mo}_6\text{N}_2(\text{CCN})_4\}(\text{CN})_{16}]^{10-}$ (IV) was obtained, which structure and charge similar are those of III. Replacing the internal ligands $\mu_4\text{-O}^{2-}$ on $\mu_4\text{-N}^{3-}$ did not lead to a change in the charge of the cluster anion, but resulted in a change of oxidation state of metal atoms in the cluster: $\text{Mo}^{\text{III}}_2\text{Mo}^{\text{IV}}_4$ in III and W^{IV}_6 in IV, which compensates the charge change introduced by the ligand environment.

The molecular structures of these compounds were revealed by X-ray single-crystal diffraction and supported by mass spectrometry. Presence of CCN^{3-} ligands was additionally confirmed by ^{13}C NMR, while $\mu_4\text{-O}^{2-}$ ligand was evidenced by ^{17}O NMR spectroscopy.

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DEVELOPING OF THERANOSTIC AGENTS FOR PHOTODYNAMIC THERAPY BASED ON BACTERIOCHLORIN AND NAPHTHALIMIDE DERIVATIVES

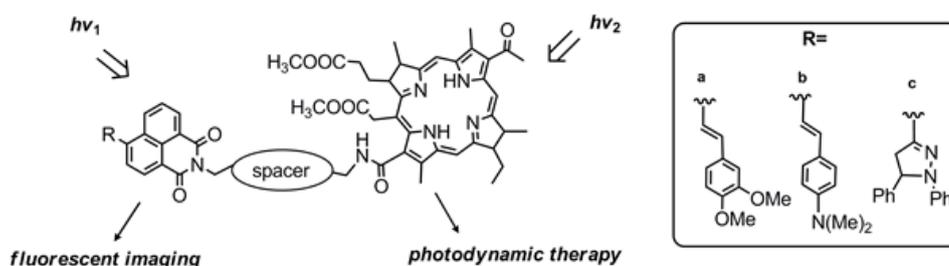
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Photodynamic therapy (PDT) is known to be one of the most perspective and progressing methods of treatment of cancer tumors. In lines of advance of the PDT effectiveness, the design of theranostic agent for both photodynamic therapy and fluorescent tumor imaging seems to be a challenging task.

The aim of this work is the synthesis and photophysical study of conjugates combining two covalently bonded functional fragments: photosensitizer (bacteriochlorin) and fluorophore (naphthalimide), which could be excited by different wavelengths to serve therapy or fluorescent diagnostics.



In this work we propose a synthesis of conjugates by the click-reaction of azide-naphthalimide derivatives and bacteriochlorin-e containing a propargyl group as well as their luminescent properties studying. Photophysical studies revealed that the emission from the naphthalimide chromophore in conjugates was quenched due to Förster resonance energy transfer (FRET) between the photoactive components. The effectiveness of FRET-process was evaluated by steady-state and time-resolved fluorescent spectroscopy, also we esteemed an influence of spacer nature on FRET.

Studying the efficiency of singlet oxygen generation, as well as biological tests conducted on human adenocarcinoma cells, and then in vivo in mice, showed that the resulting conjugates based on bacteriochlorin and naphthalimide are promising therapeutic agents for PDT, since they demonstrate high quantum yields of singlet oxygen, antitumor efficacy and allow to obtain contrast images of cells.

Acknowledgements. We thank the Russian Foundation for Basic Research 18-33-20111.

SUPRAMOLECULAR POLYFUNCTIONAL SYSTEMS: SELF-ORGANIZATION AND PRACTICAL APPLICATION

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Supramolecular systems are of high fundamental and practical importance due to their biomimetic character, nanoscale size, noncovalent nature of intermolecular bonding, versatile morphology, and stimuli responsibility. In our studies, a variety of nano-systems based on single amphiphilic compounds and their multicomponent mixtures with polymer, macrocycles and metal ions were designed, with the correlations 'structure-activity' established. These supramolecular systems are revealed to demonstrate polyfunctional activity as biomimetic catalysts accelerating the cleavage of organophosphorus toxic pollutants, nanocontainers for hydrophobic probes and drugs, nonviral vectors for transfection of eukaryotic cells, viscoelastic compositions, adjuvants, etc.

In biomedical applications much attention is paid to cationic surfactants, which is due to their high affinity to negatively charged biomolecules and biosurfaces, including DNA, intracellular organelles, and cell membranes. Therefore one of key scientific directions is the fabrication of nanocontainers based on cationic amphiphiles, including micelles and microemulsions, nonviral vectors and liposomes modified with cationic surfactants. For this purpose homological series of novel amphiphilic compounds with positively charged head groups were designed and synthesized and their self-assemble behavior studied both in single systems and with biopolyanion added. Special attention was paid to geminis and surfactants bearing hydroxy-groups and cleavable fragments.

Within framework of this study, novel hybrid liposomes functionalized with imidazolium and phosphonium surfactants were fabricated and loaded with drugs of different chemical nature and functionality. These liposomes demonstrated high stability in time, prolonged release of drug, ability of overcoming biological barriers and improved therapeutic effects of formulated preparations compared to free drugs.

This work was supported by the Russian Science Foundation, the project 19-73-30012.

SELF-ASSEMBLY OF SUPRAMOLECULAR WIRES FROM LUTETIUM DOUBLE-DECKER CROWN-SUBSTITUTED PHTHALOCYANINE

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Herein we report a new strategy for fabricating extended conductive nanowires through self-assembly of double-decker tetra-15-crown-5-substituted lutetium phthalocyanine (LuL_2), potassium ions and ceria nanoparticles. The supramolecular structures were synthesized through a two-step procedure. The certain amount of CeO_2 was introduced into the solutions of LuL_2 from their hydrosol to form a layer of ligands on the particle surface. These modified particles act as crystallization seeds, which promote the formation of the supramolecular aggregates. The growth of supramolecular structure then proceeds through a coordination of crown-ether groups of LuL_2 with potassium ions after the adding of metal salt into the system. The as-formed crystalline structures were deposited onto the solid supports via dip coating. The hybrid assemblies were examined by SEM and X-ray methods showing the formation of 1D crystals with ultra-high aspect ratio and length up to 100 microns. The nanowires exhibited better electrical properties than those of previously reported one-dimensional organic nanostructures. We believe that these phthalocyanine-based nanowires might be useful for fabrication of organic electronic devices such as solar cells, transistors and sensing devices.

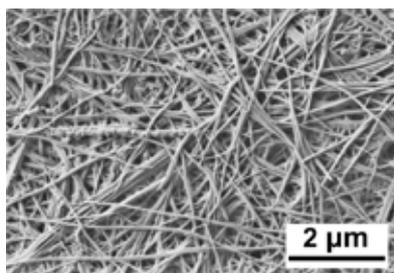


Figure 1. SEM image of phthalocyanine-based wires.

Acknowledgements. The authors wish to thank Russian Foundation for Basic Research (grant mk_18-29-04026), Ministry of Science and High Education RF. X-ray diffraction was performed using the equipment of CKP FMI of IPCE RAS.

FUNCTIONALIZED PYRAZINOPORPHYRINS FOR CATALYSIS

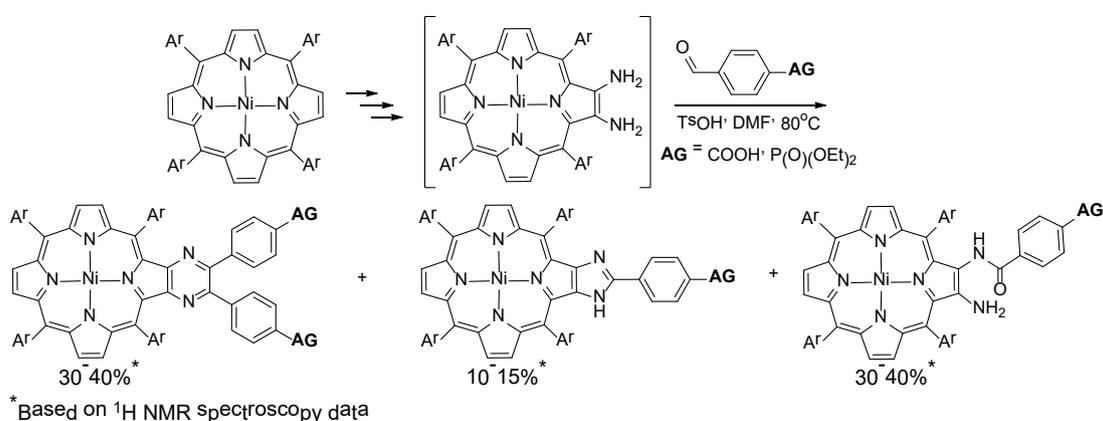
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One of the most promising areas of porphyrin chemistry is the development of novel catalyst for the transformations of organic compounds. Recyclable heterogeneous catalysts prepared by immobilization of active molecules on solid supports attract a special interest. Design of such catalytically active materials implies the introduction of anchoring groups to the periphery of macrocycle. This requires the development of novel synthetic strategies allowing effective functionalization of porphyrin macromolecules.

Recently the synthetic approach towards functionalized pyrazinoporphyryns from 2,3-diaminoporphyryns and aromatic aldehydes was developed by us.¹ Within present work this method was used for the introduction of anchoring group to the periphery of tetraarylporphyryns. Thus, diamino-derivatives were condensed with aldehydes bearing carboxyl or phosphoryl terminal group (Scheme 1). These reactions led to the formation of products mixture that demanded troublesome separation. The alternative synthetic pathway to the target functionalized compounds consists in the modification of precursors bearing 4-bromophenyl substituents using metal-catalyzed reactions.



Scheme 1. Interaction of 2,3-diaminoporphyryns with aromatic aldehydes.

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This work was supported by Council of the President of Russian Federation for support of young scientists (MK-1454.2019.3).

SYNTHESIS OF NEW PHOTOSWITCHABLE MOLECULAR TECTONS BASED ON THIACALIX[4]ARENES AND [1.1.1.1]METACYCLOPHANES IN 1,3-ALTERNATE CONFORMATION AND STUDY THEIR BEHAVIOUR IN SOLUTION

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Design of supramolecular systems is one of the most developing area in modern chemistry. Supramolecular assemblies, molecular networks possessing of translation symmetry in crystalline phase, may be successfully designed by using the molecular tectonics approach based on interaction of molecular tectons – active building blocks capable to molecular recognition. [1]. Organic compounds containing azo groups presents attractive building blocks (so called tectons) for design of photoswitchable molecular networks with controlled physical properties (porosity or luminescence, for example) [2]. Here we report the synthesis of new low rim tetrasubstituted thiacalix[4]arene derivatives adopting 1,3-alternate conformation and containing four carboxyl groups as coordinating sites and azobenzene groups as photoswitchable sites (fig 1). The ability of these compounds to form nanoassociates in solution with d and f metal cations under UV-irradiation have been studied by UV-spectroscopy and Dynamic Light Scattering (DLS) (fig 2).

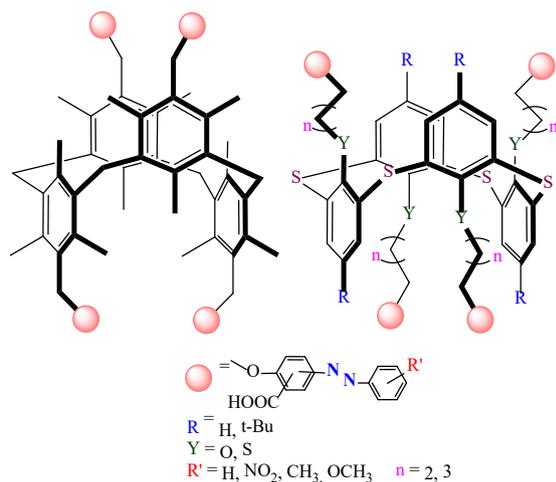


Figure 1

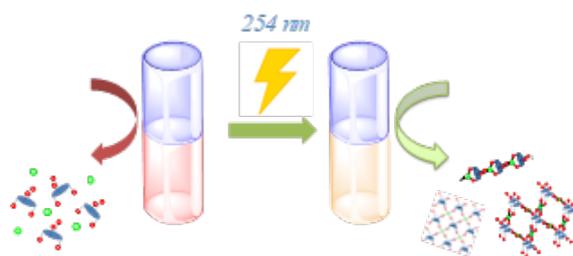


Figure 2

References:

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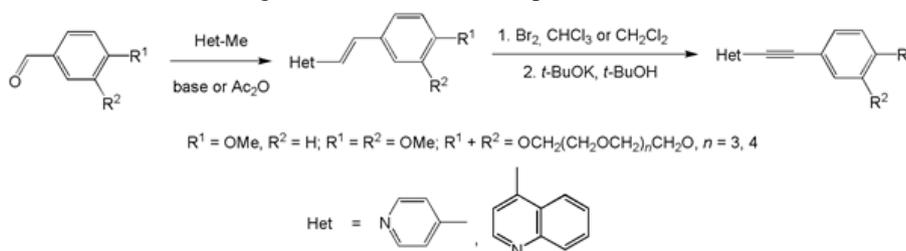
Acknowledgements - This work was supported by the RSF № 17-73-20117.

PHOTOACTIVE CROWN CONTAINING UNSATURATED COMPOUNDS: SYNTHESIS AND SUPRAMOLECULAR COMPLEXES WITH CAVITANDS

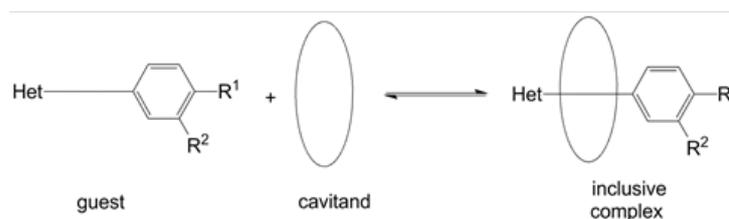
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Unsaturated crown-containing and methoxy-substituted styrylheterocycles of the 4-pyridine and 4-quinoline series were synthesized by condensation of methyl-substituted heterocycles with benzaldehydes in the presence of base. Synthesis of 18-crown-6-containing styrylpyridine by condensation of the reagents in Ac₂O was developed.



A simple and efficient method for the preparation of crown-containing and methoxy-substituted hetarylphenylacetylenes by the bromination followed by dehydrobromination reactions of the corresponding styrylheterocycles.



Complex formation of styrylheterocycles and hetarylphenylacetylenes with macroheterocyclic compounds (cavitands) – β -cyclodextrins and cucurbit[7]uril – was studied by electronic and ¹H NMR spectroscopy methods. It was established pseudorotaxane structure and stability constants of the inclusive complexes of the “host–guest” type.

This work was supported by the RFBR (project № 18-03-00214) and the Russian Science Foundation (project № 19-13-00020).

PROCESSES OF SELF-ASSEMBLING IN SUPRAMOLECULAR SYSTEMS OF N-ACETYL-L-CYSTEIN AND L-CYSTEIN WITH SILVER ACETATE

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Study of supramolecular hydrogels formed by low molecular weight compounds (amino acids, peptides, etc.) has a scientific interest because of biocompatibility, bioactivity and low concentration of the initial components determine a various area of their possible application - pharmacology, tissue engineering, etc. The purpose of this work is to study the processes of self-assembly in supramolecular systems based on the amino acid L-cysteine (L-Cys) and its derivative N-acetyl-L-cysteine (NAC) with silver acetate (AgAcet). It is known that the formation of silver mercaptide (MS) clusters is the first stage in the formation of a gel precursor in the L-Cys-AgAcet system, but the role of the amino and carboxyl groups in the process of structure formation has not fully studied. For this purpose, NAC has been used and using the methods of dynamic light scattering (measurement of dimensions and zeta potential), UV spectroscopy, and viscometry authors have studied the processes of self-assembly in the NAC-AgAcet and L-Cys-AgAcet systems were studied.

It was established that under the same synthesis conditions in systems based on NAC, the relative viscosity (~ 3.5 mPa·s) is in 1.5 times higher than in systems based on L-Cys (~ 2.5 mPa·s). Comparison of electronic spectra shows a different configuration of supramolecular aggregates formed in these systems. The NAC-AgAcet spectra contains an intense absorption bands of ~ 270 and ~ 310 nm, while L-Cys-AgAcet systems have absorption bands of ~ 314 and ~ 390 nm. The results of the DLS shows that the size of the aggregates in the systems varies in a wide range of ~ 50 – 300 nm. The value of the Z potential in the L-Cys-AgAcet system is ~ 60 mV, and in the NAC-AgAcet system is ~ -35 mV. Thus, the role of the amino group in the processes of self-assembling of supramolecular aggregates in the NAC-AgAcet and L-Cys-AgAcet systems is obvious.

The work was performed as part of the implementation of the basic part of the state assignment in the field of scientific activity (Project No. 4.5508.2017 / BC) using the equipment of the spectroscopy laboratory of the Center for Collective Use.

FORMATION OF NANOAGGREGATES IN AQUEOUS SYSTEMS BASED ON GLYCINE-AGNO₃-PVA

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Glycine (Gly) is the simplest amino acid, doesn't have optical isomers, but is the structural materials for all proteins, including the protein of muscles. Glycine plays an important role in adsorption of calcium and performs a protective function in body tissues. The systems based on aqueous solutions of Gly, AgNO₃ and PVA could find an application in medicine, for example for wound healing. In this work self-assembly in different systems based on Gly, silver salt and PVA were studied by means of UV and FTIR spectroscopy, dynamic light scattering (DLS).

A number of samples was prepared from aqueous solutions of PVA (5 and 10%), Glycine (0,01 M), AgNO₃ (0,01 M). Particle size distributions for the systems Gly-AgNO₃-H₂O and Gly-AgNO₃-PVA (0,1%), obtained by means of DLS at equal concentrations of the initial components, shows decreasing the nanoaggregates size from ~390 nm to ~160 upon addition of PVA. That can be explained by various nature of intermolecular interactions between Glycine and PVA. The results obtained by means of UV spectroscopy showed that the self-assembly in the systems depends mainly on composition, concentration, molar ratio of the initial components. In FTIR spectra of the Gly-PVA films with various ratio of the initial components (0,6/0,4; 0,5/0,5; 0,4/0,6; 0,2/0) some differences were observed in the range of 3290-3269 cm⁻¹, 1568 cm⁻¹, 1665 cm⁻¹, which can be attributed to the stretching vibrations of OH groups and deformation vibrations of NH₃⁺ and NH₂ groups, respectively.

Thus, it is found out that self-assembly in the systems based on Gly-AgNO₃-PVA occurs due to intermolecular interactions, in which Glycine connects PVA macromolecular as a flexible linker. Formation of nanoaggregates in the samples depends on concentration, molar ratio of the initial components and time of storage, what can be explained by multiple hydrogen bonding between functional groups of PVA and Glycine.

The work is performed under financial support of the Ministry of Education and Science of the Russian Federation in the frame of realizing of the State task in the field of the scientific activity, project N 4.5508.2017/BP. This work is performed by means of the Equipment Center for collective Use of Tver State University.

SOLUBILIZATION OF DINITROBENZOFUROXANE IN THE SYSTEM BASED ON NEONOL APh_{9,9} IN BINARY SOLVENT DMSO-WATER. PLANNING AND OPTIMIZATION

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The study of the solubility of practically important compounds, the finding of compositions that promote its growth, is an urgent problem, since it significantly simplifies some processes. In this work, as a solubilize, we used 4,6 –nitrobenzofuroxan, DNBPhO, which is attractive in that it belongs to energy-saturated compounds. Its molecules have a certain amount of chemical energy and can specifically interact with surface-active substances. The micellar system neonol, APh_{9,9} –sodium dodecyl sulphate, DSN - H₂O - dimethyl sulfoxide, DMSO - NaCl was chosen as the solvent, where $\alpha \text{ APh}_{9,9} = 0,800$ ($\alpha = C \text{ APh}_{9,9} / C \text{ DSN}$); $C \text{ NaCl} = 0.0216$ mol / l; $\omega (\text{DMSO}) = 0.096$ (9.6%), and the value of the critical concentration of micelle formation, CMC, $3.0 \cdot 10^{-4}$ mol/l. The determination of the solubility was performed by UV spectroscopy by the intensity of the absorption band at 450 nm, A_{450} . To determine the optimal solubility conditions for DNBPhO, we used the response surface methodology and the three-level Box-Behnken plans. In our case, the main factors selected are: mass DNBPhO (X_1), concentration APh_{9,9} (X_2) and mixing time (X_3). The best model in the selected ranges of factors is a second-order polynomial with the value of the coefficient of determination ($R^2 = 1$): As follows from the Pareto chart, the increasing of concentration of APh_{9,9} to a greater extent contributes to the increase in solubility. The mass of DNBPhO and the mixing time give a lesser effect. The analysis of the response surface for the dependence $A_{450} = f(C \text{ APh}_{9,9}; m \text{ DNBPhO})$ the influence of $m \text{ DNBPhO}$ and the concentration of APh_{9,9} has extreme. Before CCM, the A_{450} is smaller than with the formation of micelles. The solubilization of DNBPhO in micelles leads to an increase in the intensity of A_{450} nm. The effect of the mass of DNBPhO is extreme due to the fact that mixed micelles have a certain solubilization capacity. An increase in $m \text{ DNBPhO}$ leads to a redistribution of DNBPhO into a non-micellar medium. The latter is accompanied by a decrease in A_{450} nm. We found the coordinates of the optimal value A_{450} .

EFFECT OF ONE- AND TWO-ELECTRON REDUCTION OF TERBIUM DOUBLE-DECKER PHTHALOCYANINE ON SINGLE-ION MAGNET BEHAVIOR AND NIR ABSORPTION

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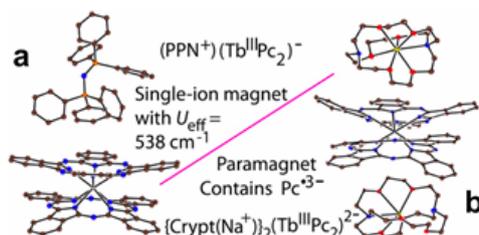
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Deeply reduced terbium(III) double-decker phthalocyanine species depending on the synthetic pathway could manifest either SIM behavior or lowest-energy NIR absorption bands among all the reduced metal phthalocyanines known.

One-electron reduction of $\text{Tb}^{\text{III}}\text{Pc}_2$ by sodium fluorenone ketyl yields $[(\text{PPN}^+)\{\text{Tb}^{\text{III}}(\text{Pc}^{2-})_2\}^- \cdot 2.5\text{C}_6\text{H}_4\text{Cl}_2]$ (1) containing the dianionic Pc^{2-} macrocycles (Fig. 1, a). The compound demonstrates¹ single-ion magnet behavior with a large spin-reversal energy barrier of $U_{\text{eff}} = 538 \text{ cm}^{-1}$, which is noticeably larger when compared with previously studied $[(\text{Bu}_4\text{N}^+)\{\text{Tb}^{\text{III}}(\text{Pc}^{2-})_2\}^-]$ ($U_{\text{eff}} = 230 \text{ cm}^{-1}$).



A stronger $\text{NaCpCo}(\text{CO})_2$ reductant in the presence of an excess of cryptand yields two-electron-reduced $[\{\text{Cryptand}(\text{Na}^+)\}_2\{\text{Pc}^{2-}\}\text{Tb}^{\text{III}}(\text{Pc}^{3-})\}^{2-}]$ (2) containing the Pc^{3-} radical trianionic macrocycle. In addition to the characteristic bands of Pc in the UV and visible spectral range, 2 manifests¹ the lowest energy absorption band in solid-state spectra even in the near IR range at 4700 cm^{-1} (2130 nm).

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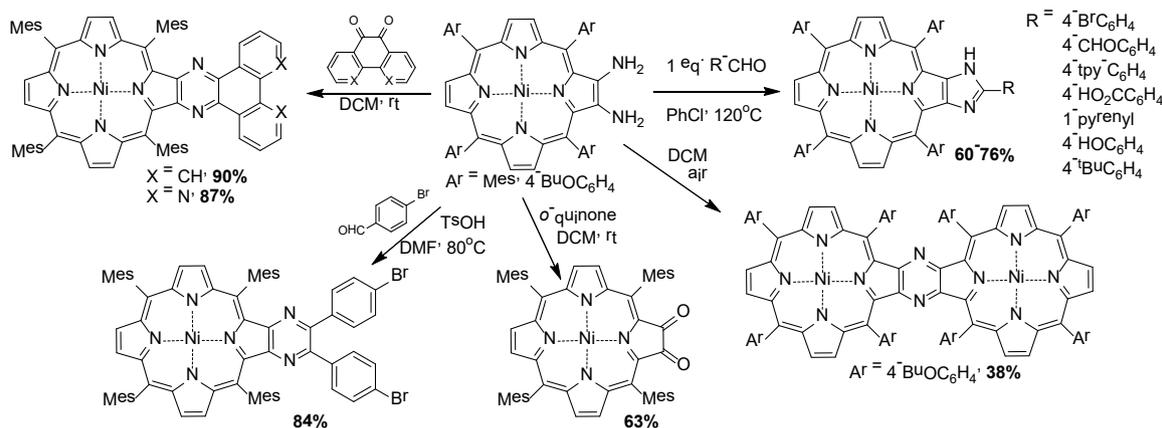
The work was supported by RSF Grant № 17-13-01215, № 18-73-10174 (the synthesis and characterization of TbPc_2)

DIAMINOPORPHYRINS FOR THE SYNTHESIS OF FUNCTIONALIZED DERIVATIVES

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The application of porphyrins in modern research areas requires the development of the efficient strategies for their preparation. Recently we have demonstrated that 2,3-diaminoporphyrins can be converted into functionalized heterocycle-appended derivatives depending on the synthetic conditions.¹ In the present work we have evaluated the scope of this synthetic approach. First, the nucleophilic amination of various 2-nitroporphyrins was investigated, that revealed the possible side substitution processes in the presence of active electrophilic groups in the substrates. In this respect further transformations were performed with porphyrins bearing unreactive peripheral moieties.

The reduction of the 2-nitro-3-aminoporphyrins smoothly provides the corresponding 2,3-diaminoporphyrins. Variation of the reaction conditions allows preparation of a variety of products, namely imidazo- and pyrazine-appended porphyrins, dioxochlorines or pyrazine-fused dimeric species (scheme 1). Thus, the condensation with aromatic α -diones provides the π -extended derivatives. The condensation with aromatic aldehydes allows the preparation of imidazo- or pyrazinoporphyrins. The oxidation by different agents may provide the 2,3-dioxochlorines as well as pyrazine-bridged dimeric porphyrins. Altogether the mentioned transformations testify that despite their low stability 2,3-diaminoporphyrins could be valuable compounds for the design of functional molecules.



Scheme 1. The investigated transformations of 2,3-diaminoporphyrins.

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INTERACTION OF Ag⁺ WITH POLYNUCLEAR MOLYBDENUM OXOCOMPLEXES AND CLUSTERS

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Polyoxometalates (POM) can be formulated as polynuclear metal-oxide anions, built on the basis of metals of groups V and VI in the highest oxidation states. Polyoxometallates are the subject of a large number of studies due to their interesting properties (stability, ease of modification, redox activity, etc.), which lead to their use in many areas, including catalysis, magnetism, electrochemistry, photochemistry, etc. Moreover, they can be considered as inorganic polydentate oxygen-donor ligands, which are able to coordinate different heterometals. Particular attention among complexes of this type deserve POM complexes containing silver. Silver ions are capable of forming various polynuclear compounds based on inorganic templates, which can also be transition metal clusters.

In this research, new materials based on the combinations "silver-POM", "silver-cluster" were obtained. In the case of the interaction $(\text{NBu}_4)_4[\text{Mo}_8\text{O}_{26}]$ with two equivalents of AgNO_3 and two equivalents of various organic ligands ($\text{P}(\text{Ph})_2\text{Py}$, XPh_3 , etc.), complexes containing the anion $[(\text{LAg})_2\text{Mo}_8\text{O}_{26}]^{2-}$ were obtained and characterized by XRD, EA, IR, their luminescent properties were studied. As a result of the reaction $(\text{NBu}_4)_2[\text{Mo}_6\text{O}_{19}]$ with two equivalents of AgNO_3 and two equivalents of $\text{P}(\text{Ph})_2\text{Py}$ in DMF, the complex salt $[(\text{P}(\text{Ph})_2\text{PyAg}(\text{DMF}))_2][\text{Mo}_6\text{O}_{19}]$ was obtained.

As a result of the interaction of molybdenum iodide-nitrate cluster $(\text{NBu}_4)_2[\text{Mo}_6\text{I}_8(\text{NO}_3)_6]$ with six equivalents of tBuSAg and two equivalents of AgNO_3 , a complex based on a polynuclear silver-containing anion and a cluster cation was obtained. Its chemical and photophysical properties are currently being studied.

This work was supported by RFBR (grant number 18-33-20067).

π -HOLE DONOR ABILITY OF FLUORINATED IODOARENES

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Noncovalent interactions play an important role in many advanced areas of modern science spanning from supramolecular chemistry to molecular biology. While amount of studies on hydrogen bonding (HB), halogen bonding (XB), π - π -stacking, and metallophilic interactions is gradually stabilized, many novel types of noncovalent forces including, e.g., anion- π or, more generally, lone pair- π (lp- π) interactions classified in Figure 1 were recognized only recently thus providing a new tool for crystal engineering.

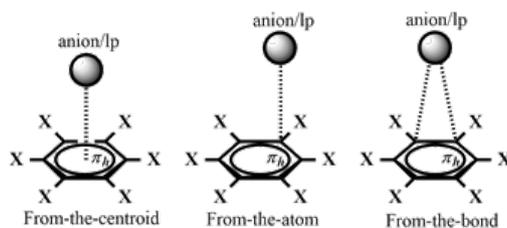


Figure 1. (Anion/lp)- π binding motifs.

In this work, we demonstrated that fluorinated electron deficient iodoarenes (FIBs) such as iodopentafluorobenzene, 1,4-diiodotetrafluorobenzene, and 1,3,5-triiodotrifluorobenzene co-crystallize with square planar platinum(II) and nickel(II) complexes, viz. $[n\text{-Bu}_4\text{N}]_2[\text{Pt}_2(\mu\text{-I}_2)\text{I}_4]$ and $[\text{Ni}\{\text{NH}=\text{C}(\text{NRR}')\text{NN}(\text{O})\}_2]$ ($\text{RR}' = \text{Me}_2$, $\text{RR}' = \text{MePh}$, $\text{RR}' = (\text{CH}_2)_5$), giving supramolecular structures held by several types of weak contacts.^{1,2} Upon analysis of noncovalent forces in the structures of obtained adducts, in addition to rather conventional HBs and XBs, we recognized hitherto unknown (anion/lp)- π interactions involving FIBs acting as π -hole donors. The types of (anion/lp)- π interactions revealed by us represent novel noncovalent bonding patterns involving FIBs and open up an avenue to the focused application of these synthons in supramolecular chemistry as building blocks exhibiting π -hole or mixed σ -hole/ π -hole donor properties.

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THERMOSENSITIVITY OF HYBRID MOLECULAR BRUSHES WITH POLYOXASOLINE SIDE CHAINS

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Polymer brushes with hydrophilic polyoxazoline side chains are perspective for biomedical applications, in particular because they exhibit thermosensitivity in aqueous solutions. To determine the specific parameters of the use of such polymers, it is necessary to study their conformational properties and behavior in aqueous solutions when heated.

This paper compares the characteristics of molecular brushes with an alkylene-aromatic polyester backbone and poly-2-ethyloxazoline (APE-graft-PEOZ) or poly-2-isopropyl-oxazoline (APE-graft-PIPOZ) side chains. The polymerization degree of the main and side chains and the grafting density of the latter for the studied polymers were close.

Molecular hydrodynamics and light scattering methods were used to study samples of the APE-graft-PEOZ and APE-graft-PIPOZ, as well as the lateral linear PIPOZ chain. Their molecular weights and hydrodynamic sizes were obtained. For dilute aqueous solutions of the studied polymers, the dependences of the intensity of light scattering, optical transmission, hydrodynamic radii, and the composition of the scattering particles on temperature were determined. The concentration dependences of these parameters were studied in a wide range of concentrations. It is shown that the phase separation temperature T₁ upon heating of the APE-graft-PIPOZ is lower than T₁ determined for the APE-graft-PEOZ and for the PIPOZ side chain. This is a consequence of higher hydrophobicity of the APE-graft-PIPOZ.

Acknowledgements. This work was supported by the Russian Foundation for Basic Research (Project 18-03-00356_a).

DONOR-ACCEPTOR COMPLEXES OF CYANINE DYES CONTAINING TERMINAL AMMONIUM GROUPS WITH BIS(18-CROWN-6)STILBEN

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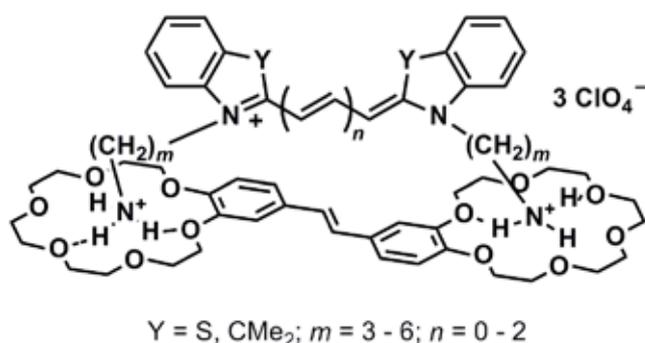
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Self-assembled photoactive supramolecular systems formed by non-covalent interactions attract considerable attention. Cyanine dyes can be employed as light-sensitive components for the design of such supramolecular systems.

We investigated the possibility to construct photoactive "host-guest" complexes based on cyanine dyes as guests and the influence of their structure on the properties of supramolecular complexes.

The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of the dye with crown molecules to form supramolecular complexes.



We demonstrated the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl *N*-substituents using their complexes with bis(18-crown-6)stilbene as an example. It was shown that the components form highly stable bimolecular and relatively unstable trimolecular complexes in which the dye ammonium groups are hydrogen-bonded to the crown ether moieties of stilbene and their π -conjugated moieties are located one above the other. The stability constants for some of these complexes were determined, and the stability of the complexes was shown to depend on the dye structure, in particular, on the geometric matching of components, which is manifested as the distance between the ammonium groups of the dye and the stilbene binding sites.

The synthesized cyanine dyes and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

This work was supported by the Russian Science Foundation (project № 19-13-00020).

N-HETEROCYCLIC TRANSITION METAL COMPLEXES BASED ON AMPHIPHILIC P-TERT-BUTYLTHIACALIX[4]ARENE DERIVATIVES: SYNTHESIS AND CATALYTIC APPLICATIONS

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The idea of creating micellar catalysts that can solubilize water-insoluble substrates and conduct traditional organic transformations in water have attracts much attention of scientist. Thiacalix[4]arene macrocycles and their derivatives are an attractive platform for creating such catalysts. Molecules of thiacalix[4]arenes can be modified by various fragments, which allow the synthesis of combined pre-organized amphiphilic structures, which can form various functional nanosystems used in micellar catalysis.

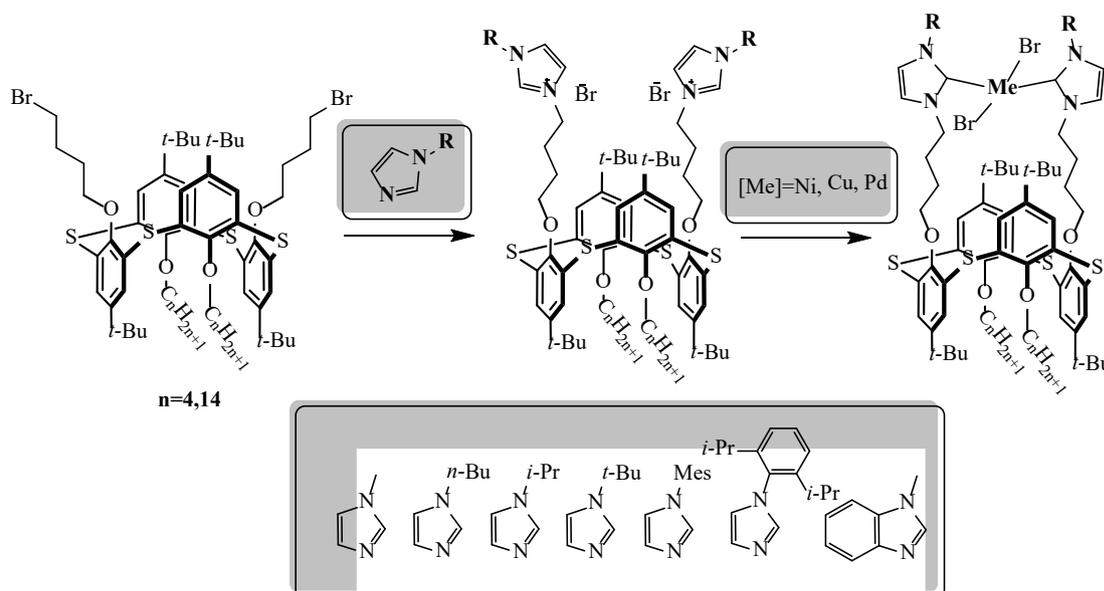


Fig. 1. The general scheme for the preparation of NHC palladium complexes with various substituents.

As a result of this work, an approach was proposed to the synthesis of new palladium complexes based on imidazolium derivatives of *p*-tert-butylthiacalix[4]arene in the stereoisomeric form of *1,3-alternate*, which makes it possible to obtain the target compounds with high yields. Palladium complexes showed high catalytic activity and selectivity in cross-coupling reactions, as well as in the reduction reaction in water-organic systems.

This work was supported by the Russian science Foundation (grant № 18-73-10033)

NEW AMPHIPHILIC NHC-FUNCTIONALIZED DERIVATIVES OF CALIX[4]ARENE AS PROMISING MOLECULES IN METAL COMPLEX CATALYSIS

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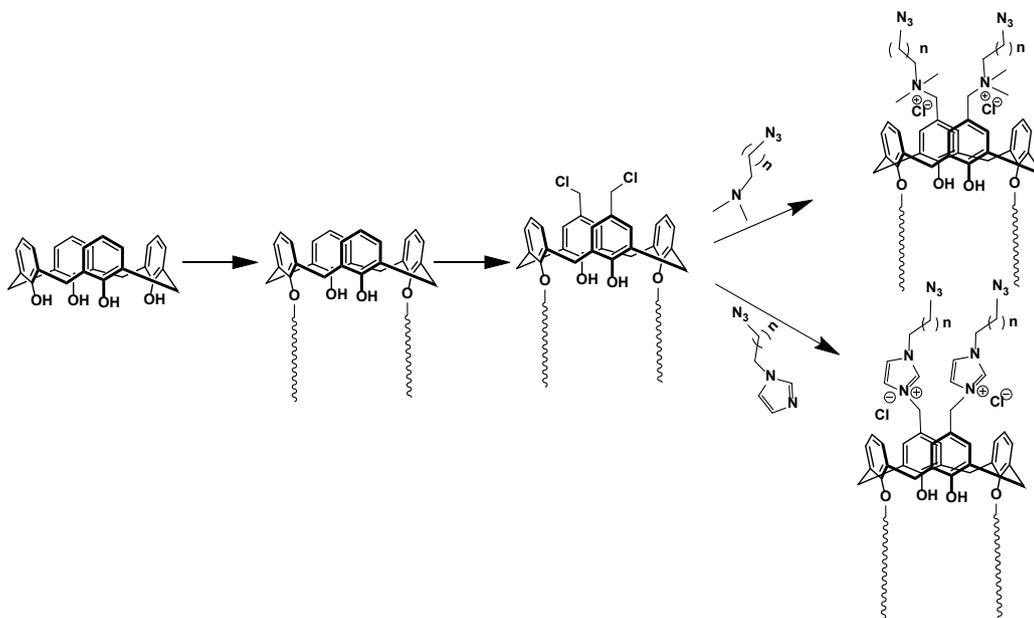
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Transition metal complexes with N-heterocyclic carbene ligands are very promising in homogeneous metal complexes catalysis. The interest in nitrogen-containing heterocyclic carbenes as ligands is due to their enhanced thermal and hydrolytic stability and high catalytic activity¹.

Combination of a calix[4]arene platform with NHC- ligands will significantly expand the potential of subsequent transition metal complexes. The possibility of selective functionalization of the upper rim of the macrocycle allows to regulate the number and location of NHC- ligands in accordance with the required properties.

This work presents the strategy for the synthesis of amphiphilic calix[4]arene derivatives with imidazolium and azidoalkyl fragments on the upper rim (scheme 1) for use in polymeric NHC-metal complexes.



Scheme 1.

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SUPRAMOLECULAR ENSEMBLES BASED ON CROWN- AND PHOSPHORYL-SUBSTITUTED METAL PHTHALOCYANINES IN ORGANIZED MICROHETEROGENEOUS MEDIA

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Using absorption and fluorescent spectroscopy, small angle X-Ray scattering, etc, supramolecular organization of crown and phosphoryl-containing phthalocyanines $Mg[B15C5O]_xPc$ ($x = 4,8$), $Mg[(15C5)_4Pc]$ and $M[R_4Pc]$ $\{R = -OPhP(O)(OH)(OR')\}$; $M = 2H^+$, $R' = H, C_2H_5, C_5H_{11}$; $M = Zn, R' = C_5H_{11}\}$ in microheterogeneous media based on anionic (sodium dodecylsulfate, sodium dodecylbenzenesulfonate and bile salts - SDS, SDBS and BS) and cationic (cetyltrimethyl ammonium bromide and cetyltriphenyl phosphonium bromide - CTAB and CTPB) surfactants were studied. In micellar solutions of conventional SDS and SDBS, crown-substituted $Mg[B15C5O]_xPc$ ($x = 4,8$) and $Mg[(15C5)_4Pc]$ are in the monomeric form. In the case of biocompatible BS, the Pc solubilization depends on the methods of introduction of crown-ether groups into macrocycle, their number and changes in the series of $Mg[B15C5O]_8Pc > Mg[B15C5O]_4Pc \gg Mg[(15C5)_4Pc]$. In microheterogeneous media of cationic CTAB and CTPB, phosphoryl-substituted phthalocyanines exist as monomers. According to absorption and fluorescent spectroscopy, addition of oppositely charged synthetic and natural surfactants to aggregated solution of zinc phthalocyaninate bearing oxy(pentyloxy)phosphoryl groups in peripheral substituents of the macrocycle leads to its monomerization. In the aqueous solution of poly(N-vinylpyrrolidone), this compound predominantly exists also as a monomer.

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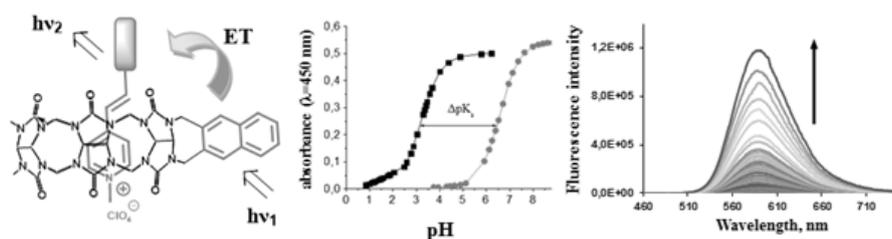
CHANGES OF PROTOTROPIC AND FLUORESCENT PROPERTIES OF STYRYL DYES IN COMPLEXES WITH CUCURBITURILS

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The encapsulation of organic molecules into the cavity of a macrocyclic host is often accompanied by modification of the physicochemical and spectral-luminescent properties of the guest molecules. The supramolecular strategy is widely used in such fields of organic and bioorganic chemistry as the creation of fluorescent sensors, systems for bioimaging and targeted drug delivery¹. Cucurbiturils have a special place among various classes of synthetic receptors. They have a high affinity for cationic molecules and they also cause a dramatic effect on the properties of chromophores.

The study is devoted the complexation of styryl dyes with cucurbit[7]uril (CB7) and naphthyl-cucurbit[6]uril (Np-CB6), as well as the effect of encapsulation on the fluorescent properties and prototropic equilibrium of the dyes.



It has been shown that the pKa value of the ligand increases with complexation. In addition, a significant increase in the fluorescence quantum yield of dyes was observed. It was shown that the self-organization of a styryl dyes and a modified cucurbit[6]uril results in a system in which the photoinduced energy transfer between its components is realized.

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SUPRAMOLECULAR SELF-ASSEMBLY OF POLYELECTROLYTE-BASED COMPLEXES CONTAINING PORPHYRIN DERIVATIVES

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Polyelectrolyte complexes are considered as promising supramolecular systems for biomedical applications, especially for targeted drug delivery¹. Polyelectrolyte-porphyrin nanoassemblies are known to be photocatalytically and biologically active systems²⁻⁴. Combination of the photosensitizing properties and catalytic activity of porphyrin molecules with the cooperative stimuli-responsive behavior of polyelectrolyte complexes (PECs) allows to obtain hybrid photoactive supramolecular systems with emergent properties.

Here we report the aggregation behavior and photophysical properties of cationic (TMPyP), anionic (TSPP, TCPP) and neutral (TPP, THPP) porphyrin derivatives within soluble non-stoichiometric polyelectrolyte and polymer-surfactant complexes obtained from biological and synthetic polymers.

Electrostatic binding to the oppositely charged polyelectrolytes results in the porphyrin fluorescence quenching due to the dipole-dipole interactions between the macrocycles bound to the neighboring units of the polymer chain. In non-stoichiometric polyelectrolyte complexes the spectral properties of the porphyrin molecules are similar to those in an aqueous solution of the excess polyelectrolyte / surfactant. Phase-separated coacervate droplets were shown to accumulate fluorescent porphyrin derivatives in a monomolecular form from the bulk solution with the partition coefficient determined both by the microparticle surface charge and the HLB value of the porphyrin molecule.

The above photochemically-active porphyrin-loaded coacervate droplets can be considered as the primitive protocell models⁵⁻⁶, and hence, the data obtained contributes to the origin of life studies.

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SUPRAMOLECULAR REGULATION OF THE PHOTOPHYSICAL PROPERTIES AND PHOTODYNAMIC ACTIVITY OF AMPHIPHILIC CATIONIC CHLORIN E_6 DERIVATIVES IN AQUEOUS MEDIA

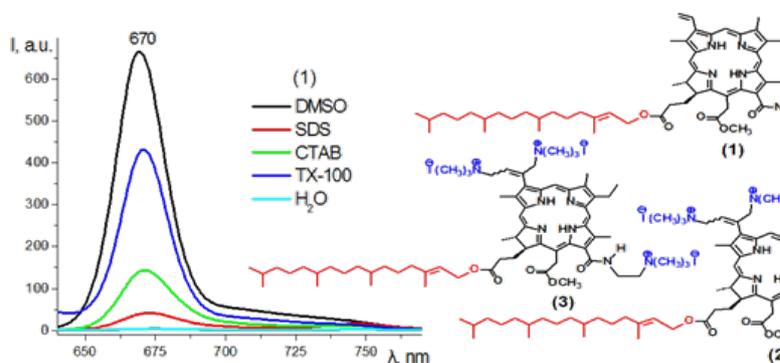
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Amphiphilic chlorin e_6 derivatives with cationic $-N(CH_3)_3^+$ groups on the periphery of the macrocycle are promising photosensitizers for antimicrobial photodynamic therapy¹. The presence of a hydrophobic phytol residue in the molecule results in the increased affinity to the phospholipid membranes and the decreased stability towards aggregation in aqueous media. In this report we compare photophysical properties and photochemical activity of amphiphilic cationic Chl e_6 derivatives in different polymer- and surfactant-based carriers.



The nature of surfactant molecules strongly influences the photophysical properties and photodynamic activity of cationic chlorins in micellar systems with the non-ionic surfactants and polymeric micelles being the most effective solubilizing systems. Polyanions induce aggregation of cationic chlorins due to electrostatic binding at the neighboring monomeric units of the polymer chain. Polyelectrolyte complexes and polymeric micelles effectively prevent monomolecular chlorins from aggregation and enhance their bioavailability.

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This work was financially supported by the Russian Foundation for Basic Research (Project No 18-03-00539).

SELF-ASSEMBLY OF J-AGGREGATES FROM OLIGOETHYLENE GLYCOL SUBSTITUTED PYROPHEOPHORBIDE-*A* DERIVATIVES

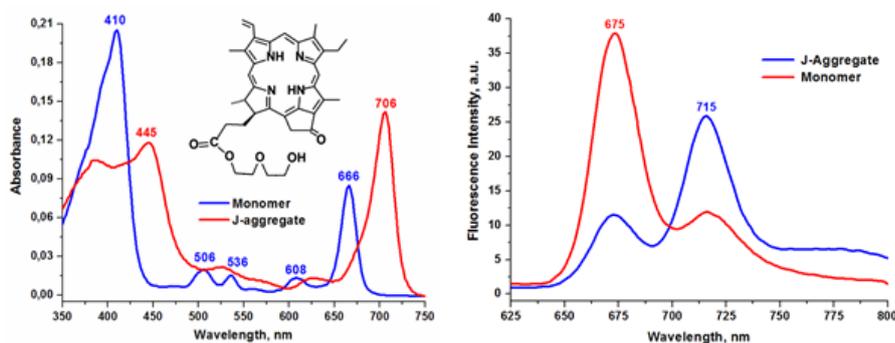
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Chlorophyll *a* derivatives with oligoethylene glycol substituents on the periphery of the macrocycle demonstrate bioavailability, low dark and high photoinduced cytotoxicity in tumor cell cultures in vitro, and hence, can be considered as promising photosensitizers for photodynamic cancer therapy¹. However, the chromophore aggregation in aqueous media usually decreases singlet oxygen quantum yields and reduces the photodynamic efficiency of the photosensitizers. This report describes conditions of J-type aggregate formation in oligoethylene glycol substituted pyropheophorbide *a* derivatives.



J-aggregate formation in aqueous media is accompanied by the 40-nm bathochromic shift of the absorption bands and a significant fluorescence quenching. However, the aggregated species demonstrate a new emission band at 715 nm. The addition of surfactants in submicellar concentration both promotes J-type aggregate formation and increases the colloidal stability of the resulting suspension with a wide particle size distribution.

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This work was carried out in the framework of the State Assignment of Ministry of Science and Higher Education of the Russian Federation (project 0082–2018–0006, registration code AAAA-A18-118020890097-1).

NONCOVALENT INTERACTIONS IN SYNTHESIS, CATALYSIS AND DESIGN OF MATERIALS

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Intermolecular weak forces were firstly taken into consideration by van der Waals, helping to revise the equation of state for real gases. Now, due to the use of modern techniques, such as NMR or X-ray diffraction analysis, new types of inter- and intramolecular noncovalent interactions, such as hydrogen, halogen, chalcogen, pnictogen, tetrel and triel bonds as well as cation- π , anion- π , π - π interactions, etc. have been identified [1–6]. Usually the energy of these weak bonds is much lower than that of typical covalent bonds, but, on account of their cooperation, multiplicity and facile transformation, their overall influence on the course of a reaction can be decisive. In fact, selectivity in chemical reactions, particularly in catalytic processes, is often an orchestral action of various noncovalent interactions occurring in intermediates and transition states. Therefore, an in-depth understanding the nature of these weak interactions – directionality, tunability, hydrophobicity, donor atom size, multiplicity, etc. may be the key to designing new catalytic materials and to a better control of the reactivity.

The hydrogen bond, agostic, anagostic, cation- π , anion- π , and π - π interactions are the most versatile and explored/understood noncovalent interactions in synthesis and catalysis. However, the use in synthesis and catalysis of the "young" noncovalent interactions, such as halogen, chalcogen, pnictogen, tetrel and triel bonds, is still in its early stages.

The results obtained in the authors laboratory towards the use of noncovalent interactions in the synthesis of organic and coordination compounds, as well as in catalysis, are highlighted herein.

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SINGLE-LAYER SURFACE COATINGS OF GRAPHENE OXIDE

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Graphene oxide (GO) is an oxidized form of graphene decorated with a large number of hydroxyl, carboxyl and epoxy groups. It is a ground breaking material for many applications such as electronics, chemical sensing, catalysis etc. This functionalized 2D carbon can be packed into monolayers on solid surfaces there by serving as perfectly flat templates for bottom-up self-assembly or as a precursor of conductive films on glasses. However, the methods for the deposition of the GO layers with controlled packing density remain to be developed. Herein we describe a strategy for the formation of uniform films of GO on solid surfaces depending on the applied experimental parameters.

The GO surface films were formed by a vertical transferring of the self-assembled GO monolayers from the oil/GO hydrosol interfaces onto the silicon wafers. The quality of the resulting films was evaluated by SEM examination in combination with the measurements of the contact angles of the silicon substrate before and after the transferring of GO monolayer onto the solid support (Figure 1). The contact angle steadily decreased with the increase of the packing density of GO on the surface. The increase of the hydrosol concentration also led to the increase of the packing density. The chemistry of non-polar solvent did not have a significant effect on the morphology of the GO films. However, the morphology of the films significantly depended on temperature. Based on these observations, we suggested a procedure for the increase of packing density of GO in films via subsequent reduction and deposition protocol.

We believe that our method can be used as a simple “soft matter” approach to the fabrication of monolayer films of 2D carbons and can be extended to the large-scale manufacturing of graphene-based materials.

Acknowledgements. The authors wish to thank Russian Foundation for Basic Research (grant 18-33-00746_mol_a), Ministry of Science and High Education RF. Raman spectroscopy was performed using the equipment of CKP FMI of IPCE RAS.

HOST-GUEST SYSTEMS OF RHENIUM CLUSTERS WITH CYCLODEXTRINS: CHAOTROPIC EFFECT AND SIZE-MATCHING

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Octahedral rhenium cluster complexes due to their photoluminescent, redox and X-ray contrast properties are very promising for application in different fields of human life – medicine, biology, functional materials, etc. On the other hand, cyclodextrins (CD) – cyclic oligosaccharides formed of 6, 7 or 8 glucopyranose units, are well known in medicine as a capsule for medical drugs. Such combination of clusters and CD should improve the biocompatibility increasing potentialities of their applications.

In this work, we studied the interactions in the system cyano rhenium clusters [$\{Re_6Q_8\}(CN)_6\}^+$ (Q = S, Se, Te) and cyclodextrins (α , β , or γ) by a set of physicochemical methods in solution and solid state as well as influence of CD on the photophysical and redox properties (Fig. 1). This study reveals that inclusion compounds exist in both solution and solid state and the strength of interaction depends either on size of cyclodextrin or on the inner ligand of cluster. The main driving force of the process is size-matching as well as the properties of the cluster-solvent interfaces, named chaotropic effect, which plays a preponderant role.

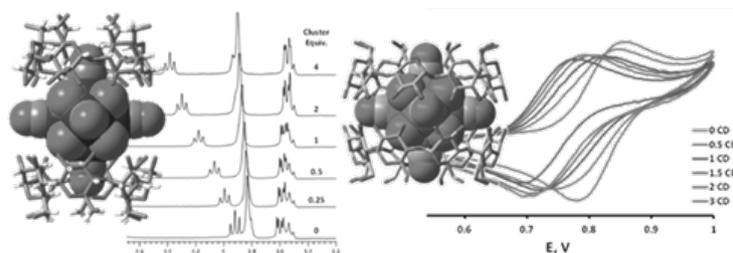


Figure 1. Fragment of crystal structure of inclusion compounds and influence of cluster on 1H NMR of CD (left) and CD on CV of cluster (right).

This work was supported by the Russian Science Foundation (project No 15-15-10006).

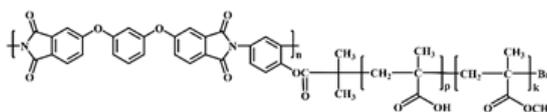
AMPHIPHILIC MULTICOMPONENT MOLECULAR BRUSHES BASED ON POLYIMIDE: SYNTHESIS AND SELF-ASSEMBLY

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The precise synthesis of macromolecules with controlled molecular weight, topology, composition and functionality, followed by their self-assembly into nanostructures (NS) opens up avenues to new materials for many potential applications in nanotechnology and biomedical fields. Molecular brushes (MBs) that consist of a backbone with densely grafted side chains have received a significant attention, since properties of MBs can be tuned by the grafting density and length of side chains, their chemical nature and architecture. Among MBs, those comprising di-block copolymer side chains are of special interest due to their unique core-shell NS and their potential application in preparing core-shell nanomaterials.



The self-assembly of diphilic MBs with a polyimide (PI) backbone and amphiphilic block-copolymer side chains, involving inner hydrophilic block of polymethacrylic acid (PMAA) and outer hydrophobic block of poly(methyl methacrylate) (PMMA) in ethanol was investigated by DLS and TEM. The target MB were synthesized by atom transfer radical polymerization (ATRP) via grafting of *tert*-butyl methacrylate (*t*BMA) from multicenter PI initiator followed by chain extension of MMA from living chain ends of copolymer, obtained on the first step. Amphiphilic MB were obtained by acidic hydrolysis of *Pt*BMA blocks in side chains. The conditions to allow regulation of grafting density and length of each block were determined.

It was shown that PI-*g*-(PMAA-*b*-PMMA) brushes tend to self-assembly in ethanol with formation of stable supramolecular NS. The effect of structural parameters of MB on the size and shape of the self-assembling NS was established. The possible mechanism of self-assembly of MBs in selective solvent was proposed.

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MECHANICAL UNFOLDING OF AMPHIPHILIC COMBLIKE COPOLYMER IN SELECTIVE SOLVENT STUDIED BY THE SELF-CONSISTENT-FIELD MODELING

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Recent advances in synthetic polymer chemistry have made it possible to produce macromolecules of complex and well-defined topology with precise control of molecular parameters, in particular, comblike copolymers – polymer chains with regularly grafted side chains. Modification of the main chain by grafted chains of different chemical nature allows to significantly change the properties of macromolecules in solution.

The present work is devoted to the theoretical study of an amphiphilic comblike macromolecule with a solvophilic backbone and solvophobic side chains. Such a macromolecule can form a unimolecular micelle of spherical shape with the solvophobic core made of side chains and the soluble corona made of the loops of the backbone.

By using the Scheutjens-Fleer self-consistent field numerical approach, we investigated the mechanical unfolding of an amphiphilic comblike macromolecule in a selective solvent. It was assumed that the solvent is good (athermal) for the main chain but poor for the side chains.

The force-extension curves were obtained for a large set of comblike macromolecules differing in the side chains' length, the side chains' grafting density, and the solvent quality for the side chains. It was shown that for loosely grafted combs at any solvent quality for the side chains and in the case of a more dense grafting in a moderately poor solvent, when the micelle is not formed, the stretching of the comblike macromolecule is completely determined by the backbone. In the poor solvent for the side chains, unfolding of the unimolecular micelle by the ends of the backbone occurs via three main stages and is accompanied by a microphase segregation into "head" and "tail".

In the case of the densely grafted comblike macromolecule and strong effective attraction of the side chains to each other, the deformation curve has a complex sawtooth-like pattern. This is associated with the formation of small globular clusters of several side chains on the tail.

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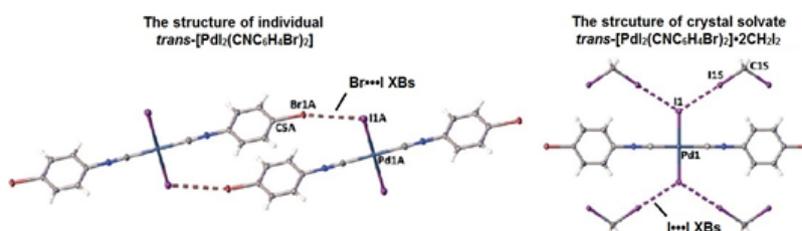
THE INFLUENCE ON SOLUBILITY OF THE METAL ORGANIC COMPLEX...SOLVENT HALOGEN BONDING

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Metal organic compounds are among frontier fields of research because of application in catalysis, biological activity and other relevant areas. High reactivity and intrinsic instability of organometallic species preclude the use of many common solvents for their dissolution. Solvation, as a process leading to a dissolution of compounds, encompasses several different types of intermolecular interactions between a solute and a solvent. Among weak interactions, contribution of HB is frequently taken into account, while impact of XB is rarely considered and needs an in-depth study.

For determination of XB role in solubility of complexes we employed a series of $[MX_2(CNC_6H_4X')_2]$ (1–16) and study their solvation in range of haloalkanes. It was found that solubility and the positive potential on the halogen atom (donating ability of a solvent) as a rule increases symbiotically. [1]. Moreover, CH_2I_2 , the solvent with the most XB donor ability, demonstrate 2–15 times better solvation properties than the most common NMR solvent $CDCl_3$. Exceptional solvation properties of CH_2I_2 and its inertness towards organometallics make this solvent a good candidate for NMR solvent-of-choice. Thus, complex...solvent XBs may play crucial role in solvation.



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These studies were funded by the RFBR (18-33-20073) and RSCF (17-73-10130). Measurements were performed at the Center for Magnetic Resonance, the Center for X-ray Diffraction Studies, the Center for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belonging to Saint Petersburg State University).

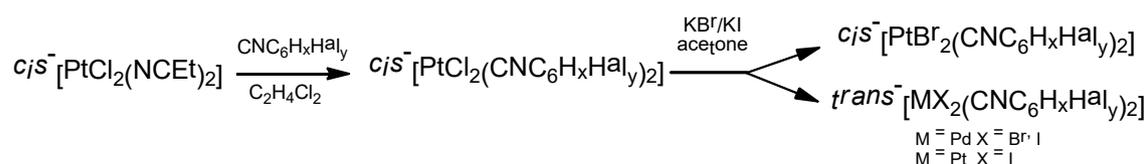
SUPRAMOLECULAR STRUCTURES ON THE BASIS OF PLATINUM AND PALLADIUM(II) ISOCYANIDE COMPLEXES

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Crystal engineering is perspective method connecting molecular and supramolecular structure on the basis of intermolecular interactions. Isocyanide complexes of platinum group metals(II) appear to be perspective building blocks in crystal engineering in consequence of square-planar environment and very slow isomerization of cis and trans-forms [1]. The introduction of halogens in isocyanide ligands leads to formation of halogen bonds (XB) and semicoordination bonds $M \cdots Hal$ [2].

In this work dihalogenides of platinum and palladium(II) halogen-substituted phenylisocyanides were received $[MX_2(CNR_2)]$ ($M = Pd, Pt$; $X^1 = Cl, Br, I$; $R = 4-Br-2-F-3-Cl-C_6H_2, 4-I-2F-C_6H_3$).



The compounds were characterized by ESI-MS 1H , $^{13}C\{^1H\}$, $^{195}Pt\{^1H\}$ NMR, FTIR spectroscopies. Intermolecular interactions were studied by means of X-ray crystallography. It was showed that changing of halogens in isocyanide ligands leads to controllable self-assembly of supramolecular structures.

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These studies were funded by the Russian Foundation for Basic Research (18-33-20073) Measurements were performed at the Center for Magnetic Resonance, the Center for X-ray Diffraction Studies, the Center for Chemical Analysis and Materials Research, and the Chemistry Educational Centre (all belonging to Saint Petersburg State University).

SYNTHESIS OF NEW POLYNUCLEAR LANTHANIDE BASED CLUSTERS USING PHOTOSWITCHABLE DERIVATIVES OF SALICYLIC ACID

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Single-molecule magnets or *SMMs* are a class of hybrid metal-organic materials, which show «superparamagnetic» behavior of purely molecular origin below a certain blocking temperature [1]. Due to their unique magnetic properties *SMMs* attract a growing interest because of their protentional application in different fields (data storage, magnetic coolers etc). Possessing of the hybrid nature the properties of *SMMs* can be tuned by the rational design of organic ligands and proper choice of paramagnetic centers (metal cation) they are made from. In this regard, the Ln based *SMMs* are of particular interest because of their large magnetic anisotropy [2-3] which may significantly increase the blocking temperature of *SMMs*. From another side, when surrounded by ligands containing light harvesting groups exhibiting the “antenna” effect, the lanthanide based coordination compounds are able to be used as luminescent materials [4]. Moreover, the presence in the ligand structure of azo-groups makes them attractive for design of new photoswitchable *SMMs*. Here we report the synthesis and crystal structure of new lanthanide (III) based clusters (Figure 1) (Ln=Gd; Dy; Tb).

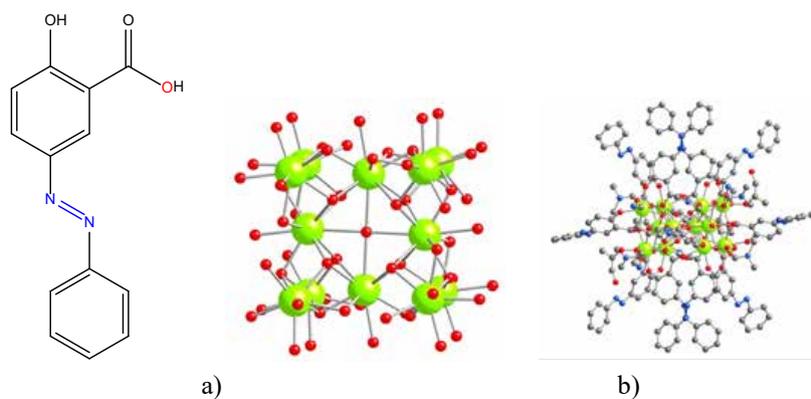


Figure 1.

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SYNTHESIS AND CHARACTERIZATION OF STAR-SHAPED POLY-2-ALKYL-2-OXAZOLINE WITH HEXAASE[2₆]ORTHOPARACYCLOPHANE CORE

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The aim of this work is the synthesis and investigation of new thermosensitive six-arm star-shaped poly-2-alkyl-2-oxazolines (PaOZ). Hexaase[2₆]orthoparacyclophane, which is characterized by the ability to form stable complexes with low molecular weight compounds, is used as a core. Samples were prepared by the cationic polymerization. The arms of PaOZ were poly-2-ethyl-2-oxazoline (PeOZ) and poly-2-isopropyl-2-oxazoline (PipOZ) (Fig. 1).

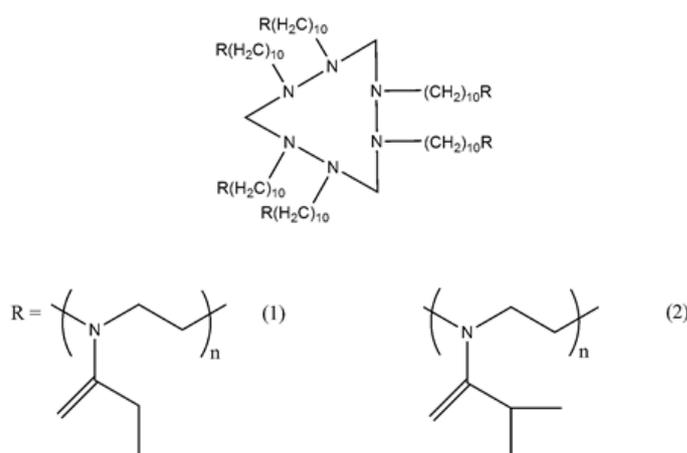


Figure 1 – Structure of star-shaped PeOZ (1) and PipOZ (2)

Molar mass, hydrodynamic and conformational characteristics of star-shaped PaOZ were determined using static and dynamic light scattering, sedimentation-diffusion analysis and viscometry. Self-organization processes were investigated in aqueous and water-salt solutions in wide interval the concentration and temperature. The values of optical transmission I^* , intensity of scattered light I , hydrodynamic radii R_h of scattering objects and their fraction of S_i in solutions depending on temperature were obtained. The temperature dependences of the characteristics of the PaOZ solutions and the phase separation temperatures were determined.

RADIATION-CHEMICAL METHOD FOR SYNTHESIS BIMETALLIC NANOPARTICLES IN POLYMER MATRICES AND COATINGS

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$\text{Cu}_{\text{shell}}/\text{Ag}_{\text{core}}$ and $\text{Cu}_{\text{shell}}/\text{Au}_{\text{core}}$ bimetallic nanoparticles (BNs) were synthesized in situ in films of interpolyelectrolyte (IPEC) complexes containing both Ag (or Au) and Cu ions by irradiation with x-ray and e-beams accelerator. HRTEM data demonstrate the core-shell structure of nanoparticles. XRD data shows that irradiation lead to formation of the nanoparticles cores (Ag or Au) at early stage of irradiation while increase of the irradiation dose result in the growth of copper shell. Also, by XANES and EXAFS it was found that initial stage of Cu_{shell} formation goes through intermediate Cu_2O and CuO structures. On the BNs sizes and core-shell ratio affect the irradiation doze and initial concentration of metal ions in IPEC. Thus, we have demonstrated that the radiation-induced reduction of metal ions in the IPEC matrices can be used for the single-stage preparation of nanocomposite films containing the bimetallic nanoparticles with controllable core-shell ratio¹.

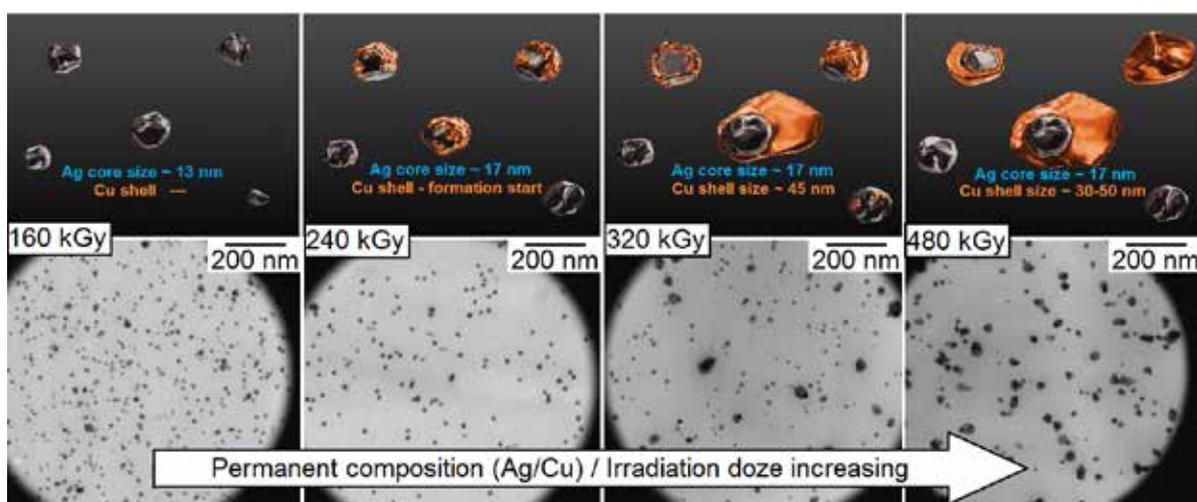


Figure 1. TEM images and 3d-model of corresponding bimetallic nanoparticles of sample containing 1 Ag wt.% and 10 Cu wt.% under different irradiation dozes

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SYNTHESIS AND STRUCTURE OF NEW HEXA AND OCTA NUCLEAR MANGANESE CLUSTERS BASED ON CALIX[4]ARENE

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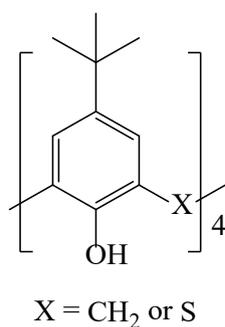
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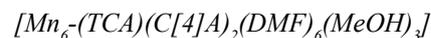
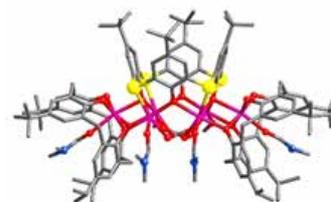
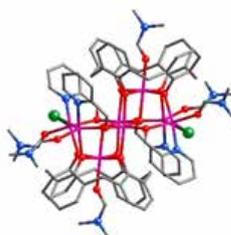
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(Thia)calix[4]arenes (Figure 1a) are versatile ligands, which are particular suitable for formation of a wide variety of polynuclear clusters comprising 3d metal cations, especially, manganese cations displaying the single molecular magnet behavior. [1]. Moreover, the using of auxiliary organic ligands containing the chelate cavity in combination with calix[4]arene may improve the magnetic properties of obtained complexes.

In this report we present the synthesis and structure of new manganese based clusters supported on the calix[4]arene adopted in *cone* conformation, containing 5, 6 and 8 manganese cations in the metallic nodes involving the pyridine methanol and thiacalix[4]arene as co-ligands (Scheme 1).



a



b

Figure 1.

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SYNTHESIS, STRUCTURE AND COORDINATION ABILITY OF SALEN-TYPE SCHIFF BASES BASED ON CALIX[4]ARENE MOLECULAR PLATFORM

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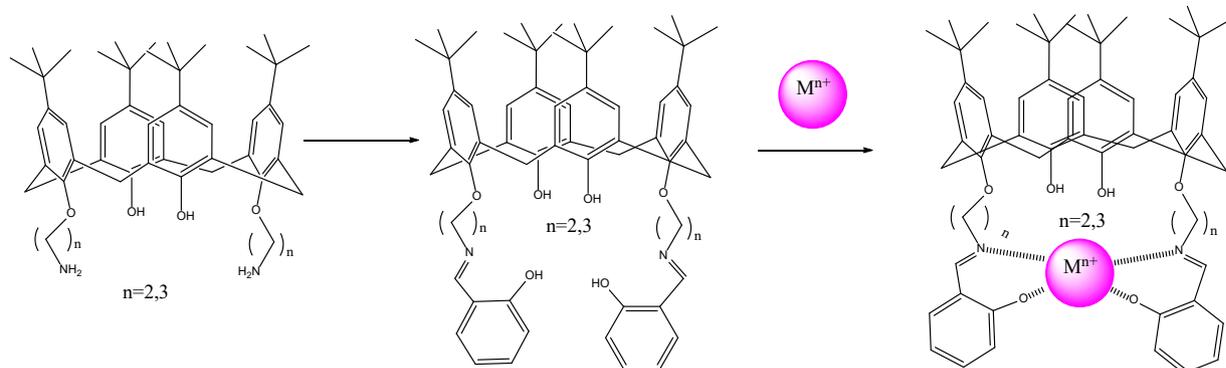
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One of the main aim of supramolecular chemistry is to discover the regularities governing the self-assembly of molecular building blocks using the weak interactions (especially coordination bonding) leading to creation of new functional materials. It is known that salen-type compounds are able to form stable complexes with transition and lanthanide cations affording to formation of complexes displaying spin-crossover (SCO) properties and can be applied for development of new molecular devices [1].

Herein we report the synthesis of salen-type ligands based on lower rim disubstituted calix[4]arene Schiff base derivatives (Scheme 1). Their coordination ability towards transition metal as well as lanthanide cations in solution and in the crystalline phase will be also discussed.



Scheme 1.

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METAL-ORGANIC FRAMEWORKS BASED ON RHENIUM OCTAHEDRAL CLUSTER ANIONS $[\text{Re}_6\text{S}_8(\text{CN})_6]^{4-}$ AND CUBANE CATIONS $[\text{Ln}_4(\mu_3\text{-OH})_4]^{8+}$ Litvinova Y.M.,^a Gayfulin Y.M.,^a Samsonenko D.G.,^{a,b} van Leusen J.,^c Mironov Y.V.^{a,b}^a*Nikolaev Institute of Inorganic Chemistry SB RAS, 630090, 3, Acad. Lavrentiev ave., Novosibirsk, Russian Federation, e-mail: litvinova@niic.nsc.ru*^b*Novosibirsk State University, 630090, 2, Pirogova str., Novosibirsk, Russian Federation*^c*RWTH Aachen University, Institute of Inorganic Chemistry, Landoltweg 1, 52074 Aachen, Germany*

For the last few decades, much attention has been focused on the synthesis and investigation of metal-organic frameworks (MOFs) due to their various and potentially useful physicochemical properties. One of the most effective and simple route for obtaining of MOF is their self-assembly in the solution from pre-synthesized building blocks. Among the numerous building blocks based on *d*-metals, octahedral cluster rhenium complexes $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ (S, Se, Te) were chosen as pre-made species. Intensive red luminescence and reversible oxidation accompanied with drastic color change and luminescence quenching makes these clusters interesting from the point of view of constructing of multifunctional coordination polymers. For the last few years, constructing of MOF based on the $[\text{Re}_6\text{Q}_8(\text{CN})_6]^{4-}$ anions and cationic complexes of lanthanides was our goal.¹ Among the compounds based on the cations Ln^{3+} , polynuclear oxo-bridged assemblies have a lot of interests because of presence of short Ln–Ln contacts, which can yield an interesting luminescent and magnetic properties. Inclusion of such assemblies in the MOF structure is an attractive research field. In this work we were able to construct Ln-MOFs consist of cubane clusters $\{\text{Ln}_4(\mu_3\text{-OH})_4\}^{8+}$ (Ln = Pr–Er) connected by isonicotinate linkers in zig-zag chains which are, in turn, connected by the rhenium cyanide cluster forming the framework structures. Note that these compounds are the first MOFs based on the tetrahedral lanthanide complexes and cyanometallate building blocks. Structural features, luminescent properties and magnetic susceptibility of nine new compounds were investigated.

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PHOTOCHEMICAL SYNTHESIS OF A 1-PYRIDYL-2,3,4-TRIPHENYL CYCLOBUTANE DERIVATIVE VIA MOLECULAR SELF-ASSEMBLY IN SOLUTION

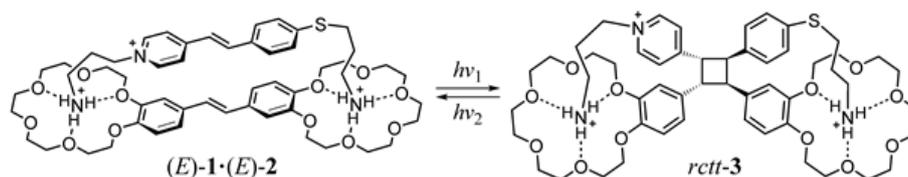
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To date, a variety of supramolecular approaches have been developed to control the efficiency and selectivity of the [2+2]-photocycloaddition (PCA) reaction both in solution and in the solid state.¹ Most attention has been paid to auto-PCA, i.e. [2+2]-photodimerization, whereas supramolecular cross-PCA reactions remain less studied.² This especially concerns the reactions between electron-donor and electron-acceptor olefins, when photoinduced electron transfer (PET) can be a competing process. In this case, it is difficult to predict the PCA efficiency, because both competing photoreactions are significantly dependent on the geometric properties of the supramolecular assemblies.

In this work, we have shown that styrylpyridinium dye (E)-1, which was synthesized for the first time, forms a highly stable bimolecular complex with bis(18-crown-6) stilbene (E)-2 in solution owing to ditopic coordination via hydrogen bonds. The complex formation leads to much faster deactivation of the excited states of both compounds, which is explained by PET from the stilbene derivative to the dye. Despite this, the complexed olefins undergo cross-PCA upon selective excitation of the dye to afford solely the syn-cycloadduct (rctt-3). The retro-PCA reaction occurs readily upon UV irradiation of cyclobutane rctt-3 and leads to the initial bimolecular complex.



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ULTRATHIN FILMS BASED ON EUROPIUM(III) BISPHTHALOCYANINATES: TUNING OF TRANSVERSAL CONDUCTIVITY BY PERIPHERAL SUBSTITUTION

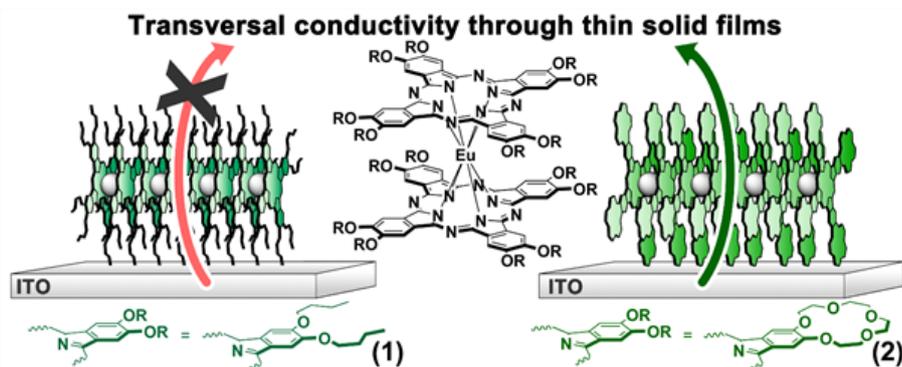
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In the light of increasing demand for development of novel thin film devices for optoelectronic applications, phthalocyanine compounds attract special attention due to the number of unique physicochemical properties including multistability as a basis for elaboration of smart materials.¹

In the present work we study in detail the influence of peripheral substitution on the transversal conductivity and electrochemical activity of ultrathin films based on Eu(III) bisphthalocyaninates. We show that butoxy-substituted complex $\text{Eu}[(\text{BuO})_8\text{Pc}]_2$, **1** does not allow transfer of charge in direction perpendicular to its densely packed films. This feature can be useful in such applications as organic field-effect transistors, where lateral conductivity is required and transversal charge transfer would be undesired. To the contrast, crown-substituted complex $\text{Eu}[(15\text{C}5)_4\text{Pc}]_2$, **2** exhibits excellent redox multistability in monomolecular ultrathin films, which points to good perspectives in molecular logic and information storage applications.



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INJECTABLE SOFT HYDROGEL IMPROVED BY NANOCCLAY

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Injectable nanocomposite hydrogels represent an evergrowing class of nanomaterials possessing a unique combination of physical and chemical properties. For the injection applications the hydrogels should demonstrate a shear-thinning behavior resulting in a significant decrease in viscosity when subjected to shear strain and a fast recovery of the initial state, when the deformation is no longer applied. Such hydrogels can be used as control delivery systems since they can be delivered in a minimally invasive manner because the final form and shape are defined by the space into which they are injected¹.

Another type of injectable hydrogels is based on wormlike micelles (WLMs). Such micelles are often compared with polymers and even gained the name of living polymers, because they incessantly break and recombine. With increasing surfactant concentration solutions of WLMs become viscoelastic and at certain conditions, a transient network of entangled micellar chains is formed. Such network possesses gel-like properties.

The nanocomposite WLM-based soft hydrogels containing tactoid particles of bentonite organoclay are developed. A pronounced enhancement of rheological properties of transient WLM network induced by nanoclay was observed. It was explained by the formation of particle-WLM physical junctions reinforcing the network. The changes of rheological properties of WLM-based hydrogels induced by shear are more significant in compare with polymer-based physical nanocomposite hydrogels. It was explained by subchains disruption of the WLM network under shear action in contrast to only cross-links disruption of polymer-based system. The observed properties make WLM-based nanocomposite hydrogels promising candidate for injectable applications, where tactoids of the nanoclay can be useful as delivery vehicle⁵.

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SELF-ASSEMBLED NETWORKS OF WORMLIKE MICELLES AND NANOPARTICLES

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Stimuli-responsive soft magnetic nanocomposites (SMN) with embedded magnetic particles have attracted increasing attention, because their mechanic properties can be changed continuously, rapidly and reversibly, by applying a magnetic field. Recently, a new type of tunable matrix for magnetic particles was proposed¹. It is based on soft matrix of wormlike micelles (WLMs) of surfactants. The advantage of such SMNs is a linear viscoelasticity of the WLM network². Also, the WLMs are “living” objects, they can reversible break under stress that makes them perspective as a matrix where particles can move freely enough even at low particles content. It shows that WLMs are perfect for the stabilization of the suspensions of particles, because they are able to link to the particles by their end-caps¹. The viscoelastic properties of SMNs were examined under the action of magnetic field at different volume fraction of particles^{3,4}. It was demonstrated that the SMNs combine features typical for magnetorheological fluids based on Newtonian liquid with some features of magnetorheological elastomers/gels. A broad region of linear viscoelasticity demonstrated by SMNs allows one to measure mechanical properties of the SMNs under oscillating stress thus modelling conditions of the practical applications of magnetoresponse smart materials as damping and amortization material. Thus, transient network of entangled WLM is a promising matrix for preparation of SMNs with prospective mechanical properties suitable for various applications. The demonstrated specific interaction of wormlike surfactant micelles and particles is very promising novel route for soft stimuli-responsive nanocomposites preparation⁵.

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SYNTHESIS OF RHODIUM, IRIDIUM AND PLATINUM CONTAINING POLYOXOMETALATES

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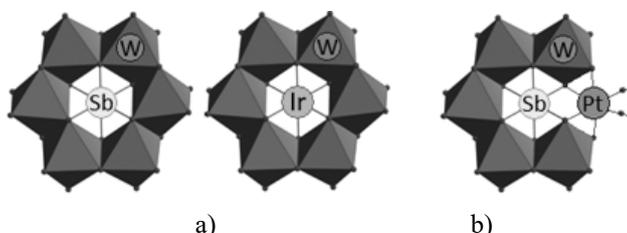
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Transition metal polyoxocomplexes (POMs) demonstrate numerous applications in catalysis (oxidation, photo and redox activity), biological activity, molecular magnetism, etc. POMs with noble metals are of particular interest due to such systems can provide synergistic effect in the catalysis of a wide range of reactions.

In this work synthetic routes to iridium and platinum containing Anderson-Evans type ions $[XW_6O_{24}]^{n-}$ have been investigated. In the case of iridium complex $K_{5.47}Na_{2.3}[Ir_{0.17}Sb_{0.83}W_6O_{24}](NO_3)_{0.6}$ was isolated and characterized. According to XRD data this is a solid solution of two anions (picture 1a) with antimony and iridium is the central atom correspondingly. In the case of platinum $K_5Na_2[H_2SbPtW_5O_{24}]$ was prepared. In this complex platinum replaces tungsten in the belt of Anderson-Evans structure $[SbW_6O_{24}]^{7-}$ (picture 1b).



Picture 1. a) the structure of anions $[SbW_6O_{24}]^{7-}$ and $[IrW_6O_{24}]^{8-}$ in the composition of the solid solution $K_{5.47}Na_{2.3}[Ir_{0.17}Sb_{0.83}W_6O_{24}](NO_3)_{0.6}$; b) the structure of $[H_2SbPtW_5O_{24}]^{7-}$.

Reaction of $[H_2P_8W_{48}O_{184}]^{40-}$ and $[Pt(OH)_4(H_2O)_2]$ gives platinum containing macrocyclic complex $K_{21}(NH_4)_8[H_3\{Pt(OH)_3(H_2O)\}_8P_8W_{48}O_{184}]$. According to XRD data 8 platinum ions are included in the central cavity of the original polyoxometalate.

Reaction of $Na_9[SbW_9O_{33}]$ with rhodium (II) acetate has been studied. According to XRD, elemental analysis and ESI-MS the composition of the product can be formulated as $((CH_3)_2NH_2)_9H_2[\{Rh(H_2O)\}SbW_{17}O_{59}]$.

THE SUPRAMOLECULAR COMPLEXES OF CYANINE DYES CONTAINING TERMINAL AMMONIUM GROUPS WITH MACROHETEROCYCLIC MOLECULES

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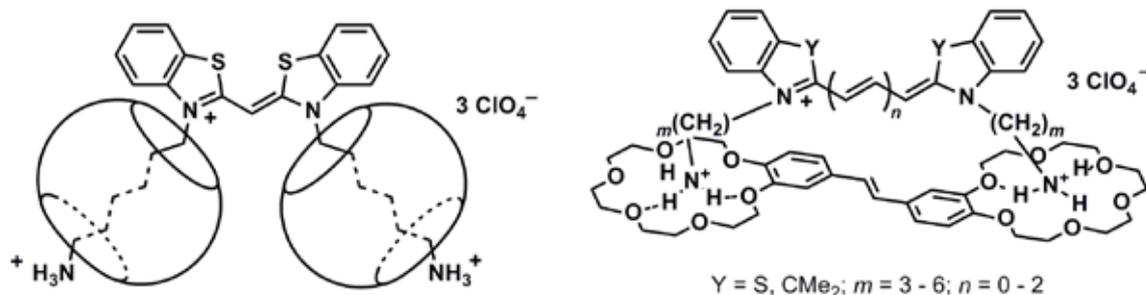
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In order to elucidate the possibility to construct photoactive "host-guest" complexes based on cyanine dyes as a guest and the influence of their structure on the properties of supramolecular complexes, we synthesized cyanine dyes with terminal ammonium groups in the *N*-substituents of heterocyclic residues. The presence of primary ammonium groups capable of hydrogen bonding enables self-assembly of the dye with macroheterocyclic molecules containing electron-donating oxygen heteroatoms to form supramolecular complexes.



We demonstrated the possibility to construct the supramolecular systems based on cyanine dyes with two ammonioalkyl *N*-substituents using their complexes with cucurbit[7]uril and bis(18-crown-6)stilbene as examples.

It was shown that inclusion of the dye molecule into cucurbituril cavity highly influence dye fluorescence spectra. It was also shown that stilbene form highly stable bimolecular and relatively unstable trimolecular complexes in which the dye ammonium groups are hydrogen-bonded to the crown ether moieties of stilbene and their π -conjugated moieties are located one above the other. The stability constants for some of these complexes were determined, and the stability of the complexes was shown to depend on the dye structure.

The synthesized cyanine dyes and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

This work was supported by RFBR (project № 18 03 00214).

PHOTOCATALYTIC ACTIVITY OF COMPOSITE MATERIAL BASED ON GRAPHENE OXIDE AND PORPHYRIN METAL-ORGANIC FRAMEWORK

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Photocatalytic degradation of toxic organic compounds is one of the most promising methods of wastewater treatment. Metal-organic frameworks (MOFs) have high surface area, catalytic activity and porosity, that makes them good candidates for such an application.¹ However, their stability often is not satisfactory, and a stabilizing matrix is required.²

Herein, graphene oxide (GO) sheets were used as a matrix and porphyrin-based MOFs as a catalytic component. Zinc (II) acetate and two different porphyrins (*meso*-tetra-(4-pyridyl)-porphyrin (TPyP) and *meso*-di(4-pyridyl)-di(4-carboxyphenyl)porphyrin (DPyPDCPP)) were applied as a metal source and organic linkers for the metal-organic frameworks.

The composite catalyst was obtained by the emulsion synthesis from water/chloroform and DMSO/hexane systems in the case of TPyP and DPyDCPP correspondingly. The DPyPCPP based material demonstrated its high efficiency for photobleaching processes of rhodamine-6G (Fig.1) and 1,5-dihydroxynaphthalene (DHN) under visible light irradiation, monitored by UV-Vis spectroscopy.

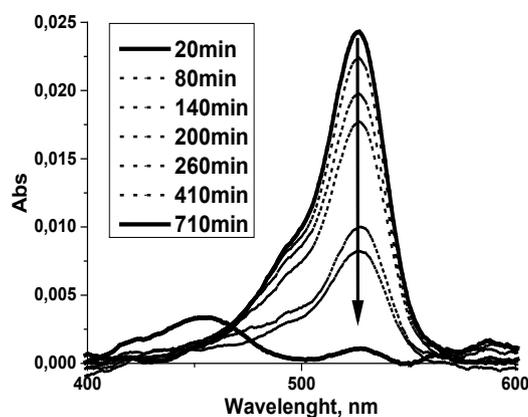


Figure 1. UV-Vis spectra of the photobleaching process of a solution of rhodamine 6G under visible light irradiation in the presence of the composite based on DPyPDCPP MOF.

Acknowledgements: This work was supported by the Russian Foundation for Basic Research (grant no. 18-29-04026 MK).

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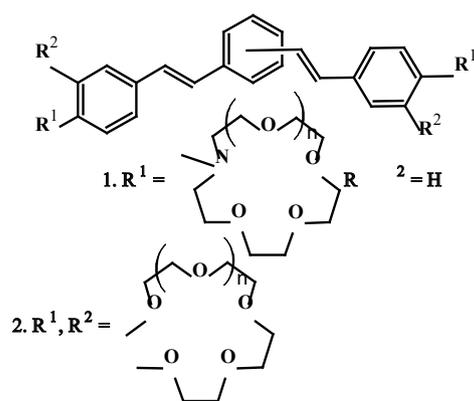
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STILBENES AND DISTYRYLBENZENES MOUNTED OFF WITH CROWN-ETHERS – THE PATHWAY TO SUPERMOLECULE

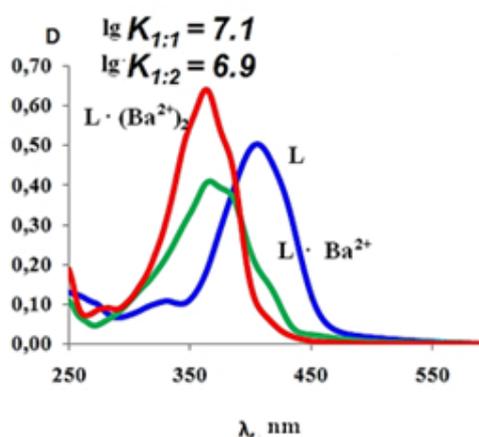
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Styryl dyes is the popular class of unsaturated polyconjugated compounds with intrinsic by itself fascinating spectral properties. Such representatives as stilbenes and distyrylbenzenes nowadays concerned as mainstream materials in creation of molecular sensors and luminophores for optoelectronic.¹ Inserting of crown-ether moieties in styryl basic framework, at the one hand, influences on their electronic properties, other side, allows to tune fine supramolecular systems, e.g., in the photochemical switching.² We developed and clean easy pathway to synthesis the set of styryl-type bis-crown containing compounds.



1, 2 (metha, para, n = 1, 2)



Spectrophotometric titration 1 (para, n = 2) Ba(ClO₄)₂

Comparing and analysis of UV and fluorescence spectra of these ligands in the presence of alkaline and alkaline earth metal ions proved an evidence of their tendency to various supramolecular self-assembling.

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INFLUENCE OF METAL SALTS ON THE PROCESS OF SELF-ORGANIZATION IN CYSTEIN SILVER SOLUTION

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At present, hydrogels derived from bioactive substances with a low content of the dispersed phase (~ 0.01 M) in solution are of particular interest. Hydrogels based on cysteine-silver solution (CSS) represent a unique model system for studying the processes of self-organization in a dilute aqueous solution. The aim of the work is to study the process of self-organization in the CSS under the influence of chlorides and sulfates of metals by the methods of vibration viscometry, dynamic light scattering (DLS), measurements of electrical conductivity and UV spectroscopy.

Hydrogels were obtained on the basis of an aqueous solution of L-cysteine and silver nitrate (1:1.27) by introducing electrolyte into the CSS. Aqueous solutions of metal chlorides and sulfates (Na^+ , Cu^{2+} , Al^{3+}) were used as electrolytes. The method of vibration viscometry has established that the hydrogels with Cu^{2+} salts have the highest viscosity, and the lowest viscosity with Al^{3+} salts. This, apparently, is due to the fact that Cu^{2+} is a stronger complexing agent. Measuring the conductivity of the CSS with the introduction of the electrolyte showed that its values in the CSS in the process of gelation is significantly reduced with an increase of the cation charge of the introduced electrolyte. So, when the concentration of the electrolyte solution is $2.0 \cdot 10^{-5}$ M, the electrical conductivities in the gel were ~ 1110 for Na^+ , $\text{Cu}^{2+} \sim 870$ and $\text{Al}^{3+} \sim 820$ $\mu\text{S}/\text{cm}$, that is, hydrogels with the introduction single charged cations due to their greater lability (smaller size and charge) had the highest electrical conductivity compared to the introduced double and triple charged cations. The process of self-organization in the CSS by changing the intensity of the absorption bands at 310 and 390 nm, indicating the formation and growth of oligomeric chains (clusters) of silver mercaptide molecules, was studied by UV spectroscopy. Using the DLS method, the sizes of the formed clusters at the initial stage of gelation are determined. It has been established that when an electrolyte is added, the process of gelation starts, and the size of particles in hydrogels directly depends on the concentration and charge introduced into the CSS of the electrolyte.

The work was done with the financial support of the Ministry of Education and Science of the Russian Federation as part of the implementation of public works in the field of scientific activity (project No. 4.5508.2017/BP) on the equipment of the Center for Collective Use of Tver State University.

THE PROCESSES OF SELF-ASSEMBLY IN AQUEOUS SOLUTIONS ON THE BASIS OF L-CYSTEINE, ITS DERIVATIVES AND SALTS OF SILVER

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In recent times increased attention focus on the study of the process of gelation involving low molecular weight compounds. Among such compounds, the amino acid L-cysteine is of particular interest, since in its aqueous solution with the participation of nitrate AgNO_3 [1] and silver nitrite AgNO_2 [2] at a low concentration of the dispersed phase (~0.01%), a self-organization process occurs, leading, under certain conditions, to the formation of a supramolecular hydrogel.

For a detailed elucidation of the mechanism of cluster formation, the set of studied systems should be expanded. For this aim we used various L-cysteine's derivatives - Cysteamine (CA), Mercaptopropionic acid (MPA) with addition AgNO_2 , AgNO_3 . The aim of the work was to clarify the possibility of formation of oligomeric chains and clusters and to investigate self-organization processes in aqueous solutions of in systems based on L-cysteine derivatives, as well as the study of the gels. Self-organization processes in solutions were studied using pH-metry, dynamic light scattering (DSR), transmission electron microscopy (TEM), UV and IR spectroscopy.

The obtained data suggest that the structure of the fragment of molecules ($\text{Ag-S(R)-Ag-S(R)-Ag-S(R)}$, (R is the rest of the molecule with mercapto group) formed by the silver ion with CA and MPA remains the same as for L-cysteine. The study of the morphology of these aqueous solutions by TEM shows that extended linear chains are indeed formed in the system, and the probability of the formation of a spatial gel-network in the presence of such precursors is high.

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STRUCTURE AND MECHANICAL PROPERTIES OF NETWORKS OF A STIFF POLYELECTROLYTE

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The paper is devoted to the study of networks based on stiff-chain polysaccharide xanthan. Unperturbed structure of these systems was visualized by freeze-fracture transmission electron microscopy. It was shown that in xanthan solutions without a cross-linker, a side-by-side association of xanthan double helices occurs at polymer concentrations close to the transition from unentangled to entangled regime. At higher polymer concentrations, aggregated macromolecules were shown to form a rather dense skeleton typical for phase-separated structures. One can suggest that the formation of the network of percolated polymer-rich domains occupying the whole volume of the system permits to get an optimum arrangement of stiff-chains with respect to each other without restriction of the motion of free ions.

The cross-linking by chromium induces additional aggregation between macromolecules enhancing the microphase separation. The increase of the cross-linking density leads to the thickening of the polymer skeleton and simultaneous decrease of the network mesh size, which results in the enhancement of the mechanical properties.

It was demonstrated that the mechanical properties of the networks can be significantly modified by surfactant addition. Responsive structure of surfactant aggregates allows easy altering of the mechanical properties of the polymer-surfactant networks thus providing a tool to get polymer matrix with desirable characteristics for a given application.

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WETTING PROPERTIES OF A SURFACTANT CONTAINING SHORT PERFLUOROALKYL CHAINS COMBINED WITH CONVENTIONAL BRANCHED SURFACTANTS

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Fluorinated surfactants are known as unsurpassed surface-active agents for reducing the surface tension of water and various solvents up to ultra-low values. However, disadvantages of the surfactants containing long C_6F_{13} - C_8F_{17} -chains are related to their environmental impact, associated with their worth biodegradation, bioaccumulation, and toxicity [1]. A proper alternative to such surfactants is a new type of amphiphiles containing several short perfluoroalkyl chains. These surfactants are not subject to restrictions on marketing and use whereas their effectiveness is almost the same as of long-chain fluorinated surfactants [2-4].

Our study focuses on the wetting properties of Tivida FL 2300 (TFL), new fluorosurfactant kindly provided by Merck KGaA. This eco-neutral anionic surfactant contains three perfluoropropyl chains connected via a spacer to hydrophilic group. Surprisingly, aqueous solutions of this fluorosurfactant in a certain range of concentrations exhibit synergistic wetting of Parafilm M with ethoxylated ($\times 5$ EO and $\times 6$ EO) wetting agents, derivatives of branched decanol (Guerbet alcohol). The wetting rate and contact angles on the Parafilm surface were examined for solutions of the surfactants and their mixtures using a digital camera in video mode at 25°C.

It was shown that the even small additives of TFL to ethoxylated alcohols significantly accelerate the spreading of water drops on the hydrophobic Parafilm surface. Probably, this nonideal behaviour is essentially of the same kind as the known cases of "fluorophobic effect", which is typical for other mixtures of a fluorinated surfactant and hydrocarbon molecules. On the other hand, the attractive interaction of hydrophilic moieties can take place. Associative behaviour of TFL and branched alcohol ethoxylate in mixed solutions is examined by various methods. Anyway, anionic TFL and ethoxylated alcohols show a certain independence of their action at the liquid/air surface and the liquid/solid interface. As it was proposed before [5], the comparison of isotherms $\gamma = f(\log C)$ and $\gamma \cdot \cos\theta = f(\log C)$ offer the suggestion on the concentration ranges of surfactant adsorption on these surfaces. TFL adsorption at the Parafilm/air surface is possible as revealed by Zisman's plot. The obtained data allow us to conclude that the synergistic mixtures of short-chain fluorinated surfactant and branched decanol ethoxylates represent a promising eco-friendly and cost-effective alternative to other wetting agents, particularly with regard to the high adsorption rate and proper wetting in such compositions as sprayable coatings, inks, and surface cleaners.

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NEW PORPHYRINS FOR ANCHORING TO NANOPARTICLES

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The development of green chemistry approaches in the chemical technology is an actual task of modern research. Over the past decades porphyrins have proved to be efficient photoactive compounds for multiple applications. Moreover, it is known, that the conjugation of porphyrins with nano-sized materials may significantly alter their physical-chemical properties. In this respect the development of the approaches for the preparation of the porphyrin building blocks bearing anchoring groups is an actual task. Carboxy-groups and particularly the citrate moiety is expected to be efficient in this area (figure 1).

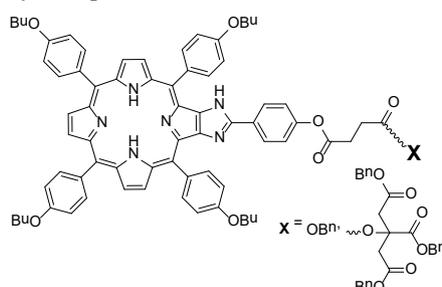
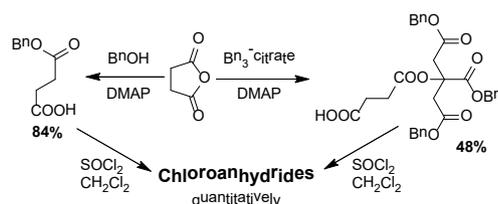
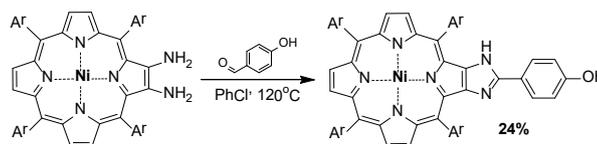


Figure 1. The structure of the target porphyrins.



Scheme 1. The synthesis of precursors of anchoring groups.



Scheme 2. The synthesis of precursors of anchoring groups.

In the present work we have investigated the strategies for the preparation of new carboxy-substituted porphyrins. Despite the crucially low reactivity of the hydroxy-group of the citric acid we succeeded to perform the acylation with succinic anhydride, while mono-benzylsuccinate was prepared as reference compound (scheme 1). In turn, the condensation of the diaminoporphyrin with 4-hydroxybenzaldehyde similar to our published procedure¹ provided the corresponding imidazoporphyrin (scheme 2).

Concluding, two strategies could be used for the preparation of citrate-substituted porphyrins, namely the condensation of the diaminoporphyrin with carboxy-functionalized benzaldehyde or the acylation of porphyrin precursor.

Acknowledgements. The authors are grateful to RFBR (grant №19-33-70036).

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RHENIUM TRIIODIDE AS A CONVENIENT PRECURSOR FOR METAL CLUSTER COMPLEXES

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Cluster complexes represent a unique class of inorganic compounds, which exhibit remarkable physicochemical properties linked to their vast structural diversity. Coordination chemistry of the cluster compounds dates back to 1964 when F. Cotton introduced the term “cluster” to describe compounds based on a framework of metal atoms held together by metal–metal bonds. Since then the chemistry of clusters has developed rapidly, yielding a large number of fascinating compounds with a wide variety of interesting structures, chemical and physical properties, and numerous applications.

The use of transition metal chlorides and bromides for the synthesis of cluster compounds is quite typical, while iodides are only rarely used. Recent data for tungsten¹ and rhenium² iodides have, however, demonstrated a significant difference of the iodides from the corresponding chlorides and bromides in metal cluster synthesis reactions.

In this work we demonstrate that rhenium (III) iodide can be successfully used for the syntheses of previously unknown rhenium compounds based on a well-known tetrahedral metallocluster, but with new types of inner ligands. Specifically, new ligands PO₂³⁻, AsO³⁻, CCN³⁻ have been obtained in the reaction of ReI₃, KCN and the elements of Group 15 at high temperature and stabilized as inner ligands in the cluster anions. Note that the ligands PO₂³⁻ and AsO³⁻ have never been previously described not only in cluster chemistry, but even in general coordination chemistry.

The compounds obtained were characterized by various physicochemical methods, including the single-crystal X-ray diffraction and NMR-spectroscopy. Redox properties of the synthesized cluster complexes were investigated and the possibility of formation of coordination polymers was shown.

Therefore, our new fundamental results are of strong interest for the whole cluster chemistry community, as it opens the door for the possibility to stabilize unusual ligands in the cyanide rhenium cluster complexes.

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MICELLES BASED ON PLA/PEO BLOCK COPOLYMERS WITH DIFFERENT MOLECULAR STRUCTURE IN DILUTE AQUEOUS SOLUTIONS

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Effect of molecular structure of block copolymers based on amorphous (D,L)-lactide or crystalline (L)-lactide and ethylene oxide on the micellization process and characteristics of micelles in dilute aqueous solutions was comprehensively studied.

Four series of di- P(D,L)LA_x-b-PEO₁₁₃ (x = 40 ÷ 210), P(L)LA_y-b-PEO₁₁₃ (y = 65 ÷ 420) and tri- P(D,L)LA_m-b-PEO₉₁-b-P(D,L)LA_m (m = 15 ÷ 65), P(L)LA_n-b-PEO₉₁-b-P(L)LA_n (n = 30 ÷ 120) block copolymers were synthesized. Micelles were prepared by dialysis. It was shown that amorphous P(D,L)LA/PEO block copolymers form in aqueous solutions spherical micelles with insoluble amorphous P(D,L)LA core and soluble PEO corona. It was established that size of the micelles is dependent both on the block copolymer structure and on the P(D,L)LA block length. In addition to individual micelles, a small number of their dense aggregates were observed. Crystalline P(L)LA/PEO block copolymers form non-spherical micelles with partially crystalline P(L)LA core and soluble PEO corona. It was shown that size of the partially crystalline micelles is weakly dependent both on the block copolymer structure and on the P(L)LA block length. In addition to individual micelles, a small number of their loose aggregates were detected with characteristic distance between adjacent micelles decreasing with an increase in P(L)LA block length. This effect was explained by the change in the tethering density of PEO corona. Force spectroscopy measurements also support this assumption.

It has been shown that such micelles can be used as drug carriers both as individual micelles and as components of multiliposomal complexes.

This work was supported by the Russian Science Foundation (grant no. 18-73-10079).

INFLUENCE OF ARM NUMBER ON THE BEHAVIOR OF THERMOSENSITIVE POLY(2-ISOPROPYL-2-OXIAZOLINE) SPHERICAL BRUSHES IN WATER

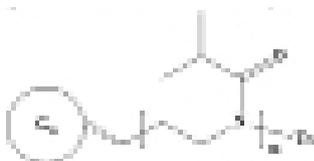
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The performance establishment of the «structure-properties» correlation for thermosensitive polymers reveals the dependence of self-organization and phase separation processes on the chemical structure and macromolecule architecture, which will allow carrying out the conditions for the synthesis of new polymer systems, in particular, for biomedical applications.

The aim of this work is to analyze the influence of the arm number on the behavior of thermosensitive poly(2-isopropyl-2-oxazoline) (PIPrOx) spherical brushes in water. Carbosilane dendrimers of the first and second generation were used as the spherical core. Four- (PIPrOx₄) and eight-arm (PIPrOx₈) poly(2-isopropyl-2-oxazolines) were studied. The degree of polymerization N of PIPrOx₄ and PIPrOx₈ were close ($N = 23$ and 25 , respectively).¹



The behavior of PIPrOx samples in water was studied by methods of light scattering and turbidimetry at temperatures from 15 to 65 °C within the hundred-fold concentration range. The formation of unimolecular micelles with dendrimer core and PIPrOx shell is observed. In addition, hydrophobic interactions between the cores lead to the formation of micelle-like and loose aggregates. It was shown that heating of solutions leads to macromolecule shrinking at temperate temperatures and aggregation near phase separation temperature T_{phs} . The T_{phs} increases with dilution and in dilute regime T_{phs} values for both systems coincide.

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This work has been supported by the State Program for Support of Leading Scientific Schools (grant no. 14.W03.31.0022).

"REVERSE" ARENE PLATINUM AND PALLADIUM SANDWICHES BASED ON π -HOLE \cdots [M^{II}] INTERACTIONS

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The diketonate complexes M(acac)₂ (M = Pd, Pt, Hacac = acetylacetonate), Pd(ba)₂ (Hba = benzoylacetonate) upon co-crystallized with highly electron-deficient arene systems to form «reverse» sandwich structures, packed as infinite stack due to π -hole \cdots [M^{II}] (M = Pt, Pd) and C \cdots F interactions.

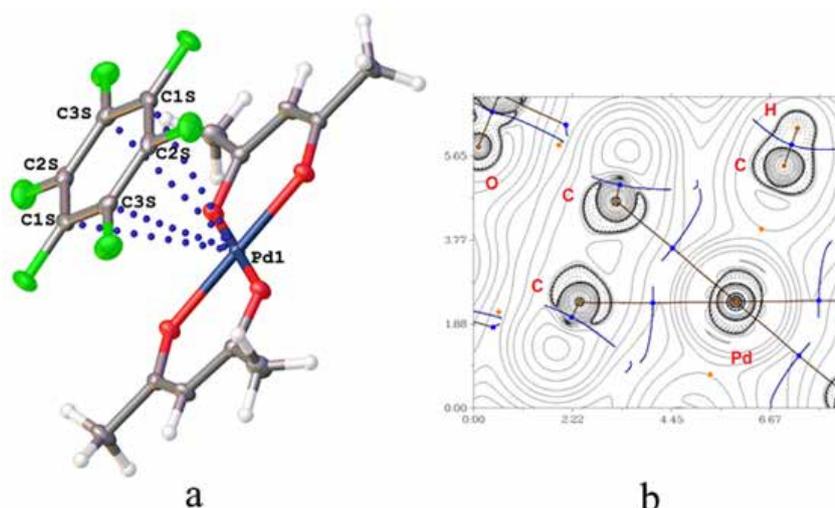


Figure 1. The fragment of adduct Pd_{(acac)₂}·C₆F₆ (a) and the contour line diagram of the Laplacian distribution in Pd_{(acac)₂}·C₆F₆ (b).

X-Ray analyses and ESP calculation of adduct indicate that in π -hole \cdots [M^{II}] contacts, [M^{II}] plays the role of a nucleophile.
This work was supported by RSF (17-73-10078).

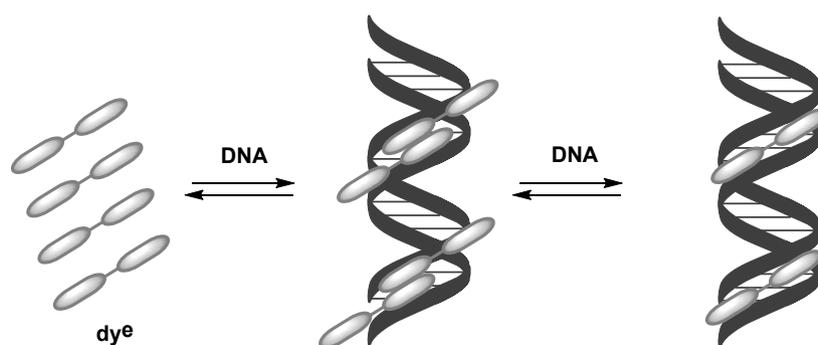
NOVEL BISSTYRYL DYES AS FLUORESCENT PROBE FOR NON-COVALENT INTERACTION WITH DNA

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The styryl dyes are one of the most widely used and important groups of functional dyes¹⁻². The interest of researchers is due to the relative ease of obtaining them, as well as a set of unique physicochemical and optical properties. The study of the interaction of organic molecules with DNA is of considerable interest to medicine and biological research. Such studies help to understand the mechanism of action of drugs, as well as contribute to the creation of a wide range of fluorescent markers for visualizing biological objects in fluorescence microscopy, gel electrophoresis, cytometry, etc.

In this work a series of new bisstyryl dyes in which the styryl moieties are bound by an alkyl linker is obtained and characterized.



The binding of dyes with DNA calf thymus has been evaluated using the UV-vis, fluorescence and circular dichroism spectroscopy. The dyes were found to have negligible fluorescence in a buffer solution, but exhibited a significant emission increase upon binding to DNA. The results obtained are consistent with a groove binding mode between bisstyryl dyes and DNA.

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Acknowledgements. We thank the Russian Foundation for Basic Research 18-33-00971 mol_a for financial support.

NOVEL SOLUBLE CROWN-SUBSTITUTED Cu(II) NAPHTHALOCYANINE COMPLEXES

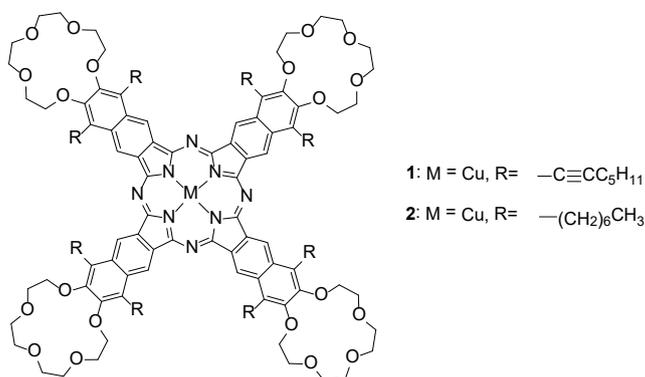
Safonova E.A.,^a Polovkova M.A.,^a Martynov A.G.,^a Gorbunova Yu.G.,^{a,b} Tsivadze A.Yu.^{a,b}

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Naphthalocyanines (Nc's) are in focus of interest as π - extended phthalocyanine derivatives with absorbance in NIR range, that affords their application as materials for optoelectronics, nonlinear optics, etc. One of the main problems of naphthalocyanines is their high tendency to aggregation leading to low solubility, fast deactivation of the excited states and ability of singlet oxygen generation.

In this work the novel tetra(15-crown-5)substituted Ncs bearing heptyl and heptynyl groups were synthesized. Copper(II) was chosen as a central cation because of the photostability of Cu(II) phthalocyanines. The complexes were obtained from corresponding naphthalonitriles by template reactions. It was shown that application of Cu(I) salts in this reaction is more effective than Cu(II) probably because of the high tendency to oxidation of naphthalocyanines.



The introduction of heptyl and heptynyl groups in 5 and 8 positions of naphthalocyanine ring dramatically increases solubility of CuNc's in organic solvents. On the other hand, it was observed that it does not have notable effect on the UV-Vis spectra of these compounds. The electron spin resonance spectra of obtained CuNcs show the characteristic pattern expected for Cu(II) cation. The UV-Vis investigation of cation-induced supramolecular aggregation of such complexes has shown that heptynyl groups in 2 make the formation of cofacial dimers more difficult while heptyl groups totally prevent this process.

This work was supported by the Russian Foundation for Basic Research (grant #18-33-00887-mol_a).

THE REGIOSELECTIVE [2+2] PHOTOCYCLOADDITION REACTION OF 2-(3,4-DIMETHOXYSTYRYL)QUINOXALINE IN SOLUTION

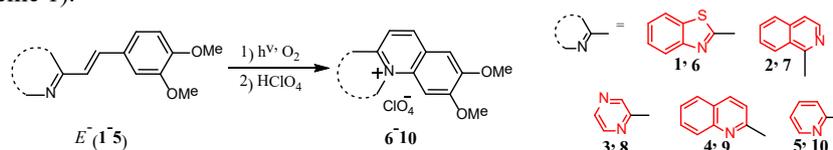
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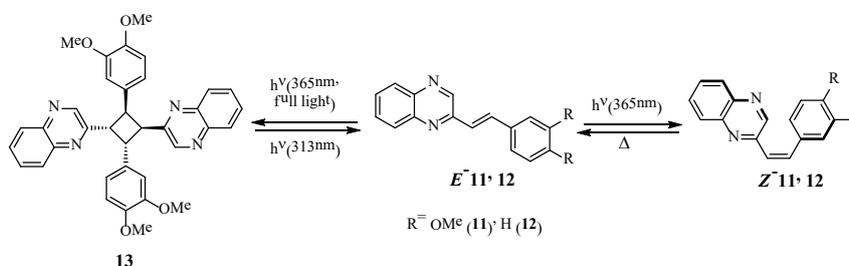
Although the photochemistry of stilbenes and its derivatives has been well studied,¹ only few studies have been reported on the photolysis of stilbene derivatives with nitrogen-bearing rings.

Recently, we have demonstrated that *ortho*-styryl-substituted *N*-heterocycles comprising one and two nitrogen atoms generally undergo regioselective C–N bond formation during photocyclization, resulting in the formation of a family of (aza)benzo [c]quinoxalinium derivatives (Scheme 1).²



Scheme 1

In our study, we present the results of the investigation of the photochemical behavior of the quinoxaline derivatives 11 and 12 to provide understanding of the influence of the heterostilbene structure on its photochemical transformation (Scheme 2).



Scheme 2

The observed photocycloaddition reaction of *E*-11 could be considered as a photoreversible photochromic process. Also, it provides an easy way for obtaining the cyclobutane derivative.

Acknowledgements. This work was supported by RFBR (№19-03-00535) and by Russian Science Foundation (грант №19-43-04127).

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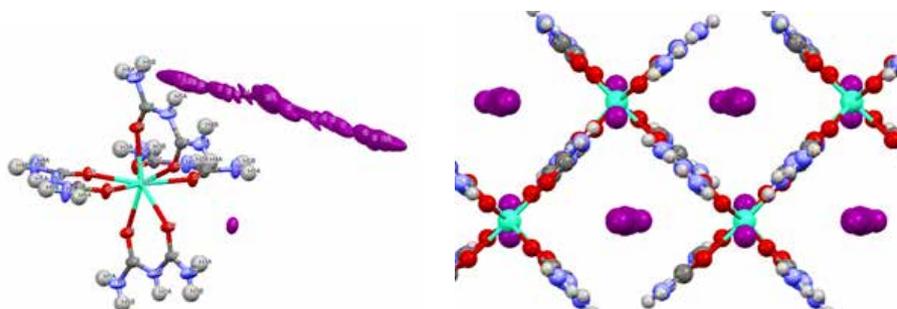
STABILIZATION OF LINEAR POLYIODIDE CHAINS BY RARE-EARTH COMPLEXES OF BIURET

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Reactions of rare-earth iodides with biuret ($\text{H}_2\text{NCONHCONH}_2$, BU) in aqueous solution in air produced black crystals of corresponding polyiodides. The gadolinium compound was studied by X-ray diffraction. Its crystals are monoclinic, space group $C2/c$, $a = 16.1089(13)$, $b = 19.9191(15)$, $c = 12.2367(9)$ Å, $\beta = 124.291(2)^\circ$, $Z = 4$. They contain $[\text{Gd}(\text{BU})_4]^{3+}$ complex cations with bidentate biuret ligands (coordination number 8), isolated iodide ions and highly disordered polyiodide ions. The formula of the compound can be presented as $[\text{Gd}(\text{BU})_4]_2\text{I}_{13}$ or $[\text{Gd}(\text{BU})_4](\text{I})_2\text{I}_{4,5}$. Complex cations and anions form walls of square channels incorporating nearly linear polyiodide chains which seem to be built of pentaiodide and triiodide ions, similar to starch-iodine¹ or pyrroloperylene-iodine complex². The structure is stabilized by N–H⋯I hydrogen bonds between biuret ligands and polyiodide ions. Isolated iodide ions form no short contacts.



Elemental analysis, IR spectroscopy (including long-wave region) and X-ray powder diffraction showed that lanthanum and samarium compounds have the same composition and structure.

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LIOTROPIC LANTHANIDOMESOGENS - PERSPECTIVE MEDIA FOR MOLECULAR ELECTRONICS AND BIOMEDICINE

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The creation of soft luminescent materials attracts great interest due to the wide range of their practical application in biomedicine and molecular electronics. Of particular interest are anisotropic molecularly organized media - lyotropic liquid crystals (LLC). Due to its unique properties and structure, lyomesophases have broad concentration limits of encapsulation and are capable of transferring both hydrophobic and hydrophilic substances. The structural and phase diversity of LLCs makes them potential template for the synthesis of nanostructures with different spatial organization. Supramolecular assemblies of metal complexes in anisotropic LLC phases are of great interest and provide new promises in today's materials science.

The paper presents a study of the liquid-crystal, structural, luminescent properties of lyotropic metallomesogens based on low molecular weight (non-ionic surfactants), polymeric (block copolymers, biopolymer) and macrocyclic (calixarenes) compounds and complexes of lanthanides in the series (Ln (III) = La, Eu, Tb, Dy). Using a complex of physico-chemical research methods, the influence of the nature and structure of the ligand on the lyotropic mesomorphism and the optical properties of the systems was revealed.

Biocompatible systems with luminescent properties are of considerable interest for bioassay and medical diagnostics. New biomesogens based on cholesteryl oligo(ethylene oxide) amphiphile and Ln (III) = La, Eu, Tb, Dy were synthesized. These systems demonstrate high luminescence characteristics¹. For binary systems CholEO₁₀/Ln, CholEO₁₇/Ln the smectic phases were obtained. In ternary systems in the present of water (5-30% wt) the lyotropic mesomorphism were observed.

New biocompatible LLCs based on biopolymer chitosan and lactic acid are proposed as transport systems for the delivery of bioactive substances. Concentration and temperature regions of lyotropic mesophase formation were found. The possibility of controlled release of vitamin B2 by varying the structure of the mesophase is shown.

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This work was supported by the RFBR, project 18-03-00173

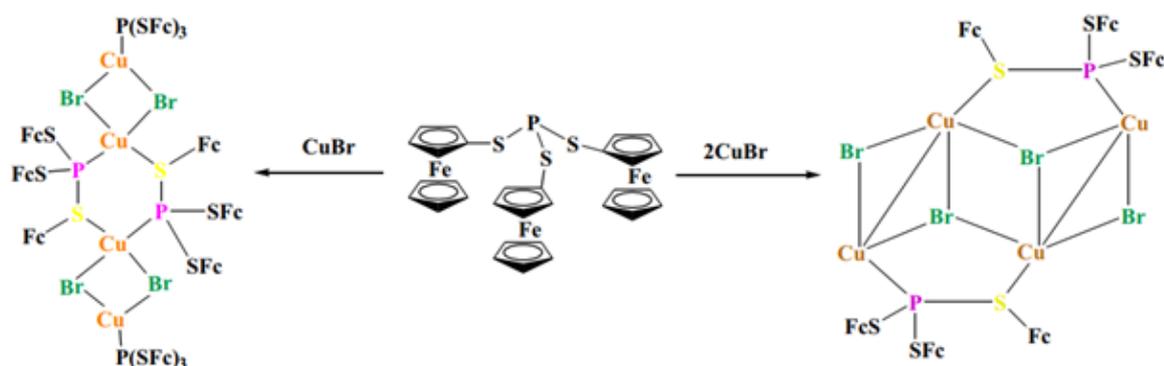
THE TRIFERROCENYLTRITHIOPHOSPHITE COPPER(I) BROMIDE COMPLEXES

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The trithiophosphite has a significant interest as potential ligands. Ability both phosphorus and sulfur atoms to bonding with metal ions lead to realization of different coordination modes that result formation of polynuclear complexes and clusters. The complexation properties of trithiophosphites clearly depend on the metals.

We have found that triferrocenyltrithiophosphite react with copper (I) bromide to form two type complexes depending on stoichiometry of initial reagents with different coordination mode of triferrocenyltrithiophosphite with copper atoms.



Stirring mixture of copper (I) bromide and triferrocenyltrithiophosphite in ratio 1:1 lead to formation of tetrakis((triferrocenyltrithiophosphite)copper(I)bromide) almost with quantitative yield. Changing the ratio triferrocenyltrithiophosphite/CuBr result the formation of complex another mode type and contain four copper atoms connected by bromide atoms and two molecule of triferrocenyltrithiophosphite as bridged ligands. The all four membered cycles CuBrCuBr are planar that is typical for copper (I) bromide.

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The work was financially supported by the grant of President of the Russian Federation (MK-3375.2019.3)

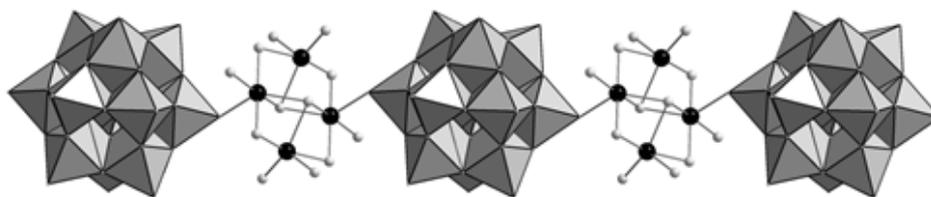
SELF-ASSEMBLY OF Ag⁺ AND POLYOXOMETALATES IN NON-AQUAEOUS CONDITIONS

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Polyoxometalates (POM) represent a specific, large and important class of inorganic compounds of seemingly endless versatility in composition and structure, impacting such fields as homogeneous and heterogeneous oxidation catalysts, photochemistry, material science in general and artificial supramolecular systems. In particular silver containing polyoxometalates refer to rather fascinating class of compounds that is the key to making photocatalytically active materials.

We studied the self-assembly of Ag⁺ and Keggin type anions [PW₁₁NbO₄₀]⁴⁻ and [SiW₁₂O₄₀]⁴⁻ under various conditions. We obtained Ag₄(MeCN)_{14,5}[PW₁₁NbO₄₀] and Ag₄(MeCN)₁₄[SiW₁₂O₄₀]. In case of Ag₄(MeCN)_{14,5}[PW₁₁NbO₄₀] MeCN molecules are rather labile and can be replaced with dimethylacetamide to form Ag₄(MeCONM₂)₄[Ag₃(MeCONM₂)₆][PW₁₁NbO₄₀]. Direct synthesis of this compound is impossible due to the protonation of the solvent and formation of ((MeCONM₂)₂H)₄[PW₁₁NbO₄₀]. We also obtained bright yellow colored Ag₄(DMF)₁₂[PW₁₁NbO₄₀]. Its color may indicate the presence of interesting Ag-Ag interactions. But this substance is unstable in air conditions, the loss of DMF leads to the compound transformation into Ag₄(DMF)₁₀[PW₁₁NbO₄₀] with other structure. So depending on the conditions, self-assembly leads to the formation of tri- or tetranuclear silver clusters.



The polymer structure of Ag₄(DMF)₁₂PW₁₁NbO₄₀ (Ag ions are black, O from dmf are white, another parts of dmf molecules are omitted for clarity)

This work was supported by Russian Foundation for Basic Research (grant number 18-33-20067)

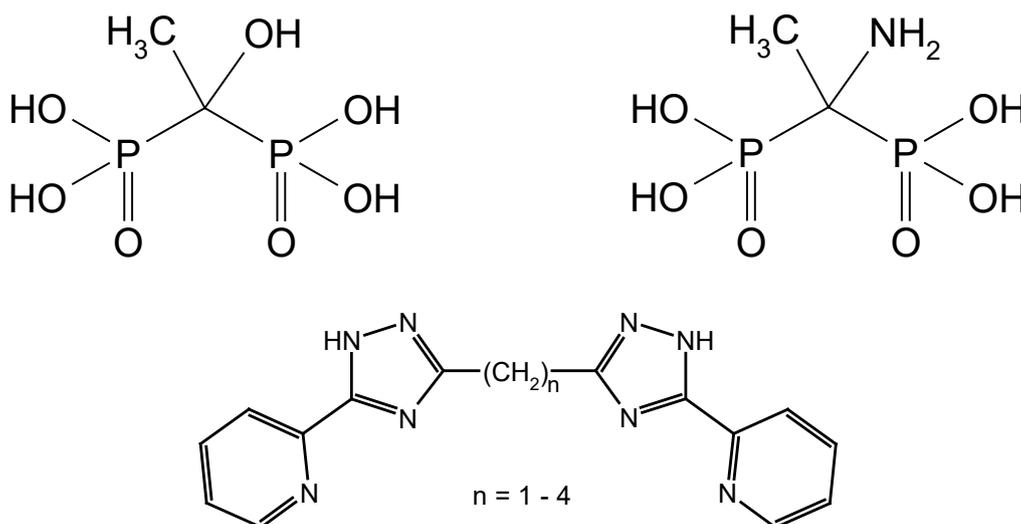
THE METALS BISPHOSPHONATES COMPLEXES WITH SPACER-ARMED 2-PYRIDYL-1,2,4-TRIAZOLES

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Bisphosphonates can show multiple coordination modes, and this combined with the different geometries of the metal polyhedron lead to a large number of compounds with versatile structures. Most of them display layered structures with different layer topologies and the organic groups filling in the interlayer spaces. Low dimensional metal bisphosphonates such as chains, clusters and coordination polymers can be obtained at additional functional groups and organic extra ligands introducing.

Here we describe the synthesis and structure heteroleptic metals complexes of same bisphosphonates and spacer-armed 2-pyridyl-1,2,4-triazoles, which are a convenient matrix for for assembling coordination compounds of various nuclear and topology.



Coordination compounds were characterized by various means including elemental analysis, UV-Vis, IR-spectroscopy, EPR and X-Ray analysis.

The modes of binding and types of structures formed during self-assembly of the complexes are studied. It is shown that the of bridging ligands binding is determined by the length of polymethylene spacer. The some types of complexes have been described.

Acknowledgements. Authors would like to acknowledge the financial support from the RSF (project № 18-13-00024).

CHARACTERISTICS OF SOLUTIONS OF STIMULI-RESPONSIVE POLYMERS ON BASIC N-[3-(DIALKYLAMINO)ALKYL)-(METH) ACRYLAMIDES WITH VARYING pH AND CONCENTRATION

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The aim of this work is to investigate behavior of buffer solutions for double stimuli-responsive polymers on basic N-[3-(dialkylamino)alkyl]- (meth)acrylamides. Synthesis was carried out by method of radical polymerization at 70°C. Molar masses and hydrodynamic radii of scattering objects were determined in chloroform solutions by static and dynamic light scattering. It was shown that for all studied polymers of N-[3-(dialkylamino)alkyl]- (meth) acrylamides chloroform is good solution. Homopolymers have different molar masses it can be explained by the fact, that addition of methyl substituent in vinyl group gives difference in reaction activity for acrylic and methacrylic monomers and consequently difference in ratio of propagation and termination constants of macroradical chain.

Temperature dependences of light scattering intensity, optical transmission, hydrodynamic radii and molecular masses of scattering objects were obtained in wide concentration and pH range in buffer solutions (from 2 to 13), depending of structures of monomer units.

It was established that decrease of concentration and pH leads to increase of phase separation temperatures.

The financial support was provided by The Russian Foundation for Basic Research (project № 18-33-00576 mol_a).

INFLUENCE OF SALT CONCENTRATION ON THE BEHAVIOR OF TERMOSENSITIVE FOUR-ARM STAR-SHAPED POLY-2-ETHYL-2-OXAZINE

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The aim of this work is an analysis of influence of salt concentration on the behavior of termosensitive four-arm star-shaped poly-2-ethyl-2-oxazine (PEOZin) in water-salt solutions.

Molar mass ($M_w = 7100 \text{ g mol}^{-1}$) was determined by static light scattering in nitromethane. The water-salt solutions were studied by the light scattering and turbidimetry. Solutions with concentration $c = 0.005 \text{ g cm}^{-3}$ was investigated at NaCl concentration $c_{\text{NaCl}} = 0.72 \times 10^{-3}$, 9.05×10^{-3} and $36.5 \times 10^{-3} \text{ M}$, which results in content of one NaCl per one macromolecule, one arm and one monomer unit of PEOZin. Also, PEOZin solutions in water and saline were investigated too.

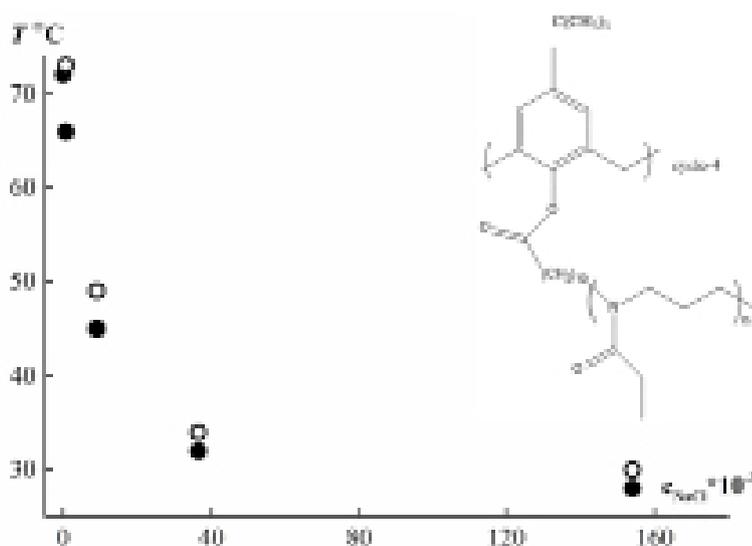


Fig. 1. The phase transition temperatures vs. NaCl concentration for solutions of polymer concentration $c = 0.005 \text{ g cm}^{-3}$.

It is shown that an increase in the salt content leads to a strong decrease in phase separation temperatures (Figure1). Even a minimum amount of NaCl ($c_{\text{NaCl}} = 0.72 \times 10^{-3}$ - of one NaCl per one macromolecule) cause to a reduction in the temperature of the beginning of the phase transition by 10 °C.

PORPHYRIN-BASED METAL-ORGANIC FRAMEWORK INTERCALATED IN LAYERED EUROPIUM HYDROXOCHLORIDE

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Porphyrin metal-organic frameworks (MOF) are the coordination polymers assembled from porphyrin metal complexes as functional linkers. These porous materials exhibit a range of useful properties of stable and functionally versatile selective catalysts. However, MOFs may not be sufficiently stable in a course of the interactions with the reactive components. A possible strategy for solving this problem is the immobilization of MOF on the solid surface of layered inorganic particles. This approach makes it possible to obtain a stable hybrid material, which might exhibit a synergistic effect due to a combination of the properties of integrated organic and inorganic components. In this work we realized this idea through the intercalation of 5,10,15,20-tetrakis(4-carboxyphenyl) zinc porphyrinate (ZnTCPP) and a binuclear complex of zinc acetate as the MOF components into the microparticles of layered europium hydroxochloride (EuLH).

The catalytic activity of the material was demonstrated in a course of the hydrolysis of bis(4-nitrophenyl) phosphate, which is widely used as a model reaction for DNA phosphodiesterase. The UV-vis absorption spectroscopy was used to monitor the reactions with the hybrid catalyst and the control system of pure EuLH. The data showed a difference in the reaction mechanisms in these two systems. We analyzed the composition of the reaction products in the hybrid catalyst to study the origin of this difference. The analysis was carried out using a combination of methods: X-ray diffraction, IR- and Raman-spectroscopy and MALDI-TOF mass-spectrometry. We pioneered the application of MALDI-TOF mass-spectrometry for a direct qualitative detection of low-molecular-weight organic components (BNPP and its products of hydrolysis) immobilized within solid colloids. These observations provided a basis for understanding the mechanism underlying the catalytic process in the hybrid system by separating the contributions of both components.

We believe that our method can be extended to other classes of layered inorganic colloids as templates for self-assembly of functional MOF-based structures potentially useful as efficient synergetic catalysts and sensing systems.

Acknowledgements: The work was supported by the Russian Foundation for Basic Research (grant 18-29-04026 MK), and the Ministry of Science and High Education RF. XRD was performed using the equipment of CKP FMI of IPCE RAS.

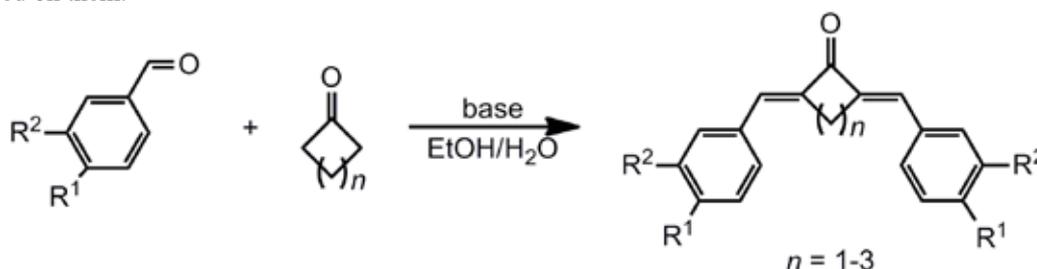
SYNTHESIS OF BIS(AZACROWN)DIENONES AND SPECTROSCOPIC STUDY OF SUPRAMOLECULAR COMPLEXES WITH ALKALINE AND ALKALINE EARTH METAL CATIONS

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The purpose of this study was to synthesize a series of dienones with various donor substituents, including azacrown-containing dienones, to study the photophysical properties of the obtained compounds and the possibility to construct photoactive supramolecular systems based on them.



$R^1, R^2 = H, OMe, SMe, NEt_2, \text{azacrown-ether}$

Dienones with various donor substituents and azacrown-containing dienones were obtained by the alkaline aldol-crotonic condensation of aromatic aldehydes with cyclic ketones in the presence of a base (Claisen-Schmidt reaction). The structure of the obtained dienones was determined by NMR-, IR-, UV spectroscopy and elemental analysis.

The formation of supramolecular complexes of azacrown-containing dienones with alkaline and alkaline earth metal cations was studied by electronic spectroscopy methods. The complexation is accompanied by changes in the absorption and fluorescence spectra of dienones. It was found that azacrown-containing dienones forms complexes of different stoichiometry with metal cations. The stability constants of the complexes were determined.

The synthesized dienones and supramolecular systems based on them may be used as components of photoactive supramolecular devices, optical molecular sensors.

This work was supported by the RAS (Program №38 of the Presidium of RAS) and the Russian Science Foundation (project № 19-13-00020).

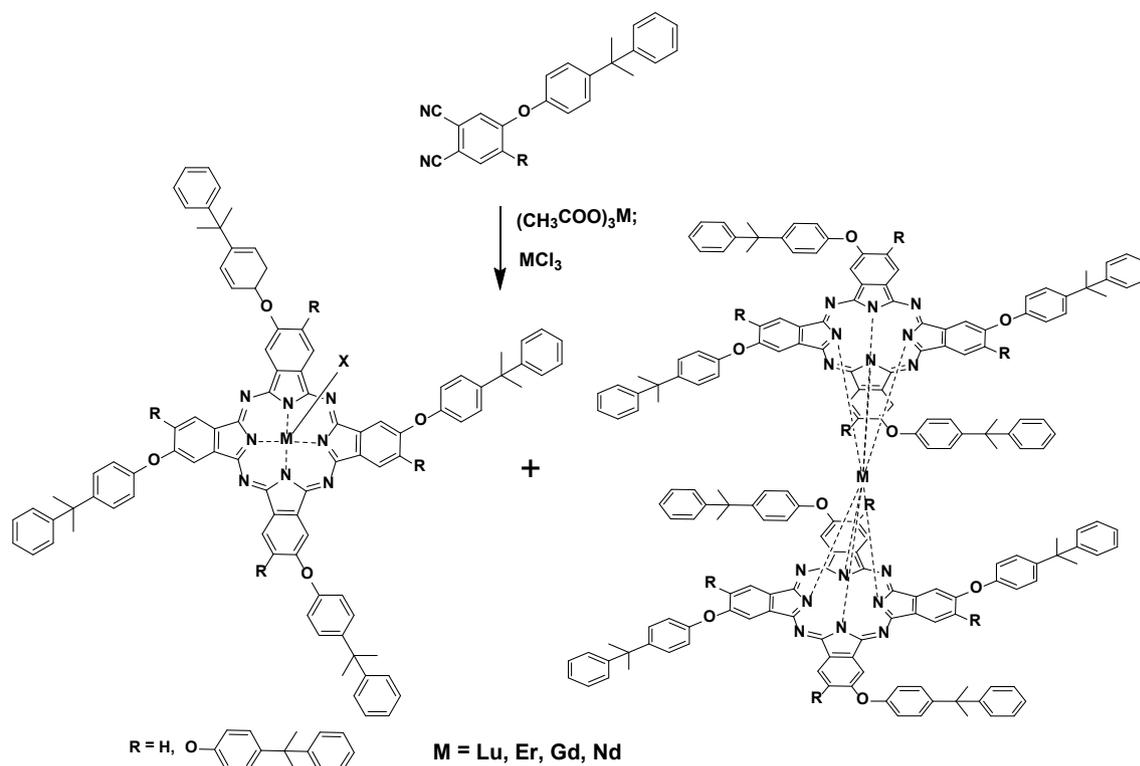
ARYLOXY-SUBSTITUTED PHTHALOCYANINES COMPLEXES WITH
f- METALS

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The development of directed lanthanide complexes with aryloxy- substituted phthalocyanine derivatives planar and sandwich structures synthesis methods is relevant since the main problem in achieving this goal is hardly separable mixture formation of different structures products. Present work describes synthetic ways to obtaining novel phthalocyanines metal complexes, containing on the periphery 4-(1-methyl-1-phenylethyl)phenoxy- groups with lutetium, erbium and gadolinium in a different ratios.



The synthesis was carried out by template condensation of corresponding nitriles with excess of metal salt in boiling *i*- amyl alcohol in the presence of DBU. The structure of all the compounds obtained was confirmed by elemental analysis, MALDI-TOF spectrometry, ^1H NMR, IR and absorption spectroscopy.

The work was supported by the Russian Science Foundation (project No. 17-73-20017).

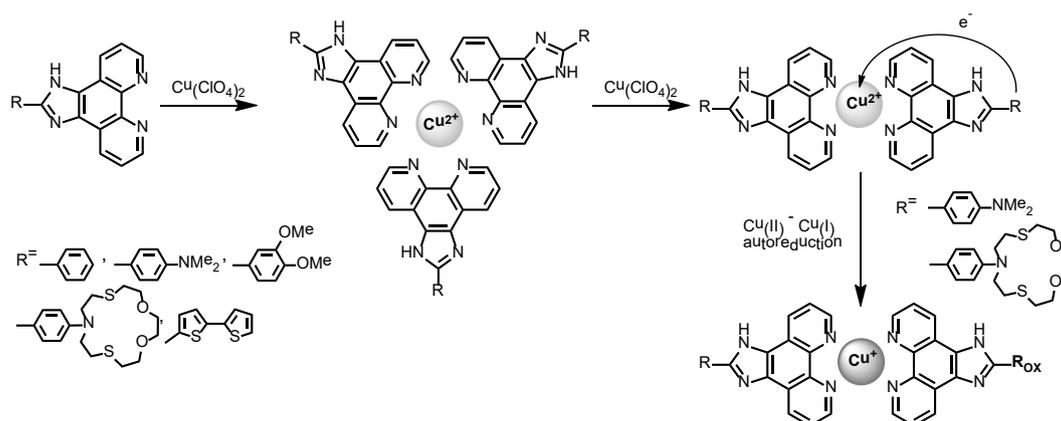
INTRAMOLECULAR ELECTRON TRANSFER IN ARYL-IMIDAZO-1,10-PHENANTHROLINE COMPLEXES WITH COPPER (II)

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Imidazo [4,5-f] [1,10] phenanthrolines as N-donor ligands demonstrate suitable structural characteristics for coordination with different types of metal cations (Zn^{2+} , Mn^{2+} , Cd^{2+} , Co^{2+} , Pt^{2+} , lanthanides (III), Ru^{2+}). In addition, imidazo-[4,5,f][1,10]-phenanthrolines are the universal chelating ligands used in the development of metal-containing DNA intercalators. In turn, organic copper complexes represent an important class of compounds in terms of bioorganic chemistry, catalysis, etc.



Imidazo[4,5-f][1,10]phenanthrolines containing phenyl- (1), 4-(N,N-dimethylamino)phenyl- (2), 4-(azadithiacrown-ether)phenyl- (3), 3,4-dimethoxyphenyl- (4) and 2,2'-bithiophen-5-yl- (5) were synthesized and their $Cu(II)$ complexes were studied to determine the effect of substituent, geometry of complex and solvent nature on the spectral and redox properties of the copper complexes. It was found that in case of 4-(N,N-dimethylamino)phenyl- and 4-(azadithiacrownether)phenyl substituents the formation of L_2Cu^{2+} complex of pseudo-tetrahedral geometry causes the appearance of an intense ligand-to-metal charge transfer (LMCT) band at the visible region and induces a positive shift in the reduction potential providing the occurrence of autoreduction of $Cu(II)$. Electrochemical study showed that the autoreduction is observed when Cu^{2+}/Cu^+ transfer and oxidation of ligand occur at the closed electrochemical condition.

The reported study was funded by RFBR according to the research project №18-33-00715.

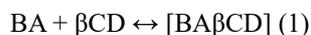
THERMODYNAMICS OF β -CYCLODEXTRIN-BENZOIC ACID INCLUSION COMPLEX FORMATION IN H_2O - $EtOH$ AND H_2O - $DMSO$ SOLVENTS AT $T = 298.15$ K

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Benzoic acid (BA) and its sodium salt are widely used as anti-microbial preservatives in food, beverages and cosmetics. To improve bioavailability, ensure maximum effectiveness of the treatment, reduce toxicity, the solubility of drugs have to be increased. One of simple and effective ways is an encapsulation by cyclodextrins. The process of complex formation of β -cyclodextrin (β CD) with benzoic acid is described as follows:



In this study the thermodynamic parameters for the reaction of $[BA\beta CD]$ complex formation in H_2O - $EtOH$ and H_2O - $DMSO$ solvents were determined from calorimetric experiments carried out by means of the calorimetric titration system TAM III (TA Instruments) at $T = 298.15$ K. The heat effects of mixing β CD solutions with BA were obtained in water-organic mixed solvents containing $X(EtOH)=0.00, 0.10, 0.20, 0.30$ and $X(DMSO)=0.05$ mol. fr. at pH = 3.6 at $T = 298.15$ K.

However, at $X(EtOH)=0.30$ mol. fr., according to the calorimetric titration data, no complex formation occurs. When transferring from H_2O to H_2O - $EtOH$ organic solvents complex stability decreases from $\lg K = 2.4$ to $\lg K = 0.7$, therein reaction exothermicity increases from -12.2 kJ/mol to -44.3 kJ/mol. A decrease in the entropic contribution to changing the reaction Gibbs energy was observed.

The calorimetric measurements reported in this work were carried out at the Institute of Thermodynamics and Kinetics of Chemical Processes of the Ivanovo State University of Chemistry and Technology (ISUCT) using the equipment of the Centre for Collective Use of ISUCT.

This work was funded by RFBR and VAST according to the research project №19-53-54004.

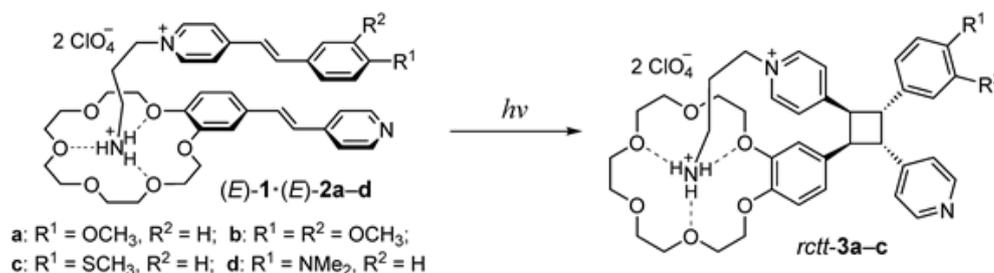
PROPERTIES OF SUPRAMOLECULAR PSEUDODIMERIC COMPLEXES OF STYRYLPYRIDINE DERIVATIVES

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Crown ether-containing styrylpyridine (*E*)-1 is able to bind styrylpyridinium dyes (*E*)-2a–d via hydrogen bonding to form complexes (*E*)-1·(*E*)-2a–d in which the styrylpyridine and styrylpyridinium moieties are arranged one over the other owing to stacking interactions.^{1,2}



The photochemical properties of dyes (*E*)-2a–d in free forms and in complexes with styrylpyridine (*E*)-1 were studied by electronic spectroscopy methods. It was found that the complexation of (*E*)-2a–c with (*E*)-1 induces a stereospecific [2+2]-cross-photocycloaddition reaction yielding cyclobutanes rctt-3a–c. The quantum yields of this photoreaction were measured upon selective excitation of the dye. An unexpected result is that with an increase in the S₁ excited state lifetime of the dye (2a < 2b < 2c, more than 20 times), the photocycloaddition quantum yield decreases (2a > 2b > 2c, twofold). In order to interpret this effect, the structures of complexes (*E*)-1·(*E*)-2a,c in MeCN were studied using density functional theory calculations.

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FRET-BASED METAL ION SENSING BY CROWN-CONTAINING BISSTYRYL DYE

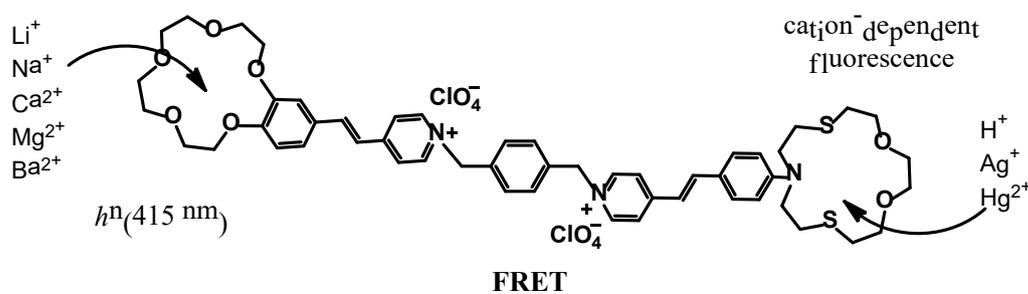
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Styryl dyes are one of the known classes of organic photosensitive compounds that are widely used due to their unique optical properties.¹ The possibility of energy transfer (FRET) in the dye molecules helps to avoid errors in the fluorescence spectra associated with the effects of self-quenching and backscattering.² This is why FRET based chemosensors are considered as promising for applications in biochemistry and environmental research.

Asymmetric bisstyryl dye containing benzocrown- and azaditiacrown-ethers was obtained and characterized. The chemosensor based on such bisstyryl dye demonstrates a distinct fluorescence changes upon interaction with Na⁺, Li⁺, Mg²⁺, Ca²⁺, Ba²⁺, H⁺, Hg²⁺, Ag⁺ perchlorates.



The complex formation of crown-containing bisstyryl dye with various metal cations and effect of this process on the flow FRET were studied by optical spectroscopy. The stability constants and quantum yields of fluorescence of complexes were calculated. Thus, it was shown that using a bisstyryl dye of such structure it is possible to recognize metal cations of different nature.

Acknowledgments. We thank the Russian Foundation for Basic Research 19-03-00535 for financial support.

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SOLUBILIZATION OF DINITROBENZOFUROXANE IN POLYETHYLENIMINE SOLUTIONS

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This report presents the results of the study of the process of solubilization of 4,6-dinitrobenzofuroxan, DNBFO, in solutions of branched polyethyleneimine molecular weight 1200. The area of existence of PEI 1200 in the unfolded conformation and the form of a coil was determined by the viscometric method. According to the results of potentiometric titration using Henderson-Hasselbalch equation, the ionization constants of polyethylenimine at its various concentrations were determined. As a result of single-factor experiments, which were performed by the spectrophotometric method, the absorption regions of PEI 1200 and DNBFO in various solvents and at different values of the acidity of the medium were determined. Polyethyleneimine 1200 was shown to have no absorption band in the visible region of the spectrum, and dinitrobenzofuroxane absorbs in the range 400-460 nm, depending on the pH of the medium. Solubilization of dinitrobenzofuroxan was determined spectrophotometrically using the optical density of the absorption band at 460 nm. To search for optimal conditions for solubilization of DNBFO in a polyethylenimine environment, the response surface methodology and three-level Box – Benken plans were used. For this purpose, 15 experiments were carried out at different values of the selected factors (C PEI 1200, pH, time of dissolution, t). Using the program “Statistica 10”, graphs of response surfaces of the $A_{460} = f$ dependence (C PEI, pH) were created; $A_{460} = f$ (C PEI, t); $A_{460} = f$ (t, pH), which allow to determine and predict the effect of these factors on optical density. Using the data obtained, a mathematical model was constructed for the dependence of the optical density on the factors under study. The model was optimized and the optimal composition was obtained to solubilize dinitrobenzofuroxan in the PEI 1200 - water system.

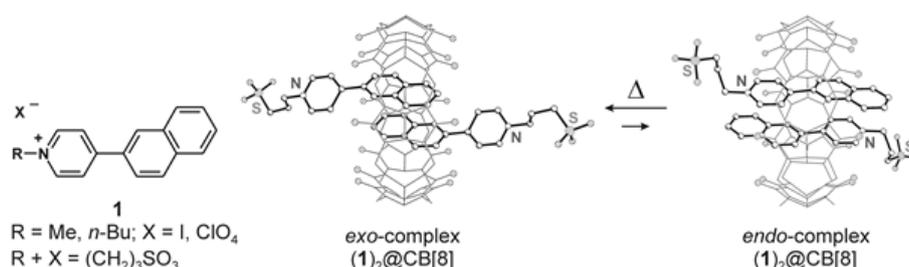
SELF-ASSEMBLY OF CAVITANDS AND NAPHTHYLPYRIDINE DERIVATIVES TO SUPRAMOLECULAR STRUCTURES

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Quaternary 4-(2-naphthyl)pyridinium salts **1** with various *N*-substituents were synthesized. The structure of these salts was determined by X-ray crystallography. The self-assembly of **1** with cavitand molecules – β - and γ -cyclodextrins and cucurbit[7,8]urils – in aqueous solutions was studied by electronic spectroscopy and ¹H NMR spectroscopy.



The formation of inclusion complexes of different stoichiometry and stability, was observed, depending on the structure of *N*-substituent in **1** and the cavitand nature and cavity size. The complex formation with cucurbiturils results in considerable changes in the absorption and fluorescence spectra of naphthylpyridine derivatives. Motion of the guest molecules in the cavitand cavities was detected. The X-ray diffraction study was carried out for two polymorphs of 2:1 complexes formed by betaine type naphthylpyridine derivative and cucurbit[8]uril, in which the cavitand was located either above the naphthalene residues of a dimeric pair of guest molecules or above the centers of their conjugated moieties.¹

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This work was supported by the Russian Foundation for Basic Research (project 18 03 00214).

BIOLOGICALLY ACTIVE COMPOSITIONS BASED ON CYSTEINE, SILVER NITRATE AND WATER-SOLUBLE POLYMERS

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In this research, we have obtained the first results on the synthesis and study of the properties of hydrogels based on cysteine-silver solution and bioactive biocompatible polymers of different molecular weight and chemical nature (polyvinyl alcohol - PVA, polyethylene glycol - PEG, polyvinylpyrrolidone - PVP).

Gels based on cysteine, silver nitrate and polymers were obtained in two stages. On the first, the cysteine-silver aqueous solution (CSS) was prepared [1]. Further, the polymer of different concentrations (0.002, 0.01, 0.02, 1 and 2 % w/w) was added to the mature (24 h) CSS solution and finally sodium sulfate (fixed concentration) as the initiator of gel formation was added to the resulting mixture.

Using UV and IR spectroscopy, it was found that the polymer macromolecules interact with CSS supramolecules without changing the structure of the latter. The study of the rheology of obtained compositions by the vibrational viscometry showed the addition of a polymer induces an increase the viscosity characteristics of hydrogels compared to the control sample (hydrogel without polymer). At the same time, PVA showed the strongest influence on the viscosity of the system. Rheological test also confirmed that gels with PVA are the most stable in time.

Methods of pH analysis, measurement of the size of the formed units and their zetta potential (DLS) confirmed the interaction of CSS and polymers through the formation of hydrogen bonds.

The study of the morphology of hydrogels (SEM) revealed a strong difference in their structure. For PVA, regardless of the molecular weight, a regular porous structure was obtained, whereas for PVP and PEG – an irregular porous structure.

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The work was carried out with the financial support of the Ministry of education and science of the Russian Federation in the framework of public works in the field of research (project №4.5508.2017/BP) on the equipment of the center for collective use of Tver State University.

SELF-ORGANIZATION PROCESSES IN SUPRAMOLECULAR SYSTEMS L-CYSTEINE -ACETATE - D₂O

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Hydrogels based on low molecular weight compounds (amino acids, peptides) are now in great demand in medicine, and therefore they attract the attention of researchers. There was discovered gelation in low-concentrated aqueous solutions of the amino acid L-cysteine (L-cys) and silver acetate (AgAcet) when adding electrolytes (sulphates or metal chlorides). The work purpose is determining the impact of the replacement of the solvent ($H_2O \rightarrow D_2O$) on the processes of self-building and gelation in supramolecular systems based on L-cys and AgAcet using the methods of UV and NMR spectroscopy, dynamic light scattering.

There was established when mixing solutions of L-cys and AgAcet in D_2O , the formation of cysteine silver solution (CSS/ D_2O) occurs similarly to systems based on H_2O . Absorption bands (~ 308 and 388 nm) give evidence about it in the electronic spectrum of CSS/ D_2O samples. Gelation with the addition of salt-initiators in systems with D_2O flows faster than in systems with H_2O . Distributions of particles by size (according to dynamic light scattering) are bimodal in both of systems, however, the diameter of germinal clusters and main aggregates in systems with H_2O is equal according to ~ 9.7 and 72.6 nm and with D_2O – ~ 20.0 and 187.9 nm. These results indicate a special role of the solvent (H_2O and D_2O) in the formation of supramolecular aggregates due to hydrogen bonding.

D_2O -based CSS and gels were studied by method of NMR spectroscopy. It was found that in the CSS sample (compared with AgAcet) there is a strong shift of CH_3 -group protons (0.14 ppm) in the region of the weaker field, which indicates the formation of supramolecular chains, as well as the possible localization of the acetate charged group in the nucleus of the cluster.

In the transition from CSS to hydrogel, the shift of the CH_3 group is not observed, which confirms the predominant formation of the gel network by surface interactions of clusters.

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The study was carried out with the financial support of the Ministry of education and science of the Russian Federation in the framework of public works in the field of research (project №4.5508.2017/BP) on the equipment of the center for collective use of Tver state University.

SYNTHESIS AND CHARACTERIZATION OF NOVEL BENZOANNULATED PHTHALOCYANINES

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Development of approaches towards low-symmetry phthalocyanines with extended aromatic systems modified by the anchor groups is an actual task both from the fundamental and practical points of view, because it can pave way to new hybrid optical materials.

In this work, we firstly performed template condensation of butoxyphthalonitrile A and naphthalonitrile with fragments of diethylene glycol B, using magnesium as a template. The reaction resulted in mixture of symmetric phthalocyanine MgA_4 and low-symmetry complex MgA_3B bearing one naphthalene unit. Demetalation of this mixture with trifluoroacetic acid and chromatographic separation afforded metal-free ligands H_2A_4 and H_2A_3B . The obtained compounds were characterized by a set of physicochemical methods (NMR, UV-Vis spectroscopy, mass spectrometry, etc.). Notably, the Q-bands of H_2A_3B are shifted bathochromically in comparison with symmetric phthalocyanine H_2A_4 which evidences of extension of aromatic system upon introduction of additional benzene ring.

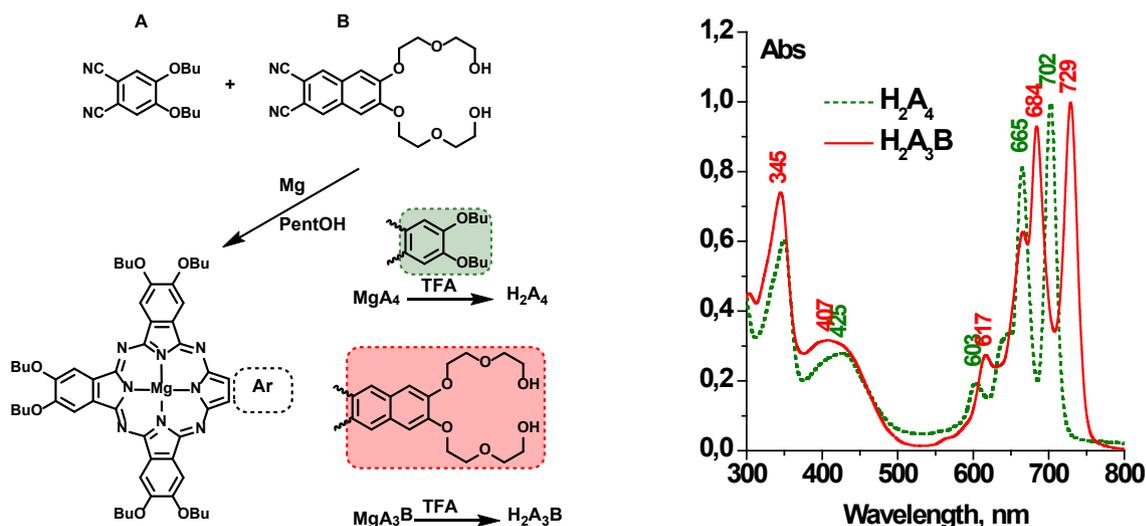


Figure 1. Synthesis (left) and UV-Vis spectra (right) of phthalocyanines H_2A_4 and H_2A_3B .

This work was supported by the Russian Science Foundation (№19-73-00332)

HYDROGELS BASED ON L-LACTIDE AND ETHYLENE GLYCOL TRIBLOCK COPOLYMERS

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The cellular technologies allow opening the opportunity of restoring or replacing damaged body tissues, without resorting to transplantation of donor organs. The main tool of regenerative medicine is tissue-engineering design, which includes cells (often stem) of the body and the scaffold - the extracellular matrix. Special requirements for the cultivation of stem cells are imposed on the matrix: 1) bioengineering scaffold should not cause inflammatory reactions; 2) stem cells must attach, proliferate and differentiate into the matrix; 3) the physicochemical characteristics of the matrix should correspond to the native tissues; 4) matrixes must be resorbed within a specified period of time. Natural and synthetic biodegradable polymers are the most promising candidates for such structures.

The object of study was biocompatible and biodegradable hydrogels based on amphiphilic ternary block copolymers of L-lactide and ethylene glycol (PLLA-PEG-PLLA) with a total molecular weight of 10 to 45 kDa. The hydrogels were obtained by dialysis with a fast and slow change of the solvent quality. The hydrogels structure was studied by scanning electron microscopy and X-ray scattering using synchrotron radiation source. It was shown that the network with predominantly defected crystallites and low elastic moduli (13 kPa) is formed in the case of the fast dialysis. Hydrogels with the lamellar structure of polylactide and higher (1650 kPa) elastic moduli are formed during slow dialysis.

This work partially supported by RFBR, project №17-03-01361 A.

INFLUENCE OF THE CONTENT OF N-(3-(DIETHYLAMINO)PROPYL)-N-METHYLACRYLAMIDE ON THERMO- AND pH-SENSITIVITY OF STATISTICAL COPOLYMERS IN AQUEOUS SOLUTIONS

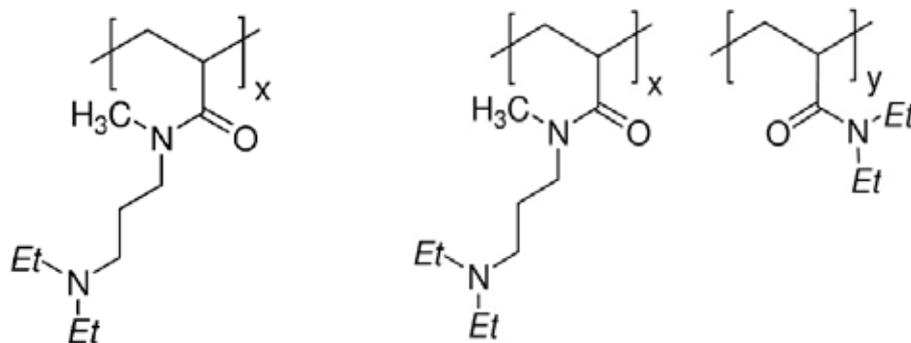
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Polymer amines are intensively studied for application in smart systems and as matrices for the design of composite materials, including bioinspired substances.

The aim of this work is to study solution characteristics the homopolymer of N-(3-(diethylamino)propyl)-N-methylacrylamide (poly-DEAPMAA) and copolymer of N-(3-(diethylamino)propyl)-N-methylacrylamide (DEAPMAA) and N,N-diethylacrylamide:



poly-DEAPMAA

copolymers with $x = 7.5$ and 60 mol %

The molar masses of the samples were equal to 30000 (poly-DEAPMAA), 32600 (copolymer with $x = 7.5$ mol %), and 36400 Da (copolymer with $x = 60$ mol %). Behavior of synthesized samples was studied in water-salt solutions using light scattering and turbidimetry methods. The experiments was carried out in pH interval from 7.01 to 13.01 and in wide range of concentrations from 0.0003 to 0.03 g/cm³. The phase separation temperatures are determined for all solutions. It was shown that the characteristics of the aqueous solutions of the copolymers depend on their composition. An increase in DEAPMAA content leads to an increase in phase separation temperatures.

The study by the coauthors from the Institute of Macromolecular Compounds RAS carried out under the financing of the Ministry of Science and Highest Education of the Russian Federation, State registration № AAAA-F16-116071450046-9.

MOLAR MASS AND HYDRODYNAMIC CHARACTERISTICS OF WATER SOLUBLE COMB-LIKE COPOLYMERS BASED ON CHITOSAN IN BUFFER SOLUTIONS

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In this work, we studied new graft copolymers of chitosan with poly-N,N-dimethylacrylamide (PDMAA) or poly-N,N-diethylacrylamide (PDEAA) obtained by grafting monomer under red-ox initiation conditions. Their structure (Figure) is confirmed by the data of IR and NMR spectroscopy and potentiometric titration. Buffer solutions (pH = 1.68, 4.01, 5.50) of copolymers were studied by static and dynamic light scattering and viscometry. Molar masses (MM), hydrodynamic radii R_h and radii of gyration R_g , the second virial coefficients A_2 and the characteristic viscosity $[\eta]$ of the initial chitosan and comb-like copolymers were determined.

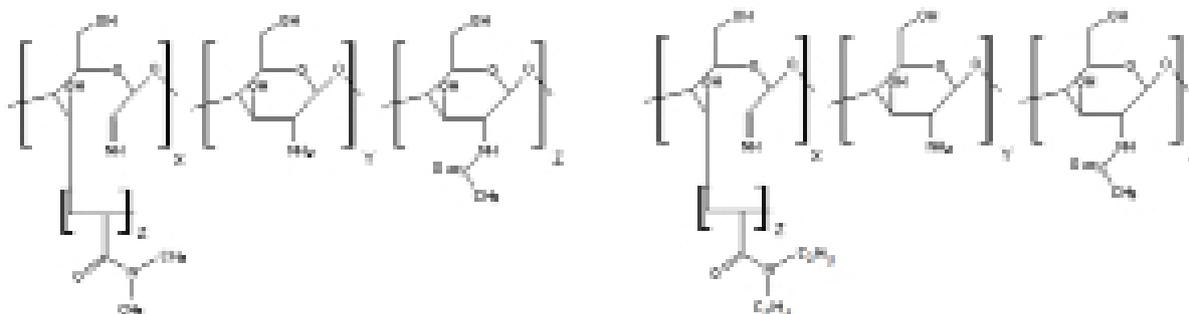


Figure 1. Structure of graft copolymers of chitosan with PDMAA (left) and PDEAA (right) side chains.

The samples of chitosans grafted by PDMAA had rather high MM: $M_w = 400$ and 710 kDa. MM of chitosans with PDEAA side chains was $M_w = 950$ kDa. The grafting density $z^* = x/(x + y + z)$ was evaluated by comparing the experimental values the MM of the graft copolymer, chitosan and the side chains. The z^* values was about 0.03 and 0.08 for samples with PDMAA and 0.15 for copolymer with PDEAA. Therefore, the synthesized samples are loose molecular brushes. It was shown, that investigate copolymers are thermo- and pH-sensitive in wide range of concentration and acidity.

The study by the coauthors from the Limnological Institute Siberian Branch RAS was carried out under the financing of the Ministry of Science and Highest Education of the Russian Federation, State registration № AAAA-A16-116122110059-3.

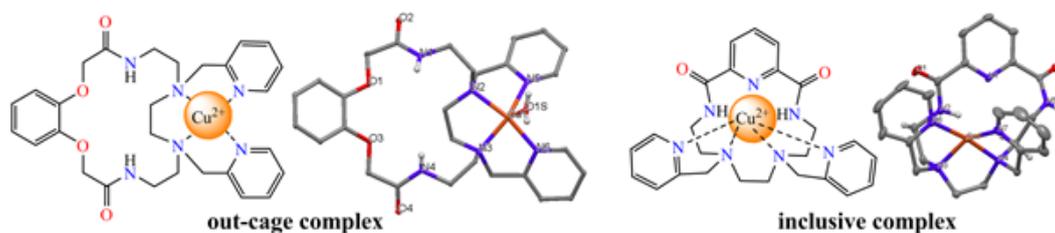
BISAMIDE AZACROWN COMPOUNDS: SYNTHESIS AND COMPLEX FORMATION PROPERTIES

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The inclusion properties of macrocyclic compounds are a very interesting subject of study – the search for selectively complexing receptors is significant in chemistry and biology as well as in medicine.¹ A design of macrocyclic receptors is governed by a number of factors, and the combination of these factors affect the specificity in host-guest recognition. Although amides often serve as anchoring groups in natural and synthetic receptors, the structure – affinity relationship studies of amide based macrocyclic receptors are still very limited. Therefore, we decided to investigate the influence of the size of the macrocycle, type and number of the chelating group on the strength and selectivity of ion heavy metal binding by amide-based receptors.



This work presents the synthesis of a novel bisamide azacrown compounds and their derivatives comprising carboxylic, pyridine and picolinate pendant arms. The potentiometric, NMR, ESI-MS and X-ray analysis were carried to study the binding properties towards heavy metal ions. The chelators demonstrated high stability constant of their complexes in aqueous solutions. The study of the structure of the obtained macrocycles showed that they have an open cavity due to the presence of rigid fragments that provides fast kinetics of complex formation.² A fundamental difference was found between types of metal binding in complexes of benzo- and pyridinecrown compounds – they form out-cage and inclusive complexes, respectively.^{3,4}

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We thank RSF №16-13-10226 and RFBR №18-33-20152 for financial support.

NITRO-DERIVATIVES OF BENZOAZACROWN ETHERS: SYNTHESIS, STRUCTURE, AND COMPLEXATION

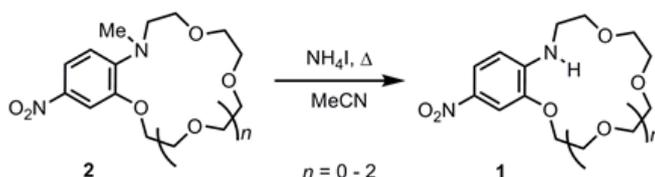
Dmitrieva S.N.,^a Kurchavov N.A.,^a Kuz'mina L.G.,^b Vedernikov A.I.,^a Churakova M.V.,^a Sazonov S.K.,^a Howard J.A.K.,^c Gromov S.P.^a

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Previously, we developed a new strategy for the synthesis of formyl and nitro *N*-alkylbenzoazacrown ether derivatives with different macrocycle size and macrocycle nitrogen atom being linked to the benzene ring.^{1,2} Nitrobenzoazacrown ethers **1** containing NH group in the macrocycle have been unknown until now.

We elaborated a method for the synthesis of nitrobenzoazacrown ethers **1** by *N*-demethylation of *N*-methyl-nitrobenzoazacrown ethers **2** on treatment with ammonium iodide, resulting in the formation of benzoazacrown ethers in 95–100% yields.³



It was shown that the stability of host–guest type complexes of nitrobenzoazacrown ethers **1** with metal and ammonium cations in MeCN-*d*₃ is lower than the stability of complexes formed by *N*-alkyl-substituted analogues with the same macrocycle size. It was shown that fluoride anions in DMSO-*d*₆ or MeCN-*d*₃ can bind to nitrobenzoazacrown ethers **1** via hydrogen bonding with the NH group of the macrocycle.

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This work was supported by the RFBR (grant No. 16-03-00267), the Ministry of Science and Higher Education within the State assignment FSRC «Crystallography and Photonics» RAS.

INTERMOLECULAR TUNING OF PHOTOCHEMICAL ACTIVITY OF TETRAPYRROLIC PHOTSENSITIZERS

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Tetrapyrrolic photosensitizers (PS) based on complexes of phthalocyanines and with *p*-, *d*⁰- and *d*¹⁰-elements of II, III and IV groups (e.g., Mg, Zn, Al, Ga, Si) have rare long-lived (0.1-1 ms) triplet excited states and absorption in the transparency region of biological tissues. Molecular design of PS macroheterocycles leads to a long-wavelength shift of their absorption band only. At the same time, PS association leading to the formation of nanosized intermolecular H- or J-aggregates significantly effects on manifestation of photosensitizing (energy transfer), photocatalytic (electron transfer) or fluorescent activity of PS. Association of PS can be controlled by including them in various supramolecular and nanosized systems.

In complexes with biocompatible nanosized carriers H-aggregates of PS exhibit selective photochemical activity in electron transfer to O₂ with the formation of ROS but the triplet-triplet energy transfer and fluorescence are impossible. Monomers and J-aggregates of PS have fluorescence and participate in the triplet-triplet energy transfer forming ¹O₂. A competing electron transfer is suppressed in this case.

The spectral properties of PS J-aggregates on ($\lambda_{\text{abs}}(\text{PS}) = 740\text{-}850\text{ nm}$, $\tau(^1\text{PS}) = 0.6\text{-}0.7\text{ ms}$) excellently correspond to the requirements of the agents for photodynamic therapy. The carriers quenching of triplet states of J-aggregates of phthalocyanines were found. The test of these PS for fluorescent diagnostics showed that they do not have a dark cytotoxic effects (apoptosis, necrosis, post-apoptotic necrosis), do not change the granularity of lymphocytes and possess intense fluorescence.

This work was supported by RFBR (project № 18-03-00539).

**STYRYL BASES AND DYES: DIMERIZATION AND PHOTOREACTIONS
WITH AND WITHOUT CAVITANDS**

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Gromov S.P.^{1,2}

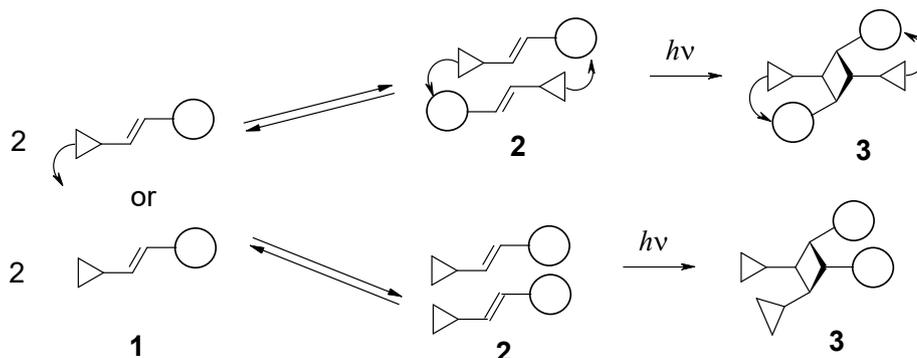
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A number of styryl dyes **1** and their corresponding bases were synthesized. It was found that dyes **1** can spontaneously form dimers **2** in both the solid state and in solution (MeCN, CH₂Cl₂). The dimers have a head-to-tail pseudocyclic structure. The dimerization stability constants for dyes **1** were estimated by ¹H NMR titration in MeCN-d₃ (logK_d up to 8.0)^{1,2}. The complexation of styryl dyes and bases **1** with cucurbit[n]urils (CB[n], n = 7, 8) and β-, γ-cyclodextrins (CD) was studied by electron spectroscopy, NMR and X-ray^{3,4}. It was found that in aqueous solutions the addition of complementary cavitands (CB[7], β-CD) to compounds **1** lead to inclusion complexes of 1: 1 with a pseudorotaxane structure. For cavitands with a large cavity size (CB[8], γ-CD), the formation of complexes **2** of higher stoichiometry is also possible.



[2+2] photocycloaddition reaction generate cyclobutane derivatives **3** (quantum yield is up to 0.38). The possibility of reaction passing depends on the nature of the compound **1** and the steric volume of its fragments. The structures of **1** **3** were studied by X-ray diffraction and NMR spectroscopy.

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SEED RAFT-POLYMERIZATION MEDIATED BY SYMMETRICAL TRITHIOCARBONATES

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Recently, one of the actively developing areas of polymer science is the synthesis of amphiphilic block copolymers, self-assembling in the process of synthesis into nanoscale particles of controlled morphology. The variety of morphology formed during dispersion of amphiphilic block copolymers in a selective solvent allows us to expect the implementation of different types of structures and heterophase synthesis of such block copolymers under conditions of reversible addition-fragmentation chain-transfer polymerization (RAFT). Dispersions of amphiphilic block copolymers particles obtained by heterophase polymerization using hydrophilic polymer RAFT-agents retain their ability to resume the "live" process with the addition of a new monomer, i.e. can be used as "seed particles" for the synthesis of ABC block copolymers of a given morphology.

In the present work, the seeding RAFT-polymerization of styrene and N-isopropylacrylamide was performed. As "seed particles" the particles of copolymer of acrylic acid (AA) and *n*-butyl acrylate (*n*-BA) obtained by heterophase RAFT-polymerization of *n*-BA in water-alcohol medium in the presence of hydrophilic precursor – PAA with trithiocarbonate group inside the chain were used. The symmetric structure of the RAFT-agent allows to obtain particles triblock copolymers, and in the process of seed polymerization – pentablock copolymers as chain growth occurs in both ends. According to MMD GPC curves of samples of the polymers gradually move in the direction of increasing molecular mass. According to the graph of Mn dependence on conversion, it can be seen that for styrene the dependence is linear, which may indicate a pseudoliving mechanism of the process.

This work was supported by Russian Foundation for Basic Research (project No 18-33-00386).

**SELF-ORGANIZED STRUCTURES IN THE SYSTEM POLYOXYETHYLATED
ALKYLPHENOL - WATER - SODIUM SULPHATE**

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The ability of polyoxyethylene surfactants to form various supramolecular structures is of great theoretical and practical importance. The formation of self-organizing ensembles due to the influence of temperature and concentration of surfactants. A distinctive feature of these compounds is the formation of two-phase systems in aqueous solutions, with increasing temperature and / or adding strong electrolytes. The study of the structure formation of micellar phases in aqueous solutions of industrial analogues of polyoxyethylated alkylphenols (for example, OP-10) expands the limits of applicability of these inexpensive, affordable drugs.

In this regard, the aim of the work was to establish the structure of the micellar phase formed in the (OP-10) -H₂O-Na₂SO₄ system at different phase separation modes.

Phase separation in the system was studied in a polythermal mode (C (OP-10) - 10%, C (Na₂SO₄) -0,2 M, temperature range 20-80 °C, the temperature of separation - 69 °C). It is established that the rate of heating and cooling affect the physico-chemical characteristics of the micellar phase (volume, viscosity). Rapid heating (mode № 1: t-80 °C, time - 10 min) and rapid cooling (t - 15 °C, time - 10 min) leads to a more compact viscous phase than with slow heating (mode № 2: 1 °C/min to 80 °C) and rapid cooling. Thermogravimetrically determined water content in the micellar phase: 57% (mode № 1) and 58% (mode № 2).

The study of the isolated micellar phases by the method of ²H NMR spectroscopy showed that mode № 1 leads to the formation of an anisotropic phase with a hexagonal structure, while under mode № 2, a mixture of isotropic and anisotropic phases. The formation of the hexagonal structure of the micellar phase was confirmed by polarization microscopy. The ²H NMR method was used to determine the phase transition from anisotropic to isotropic phase state in the temperature range 30-35 °C. Practical recommendations on the use of phase separation in optimal conditions for the extraction-spectrophotometric determination of synthetic dyes in various food products have been developed.

SOLUBILIZATION PROPERTIES OF MICELLAR SYSTEMS BASED ON METAL COMPLEXES OF ALKYLATED N-METHYL-D-GLUCAMINES AND CETYLTRIMETHYLAMMONIUM BROMIDE

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One of the most important features of solutions of surfactants, determining the possibility of their application in the field of medicine, ecology, catalysis, etc., is their ability to solubilize poorly soluble substances.¹ The effect of the mixed micellar and metallomicellar systems based on surfactants with an aminosugar fragment - alkylated derivatives of N-methyl-D-glucamine (Alk = C_nH_{2n+1}, n = 12,16) (GAM-12, GAM-16), their complexes with lanthanum nitrate ([GAM-12 × La(NO₃)₃], [GAM-16 × La(NO₃)₃]) and cetyltrimethylammonium bromide (CTAB) on the solubility of the hydrophobic substrate (Orange OT), as well as the micelle formation process in these solutions in the presence of the dye are investigated by spectrophotometric method. It is established that these systems exhibit high solubilization properties with respect to the water-insoluble agent. Solubilization activity increases with the transition from compositions based on ligands (GAM-12(16) - CTAB (1:1)) and their mixtures with inorganic salt (GAM-12(16) - CTAB - La(NO₃)₃ · 6H₂O (1:1:1)) to the compositions containing the corresponding metallosurfactants (complex - CTAB (1:1)), as well as increasing the hydrophobicity of the metal complex. The solubilization capacity of metallomicellar solutions is higher than that of the individual solutions of conventional surfactant CTAB. The increase in the solubility of Orange OT reaches more than two or three orders of magnitude, which allows us to consider these systems as nanocontainers of practically important substances, including drugs. It is shown that the presence of the dye usually does not change the aggregation threshold of the systems, determined by independent methods (tensiometry, conductometry), but has a positive effect on the process of rearrangement of the aggregates structure.

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THE EFFECTIVE LUMINESCENT SOFT MEDIA BASED ON THE LYOTROPIC MESOPHASE

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The lanthanide β -diketonate complexes are the most studied and widely used organic ligands and played a key role in fields in biology; medicine; supramolecular chemistry and nanotechnologies. However, their practical applications remains a serious problem due to their poor stability and strong luminescence quenching under of ultraviolet irradiation. Moreover, it is difficult to find organic matrices to introduce lanthanide complexes improves their luminescent efficiency and photostability. In this case, it is necessary to find and develop suitable media to overcome these problems of their practical application. A new method for creating effective and stable luminescent media with highly energy transfer by incorporating the hetero-ligand terbium β -diketonate complex and n-tert-butylcalix[4]arene as second ligand into the lyotropic mesophase was proposed. Lyotropic system based on the Pluronic P123 copolymer and $C_2H_6O_2$. The optical properties and phase behavior of P123/ $C_2H_6O_2$ systems were analyzed using polarization optical microscopy (Fig. 1a). Concentration and temperature intervals of existence mesophases are found. This supramolecular organized media is used as a platform for incorporation of a complex $[Calix][Tb(ACA)_4]$. Intermolecular interactions of hetero-ligand complex investigated by using FTIR spectroscopy.

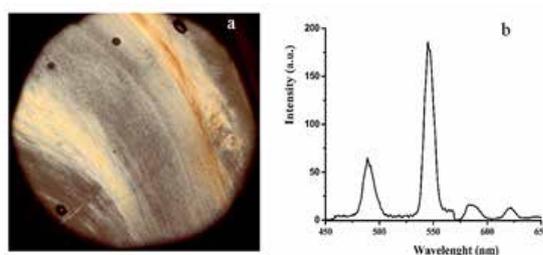


Figure 1. Texture in polarized microscope of the P123/ $C_2H_6O_2$ /[Calix][Tb(ACA)₄] system (a) and emission spectra (b)

A study of the optical properties of the P123/ $C_2H_6O_2$ /[Calix][Tb(ACA)₄] system showed high luminescence (Fig. 1b) and life-time $\tau=0,735$ ms. The data obtained in this study demonstrate that lyotropic liquid crystal can be efficient media for luminescence complexes.

This work was supported by the RFBR, project 18-03-00173

SUPRAMOLECULAR SYSTEMS BASED ON NANOPARTICLES AND BIOPOLYMERS FOR DESIGN OF HYBRID MATERIALS

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Design of the supramolecular systems based on the nanoparticles and biopolymers (SSNBs) is one of the actively developing research-technical directions (at the “junction point” of chemistry and biology, bio- and nanotechnologies). Such SSNBs are promising as fundamental models for study of the biochemical processes occurring at the interfaces and as prototypes of the functional hybrid materials¹.

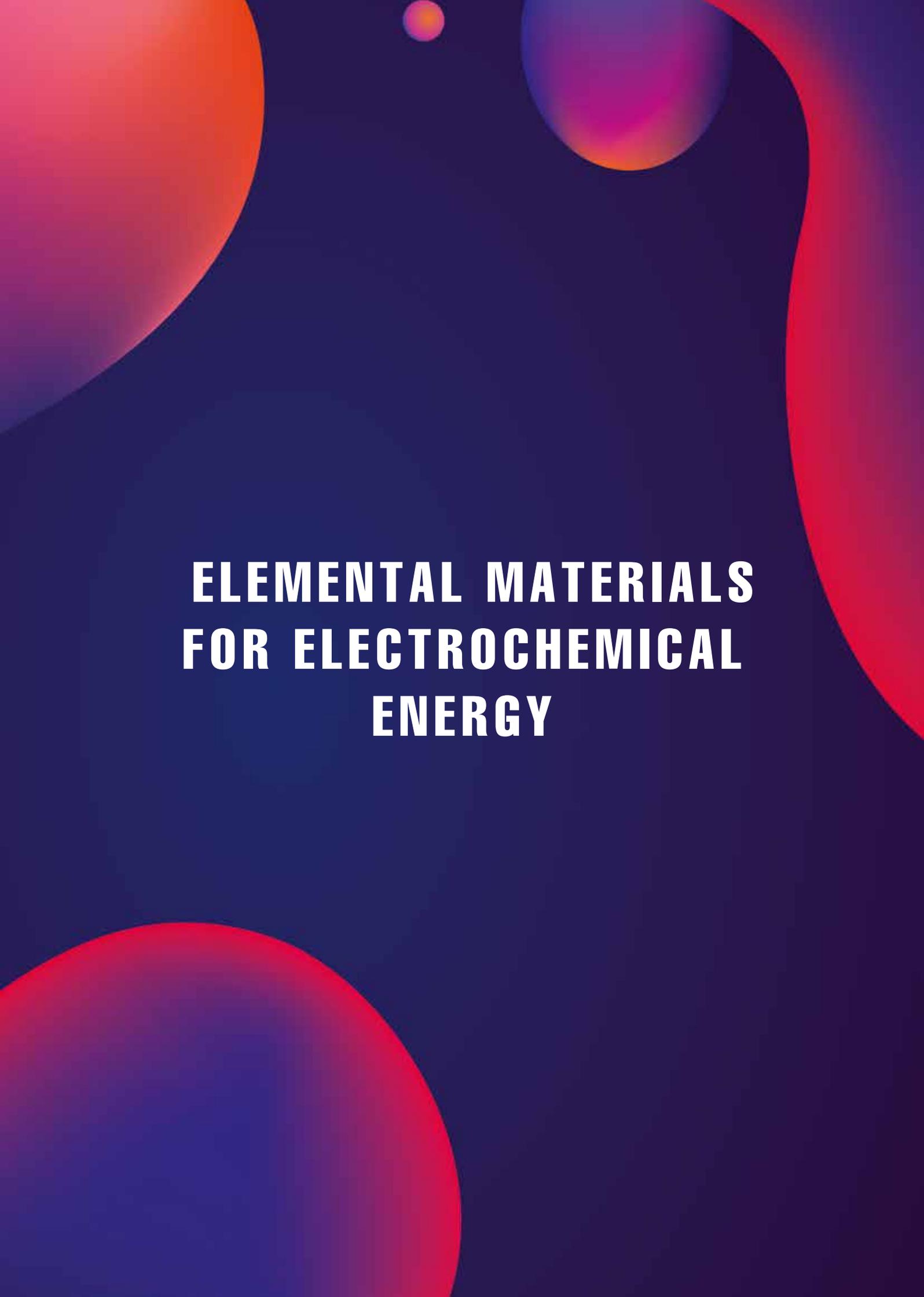
The purpose of this work was a detailed study of the features of the immobilization of lipases from various sources on nanoscale carriers, such as quantum dots, particles of metals or their oxides. Methods for the immobilization of enzymes in various variations (adsorption and covalent immobilization) and the conditions for the preparation of bionanocomposites with specified properties were studied. Comparing our data with those in the analyzed literature, we can conclude that the immobilization of lipases on various nanoscale carriers is a promising direction of preparation bionanohybrids with a sufficiently high degree of activity preservation and stability¹. However, in the reviewed methods, the inhibitory effect of nanoparticles on lipolytic materials is also often described. Our work on the immobilization of lipase on silver nanoparticles (LSN) with a modified surface showed that the decrease in the LSN activity is insignificant compared with the individual lipase. The optimal temperature at which LNS and lipase showed the maximum activity is 40°C. It is noteworthy that the activity of immobilized lipase even increased slightly with respect to free lipase at higher temperatures (about 50°C), which is consistent with the work of other authors².

This approach is not only economically more beneficial for a number of applications, it simplifies the control of the production process and allows you to reuse both the carrier and the enzyme preparation.

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This work was supported by the Russian Foundation for Basic Research, project 19-03-00717.



**ELEMENTAL MATERIALS
FOR ELECTROCHEMICAL
ENERGY**

SUPPRESSING DENDRITIC LITHIUM FORMATION IN LITHIUM METAL BATTERIES

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Owing to its ultra-high specific capacity, lithium metal holds great promise for revolutionizing current rechargeable battery technologies. Nevertheless, the unavoidable formation of dendritic Li, as well as the resulting safety hazards and poor cycling stability, have significantly hindered its practical applications. A mainstream strategy to solve this problem is introducing porous media, such as solid electrolytes, modified separators, or artificial protection layers, to block Li dendrite penetration. However, the scientific foundation of this strategy has not yet been elucidated. In this presentation, I am going to discuss the role of the porous media in suppressing dendritic Li growth and probe the underlying fundamental mechanisms based on experiments and simulation. It is found that the tortuous pores of the porous media, which drastically reduce the local flux of Li⁺ moving towards the anode and effectively extend the physical path of dendrite growth, are the key to achieving the non-dendritic Li growth. Based on the theoretical exploration, we synthesize a novel porous silicon nitride submicron-wire membrane and incorporate it in both half-cell and full-cell configurations. The operation time of the battery cells is significantly extended without a short circuit. The findings lay the foundation to use a porous medium for achieving non-dendritic Li growth in Li metal-based batteries.

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ATOMIC SCALE SIMULATIONS OF INTERFACIAL PHENOMENA IN SOLID ELECTROLYTES

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ABSTRACT

The development of robust and efficient solid electrolytes would transform mobile energy storage by enabling batteries with higher energy densities and safer operation. Developing such an electrolyte remains a challenge, however, as the candidate material must satisfy several requirements simultaneously: it must display high ionic conductivity, with limited electronic transport; it must exhibit sufficient mechanical properties to suppress dendrite initiation on the negative electrode; it should have a large electrochemical window, allowing its use with high voltage electrodes; it must be chemically stable in contact with both electrodes; finally, it should be easy to manufacture. This talk will describe atomic scale simulations aimed at understanding several of these phenomena in the prototype solid electrolyte, $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO). Emphasis is given to understanding the role played by interfaces with electrodes, and at internal interfaces (grain boundaries) within bulk LLZO. Several scenarios associated with the penetration of Li 'dendrites' through LLZO are evaluated computationally.

Keywords: Solid electrolytes, interfaces, LLZO, atomistic simulation, dendrites

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ELECTROCHEMICAL ENERGY STORAGE BEYOND LITHIUM

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Electrochemical energy storage beyond lithium is of high relevance for a sustainable energy technology. However, qualitatively new concepts are needed for suitable electrodes, especially in the case of the intercalation of larger monovalent ions like Na⁺ or K⁺ or multivalent ions like Mg²⁺, Ca²⁺ or Zn²⁺.

One example for a promising Na-ion battery is presented based on symmetrical NASICON-structured Na₂VTi(PO₄)₃ electrodes. ¹ The contribution of *in situ* synchrotron diffraction and X-ray absorption spectroscopy to unravel the underlying sodium storage mechanism and charge compensation behaviour is presented.

Model systems for multivalent-ion insertion can also include hybrid batteries with two mobile metal ions in the electrolyte, where a metal like Mg is plated at the negative electrode, while Li- or Na-ions are inserted at the positive electrode. ²⁻³ This presentation summarizes some recent results on the underlying working mechanisms in such hybrid batteries as revealed by *in operando* diffraction using synchrotron radiation in combination with X-ray photoelectron spectroscopy (XPS).

No well-working combination of materials is found yet for Mg-ion batteries with insertion-type positive electrodes and sufficiently high cell voltages. For example, V₂O₅ works only with electrolytes, which are not stable in contact with Mg-metal and steel housing. The Mg-insertion mechanism was therefore investigated for a full cell with Mg_xMo₆S₈ as a suitable negative electrode.⁴

This work contributes to the research performed at CELEST (Center for Electrochemical Energy Storage Ulm-Karlsruhe) and was funded by the German Research Foundation (DFG) under Project ID 390874152 (POLiS Cluster of Excellence).

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NA-ION BATTERIES: FROM ADVANCES IN MATERIAL-SEPARATOR-ELECTROLYTE TO PRACTICAL 18650 CELLS

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Li-ion batteries being light weight and capable of providing high energy density have conquered the transport sector, therefore, there is a sorely need for low cost batteries for grid applications linked to the use of renewable energies. In this regard, Na-ion battery technology that utilizes more sustainable materials is rapidly developing as a possible alternative. Several prototype Na-ion batteries using various chemistries have already been demonstrated; the most feasible being the two types of technologies based either on sodium layered oxides Na_xMO_2 ($x \leq 1$, M= transition metal ion(s)) or polyanionic compound such as $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ as positive electrode and carbon as negative electrode.^{1,2} To increase the specific energy of the sodium ion cells, it is essential to understand the origin of such limitations. Herein, we will first show how by manipulating the $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3$ chemistry³ and the design of new electrolyte formulations, via tedious iterations, we could master practical 18650 Na-ion batteries. Secondly, to further increase the energy density of Na-ion cells we have revisited the chemistry of the Na-based layered oxides. From structural-stability-electrochemical performance considerations we successfully design new chemically substituted layered Na-layered oxides⁴ which once implemented into practical 18650 ion cells shows greater performance than today's stellar Na-ion cells based on $\text{Na}_3\text{V}_2(\text{PO}_4)_2\text{F}_3/\text{C}$. Thirdly, as way on conclusion we discuss the pros and cons of the Na-ion technology against its Li-ion counterpart together with the market perspectives for such cells.

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ENHANCED ELECTROCATALYTIC ACTIVITIES BY SUBSTITUTIONAL TUNING OF NICKEL-BASED RUDDLESDEN-POPPER CATALYSTS FOR THE OXIDATION OF UREA AND SMALL ALCOHOLS

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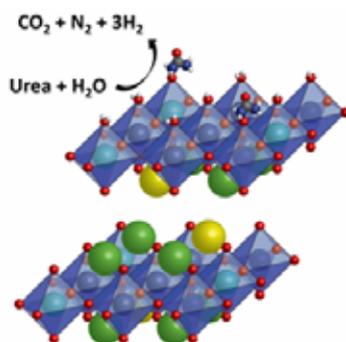
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ABSTRACT

The electrooxidation of urea continues to attract considerable interest as an alternative to the oxygen evolution reaction (OER) as the anodic reaction in the electrochemical generation of hydrogen due to the lower potential required to drive the reaction and the abundance of urea available in waste streams. In this talk the effect of Sr substitution in a series of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ Ruddlesden-Popper catalysts on the electrooxidations of urea, methanol, and ethanol are presented. We demonstrate that activities toward the urea oxidation reaction increase with increasing Ni oxidation state. The 75% Sr-substituted $\text{La}_{0.5}\text{Sr}_{1.5}\text{NiO}_{4+\delta}$ catalyst exhibits a mass activity of $588 \text{ mA mg}^{-1}_{\text{ox}}$ and $7.85 \text{ A mg}^{-1} \text{ cm}^{-1}_{\text{ox}}$ for the electrooxidation of urea in 1 M KOH containing 0.33 M urea, demonstrating the potential applications of Ni-based Ruddlesden-Popper materials for direct urea fuel cells and low-cost hydrogen production. Additionally, we find the same correlations between Ni oxidation state and activities for the electrooxidations of methanol and ethanol, as well as identify processes that result in catalyst deactivation for all three oxidations. This demonstration of how systematically increasing Ni – O bond covalency by raising the formal oxidation state of Ni above +3 serves to increase catalyst activity for these reactions acts as a governing principle for the rational design of catalysts for the electrooxidation of urea and other small molecules going forward.



ACCELERATING THE DEVELOPMENT OF INTERCALATION CATHODE MATERIALS FOR LI, NA, AND K-ION BATTERIES USING COMPUTER SIMULATION TECHNIQUES

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The portable electronic device revolution and upcoming transition to all electric vehicles, heavily relies on Li-ion battery technology, which has led to a doubling of the prices for Li precursors in several years.¹ As a result, the interest in the alternative potentially cheaper battery systems, such as Na-ion (NIB) and K-ion (KIB) has been reignited. Their commercialization depends on further improvements of batteries' specific energy, which mainly depend on the improvement of the anode, cathode, and electrolyte materials.

One emerging and promising approach for discovery and improvement of materials is computer modeling. Traditionally, providing deep understanding of materials' properties, computer modeling helped to rationalize the process of materials development. Nowadays, with the emergence of high throughput screening techniques, computer modeling allows to discover completely new materials with the desired properties.²

In this talk we show how computer modeling accelerates development of NIB and KIB cathode materials. Though we are mainly focused on quantum mechanics methods such as density functional theory (DFT), almost all aspects of battery performance including specific energy, power, and longevity are considered. In the first part of the talk the basics of DFT usage for predicting structure, intercalation potentials, diffusion characteristics, and surface effects of cathode materials are presented. In the second part we provide specific examples of DFT application for explaining several effects: intercalation mechanisms of Li⁺ and Na⁺ in NaFePO₄F; diffusion characteristics of K⁺ in KVPO₄F; origin of migration barriers for diffusion across Li, Na, and K compounds; improvement of oxide cathodes with surface segregations. The talk is concluded by showing the path to high-throughput modeling of cathode materials' properties with the help of our software SIMAN.³

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HYDROGEN IN OXIDE MATERIALS: FROM PROTONIC ELECTROLYTES TO PROTONIC CERAMIC FUEL CELLS

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Proton conducting electrolytes appear to be advanced materials for the electrochemical devices in renewable and hydrogen power generation. Contacting with hydrogen-containing atmosphere proton conducting oxide materials uptake hydrogen (and/or water), and as a result, protonic conductivity appears. Protonic conductivity is observed at the considerably lower temperatures in comparison with oxygen-ion conductivity, such that the proton conducting materials are considered as advanced materials for the development of the electrochemical devices generation and storage of energy (protonic ceramic fuel cells, electrolyzers, gas sensors, pumps etc.).

Nowadays there are lots of papers related to the proton conducting materials study. The most popular class of the proton conducting electrolytes is acceptor doped oxides with perovskite structure. In this contribution the nature of hydrogen defects, their mobility in protonic conducting oxide materials, as well as peculiarities of the hydrogen-containing gases adsorption and exchange are discussed. A special attention is paid to not only protonic oxide electrolyte materials, but also to specific electrode materials, materials for electrical commutation and sealants, which is very important for the development of the Protonic Ceramic Fuel Cells (PCFC).

PCFCs have two considerable advantages before Solid Oxide Fuel Cells (SOFC) with oxygen-ionic oxide membrane: working at lower temperature 500–700 °C and direct hydrocarbon conversion in anode.

In the Institute of High Temperature Electrochemistry of the Ural Branch of the Russian Academy of Sciences in the Solid Oxide Electrochemistry Department we work with systems based on barium zirconate-cerate and our recent developments are focused on protonic electrolyte based on lanthanum scandate, showing greater ionic conductivity and stability in both high oxidative and high reductive atmospheres.

In the framework of the joint laboratory with Company “InEnergy” and our colleagues (NeoHim, Moscow; ECON, Obninsk; OOO TSP, Gorniy Schit) we fabricated and tested new stack of protonic ceramic fuel cells based on lanthanum scandate electrolyte. This PCFC was successfully tested under direct methane-water conversion.

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NEW GENERATION OF ELECTROCATALYSTS BASED ON EARTH-ABUNDANT ELEMENTS

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Introducing fuel cell technology in mainstream applications such as automotive, electrolyzer and combined heat-and-power markets faces challenges derived from the availability of platinum and platinum group metals (PGM). Earth-abundant elements are called upon as a solution to the resource limitations of this, as well as other resource-limited technologies, providing solutions that level the field for market enterprise. Platinum Group Metal-free (PGM-free) catalysts have been extensively developed for both Proton Exchange Membrane (PEM) and Alkaline Exchange Membrane (AEM) fuel cells aiming automotive, stationary and portable applications. In this lecture we will address the critical challenges that our team has faced on the way to practical application of such catalysts.

Our team at the University of New Mexico (UNM) and now at the University of California, Irvine (UCI) has developed the Sacrificial Support Method (SSM) as a main approach for templated synthesis of hierarchically structured electrocatalysts materials. In this method the catalysts precursors are being absorbed on, impregnated within or mechanically mixed with the support (usually mono-dispersed or meso-structured structured silica), thermally processed (pyrolyzed) and then the silica support is removed by etching to live the open frame structure of a “self-supported” material that consists of the catalysts only.

The makeup and structure of the active site/sites of the PGM-free ORR electro-catalysts, including geometry (coordination) and chemistry (composition and oxidation state) remain contentious even after 50 years of research. There is an emerging agreement that iron and nitrogen functionalities, displayed on the surface of the carbonaceous substrate/support, govern ORR activity. This is often combined with a broadly accepted hypothesis that micro-porous surface area plays a critical role forming the active site. Candidate structures participating in ORR include multitudes of nitrogen defect motifs in the carbon matrix of different degrees of graphitization, with metal incorporated as metal nano-particles, corresponding (native) oxides and/or as atomically dispersed, oxidized metal species, linked (coordinated) to nitrogen defects in carbonaceous matrix in a variety of possible configurations. This lecture will attempt to address rational design metrics of M-N-C electrocatalyst based on a broad experimental set of data.

This presentation will review the applications of this new class of electrocatalyst across several fuel cell applications: from automotive to microbial and from regenerative electrolyzer/fuel cell units to water purification and desalination devices.

ALLUAUDITE BATTERY CATHODES

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Electrochemical energy storage, particularly rechargeable batteries, form a key sector in the energy-hungry 21st century having myriads of application ranging from portable electronics, hybrid vehicles and (remote area) grid storage. While the former two sectors are ruled by Li-ion batteries owing to their higher gravimetric/ volumetric energy density, stationary applications like grid storage can be served by low cost Na-ion batteries. To realize efficient sodium-ion batteries, various Na_xMO₂ oxides and polyanionic insertion compounds have been developed. While the metal oxides have higher theoretical capacity, polyanionic systems offer moderate capacity with tunable redox potential.¹ Exploring SO₄-based polyanionic systems guided by inductive effect as proposed by Goodenough,² recently alluaudite framework Na₂Fe₂(SO₄)₃ cathode has been reported as a 3.8 V sodium battery materials.³ It has led to wide attention to alluaudite framework insertion compounds for low cost sodium-ion batteries.

Alluaudites are named after certain family of minerals with general formula A(2)A(1)(M1)(M2)₂(XO₄)₃ [X= P, S, V, W, Mo]. It has edge-sharing MO₆-MO₆ dimers, which are interconnected by XO₄ tetrahedra delimiting large tunnels along b-axis. We have produced SO₄-based Fe-containing alluaudite using non-aqueous as well as aqueous routes delivering capacity over 80 mAh/g with high redox potential (ca. 3.7-3.8 V vs. Na).⁴ The current work will highlight (i) three energy-savvy solvothermal synthesis of alluaudites, (ii) the first demonstration of aqueous synthesis of SO₄-based electroactive compounds and compositional flexibility, (iii) benchmarking the lowest annealing temperature (ca. 200 °C) and annealing time (ca. 6 h), (iv) discovery of three new Mn/Co based alluaudite compounds and three distinct families of alluaudite sulfate solid-solutions (Fe-Mn, Mn-Co, Co-Fe) and (v) fundamental study on the electronic and magnetic properties of alluaudite battery cathodes.⁵⁻⁸

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COMBINING BIG DATA ANALYSIS WITH DFT MODELING FOR PREDICTION OF IONIC CONDUCTIVITY IN SOLIDS

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Prediction of structure and useful properties of functional materials is the main trend in modern materials science. An important group of the properties concerns ionic conductivity of solids; these properties are crucial in manufacturing ion batteries and other devices for energy storage. The search for new substances with specified ion-conducting properties or improving these properties for known materials require exploring their crystal structures to reveal conduction channels. More than 200,000 such structures are deposited in world-wide crystallographic databases, such as Inorganic Crystal Structure Database, Pearson's Crystal Data, or Powder Diffraction File. To review such a huge amount of information we need special algorithms and methods, which determine the application of the modern big data analysis in materials science.

Here we present a geometrical-topological approach, which is based on the representation of the crystal space as Voronoi partition built for the atoms of the structure framework. The approach is implemented in the program package *ToposPro*.¹ The conduction channels are determined in accordance with rigorous and simple geometrical criteria, and the conductivity is predicted by the analysis of topological properties of the channel system. The method is fast enough to process thousands of structures in a reasonable time, and applicable to different classes of ion conductors. The fast screening of the experimental databases is combined with precise DFT modeling of ion-conducting properties: the most promising candidates revealed by the Voronoi analysis are then explored in detail for their ion migration energy barriers and diffusion parameters.

We provide examples of application of this approach to alkali-ion conductors, high-valent cation conductors, and anion conductors. A possible combination with other modeling methods, such as bond valence sum (BVS), Hirshfeld and procrystal models, is briefly discussed.

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ELECTROLYTES FOR LOW-TEMPERATURE ELECTROCHEMICAL DEVICES

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An electrolyte is a critical component of an electrochemical device. One of the essential functions of the electrolyte is to ensure the rapid ion transport between the electrodes (for which the electrolyte must have high ionic conductivity) while blocking electronic transfer. Also, the electrolyte separates the electrode spaces, playing the role of a gas (fuel cells, metal-gas batteries) or liquid (redox batteries, lithium-ion batteries, etc.) barrier between the electrode spaces. Often, the electrolyte is an element of the supporting structures of electrochemical devices (solid oxide fuel cells, sodium-sulfur batteries). Since it would be ideal to combine all the functions in one material, there is a constant shift in the interest of researchers and developers of electrochemical devices from liquid to polymer and then to ceramic electrolytes.

The report examined various types of electrolyte materials for low-temperature electrochemical devices, analysed their advantages and disadvantages and showed the main trends in their development. Particular attention is paid to the reasons that impede the operation of devices at low temperatures, and the prospects for overcoming them by creating new low-temperature electrolytes.

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PERIODIC TABLE AS A GUIDE TO A RATIONAL DESIGN OF HETEROMETALLIC MOLECULAR PRECURSORS FOR THE SYNTHESIS OF ENERGY-RELATED MATERIALS

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The presentation will describe our latest efforts in the design of heterometallic compounds that can be used as single-source precursors for the low-temperature synthesis of energy-related materials. This research is focused on creating heterometallic precursors with well-defined molecular structure and with a proper metal ratio for the target material. A number of strategies for a rational design of heterometallic compounds will be discussed. These techniques were shown to effectively bring about changes in the connectivity pattern within heterometallic assembly and to yield molecular precursors with required stoichiometry, while avoiding the formation of coordination polymers. The above approaches have been successfully utilized in the design of heterometallic molecular precursors for the low-temperature synthesis of prospective cathode materials of rechargeable batteries. New characterization techniques were shown as efficient tools to rationalize the important features of heterometallic precursor structure such as oxidation/spin states of transition metal atoms as well as the identities of elements with very close atomic numbers.

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ELECTRODE MATERIALS FOR SODIUM-ION BATTERIES BASED ON VANADIUM REDOX TRANSITIONS

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Sodium-ion batteries (NIB) are considered as an alternative to lithium-ion batteries (LIB) in a number of applications, e.g. for large-scaled energy storage systems.¹ Development of the cathode materials for NIB combines studies conducted in two principal directions: oxide and polyanion materials. In the field of anode materials, the main object of study is carbon non-graphitizable materials, so-called "hard carbon". Various vanadium compounds became an object of intensive research and most probable candidates for practical application in NIB due to the rich crystal chemistry of oxide and polyanionic V-based materials and a wide range of redox transitions: $V^{+2} / V^{+3} / V^{+4} / V^{+5}$.²

In our work, we studied a number of vanadium compounds for use as both cathode and anode materials for NIB. The report will address issues related to the synthesis, electrochemical properties, and phase and structural transformations during Na^+ (de)intercalation for a number of vanadium compounds: $Na_4MnV(PO_4)_3$, β - $NaVP_2O_7$, $Na_3V_3(PO_4)_4$, $VOCl$, etc. (Fig. 1).

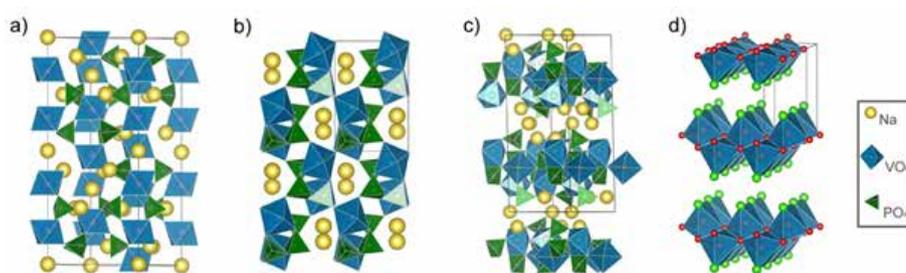


Figure 1. Crystal structure of $Na_4MnV(PO_4)_3$ (a), β - $NaVP_2O_7$ (b), $Na_3V_3(PO_4)_4$ (c), $VOCl$ (d).

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BREAKING THE ACTIVITY/STABILITY RELATIONSHIP FOR OXYGEN EVOLUTION REACTION (OER) CATALYSTS BY CONTROLLING INTERFACIAL INTERACTIONS

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The development of highly active catalysts for the oxygen evolution reaction (OER), reaction which is at the heart of electrolyzers, is currently hampered by the relative instability of transition metal oxides in these harsh operating conditions.^{1,2} At the origin for this activity/stability tradeoff is the formation of high valance intermediates on the surface of the catalysts which, upon reactivity with water, leads to under-coordinated transition metals that are prone for dissolution.^{3,4} Efforts were thus recently paid at understanding and controlling these intermediates, with however the main limitation that the driving force for transition metal oxide to be unstable not being suppressed.

Recently, we investigated different chemical strategies in order to break such activity/stability correlation relying on the control of weak interfacial interactions at the catalyst/electrolyte interface. Adopting an approach relying on the modifications of solvation properties of the electrolytes, we will discuss how these weak interactions affect not only the performances of OER catalysts but also how they can be used to control their stability by self-healing processes. We will describe a so-far neglected phenomenon for which the electrolyte can access the bulk of the catalyst to counter-balance charge transfer associated with the OER reaction and thus stabilizing the crystallographic structure of the transition metal oxides.

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NEW PLATINUM-CONTAINING ELECTROCATALYSTS FOR PEM FUEL CELLS

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Proton exchange membrane fuel cells (PEMFC) are important components of the hydrogen power engineering. The current-forming reactions realized in PEMFC occur on the active surface of Pt-containing catalysts. An important task that determines the commercialization of PEMFC is to increase the activity and stability of electrocatalysts, reducing the Pt content in their composition.

The Research and Education Center “Chemistry and Physics of Functional Nanostructured and Inorganic Materials” of the Southern Federal University for about 10 years has been conducting research, the key aspect of which is the search for technologically advanced methods for managing the composition and hierarchically organized structure of deposited Pt and PtM_x (M = Ni, Ag, Cu, Co) catalysts.

The use of original methods for the influence on the nucleation/growth of Pt nanoparticles on the surface of Vulcan XC72 carbon black particles allowed us to synthesize Pt/C catalysts that are superior to the best commercial samples.

On the basis of Pt-Cu nanoparticles with a gradient architecture, materials were obtained which demonstrate similar activity in the reaction of oxygen electroreduction and significantly higher stability compared to Pt/C.^{1,2} The conditions for the pretreatment of PtCu_x/C catalysts, leading to the formation of PtCu_{x-y} nanoparticles combined stability with high specific activity, are determined.

High functional characteristics of synthesized electrocatalysts are confirmed by results of their tests in H₂/Air membrane-electrode assembly.

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CHALLENGES FACING THE DEVELOPMENT OF MATERIALS FOR LITHIUM-AIR BATTERIES

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Lithium-oxygen chemistry can potentially enable development of rechargeable batteries demonstrating a few-fold increased specific energy in comparison to lithium-ion ones. The practical implementation of this idea, however, faces a number of significant challenges. The first one is the problem of positive electrode material stability during cycling. During lithium-air battery (LAB) operation oxygen reduction reaction occurs at the positive electrode – oxygen dissolved in the electrolyte is reduced to superoxide (O_2^-), which forms ionic pairs with Li^+ (LiO_2^-). Such intermediates are then converted to a final discharge product lithium peroxide (Li_2O_2) after transfer of second electron from the electrode or by chemical disproportionation reaction. Unfortunately, oxygen reduction products and intermediates are highly reactive species that can attack both electrolyte solvents and electrode materials. Among others, carbon materials received major attention as a positive electrode in $Li-O_2$ cells as they are freely available, porous, highly conductive and lightweight. The requirements for porous positive electrodes and their chemical stability would be discussed in the talk using carbon materials and Ti-based conductive compounds as examples. Application of a number of neutron and synchrotron-based tools (neutron reflectometry, XPS/NAP XPS and others) for monitoring the interfacial processes at positive electrodes will be demonstrated.

DESIGN OF REDOX-CONDUCTING POLYMERS FOR ENERGY STORAGE APPLICATIONS

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Design of novel kind of power sources that would combine the high power output with larger energy density represents an actual task. However, low charge diffusion coefficients, typical for "hard" condensed inorganic materials, are limiting the power density of the electrodes. A possible solution might be creation of novel "soft" organic and metalorganic materials with designed functionality. Attractive candidates for application in new generation of batteries can be found among polymers bearing organic radical substituents as high-capacitance groups, in particular, radical polymers bearing stable nitroxide-radical groups. The attractiveness of these particular polymers is due to the high potential of charging/discharging and theoretical specific capacitance. An important advantage of such materials over traditional inorganic materials is high ionic conductivity, availability and low cost of the starting materials for the synthesis of the target polymers combined with good mechanical properties of the latter such as flexibility, elasticity and ease processability. At the same time, low electron conductivity of materials based on nitroxide radicals, hampers their broad application as cathode material. In this connection, creation of novel materials based on nitroxyl radicals that would possess high conductivity while retaining high power density, is an actual task in the development of new kinds of lithium-ion batteries.

Here we report the new principles for creation of conductive materials based on polymer metal complexes bearing nitroxyl groups and assessment of such compounds as energy storage materials. A large array of organic compounds bearing nitroxyl free-radical groups (derivatives of TEMPO, 2,2,6,6-tetramethylpiperidineoxyl) and nickel and copper complexes with tetradentate ligands based on bis-imines of salicylic aldehyde derivatives (Schiff bases of salen family) was synthesized. The capacitance of the best material reaches 86 mAh g⁻¹, remaining constant at charge/discharge currents ranging from 16 to 128C. We also demonstrated high tolerance of the material to low temperatures. In particular, the capacitance of the electrode comprises 70% of the theoretical at 1C and 50% of theoretical at 100C even at -40 °C (cell temperature).

This work was supported by the Russian Science Foundation (grant number 16-13-00038). Scientific research was partially performed at the Research park of St. Petersburg State University: Interdisciplinary Resource Centre for Nanotechnology, Chemical Analysis and Materials Research Centre, Magnetic Resonance Research Centre, Chemistry Educational Centre, Centre for X-ray Diffraction Studies.

ELECTROCHEMICAL DIAGNOSTICS OF THE SLOW NUCLEATION RATE CONTROL FOR PHASE TRANSFORMING INTERCALATION MATERIALS

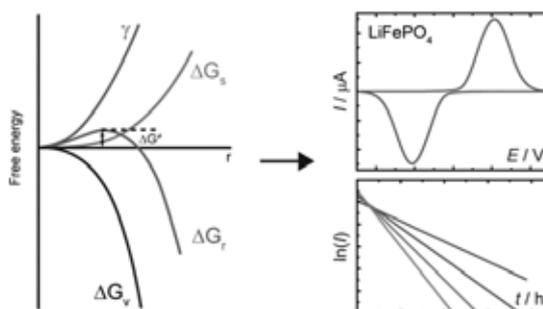
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Phase-transforming cathode materials have been extensively studied for both Li-ion (olivine LiFePO_4) and Na-ion ($\text{Na}_3\text{V}_2(\text{PO}_4)_3$) batteries. In particular, LiFePO_4 material has become a model system for the investigation of intercalation induced phase transformation mechanisms.¹ Most of the state-of-the-art research on the phase-separating intercalation materials focuses on the elucidation of phase transformation mechanisms as well as on the theoretical assessment of the nucleation barrier heights based on the evidence from structural and microscopic single particle-level experiments.²

In this work, we show that the new phase nucleation appears to be a characteristic rate-determining step for a wide range of intercalation materials (LiFePO_4 , V_2O_5 , Prussian blue analogues, etc.). We demonstrate that the nucleation rates (probabilities of critical nucleus formation) can be straightforwardly determined from the electrochemical experimental data. We propose a simple approach based on the classical nucleation theory toward interpreting electrochemical cyclic voltammetry and chronoamperometry data for phase-transforming electrodes.³ Experimental data analysis illustrates the validity of the applied approaches, which allows developing diagnostic criteria for distinguishing slow nucleation rate control from other possible rate-determining steps.



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HYDROGEN ELECTROCATALYSIS ON NI: ADVANCES AND CHALLENGES

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Anion exchange membrane fuel cells (AEMFCs) are currently attracting an increasing attention. Since hydrogen oxidation reaction (HOR) is significantly slower in alkaline compared to acid media, the future of AEMFCs largely depends on the availability of materials containing little or no noble metals and capable of catalyzing the HOR at low overpotentials. Numerous groups are trying to uncover the mechanism of the HOR in alkaline media and factors determining the electrocatalytic activity, and on the development of active and stable materials for the AEMFC anode.

In this presentation we will discuss the HOR on monometallic and bimetallic NiM electrodes (M=Cu or Mo). By joining experiments and modeling we will analyze main factors determining the electrocatalytic activity of Ni in the hydrogen oxidation and evolution reactions. We will see why the activity of a reduced Ni surface in the HOR is low, why it increases following partial surface oxidation [1], how and why the activity depends on the electrolyte pH, and why addition of Cu [2,4] or Mo [3] increases the electrocatalytic activity.

Acknowledgement. The work was supported by RFBR (17-53-150008) and CNRS (PRC n° 1553).

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LITHIUM DIFFUSION PATHWAYS IN MODERN SOLID STATE Li CONDUCTORS

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The rapid development of energy storage media permanently requires new electrode and electrolyte materials, which are cheaper, more stable/robust and have better electrochemical performance. To large extent the electrochemical energy storage and energy conversion are diffusion-based processes, where the knowledge about underlying diffusion pathways and mechanisms becomes crucial and indispensable. Unfortunately the information about preferable diffusion pathways of polycrystalline (non-cubic) materials can hardly be obtained by bulk (e.g. resistivity, impedance spectroscopy, quasielastic neutron scattering etc) or local measurements. Theoretical methods for prediction of diffusion pathways are often based on molecular dynamics simulations (either force-field or ab initio), which creates sufficient computational challenges for the modelling of diffusion properties of new materials.

On the other hand the diffusion processes in a material are determined by its crystal structure, and there are several methods to predict the preferred ion diffusion pathways with high reliability on the basis of the underlying crystal structure or more specifically the corresponding scattering density maps (electron for X-ray and nuclear ones in the case of neutrons). Their analyses in terms of probability density function from anharmonic refinements of diffraction data and/or the reconstruction of electron/nuclear densities by maximum entropy method. The latter approach has been found more robust (better performing) in the case of powder-averaged diffraction data capable to probe weak structural disorder. In the current contribution the application of high-resolution neutron powder diffraction along with the data analysis by maximum entropy method will be reported for the series of promising lithium conductors ($\text{Li}_2\text{B}_4\text{O}_7$ [1], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ [2], $\text{Li}_{1.3}\text{A}_{10.3}\text{Ti}_{1.7}(\text{PO}_4)_3$ [3], $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ [4], $\beta\text{-Li}_3\text{PS}_4$ [5] etc).

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HIGH-CAPACITY AND HIGH-RATE METAL-ION BATTERIES BASED ON ORGANIC REDOX-ACTIVE MATERIALS

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Using organic redox-active molecules provides a new paradigm for future development of metal-ion batteries. Indeed, organic materials are usually based on light elements (C, H, N, O, S) and, therefore, can enable much higher specific capacities compared to the salts and oxides of heavy transition metals. Most of organic materials are non-toxic and environment friendly, which makes easy their recycling as a common household waste. In contrast to crystalline inorganic cathodes and anodes, organic materials are soft and, therefore, can operate at high charge and discharge rates thus leading to design of ultrafast batteries. Mechanical properties of polymeric cathodes and anodes enable their application in truly bendable batteries for emerging generation of portable electronics.

Lithium-ion batteries currently represent one of the mainstream energy storage technologies. However, lithium is a scarce element and the available resources are definitely not matching the rapidly growing demand for energy storage. Therefore, sodium- and potassium-ion batteries (SIBs and PIBs) are now considered as promising scalable metal-ion battery technologies. In that context, organic redox-active materials are particularly important since they can operate efficiently with multiple mobile ions, while most of inorganic cathodes are constrained to only one specific ion matching the crystal lattice.

In this talk, we will highlight our recent results on the design of organic and metal-organic cathode and anode materials for lithium, sodium and potassium batteries. In particular, we will present ultrafast potassium-ion batteries delivering specific capacities of 169 mA h g⁻¹ at an impressive current density of 10 A g⁻¹ (charging/discharging in ca. one minute) and 245 mA h g⁻¹A at a lower current density of 50 mA g⁻¹. Specific energy of ~550-600 W h kg⁻¹ is reached for the best organic cathodes in potassium batteries. The polymer-based devices also demonstrated record-high cycling stability with no capacity decay after 4600 cycles, thus outperforming all previously reported non-aqueous K-ion batteries.

The obtained results suggest that organic electrode materials, while being at the infancy of their development, start to show commercially interesting performances thus paving a way to implementation of a new generation of post-lithium metal-ion batteries.

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UNDERSTANDING THE ROLE OF PROTONS FOR OXYGEN REDUCTION REACTION IN PT-BASED ELECTRODES FOR POLYMER ELECTROLYTE FUEL CELLS

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Pt is one of the best electrocatalyst for oxygen reduction reaction (ORR). Sluggishness of the ORR is currently limiting the efficiency and current densities of polymer electrolyte fuel cells (PEFCs). Understanding the electric double layers (EDLs) at Pt electrolyte interface is critical to enhance the ORR rates. Here, we present a comprehensive approach to interrogate the Pt electrolyte interface with a broad range of characterization techniques and to understand the role protons in ORR. We used kinetic isotope effect (KIE) to show weak dependency of ORR on protons using both Pt-disk and 40 wt% of Pt dispersed on carbon black support in perchloric and sulfuric acids. Previously, Yeager¹ show no KIE on Pt electrocatalyst but only in deuterated phosphoric acid. Although, protons do not directly participating in the rate-limiting step, they are nevertheless needed for the overall ORR.

To achieve high efficiencies for heavy-duty applications PEFCs need to operate at high potentials and low current densities. In this regime Pt charge is positive, as potential of zero charge (pzc) for Pt is ~ 0.27 V², although there are studies that report pzc reversal at higher potentials³. CO-displacement experiment was performed on actual MEAs with loadings range of 0.15 to 0.4 mg/cm². A clear trend was observed of increase in ionomer coverage with Pt loading (when normalized per loading), which can be attributed to higher affinity of sulfonic acid groups to Pt at higher loading. Furthermore, the pzc remained at 0.21 – 0.23 V independent of Pt loading. Lastly, to improve local ionic conductivity in Pt/C electrodes we utilize protic ionic liquids to penetrate smaller meso-pores. With electrochemical impedance spectroscopy (EIS) sheet resistance method we show increase in overall ionic conductivity of Pt/C electrode when ionic liquids are added, and also a shift in onset oxide region for Pt.

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CHARGE TRANSFER PARAMETERS AND STABILITY OF DIFFERENT SALEN-TYPE POLYMERIC NICKEL COMPLEXES IN ELECTROLYTES CONTAINING EXTERNAL LIGANDS

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Supercapacitors with non-aqueous electrolytes have already found commercial applications. However, at present one of the main restrictions to widespread of the technology is their limited lifetime, since the electrode materials degrade under the influence of water, which, inevitably, contains any industrial solvent. In addition to water, the main pollutions of the electrolytes are halogenic ions. Data on the degradation of salen-type transition metal complexes in the presence of these impurities, presented in the literature, are clearly not sufficient for understanding the detailed mechanism of this process, since they contain the results obtained using only electrochemical methods and refer to single complexes. As a result, the search for new materials based on such complexes for use as capacitor modifiers is often carried out by empirical method, which requires enormous time and money and is ultimately ineffective. An alternative, rational way to search for new materials is possible only with an understanding of the detailed mechanism of the degradation of salen-type transition metal complexes in dry electrolytes and in the presence of various external ligands.

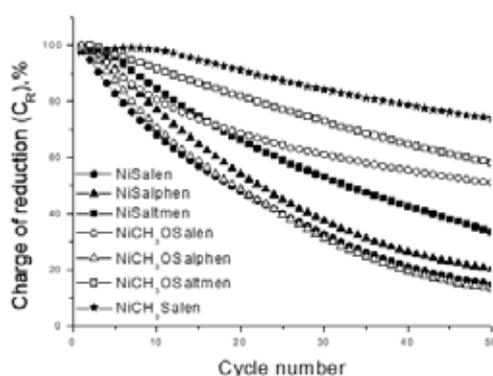


Рисунок 1 – Изменение заряда восстановления полимерных пленок саленового типа в 0,1 М $(C_2H_5)_4NBF_4$ / АН при добавлении 1% воды при циклировании в диапазоне от -0,2В до 0,8В

This research was supported by the Russian Foundation for Basic Research (project no. 18-33-00682). Scientific research were performed at the Research park of St.Petersburg State University: Geomodel, Natotechnology, Center for Studies in Surface Science and Centre for X-ray Diffraction Studies

ELECTROCHEMICAL NOISE DIAGNOSTICS OF LI-ION BATTERIES

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Electrochemical power sources state of health (SOH) evaluation is a very demanded task for today. Different methods such as voltammetry or electrochemical impedance are commonly used to solve it today¹. One of new methods which can be applied for it too, is electrochemical noise (ECN) measurement and analysis^{2,3}.

We have investigated the ECN behavior of the commercial Li-ion battery during discharge process and shown that it can be used to estimate the overdischarge condition of it⁴. The electrochemical noise of the commercial fully charged Li-ion battery was measured during charge-discharge cycling for the first time. It was shown that power spectral density (PSD) frequency dependencies level increases during battery cycling and the $1/f^n$ shape of the low-frequency part of it keeps the same with small n value increasing from 1 up to 1.3. Standard deviation (SD) calculations in the low-frequency band have shown that noise amplitude increases and linearly depends on the battery cycle number during charge-discharge cycling.

Electrochemical noise of the battery was measured using different loads to build the dependencies of the PSD values on the DC load current for the fresh and cycled battery. It was shown that these dependencies are linear in bi-logarithmic coordinates with the slope values close to 2. This value allows to attribute the low-frequency ECN nature to the fluctuations of the impedance of the battery during discharge. Statistical analysis confirms that the nature of the ECN does not change during the battery cycling as normal ECN distribution is observed both for the fresh and cycled battery.

All types of the performed in the current work calculations – SD, voltage PSD, current PSD, and ECN PSD slope values, demonstrate that the ECN technique can potentially be used for the SOH estimation of the tested Li-ion battery competitive to the EIS method.

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STUDY OF ELECTROCHEMICAL STABILITY OF LITHIUM CONDUCTING ELECTROLYTES

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The characteristics of lithium-ion batteries (LIB) are strongly dependent on the structure and properties of the electrodes active materials and the electrolyte composition. In this case, one of the important tasks is the development of electrolytes with high anodic stability. An understanding of the redox stability of the electrolyte is necessary to select the appropriate electrolyte-electrode pairs for LIB1. The physicochemical properties of liquid electrolytes are largely determined by the method of interaction between the ions of the dissolved salt and the solvent molecules. Therefore, studying of the structure and oxidative stability of the resulting complexes is an important task, which has both practical and theoretical significance.

In this work, electrolyte systems based on LiBF_4 and LiDFOB salts in solvent mixtures, including sulfolane and dimethyl carbonate, were studied. It was shown that 1 m solution of LiDFOB in the mixture of sulfolane and dimethyl carbonate (2/3) is stable to 5.6 V at room temperature and stable up to 5 V at 40 °C. The stability of the described systems to anodic oxidation was investigated using quantum chemical calculations taking into account the processes of ionic solvation in an electrolyte solution. The stability of the electrolyte was assessed taking into account the influence of the structure of the anionic solvate complex. It was investigated how the spatial coordination of the solvent with respect to the BF_4^- and DFOB^- anions changes during the oxidation reaction.

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ELECTROCHEMICAL PROPERTIES OF LITHIUM TITANATE ANODES WITH CONDUCTIVE BINDER

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We present a simple and cost-effective approach to fabricate $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrodes with enhanced functional properties by using eco-friendly water-based binder, which is an alternative to fluorine-containing binders. The obtained results show that the introduction of PEDOT:PSS/CMC binder maintains the good integrity of material and adhesion to current collector.

Electrochemical characterization was performed by galvanostatic charge-discharge experiments, cyclic voltammetry and impedance spectroscopy. The electrode with combined PEDOT:PSS/CMC binder has superior properties, in particular increased specific capacity and improved C-rate performance during charge-discharge. By using PEDOT:PSS/CMC binder instead of PVDF, the practical specific capacity was increased up to 14 % (157 mAh g^{-1} at 0.2C, normalized to total electrode mass). Highest stability during long cycling was observed for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -electrode with this binder at less than 1% decay after 100 cycles at 1C.

Electrochemical impedance spectra reveal a decrease of interfacial resistance and an increase of apparent diffusion coefficients for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode material with PEDOT:PSS/CMC binder, which supports improved functional characteristics of the electrode. As combined polyelectrolyte dispersion, the proposed conductive binder is an efficient alternative to the non-conductive PVDF binder for commercial lithium ion batteries.

We believe that an optimized composition of LTO/PEDOT:PSS/CMC anode material can be applied for fabrication in commercial lithium ion batteries. We have tested a button cell composed of a positive $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ electrode, a negative $\text{Li}_4\text{Ti}_5\text{O}_{12}$ with the same conducting polymer binder for both electrodes. The mass loading ratio of $\text{LiFe}_{0.4}\text{Mn}_{0.6}\text{PO}_4$ positive electrode and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ negative electrode was calculated before battery assembly to be 0.879. The good cycling performance observed with capacity fading of only 16 % over 1000 cycles is remarkable.

Acknowledgements: The financial support from Saint Petersburg State University (grant № 26455158) is gratefully acknowledged. The authors would like to thank the Center for X-ray Diffraction Methods and the Interdisciplinary Center for Nanotechnology Research park of Saint Petersburg State University, where data were obtained with support of RFBR grant № 19-03-00593-a.

DEFECTS GENEALOGY IN OLIVINE-TYPE CATHODE MATERIALS FOR RECHARGEABLE BATTERIES

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For materials scientists the mineral world has always been a bottomless pool of ideas. A thorough analysis of the data on natural minerals might provide valuable insights into the features of isostructural or closely related synthetic materials. In this sense, the structure of defects in minerals deserves a special attention due to its crucial role in determining and tuning the functional properties of materials.

The word “olivine”, originally coined to name a greenish (olive-colored) mineral with a basic formula of Mg_2SiO_4 , has now turned into a generic term for a class of phosphate-based cathode materials for Li-ion batteries, $LiMPO_4$ ($M = Fe, Mn, Co$)^{1,2}, which are isostructural to Mg_2SiO_4 . In fact, the practical implementation and commercialization of the most prominent material in the series, $LiFePO_4$, has been delayed due to the poor understanding of defects’ formation mechanisms, their evolution, and influence on properties. In due course, many defects in $LiFePO_4$ were literally rediscovered by materials scientists despite being intrinsic and known for years in olivine minerals systematically studied by mineralogists.

In this talk, the parallels between defects in olivine-type minerals and $LiFePO_4$ will be drawn with a focus on their formation, propagation, and structure-property relationships, which is here named “defects genealogy”. For this, we scrutinized a huge array of geological data on olivine minerals, analyzed and compared most of types of defects as well as predicted and experimentally found new H/OH-defects in $LiFePO_4$, which were widely identified and examined for olivine minerals, but unfairly omitted for cathode materials. Our results and conclusions are validated experimentally and supplemented by comprehensive high-throughput computations based on the density functional theory. The influence of the defects’ structure on the electrochemical properties of $LiFePO_4$ will also be discussed along with the recommendations on how to force defects play on your side.

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IDENTIFICATION OF NEW HIGH-VALENT IONIC CONDUCTORS BY USING COMBINATION OF TOPOLOGICAL AND DFT METHODS

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The current trend in the battery materials science is in the searching of most prospective post-lithium batteries. Traditionally, alkali metal-ion batteries (Na, K) are considered as most viable alternative to the lithium ones. However, high – valent metal-ion batteries also look very promising due to availability and low cost of raw materials and higher charge of working ions.

Here we report the recent results in theoretical searching of new high-valent metal-ion conductors. The searching procedure based on two main steps: 1) high-throughput topological screening of ICSD database, which allows for determining the size and position of cavities and channels in crystals, obtaining data on the topology of the free space, and construct a map of cavities and diffusion channels; and 2) more precise Density Functional Theory (DFT) calculations of diffusion barriers for the most prospective structures. ToposPro [1] and VASP [2] packages were used for topological and DFT analysis, respectively.

In summary, based on topological screening, we selected ca. 230 compounds with enough free space for Mg-, Ca-, Sr- or Al- ionic conductivity [3,4]. Further 20 most perspective compounds were analyzed by DFT methods: AlVO_3 , $\text{Mg}_3\text{V}_2(\text{SiO}_4)_3$, $\text{Mg}_3\text{Nb}_6\text{O}_{11}$, $\text{Ca}_3\text{Mn}_2\text{O}_7$, $\text{Ca}_3\text{Fe}_2(\text{GeO}_4)_3$, $\text{Sr}_3\text{Ti}_2\text{O}_7$, SrCr_2O_4 etc. The full database of newly identified high-valent metal-ion conductors is uploaded at <http://batteryaterials.info/> website.

The research was done using the computational facilities of SCTMS (supercomputer 'Zeolite').

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ENERGY BARRIERS FOR OXYGEN ION MIGRATION IN Pr_2CuO_4 : NEB AND VORONOI METHODS

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The layered cuprates were suggested¹ as cathode materials for creating prospective high-temperature electrochemical devices (SOFC). To provide significant oxygen ion conductivity, the presence of interstitial vacancies in the crystal structure is an essential factor. In the Pr_2CuO_4 crystal structure (sp. gr. $I4/mmm$)¹ oxygen vacancies are located between the $[\text{CuO}_2]$ and $[\text{Pr}_2\text{O}_2]$ layers. Using the geometrical Voronoi method² we have revealed that these vacancies are represented by four-membered rings of voids and channels of the migration map (Fig. 1).

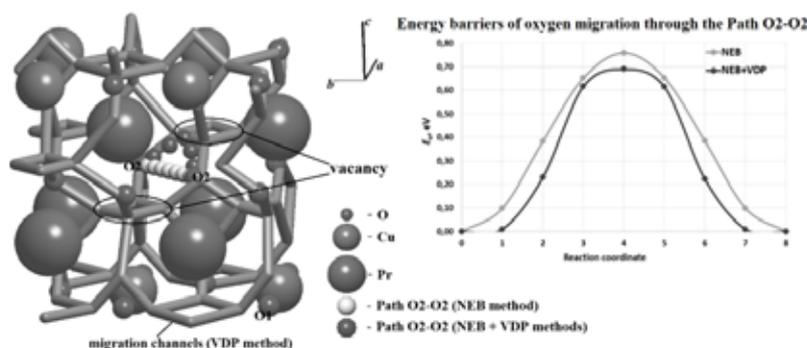


Figure 1. Energy barriers for the oxygen diffusion between two O2 positions in the Pr_2CuO_4 crystal structure. The length of the transition O2-O2 is 2.83 Å.

By means of the DFT modeling (VASP package), we have determined that the movement of the O^{2-} ions is preferable in the $[\text{Pr}_2\text{O}_2]$ layers: the migration barriers in the $[\text{CuO}_2]$ layer, $[\text{Pr}_2\text{O}_2]$ layer and between the layers are equal to 1.04 Å, 0.76 Å and 1.88 Å, respectively. Moreover, we have calculated the migration barrier using an improved Nudged Elastic Band (NEB) method (the intermediate points for the NEB trajectory were taken from the migration map calculated by means of the Voronoi method). The resulting barrier is 0.07 eV lower than the barrier calculated with the standard NEB³ method. Thus, the combination of the NEB and Voronoi methods describes more correctly the ion migration.

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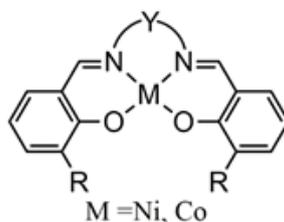
METAL CENTER – ORGANIC BACKBONE INTERPLAY DEFINING PROPERTIES AND APPLICATIONS OF SALEN-TYPE METALLOPOLYMERS

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Developmental efforts in the design and optimization of new materials with good electronic conductivity and ability to participate in multi-electron oxidation-reduction reactions is currently one of the primary strategies to obtain systems and devices with high performance in various fields such as energy storage and transformation, catalysis, electronics or medicine. Such novel multifunctional materials often come in the form of polymeric structures with molecular and supramolecular architectures built from transition metal complexes with “non-innocent” (redox active, i.e. with energetically accessible levels susceptible to oxidation or reduction) ligands capable of multi-electron transfer. Defining and adjusting of the electronic communication between transition metal and organic backbone is crucial for successful implementation of the metallopolymers in electrochemical energy systems.

We are focusing on the polymers of metal-salen type complexes that are notable for ease of preparation and structure modification of monomers via modular synthesis, ability to incorporate diverse metal centers, simple electrochemical polymerization and redox activity of the resulting polymers.



Salen-type complex

In this contribution we will present our recent results on multi-electron redox activity of the nickel- and cobalt-containing salen-type polymers leading to specific capacities up to 180 mAh/g polymer. We will discuss influence of metal centers, ligand structure and extend of their communication on these materials capacity and magnetic properties. We will demonstrate strategies of performance improvement for Li-ion batteries and supercapacitors by using salen-type metallopolymers as capacitive and conductive electrode additive.

CONDUCTIVE POLYMER BINDERS FOR LiFePO_4 CATHODES

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The energy density of conventional LiFePO_4 cathodes is limited by the amount of the added carbon conductor and inert PVdF binder which make up significant weight and volume fraction of the cathode.

We have developed composite binders based on electrically conducting poly(3,4-ethylenedioxythiophene)–poly(styrene sulfonate) (PEDOT:PSS) polymer and an ionically conducting co-binding polymer – poly(ethylene oxide) (PEO) or sulfonated poly(phenylene oxide) (SPPO). Both SPPO and PEO are miscible with PEDOT:PSS. The resulting composite binders have exhibited electronic conductivity ($1\text{--}40\text{ S cm}^{-1}$), Li^+ ionic conductivity ($10^{-5}\text{--}10^{-4}\text{ S cm}^{-1}$), and electrochemical stability over the potential range of 2.0–4.2 V vs. Li/Li^+ . The cathodes have been processed using “green” aqueous media, avoiding the use of toxic and expensive N-methyl-2-pyrrolidone.

The PEDOT:PSS/PEO binder has revealed poor cyclic performance with conventional carbonate electrolytes due to the solubility of PEO in the electrolyte solution. However, that issue has been resolved by using sulfolane-based electrolytes. The PEDOT:PSS/SPPO binder can be used in conventional carbonate electrolytes, showing high stability and cyclability.

It has been found that PEDOT:PSS increases the macroscopic electronic conductivity of cathode blends, resulting in better utilization of the active material. The addition of the co-binder (PEO or SPPO) has enhanced Li^+ conduction and the adhesion of the cathode layer to the aluminum current collector. As a result, the specific capacity and cyclic performance of the developed cathodes have been improved compared to conventional LiFePO_4 cathodes. Moreover, the packing density of the active material has been increased in the presence of the co-binders, and the resulting cathodes have exhibited enhanced volumetric capacity.

The rate capability of the cathodes is highly influenced by the cathode porosity. The cathode containing 2.5 wt.% of PEDOT:PSS, 2.5 wt.% of SPPO, and 95 wt.% of LiFePO_4/C has demonstrated the optimal porosity of 43% resulting in high volumetric energy density at discharge rates 0.1C–50C.

In summary, the developed polymer binders can replace conventionally used carbon black and PVdF in the LiFePO_4 cathode composition to enhance its specific capacity and volumetric energy density.

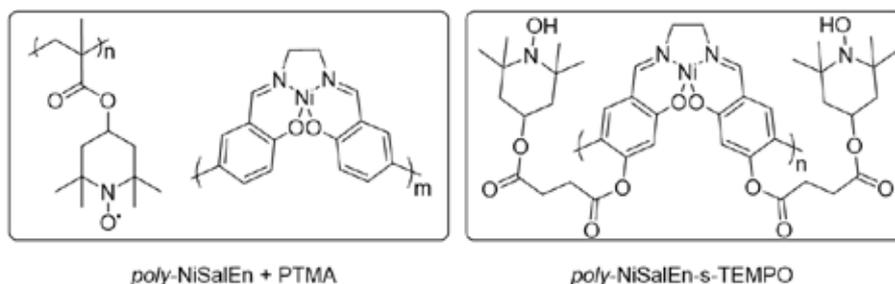
This study was financially supported by the Russian Science Foundation (project no. 17-73-30006).

DESIGN AND SYNTHESIS OF NITROXYL-DERIVED POLYMERS FOR ENERGY STORAGE

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Polymers containing the redox-active side groups may be considered as one of the promising motifs for the design of energy dense materials for electrochemical power sources.¹⁻² The nitroxyl radical compounds, possessing both high specific capacity and electron transfer rates, are widely used as such redox groups.³



The current work is devoted to the design and synthesis of NiSalEn monomers and polymers with nitroxyl fragments covalently appended to the conductive backbone. A crucial impact of the structure of the *poly-NiSalEn-s-TEMPO* on the performance of the materials derived from the materials obtained was found.⁴

This work was supported by the Russian Science Foundation (grant number 16-13-00038). Scientific research was partially performed at the Research park of St. Petersburg State University: Interdisciplinary Resource Centre for Nanotechnology, Chemical Analysis and Materials Research Centre, Magnetic Resonance Research Centre, Chemistry Educational Centre.

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COMBINED CRYSTALLOCHEMICAL AND QUANTUM-CHEMICAL METHODS FOR PREDICTION OF NEW Ag^+ -CONTAINING INORGANIC SOLID ELECTROLYTES

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Nowadays the production of Li-based power sources meet problems: they are unsafe, unstable and expensive due to depletion of natural resources. One of the main goals of materials science is the search for solid electrolytes (SE) containing other mobile cations. In this work, the search for new SE among Ag- and S-, or Se-containing ternary and quaternary compounds is presented as an alternative of Li-SE.

Prospective structures were found by using high-throughput screening of existing databases and quantum-chemical simulation of ionic transport. Totally, 1105 ternary and quaternary Ag- and S(Se)-containing compounds were selected from the ICSD (version 2018/2). A group of promising ionic conductors with 1D-, 2D-, or 3D-migration maps was identified by using the Voronoi partition algorithm as implemented in the ToposPro program package.¹

Thus, 135 ternary and 99 quaternary compounds were found, in which Ag^+ -migration is possible. Among them, 87 compounds have not been studied previously as possible Ag^+ -conductors. The modeling by the density functional theory (DFT) method was carried out for 13 compounds with the simplest migration maps. The migration energy was calculated using the Nudged Elastic Band (NEB)² method as implemented in the CP2K package.³

Such combination of fast crystallochemical and precise DFT methods can serve as an effective prediction scheme to search for new fast-ion conductors.

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RELATIONSHIPS BETWEEN MIGRATION ENERGY BARRIERS AND PROCRYSTAL ELECTRON DENSITY DISTRIBUTIONS IN SOLID ELECTROLYTES

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In the field of computational modeling of materials properties, one of the challenges is to reach high accuracy of predictions made within the reasonable computer time. Particularly, for high-throughput searching for promising solid electrolytes and cathode materials different approaches were developed. The most common among them are geometrical-topological approach¹⁻³, the bond-valence-landscape-based methods^{2,4} and their combinations with density functional theory (DFT) calculations³. The methods of the last group, such as the nudged elastic band (NEB) method, are the most precise, but the most time-consuming ones. In order to reduce the computational cost of NEB calculations, an analysis of the spatial electron density distributions could be used to guess 'correct' migration pathways in the crystal structure⁵. In this connection, we have developed a procedure of migration ion pathways selection based on topological analysis of model electron density distributions and evaluation of their contribution in conductivity based on the electron density values in their critical points. Combining the disposition of critical points calculated for the procrystal electron density distributions with the following analysis of their connectivity, we have obtained possible migration pathways. As a result, the DFT-predicted migration barriers and the electron density values on certain critical points correlate well for tested potassium- and silver-containing compounds selected as promising solid electrolytes by means of the geometrical-topological screening. The consistency of the migration energy values obtained using this method with the results of NEB calculations allows to apply this approach for screening of large datasets.

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GEL-POLYMER ELECTROLYTES FOR SODIUM-ION BATTERIES

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Polymer electrolytes have numerous advantages over traditional liquid electrolytes for many electrochemical applications including advanced metal-ion batteries. However, they usually have low conductivity, which may limit their practical use. Finding ways to improve the conductivity of polymer electrolytes is an important scientific and technical problem.

In this work, a polyacrylonitrile-based gel-polymer electrolyte for sodium-ion batteries is described that features sodium-ion conductivity greater than $1 \cdot 10^{-3} \text{ Ом}^{-1} \text{ см}^{-1}$ at room-temperature. Complete sodium-ion cells with these gel-polymer electrolytes are tested. They are capable of withstanding several hundreds charge-discharge cycles without significant deterioration of the parameters of the electrolyte both at room temperature and at -20°C . Practical aspects of conductivity measurements in polymer electrolytes are also discussed, including such issues as the cell design, types of electrodes to be used, treatment and interpretation of the impedance data to extract the electrolyte conductivity.

The work was supported by the Russian Science Foundation, grant no. 17-73-30006.

ENHANCING Na^+ EXTRACTION LIMIT THROUGH HIGH VOLTAGE ACTIVATION OF THE NASICON-TYPE CATHODES

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NASICON-type $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ delivers a highly reversible capacity of more than 110 mAh/g, showing a voltage plateau at 3.4 V corresponding to the $\text{V}^{4+}/\text{V}^{3+}$ redox couple.¹ In $\text{Na}_{3+x}\text{Mn}_x\text{V}_{2-x}(\text{PO}_4)_3$, introduction of Mn(II) lowers the cost of the material and enhances the operation voltage compared to that in $\text{Na}_3\text{V}_2(\text{PO}_4)_3$.² Here, we studied the phase transformation behavior of $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ upon charge and discharge within different voltage limits.

In $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ two well-defined steps are observed when charged to 3.8 V.² After the increase of the cut-off voltage on charge up to 4.0V the electrochemical behavior on discharge changes, namely instead of two steps as in the case of cut off at 3.8V a gradual slope is observed.³

By operando synchrotron X-ray powder diffraction we've found that symmetry reduction from rhombohedral to monoclinic occurs immediately after the start of the electrochemical desodiation, with restoring of the rhombohedral phase at 3.8 V.⁴ Cycling within 2.5-3.8 V potential range proceeds through both solid solution ($\text{Na}_4\text{MnV}(\text{PO}_4)_3 \leftrightarrow \text{Na}_3\text{MnV}(\text{PO}_4)_3$) and two-phase ($\text{Na}_3\text{MnV}(\text{PO}_4)_3 \leftrightarrow \text{Na}_2\text{MnV}(\text{PO}_4)_3$) processes. An additional voltage plateau at ~3.8-4.0 V vs. Na/Na^+ is observed, associated with re-distribution of Na cations over available crystallographic positions and "unlocking" of the Na1 site in the rhombohedral phase. Reverse insertion of Na^+ cations proceeds via a complete solid solution region. The experimentally observed reversible electrochemical capacity increases by $\approx 14\%$ after raising cut-off voltage.

This work was supported by the Russian Science Foundation (Grant No. 17-73-30006).

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ELECTROCHEMICAL INTERCALATION OF Li^+/Na^+ INTO VANADIUM (III) OXYCHLORIDE

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Layered structure of vanadium (III) oxychloride together with its high theoretical capacity (260 mAh/g per 1 alkali cation) allows considering VOCl as a perspective electrode material for metal-ion batteries¹.

Electrochemical Li^+ and Na^+ intercalation into VOCl was investigated by cycling voltammetry and galvanostatic charge-discharge using two-electrode coin-type cells assembled in argon-filled glove-box. Electrode characterization was carried out by means of *ex situ* powder X-ray diffraction and energy-dispersive X-ray spectroscopy. Structure transformation caused by Li^+ and Na^+ (de)intercalation into VOCl electrode material was studied by *operando* synchrotron X-ray powder diffraction.

Irreversible phase transition of VOCl occurring during the first charge in both Li- and Na-cell has been revealed. As a result, the isostructural phases with the structure closely related to the host structure ($a_{\text{int}} \approx 5c_{\text{VOCl}}$, $b_{\text{int}} \approx 2a_{\text{VOCl}}$, $c_{\text{int}} \approx b_{\text{VOCl}}$) are formed. Upon further cycling these phases participate in reversible red-ox reactions followed by progressive conversion with reversible capacity of ca. 100 mAh·g⁻¹.

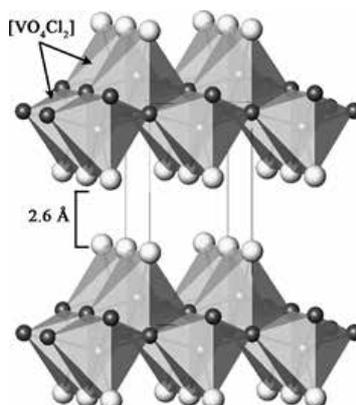


Figure 1. The crystal structure of VOCl.

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This work was supported by Russian Scientific Foundation grant No. 17-73-30006.

NICKEL-SALEN-TYPE POLYMERS CONDUCTIVITY UNDER OXIDATION

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One of the lithium-ion battery safety problem is overcharge accompanied by the heat release until a battery destruction. A possible solution of this problem is to apply protective layers based on electroconductive polymers that have conductivity dependence on electrode potential.

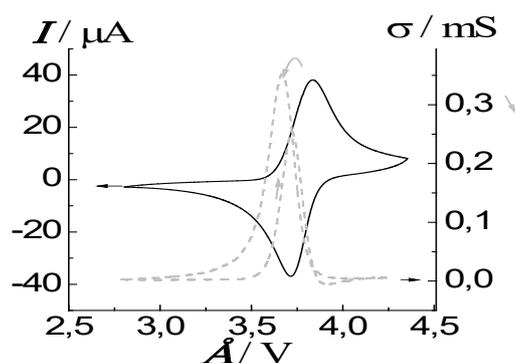


Figure 1. Cyclic voltammery of poly[Ni(Salen)] in 1 M LiPF₆ в EC:DEC (1:1) solution (10 mB/c) and a measure of conductivity dependence on potential; reference and counter electrode is lithium

In this work there were tested series of polymer complexes of nickel that have conductivity in limited potential range. Simulating battery overcharging conditions by holding at definite potential value up to 5.0 V vs Li/Li⁺ within 5 minutes we found that poly[Ni(CH₃Salen)] and poly[Ni(CH₃OSalen)] have an upper limit of stability as 4.50 V and 4.09 V, respectively. This fact allows applying them for lithium-ion protection with different cathode materials.

This work was supported by the Russian Science Foundation (grant number 19-19-00175). Scientific research was partially performed at the Research park of St. Petersburg State University: Interdisciplinary Resource Centre for Nanotechnology, Chemical Analysis and Materials Research Centre, Magnetic Resonance Research Centre, Chemistry Educational Centre.

PRODUCTION OF SOLID ELECTROLYTE PbSnF_4 FILMS BY AEROSOL VACUUM DEPOSITION

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Fluorine ion batteries are hopeful candidates in accordance to the development of battery concepts with high energy densities. PbSnF_4 has the highest conductivity of fluorine ions at room temperature among solid fluorine electrolytes $1 \cdot 10^{-5} - 2 \cdot 10^{-2} \text{ S/cm}$ depending on the method of synthesis. It is possible to significantly improve the characteristics and expand the field of application of electrochemical devices based on PbSnF_4 when obtaining this solid electrolyte, in the form of a thin layer. It should be noted that the PbSnF_4 compound decomposes upon melting ($\sim 390^\circ \text{C}$)², which creates difficulties when it is used to precipitate a high-performance and simple thermal evaporation method.

For deposition of a thin electrolyte layer, we applied “cold” aerosol vacuum deposition (AVD), which allows obtaining coatings from powders of compounds and composites without their heating and to a low substrate temperature³. The starting material for the precipitation was single-phase γ - PbSnF_4 powder with an average particle size of $5 \mu\text{m}$, obtained by mechanochemical synthesis. The coatings were deposited in a vacuum chamber in which a supersonic aerosol jet of solid particles PbSnF_4 was formed using a Laval nozzle at a pressure of 190 Pa. The substrate was placed on an X-Y platform driven stepper motors. The deposition rate on a 4 cm^2 substrate was $10 \mu\text{m}$ per minute. XRD showed the identity of the phase composition of the initial powder and the resulting coating. The ionic conductivity of the coating at room temperature, was $\sim 2 \cdot 10^{-4} \text{ S/cm}$ – same as in initial powder, measured on cold pressed tablet. Therefore, AVD is a good nondestructive method for production solid electrolyte films.

This study was carried out with the use of resources of Competence Center of National Technology Initiative in IPCP RAS

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INFLUENCE OF SYNTHESIS CONDITIONS ON THE MORPHOLOGY AND ELECTROCHEMICAL PROPERTIES OF ACIDIC CESIUM SALTS OF PHOSPHOTUNGSTIC ACID

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12-tungstophosphoric acid (TPA) and its salts are used in electrocatalysis for the modification of membranes, supports of electrocatalysts and in sensors. The acid cesium salts of TPA - $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ are particularly interesting for use in low-temperature fuel cells and sensors because of their insolubility in water, thermal and chemical stability, high acidity and proton conductivity. The kinetics of precipitation of this salt may depend on the concentration, temperature and pH of the precursor solutions. To use cesium salts of TPA in electrocatalysis, it is necessary to establish the dependencies of the synthesis conditions on their structure and properties (such as specific surface area, particle size).

In this work, we studied formation of acid cesium salts ($\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$) of TPA with varying synthesis parameters: temperature, pH, concentration. With an increase of the concentration of TPA in the initial solution, the particle size of $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ decreases regardless of the temperature at which the synthesis was carried out. The specific surface area does not depend on the particle size, but depends only on the internal porosity. The pH strongly influences the morphology and properties of the resulting salts. With any change in pH by introducing background electrolyte, the specific surface area of the salts increases. When alkalinizing the solution increases, the bimodal nature of the distribution of salt particles becomes more pronounced. Ionic conductivity depends on the water content in the sample. In samples that synthesized at $\text{pH} < 2.5$, the conductivity is constant, but when $\text{pH} > 2.5$ conductivity decreases monotonically, which is probably due to an increase of cesium content in samples.

Samples of different morphologies were tested in hydrogen sensors in air at room temperature. The sensor cell had a composition: Pt/ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /PbO₂. The concentration dependences for the hydrogen sensor for all the tested membranes are of a non-Nernst nature, indicating the establishment of a mixed potential. With an increase in the conductivity of the samples obtained, the response time of the sensor to a hydrogen pulse decreases.

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HARD CARBON ANODE MATERIALS: SYNTHESIS AND STUDY OF THE CHARGE STORAGE MECHANISM

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Hard carbon is a class of carbon materials widely used in sodium-ion batteries which are characterized by sp² hybridized carbon atoms forming highly irregular structure consisting of randomly oriented graphene layers.¹ These materials have a number of advantages including high capacity, good cycling stability, low cost and can potentially be easily up-scaled. However, hard carbon is still largely underinvestigated and its comprehensive study is of great importance. In particular, a mechanism of sodium ion intercalation should be thoroughly analyzed.²

In this study, samples of hard carbon were synthesized from D-glucose using two different approaches. In the first approach the samples were prepared via hydrothermal carbonization at 180 °C of the 2 M D-glucose solution and further hydrochars pyrolysis at 1100 °C, 1250 °C and 1400 °C under argon atmosphere. In the second approach dehydration of D-glucose powder was performed at 180 °C in air with further pyrolysis at the same temperatures from first case under argon atmosphere.

Characterization of the obtained hard carbons was carried out by different techniques such as X-ray diffraction (XRD), Raman spectroscopy and nitrogen adsorption-desorption isotherm (Brunauer-Emmett-Teller (BET)). Electrochemical methods were used to analyze the gotten materials and it was found that the samples demonstrated capacity more than 250 mAh/g. Charge storage behavior was estimated by linear voltammetry in anodic area at different sweep rates.³

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ELECTROCHEMICAL SYNTHESIS AND CHARACTERIZATION OF NICKEL SALEN-TYPE COMPLEXES-POIY(STYRENESULFONATE)

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Organometallic compounds have been extensively investigated in both fundamental research and practical applications due to their unique electrical and chemical properties. An important type of an electronically conducting coordination polymer can be produced by oxidative electrochemical polymerization of transition-metal complexes with salen-type N_2O_2 Schiff base ligands (salen is N,N' -bis(salicylidene)ethylenediamine).

The electrochemical preparation of electrically conductive composites of polymeric complexes, with a variety of carrier polymers has led to a new class of multicomponent materials with controllable electrochemical, electrical and mechanical properties. The ultimate properties result from the intrinsic properties of both the polymeric complex, and the carrier polymer, along with specific interactions between the two polymers.

Complex of nickel (II) with N,N' -ethylenebis (3-methoxysalicylideneimine) ligand doped polystyrenesulfonate (poly[Ni(CH₃O-salen)]/PSS) electroactive material have been synthesized by the electrochemical polymerization of monomer complex in the presence of tetrabutylammonium poly(styrenesulfonate) (TBA⁺PSS⁻). Their synthesis and charge transport properties have been investigated by a combination of electrochemical and gravimetric techniques using the Electrochemical Quartz Crystal Microbalance (EQCM). Electropolymerization occurs in acetonitrile (AN) solution at 0.35 V (vs. Ag/AgNO₃ in AN) and yields a polymer complex with sulfonate dopant anions from PSS. Cation-specific transport is found during electrochemical oxidation/reduction of poly[Ni(CH₃Osalen)]/PSS in 0.1 M TBAPSS and 0.1 M LiClO₄ acetonitrile solutions, as expected for a composite system with polyelectrolyte chains physically entrapped within the film.

It was determined that the diffusion coefficient of TBA⁺ cations in a poly[Ni(CH₃Osalen)]/PSS film in 0.1 M TBAPSS/AN solution is higher than that of Li⁺ in LiClO₄/AN solution. Comparison of the conductivity of the poly[Ni(CH₃Osalen)]/PSS electrode material during redox processes in acetonitrile solutions of 0.1 M TBAPSS and 0.1 M LiClO₄ showed that in TBAPSS the relative conductivity is 2 times higher than the conductivity of these films in LiClO₄.

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GRAPHENE-SILICON COMPOSITE AS MATERIAL FOR NEGATIVE ELECTRODES FOR LITHIUM-ION BATTERIES

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Different types of nanomaterials are studying as components for lithium-ion batteries (LIB). It's necessary for creating new types of LIB: more lightweight, compact and with higher capacity. One of the way of improvement of anodes material of LIB is using graphene as a part of negative electrode. Graphene has high conductivity ($2640 \text{ m}^2/\text{g}$) and able to withstand current of high density ($\sim 10^7 \text{ A}/\text{cm}^2$) [1]. It's also very stable and durable material. In the combination with silicon nanoparticles can be produced negative electrodes with high capacity and cyclical stability. Ghraphene can stabilize cylcability of silicon-based anodes, that destruct during lithium insertion-extraction.

In this work new materials based on graphen and silicon nanoparticles was studyed. Silicon nanopowder was produced by plasmo-chemical method. It was spherical nanoparticles with the average size about 40 nm. Negative electrodes was obtained by the inkjet printing method using as the active component mechanical mixture of silicon and graphene with different percentage of Si (0, 33, 75 and 80%) and also silicon particles that was covered by graphene during chemical reaction.

Negative electrodes was tested in the two-electrode electrochemical cell against Li counter electrode using electrolyte solution based on 1 M LiDFOB in the mixture EC/DMC (1/1).

It was shown that the optimum silicon percentage in the mixture is 75%. Its capacity on the 25 cycle was 900 mAh/g.

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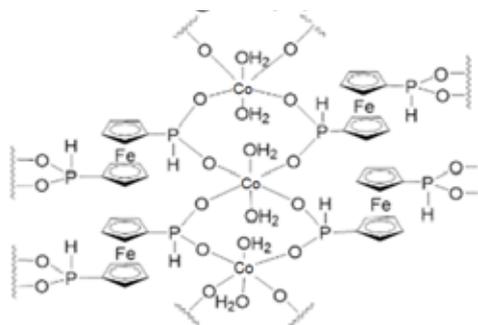
THE PERSPECTIVE OF THE USE OF NOVEL CO(II) MOF BASED ON FERROCENYL-PHOSPHINIC ACID FOR LITHIUM-SULFUR BATTERIES

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Lithium-Sulfur (Li-S) and Lithium-ion batteries (LIBs) as a promising power source have received widespread attention, owing to their convenient and good charge-discharge capacity. Suitable materials for electrodes for the batteries should have a high surface area and high values of electrical conductivity. Combination of these properties with controlled morphology and multifunctionality makes metal-organic frameworks (MOFs) to be the key research subjects for design of LIBs and Li-S batteries.

Recently new ferrocene-containing Co(II) 2D MOF have been synthesized.



The heating of the sample leads to loose of all water molecules and is accompanied by change of color from orange to blue. Detailed IR and UV/Vis-spectral analysis suggests tetrahedral environment of Co(II) ions in dehydrated MOF.¹ One can assume that in this form Co(II) can coordinate sulfur atoms to form octahedral coordination mode. At the same time, ferrocene moieties of the MOF could be attractive for Li atoms. DFT calculations provide insights on fundamental interactions between lithium polysulfides and the MOF under study. Possible locations of Li₂S, Li₂S₂ and LiSSH models have been estimated by density functional theory. Several functionals (B3LYP, PBE0, wB97xD and cam-B3LYP) were used in combination with def-TZVP basis set. Dispersion interaction was taken into account within the framework of D3 approach.

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SYNTHESIS AND STUDY OF $\text{Li}_{1+\delta}(\text{Fe},\text{M})\text{PO}_4$ (M = Mn, Co, Ni, Mg, Li) DEFECT OLIVINES AS CATHODE MATERIALS FOR LI-ION BATTERIES

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In spite of a decade of successful commercialization, LiFePO_4 and its derivatives continue to be an important part of scientific research in the field of Li-ion batteries due to their rich crystal chemistry and the number of intriguing properties¹. Presence of certain amount of defects in the crystal structure of lithium iron phosphate may not only deteriorate but also to improve electrochemical performance of the olivine-type materials. The former effect is well-studied and generally acknowledged (e.g. antisite Fe/Li disorder diminishing Li^+ diffusivity). The reasons and mechanisms of the latter (e.g. a small number of $\text{Li}_{-\text{Fe}}$ cations facilitating Li^+ diffusivity), however, are still rather vague and need to be studied even more thoroughly since they could significantly improve existing technology^{2,3}.

Series of lithium-excess olivine-type cathode materials with general formula $\text{Li}_{1+\delta}(\text{Fe},\text{M})\text{PO}_4$ (M = Mn, Co, Ni, Mg, Li; $\delta \sim 0.05$) was synthesized via solvothermal route with Li_3PO_4 as intermediate. Samples were investigated by X-ray powder diffraction, scanning electron microscopy and Mössbauer spectroscopy. The electrochemical properties and phase transformations were studied by means of galvanostatic cycling, potentiostatic intermittent titration, operando X-ray powder diffraction and Mössbauer spectroscopy. Dependence of high-C-rate performance, phase transformation behavior, electrode potential hysteresis on presence of one or two types of defects in the crystal structure is discussed in the work.

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DISTINCTION OF IMPEDANCE SPECTRA OF $\text{Li}_4\text{Ti}_5\text{O}_{12}$ -ANODES WITH DIFFERENT BINDERS

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Lithium titanate spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) is one of perspective anode materials for lithium-ion batteries because of its high structural stability during charge-discharge process, relatively high specific capacity ($175 \text{ mAh}\cdot\text{g}^{-1}$) and low cost. However, LTO has low electronic conductivity ($10^{-12} \text{ Sm}\cdot\text{cm}^{-1}$)¹.

To increase specific capacity and stability of LTO electrodes, it was suggested to change a binder in the electrode composition from polyvinylidene fluoride (PVDF) (LTO-1) to the mixture of conducting polymer poly(3,4-ethylenedioxythiophene)/polystyrenesulfonate and carboxymethylcellulose (PEDOT:PSS/CMC) (LTO-2)². As it was shown by authors, specific capacity values are grown up at high current densities for LTO-2 in comparison with LTO-1. Capacity loss during 100 cycles consists 0.5 % for LTO-2 while for LTO-1 it was 5 %.

To explain the observed increasing of specific capacity values and cycling stability, it was suggested that in LTO-based composite materials with two different types of binders difference in kinetic limitations takes place. To verify this suggestion, in this work LTO-electrodes with two binders were investigated by cyclic voltammetry (CV), electrochemical impedance spectroscopy and galvanostatic charge-discharge in coin-cells vs. Li/Li^+ . Impedance spectra were measured at two states of charges after three CVs before and after 100 cycles of charge-discharge process at current density 1 C.

It was observed that shape of impedance spectra before long cycling for both electrodes is similar and resistance of charge transfer (R_{ct}) value for LTO-1 is in 2 times higher than for LTO-2. After 100 cycles of charge-discharge process shape of impedance spectra is changed, and R_{ct} of LTO-2 electrode decreased in 3 times while R_{ct} of LTO-1 electrode decreased only in 2 times. At $E = 1.0 \text{ V}$ apparent diffusion coefficient (D_{app}) of LTO-electrodes before and after long cycling were calculated. The difference between of them constituted 2.5 times for LTO-2 and for LTO-1 changes were negligible small.

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AN APPROACH FOR IMPROVING THE SECOND LIFE PERFORMANCE OF SPENT LITHIUM-ION BATTERIES

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Today lithium-ion batteries (LIB) are used in numerous applications. Such power sources have lots of advantages, such as high specific energy and energy density, high specific power, long shelf life, etc. Today the market of electric vehicles rapidly develops increasing the demand for LIBs.

According to various estimates¹, the annual amount of LIB waste is ca. 200-500 million tons, of which 5-15% belong to cobalt - an expensive and toxic element. Due to expected even more rapid growth of LIB production the battery recycling¹ and “second life” became hot topics driven by both economic and environmental factors.

It is known that there are many reasons for the loss of battery capacity and power during its discharge/recharge cycling². One of the most serious and universal reasons for degradation is damaging of initial SEI (solid-electrolyte interphase) layer and its re-formation accompanied by lithium immobilization inside its structure (in the form of oxide, fluoride, carbonate and alkyl-carbonate). In our work we suggest a method of battery capacity recovery based on the removal of the SEI from the surface of the negative electrode and further replenishment of lithium inventory in the cell. For the SEI removal we use supercritical fluids (sc-CO₂), which has a high penetrating power and can be used for the efficient “washing” of spent cells without its full disassembly. We evaluated the possibility of the washing out of electrolyte and SEI from the negative LIB electrodes. For the electrolyte solubility analysis we performed cloud point measurements in high pressure reactor and investigated the phase diagrams for the sc-CO₂-LiPF₆-ethylene carbonate-dimethyl carbonate. Furthermore, we studied the possibility of using acetonitrile as a co-solvent. The possibility of electrolyte extraction from the high pressure reactor was confirmed by the mass-spectrometry analysis of the exhausts from the high-pressure system. The SEI removal possibility was tested using natural graphite electrodes cycled inside coin cells.

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CYCLIC VOLTAMMETRY OF LiMn_2O_4 -ELECTRODES

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LiMn_2O_4 (LMO) is a low cost, environmentally friendly material that attracts attention because of its high discharge potential (4.2 V relative to Li^+/Li). Electroactivity of LMO-electrodes is observed as well as in mixture of organic carbonates and in aqueous electrolytes¹. In this work we studied the kinetics of intercalation/deintercalation processes of lithium ions into a spinel lattice of LMO-based materials with a standard polyvinylidene fluoride (PVDF) binder in aqueous lithium-containing electrolytes by cyclic voltammetry.

Electrodes were prepared by mixing LiMn_2O_4 with carbon and binder in ratio 80% of LiMn_2O_4 , 10% of carbon black and 10% of PVDF. This mixture was cast on Ni grid and then it was dried at 120 °C for 6 hours under vacuum. LiMn_2O_4 -electrodes were investigated by cyclic voltammetry in aqueous solutions of 0.5 M LiClO_4 and 1 M Li_2SO_4 in argon atmosphere at different scan rates (0.2 – 50 $\text{mV}\cdot\text{s}^{-1}$).

It was shown that at high scan rates (1 – 50 $\text{mV}\cdot\text{s}^{-1}$) the kinetics of lithiation/delithiation process depends on diffusion of Li^+ ions because the slope of the peak current versus the sweep speed in logarithmic coordinates is close to 0.5. On the other hand at slow rates (< 1 $\text{mV}\cdot\text{s}^{-1}$) the slope $\lg I_p - \lg v$ is close to 1 which indicates kinetic control (electron transfer).

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A DETAILED DESCRIPTION OF HYDROTHERMAL SYNTHESIS OF OLIVINE-TYPE CATHODE MATERIALS.

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One of the most crucial problems in the field of producing cathode materials for advanced Li-ion batteries is to understand the influence of synthesis parameters on structural and electrochemical properties of the materials.

The focus of the presentation lies on the main features of the dependence between synthesis parameters, chemical composition, structure and electrochemical properties of cathode materials based on LiFePO_4 and Mn-doped LiFePO_4 .

The synthesis process of LiFePO_4 and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ solid solution was described, the influence of synthesis conditions such as temperature, concentration, pH value of reaction media, chemical composition ratio on the key properties of the materials was determined. The charge-discharge capacity of obtained LiFePO_4 and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ is represented in fig.1 a - b.

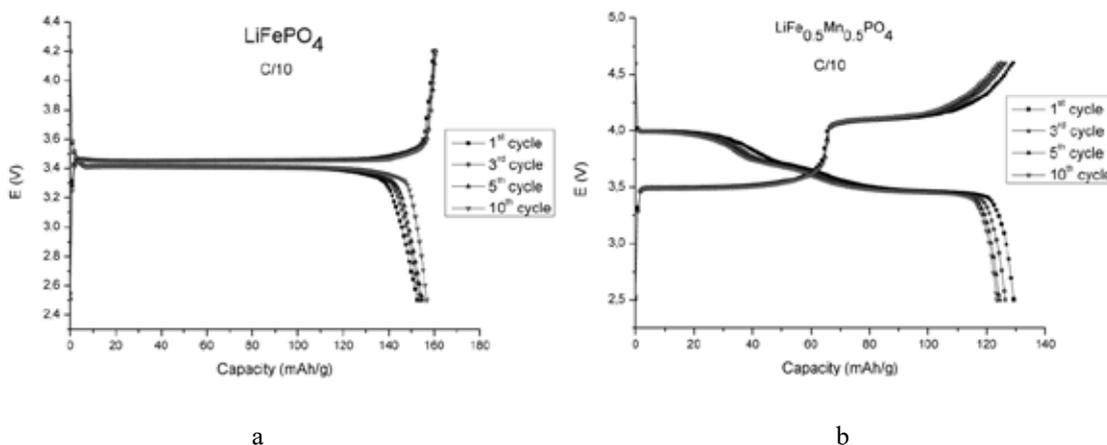


Figure 1. Electrochemical performance of LiFePO_4 (a) and $\text{LiFe}_{0.5}\text{Mn}_{0.5}\text{PO}_4$ (b)

SUSPENSIONS AND KINETICS OF THE ELECTROPHORETIC DEPOSITION OF YSZ ELECTROLYTE OF DIFFERENT DISPERSION ON A CATHODE SUBSTRATE

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One of the main streams in commercialization of solid oxide fuel cells is to reduce the operating temperature, while maintaining the relevance of the well-studied traditional electrolyte material ZrO_2 , stabilized by Y_2O_3 (YSZ), but in a thin film design, which helps significantly reduce its ohmic losses at low temperatures. For the formation of thin YSZ films, electrophoretic deposition (EPD) was used in this study. The purpose was to compare the properties of suspensions, deposition kinetics, parameters of the coatings obtained based on nanoscale YSZ powder (YSZ_L, IEP UB RAS, 54.6 m²/g) and commercial YSZ powder (YSZ_T, Tosoh, 16.8 m²/g). Suspensions for EPD in a mixed dispersion isopropanol / acetylacetone (50/50 vol. %) medium prepared using YSZ_L and YSZ_T showed a high positive zeta potential value (+27 mV) suitable for precipitation. However, a significant difference was found in the kinetics of deposition at a constant voltage from the resulting suspensions, namely, in the deposition process from the YSZ_L suspension, no decrease in current was observed, whereas for the YSZ_T suspension there was a noticeable current drop from deposition time. This affects the thickness, mass and green density of the resulting film, which were noticeably less for YSZ_T suspensions. It was shown that the YSZ_L film deposited on the La_2NiO_4 cathode substrate was completely dense after sintering at 1350 °C, whereas a higher temperature (1450 °C) was necessary to sinter the film based on the commercial YSZ_T powder. Methods were proposed for reducing the aggregation of particles in suspensions and optimal deposition regimes of YSZ powders of different dispersion were found for the practical use of the EPD method in SOFC technology.

The work was carried out within the framework of the state assignment of the IEP UB RAS and was partially supported by the RSF (project 19-13-00136). The authors are grateful to the Government of the Russian Federation for the full support of their work (02.A03.21.0006, Act 211). The facilities of the shared access centre "Composition of compounds" IHTE UB RAS were used to characterize the films obtained.

LAYERED NICKELATES AS PERSPECTIVE CATHODE MATERIALS FOR INTERMEDIATE TEMPERATURE ELECTROCHEMICAL DEVICES

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Layered oxide materials Ln_2NiO_4 , possessing high values of the mixed ionic and electronic conductivity and moderate values of the thermal expansion coefficient, are considered as perspective materials for the cathodes of intermediate temperature electrochemical devices. This report summarizes investigations made by our group on the structure of the materials in the series of Ca-doped $\text{Ln}_2\text{NiO}_{4+\delta}$ ($\text{Ln} = \text{Pr}, \text{Nd}; x = 0 - 0.6$), their thermal expansion and electrical properties, electrochemical performance of the related electrodes, include composite electrodes with electrolyte content equal to 50 wt. %. It was found that doping results in the structure stabilization, increase phase stability of the materials, decrease its chemical interaction with CeO_2 and BaCeO_3 based electrolyte materials. The dependence of the total conductivity showed extreme behavior, reaching maximum at $x = 0.5$ for the Pr-based materials (145 S/cm) and $x = 0.3$ for Nd-based materials (140 S/cm) compared to the undoped samples (60 – 70 S/cm) at 700°C. We established the preferable content and sintering conditions in the case of each electrode system in contact with oxygen ion ($\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{2-\delta}$) and proton-conducting ($\text{BaCe}_{0.89}\text{Gd}_{0.1}\text{Cu}_{0.01}\text{O}_{3-\delta}$) electrolytes. The lowest values of polarization resistance at 700°C were obtained for the $\text{Pr}_{1.9}\text{Ca}_{0.1}\text{NiO}_{4+\delta}$ (0.17 $\Omega \text{ cm}^2$) and $\text{Nd}_{1.6}\text{Ca}_{0.4}\text{NiO}_{4+\delta}$ (0.41 $\Omega \text{ cm}^2$) electrodes. However, low Ca content ($x=0.1$), was found, did not eliminate phase decomposition of $\text{Pr}_2\text{NiO}_{4+\delta}$. For application in the electrochemical devices we recommend $\text{Pr}_{1.7}\text{Ca}_{0.3}\text{NiO}_{4+\delta}$ - a compromise composition, thermodynamically stable in the intermediate temperature range, with moderate value of thermal expansion coefficient and electrochemical activity. The electrode performance of both electrode compositions selected was found to be substantially enhanced using these materials in composite electrodes in combination with related oxygen ion and proton-conducting electrolytes.

The study was partly supported by RFBR (project № 18-38-20063). The work was performed using facilities of the shared access centers “Ural-M”, Institute of Metallurgy, UB RAS and “Composition of compounds”, Institute of High Temperature Electrochemistry, UB RAS.

STRUCTURE AND PHYSICO-CHEMICAL PROPERTIES OF CU SUBSTITUTED $\text{La}_{1.7}\text{Ca}_{0.3}\text{NiO}_4$ AND ELECTROCHEMICAL PERFORMANCE OF THE RELATED ELECTRODES

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Development of cathodes with high performance and stable electrochemical characteristics is a very promising direction of modern research in the field of solid oxide fuel cells. As the object of this study layered Ruddlesden-Popper phases were selected. The materials of the $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ series ($x = 0 - 0.4$) were synthesized via citrate-nitrate combustion method and certified using conventional and high-temperature XRD (20 – 900 °C). All the materials possessed a tetragonal syngony with a space group of I4/mmm in the entire range of concentrations and temperatures. Substitution with Cu leads to a noticeable decrease in the CTE values from 14.5 to $12.8 \times 10^{-6} \text{ K}^{-1}$ at $x = 0$ and at $x = 0.4$, respectively. The results of dilatometric study were in a good agreement with those obtained by HT-XRD.

The total conductivity with Cu doping increases from 90 to 140 S/cm at 700 °C, the content of interstitial oxygen δ decreases from 0.052 to 0.017. To study the electrochemical characteristics, symmetric cells with functional $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{1-x}\text{Cu}_x\text{O}_{4+\delta}$ layers were fabricated on the $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ electrolyte substrates (95% of relative density). Substitution with Cu makes it possible to reduce the optimum temperature of electrode sintering from 1200 °C at $x = 0$ to 900 °C at $x = 0.4$. Polarization resistance of the $\text{La}_{1.7}\text{Ca}_{0.3}\text{Ni}_{1.6}\text{Cu}_{0.4}\text{O}_{4+\delta}$ at 850 °C in air was $0.15 \text{ } \Omega/\text{cm}^2$, for comparison, the polarization resistance of the base electrode sintered at the optimum temperature (1200 °C) was $0.6 \text{ } \Omega/\text{cm}^2$. Application of $\text{LaNi}_{0.6}\text{Fe}_{0.4}\text{O}_{3-\delta}$ collector layer to the Cu-containing electrodes showed deterioration of their electrochemical performance in contrast to the base composition. The electrochemical performance of Cu-rich electrodes was stable during 500 hours of testing in air atmosphere at 850 °C.

The study was performed using facilities of the shared access centres “Composition of compounds” IHTE UB RAS and “Ural-M” IMET UB RAS.

ELECTROCHEMICAL PROPERTIES AND STRUCTURAL TRANSFORMATIONS IN O3-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ AS A CATHODE MATERIAL FOR Na-ION BATTERIES

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Li-ion batteries is the most efficient technology for electrochemical energy storage. However, there are many research devoted to development of sodium-ion batteries due to large abundance and low cost of sodium compared with lithium.

O3-type NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ and related compositions are promising cathode materials for Na-ion batteries due to the high potential of Ni²⁺/Ni⁴⁺-couple and suppression of iron cations migration at desodiated state. NaFe_{1-x}Ni_xMn_yO₂ solid solution materials can deliver 130 mAh g⁻¹ of reversible capacity in a voltage range of 2.0 – 3.8 V versus Na⁺/Na, yet it shows very smooth charge/discharge curves with no significant voltage hysteresis, which may be attributed to stable electrochemical behavior¹.

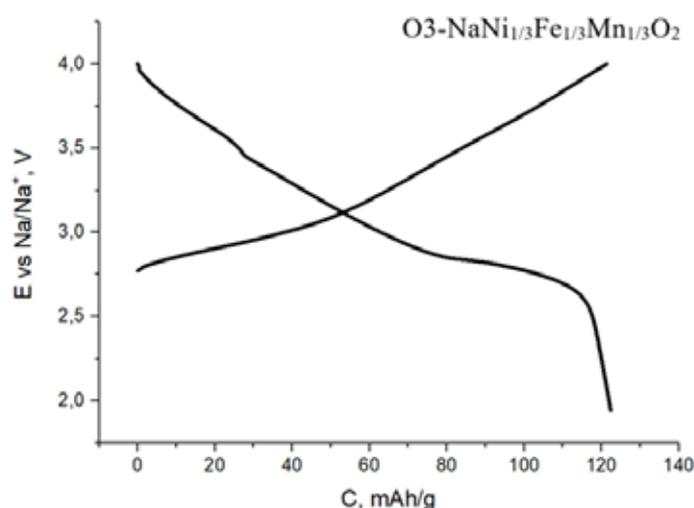


Figure 1. Charge-discharge curves of NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathode material

Figure 1. Charge-discharge curves of NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ cathode material

O3-NaNi_{1/3}Fe_{1/3}Mn_{1/3}O₂ was synthesized by co-precipitation method followed by annealing of (Ni_{1/3}Fe_{1/3}Mn_{1/3})(OH)₂ and Na₂CO₃ precursors. Electrodes demonstrate 120-130 mAh g⁻¹ of reversible capacity (fig.1). Structural transformations during charge-discharge were studied by means of X-ray diffraction and Mössbauer spectroscopy in *operando* mode.

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A REVERSIBLE PROTON CONDUCTING CELL WITH SYMMETRICAL $\text{Pr}_2\text{NiO}_{4+\delta}$ -BASED ELECTRODES

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Solid oxide systems with predominant protonic transport are considered as advanced applied materials for the energy sector. A particular interest is associated with their utilization as proton-conducting electrolytes in protonic ceramic cells, including reversible solid oxide cells that are used to convert different types of energy with high efficiency and no harmful impact.

Recently, many efforts have been made to simplify technological processes involved in the fabrication of solid oxide devices based on oxygen-ionic or proton-conducting electrolytes. One of these efforts consists in designing electrochemical cells having symmetrical electrodes as an efficient strategy for reducing fabrication costs. Moreover, this strategy can help to resolve problems associated with thermal incompatibility and electrochemical degradation if the latter has a reversible nature.

In the present work, we propose to use a $\text{Pr}_2\text{NiO}_{4+\delta}$ -based oxide as symmetrical functional layers for a reversible protonic ceramic cell. This cell was fabricated from three functional materials, including $\text{BaCe}_{0.5}\text{Zr}_{0.3}\text{Dy}_{0.2}\text{O}_{3-\delta}$ as a proton-conducting electrolyte layer, its mixture with nickel oxide as a substrate for supporting fuel electrode layer and $\text{Pr}_{1.9}\text{Ba}_{0.1}\text{NiO}_{4+\delta}$ as a basis for functional oxygen and functional fuel electrode layers. The used nickelate is stable under oxidizing conditions and almost completely decomposes at temperatures above 600 °C under H_2 -containing atmospheres, with the formation of a $\text{Pr}_2\text{O}_3/\text{Ni}$ cermet.

Utilization of the same material as the functional fuel and oxygen electrode allows minimisation of the thermo-chemical stress between the functional materials during high-temperature steps and even a reduction of these steps to one sintering stage, yielding significant techno-economic benefits. The proposed strategies can effectively be used in future to resolve a number of technological issues.

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NOVEL FORM OF NaVP_2O_7 AS A PERSPECTIVE ELECTRODE MATERIAL FOR Na-ION BATTERIES

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Sodium-vanadium phosphates, fluoride phosphates, pyrophosphates and mixed phosphates-pyrophosphates as an anionic compounds are considered as the most attractive for practical application in Na-ion batteries^{1,2}. Novel modification of sodium vanadium pyrophosphate ($\beta\text{-NaVP}_2\text{O}_7$) isostructural with KAIP_2O_7 demonstrates attractive electrochemical behavior (Fig. 1) as a Na-ion cathode material with experimentally achieved capacity of 104 mAh/g at 10mA/g current density, average operating voltage of 3.9 V vs. Na/Na^+ and only 0.4% volume change between charged and discharged states. Besides this, the $\beta\text{-NaVP}_2\text{O}_7$ framework is able to intercalate additional sodium cation at low (~ 1.5 V) potential.

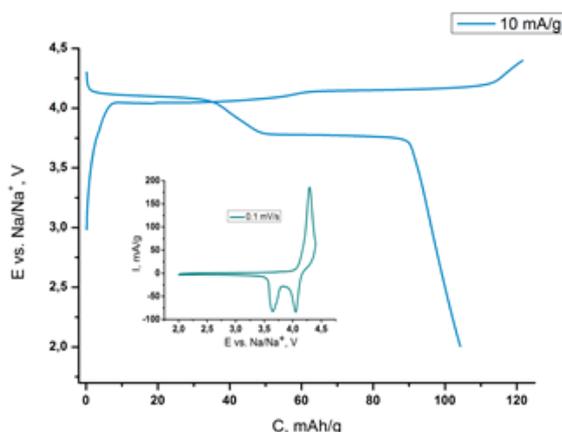


Figure 1. Galvanostatic charge-discharge curves collected at 10 mA/g current density between 2.0 and 4.4 V vs. Na/Na^+ . (Inset: CV measurement performed within 2.0 – 4.5 V vs. Na/Na^+ region at 0.1 mV/s scan rate).

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CARBON MATRIX NANOSTRUCTURED COMPOSITES AS ELECTRODE MATERIALS FOR SUPERCAPACITORS

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The development of a modern high effective integrated power supply system requires the creation of power storage and conversion devices. One of the most promising solutions is supercapacitors (ionistors, SC). Electrode materials for SC, which determine the level of their technical characteristics, most often represent nanostructured composites (NSC), consisting of highly porous, inert, conductive matrix with nanoparticles of electrochemically active substance deposited on its surface (most often metal oxides with variable valence).

A review of the authors' work on the creation and study of functionally active nanocomposites based on the group of promising carbon matrices (Kemerit, TU-145, Carbonizat, CNT, VOG, PPS, KAU) with integrated nanoparticles of different composition (Au, Ag, Pt, CrO_x, CoO_x, Co(OH)₂, Ni(OH)₂, NiO_x, MnO_x) is represented. A number of original approaches to the creation of nanocomposites was developed, including the use of thermal decomposition of high-energy materials (metal azides), the introduction of slightly soluble compounds into the matrix, and their subsequent decomposition.

The obtained nanocomposites were studied by X-ray diffraction and X-ray fluorescence analysis, small-angle X-ray scattering, thermogravimetry, electron microscopy, differential voltammetry, galvanostatic charge / discharge and impedancemetry.

The carried out research allowed to create a number of methods for the synthesis of electrode nanocomposite materials, allowing to achieve the specific capacitance of supercapacitors up to 600 F / g (at scanning rate of 10 mV / s) with good resistance (85-100%) to multiple charge / discharge processes.

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