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“NONCOVALENT INTERACTIONS IN SYNTHESIS, CATALYSIS, AND CRYSTAL ENGINEERING”

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BOOK OF ABSTRACTS

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PLENARY LECTURES

Non-Covalent Interactions with Neutral Radicals: Control of Selectivity of Bond Formation and Bond Breaking in Radical Cyclization/Fragmentation Cascades of Alkynes

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Designing an intermolecular directing group for a short-lived neutral intermediate, such as a radical, is a daunting task. I will describe how to use propargylic alkoxy groups as supramolecular chaperons for directing the Bu_3Sn radical at the correct alkyne target in multifunctional substrates.

The supramolecular directing effect is based on through-space $2c,3e$ -interactions of radicals with a lone pair of a propargylic heteroatom.²⁶ It makes the Sn radical addition to propargylic position favored both kinetically and thermodynamically over addition to diaryl substituted alkynes and other related functionalities. Such interactions enable highly efficient radical cascades of ortho-phenylene oligoalkynes.¹

I will also illustrate how non-covalent acceleration makes the directing group “traceless” as it is removed in the final aromatization step with the assistance of a through-space interaction between the departing OR radical and the SnR_3' group.²

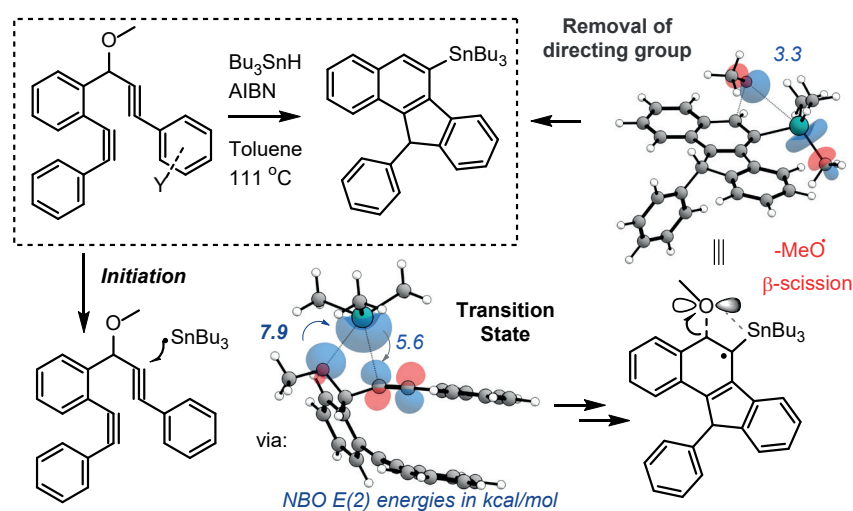


Figure 1. Non-covalent interactions with Sn- and O-centered radicals in alkyne cascade

Acknowledgements

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Hierarchical structure of catalytic systems studied with artificial intelligence algorithms

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This presentation will focus on exploring the contribution of the hierarchical organization of modern catalytic systems. According to recent studies, the dynamic nature and relationship between homogeneous and heterogeneous catalysis has now been established for C–C cross-coupling reactions [1]. The involvement of dynamic catalysis has been experimentally proven for C–N cross-coupling processes [2]. Catalytic pathways that go beyond the generally accepted assumptions have been found for C–H functionalization reactions and hydrosilylation reactions.

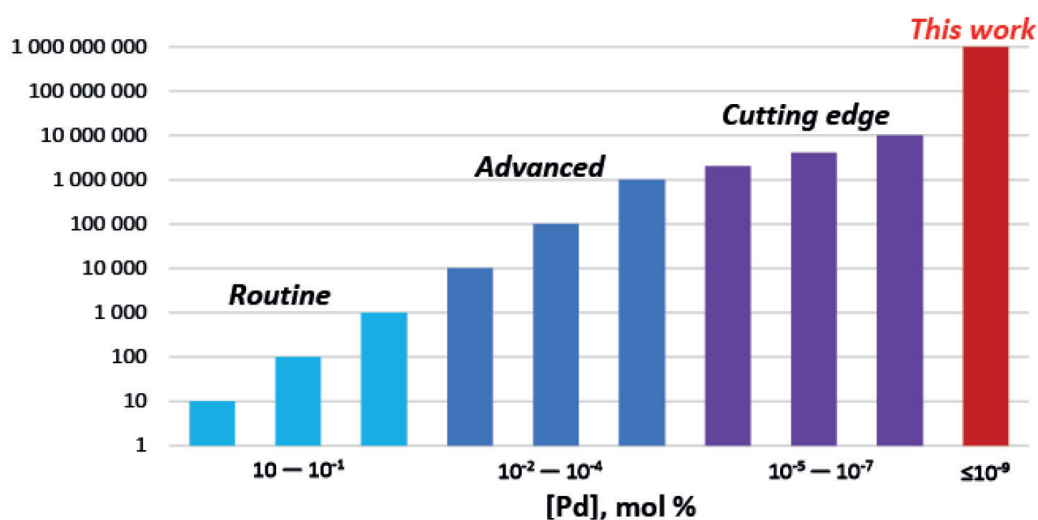


Fig. 1. Discovered superior efficiency of catalysis [5].

The dual nature of carbon groups and the participation of carbene centers have been shown for the catalytic trimerization of acetylene [3]. The use of artificial intelligence methods for the analysis of experiments on catalysis identified highly active catalytic centers with TON ~ 10⁹ (Fig. 1) and led to the discovery of the concept of Totally defined catalysis [4] and the creation of new methods for understanding the nature of homogeneous catalysis [5].

Acknowledgments

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Correlation of Noncovalent Interactions with Reactivity, a "Game Changer" for Catalyst Engineering ?

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The recent outburst of interest for C-H bond functionalization led us to address the broader question of catalyst engineering from the seldom investigated viewpoint of noncovalent interactions (NCIs).¹ Can modern theoretical methods guide reactivity exploration for the engineering of catalysts ? We first addressed this question by investigating the Ambiphilic Metal–Ligand Activation/Concerted Metalation Deprotonation (AMLA/CMD) mechanism involved in the transition metal-catalysed directed C-H bond functionalization.² This endeavor was initiated having in scope the construction of a rationale for the transposition of 4-5d metal chemistry to 3d metals. We also initiated a shift of our research towards the construction of a NCI-inclusive paradigm³ of chemical reactivity engineering based on the Independent Gradient Model and its Intrinsic Bond Strength Index (Figure 1) particularly promising for the evaluation of reductive-elimination steps in catalytically relevant reactions.^{1, 4}

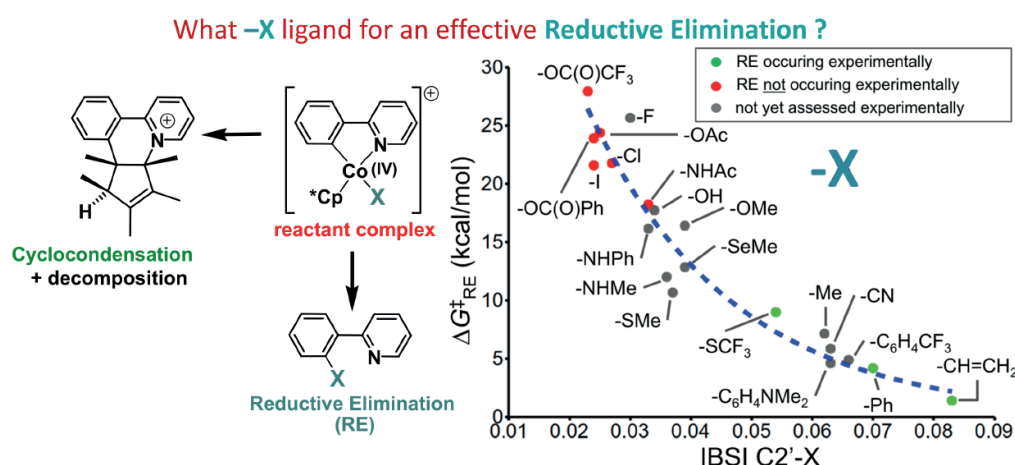


Figure 1. IGM/IBSI as a tool for engineering reductive elimination in catalytically relevant steps.

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Anion⋯anion Self-assembly via unconventional interactions

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The distribution of the electron density in bonded atoms is anisotropic. Areas of depleted or excess electron density are thus present at atoms periphery and the surface electrostatic potential (SEP) at these areas is frequently positive or negative, respectively. This is the case in both neutral and charged molecular entities. In anions SEP is negative on the whole anions surfaces, but in polyatomic anions it is less negative on the extension of the covalent bonds the “central” atom is involved in. For instance, perrhenate (ReO_4^-), permanganate (MnO_4^-), and periodate (IO_4^-) anions present four regions of local minimum electrostatic potential (σ -holes) on the extension of Re/Mn/I–O covalent bonds. The cation-anions interactions present in crystals of perrhenate, permanganate, and periodate salts further decrease the electron density on the anions to the point that the electrostatic potential at σ -holes can become positive. This offers a theoretical background to the short, directional, and attractive anion-anion interactions observed experimentally in several salts wherein O–Re/Mn/I⋯O contacts assemble anionic units into supramolecular infinite chains (Fig.1, left) or discrete adducts (Fig. 1, mid and right). Experimental and computational evidences supporting the rationalization of these short contacts as σ -holes interactions (i.e., matere bonds,¹ halogen bonds,² and coinage bonds³) will be described.

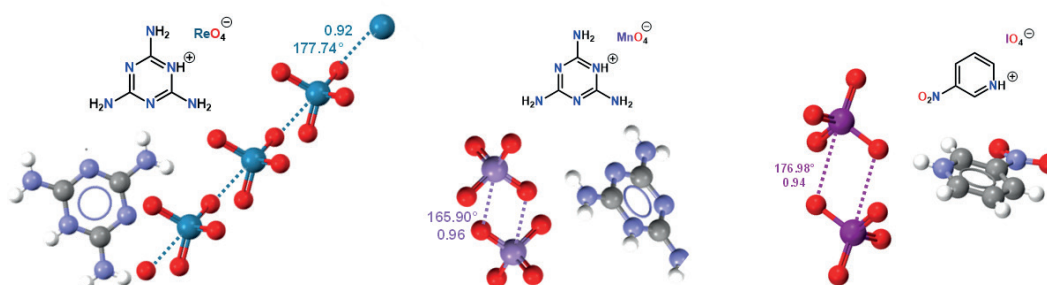



Figure 1. Molecular formula and ball and stick representation of the crystal packing of: melaminium perrhenate (left), melaminium permanganate (mid), and 3-nitro-pyridinium periodate (right). In the partial representation of the crystal packing, a single cation and the observed supramolecular anion-anion assemblies are reported. $\text{Re}\cdots\text{O}$, $\text{Mn}\cdots\text{O}$, and $\text{I}\cdots\text{O}$ short contacts are represented as teal, violet, and purple dotted lines, respectively. O–Re/Mn/I⋯O angles and normalized contacts of R/Mn/Ie⋯O separations are also given.

Acknowledgements

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The background is a solid red color. In the top-left and bottom-right corners, there are decorative geometric patterns consisting of overlapping triangles and squares in various shades of red, creating a layered, architectural effect.

KEYNOTE LECTURES

Self-assembly patterns of non-metalloid silver thiolates

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Silver thiolates show high tendency to aggregation, forming large-sized clusters which reach into the nanoscale (nanoclusters), and which represent a distinct and rapidly growing family among the coinage metal clusters. These objects can be of different nature, depending on the cluster core electronic structure and extra ligand composition, including i) Fenske-type clusters, containing only Ag⁺ and supported by S²⁻, like [Ag₄₉₀S₁₈₈(S^tC₅H₁₁)₁₁₄] as one of the most spectacular examples; ii) core-shell reduced (metalloid) clusters with mixed Ag⁺/Ag⁰ cluster cores, e.g. [Ag₃₇₄(SR)₁₁₃Br₂Cl₂]; iii) highly diverse and complicated template-assisted Ag⁺ clusters, which incorporate heteroatoms, organic ligands, polyoxometalates etc. as auxiliary ligands and templates. The template plays crucial role, initiating, sustaining and directing the cluster growth.

Self-assembly in the AgNO₃/Ag^tBu/O-donor solvent systems lead to formation of {Ag₂₀(S^tBu)₁₀} clusters (Fig. 1 left) in DMF, DMSO and NMP solutions, which can be isolated as individual complexes. Such complexes have a torus-like shape with five-fold symmetry and 2Ag:1S atomic ration and are assembled around nitrate anion acting as template. The self-assembly route can be changed into smaller {Ag₁₆(S^tBu)₈} in the presence of Br⁻ as competing template. The resulting [Br@Ag₁₆(S^tBu)₈(NO₃)₅(DMF)₃](NO₃)₂ (Fig. 1, right) is the first example of a silver thiolate framework hosting bromide.

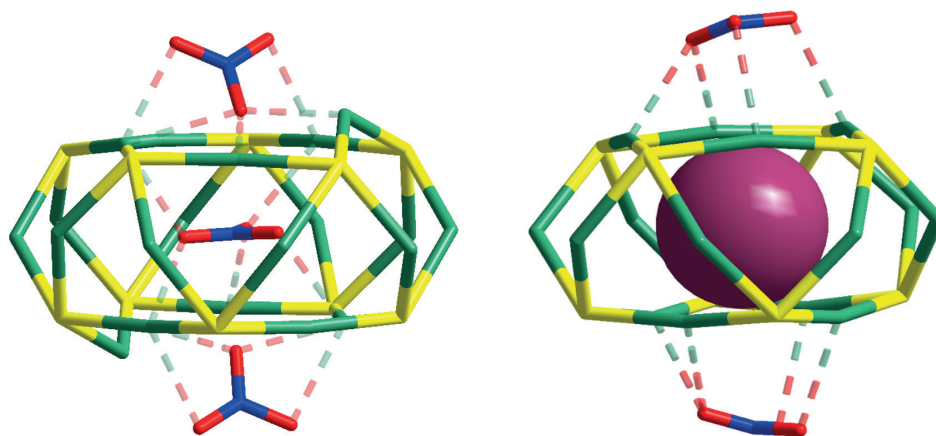


Figure 1. Structures of [NO₃@Ag₂₀(S^tBu)₁₀(NO₃)₉(DMF)₆] (left) and [Br@Ag₁₆(S^tBu)₈(NO₃)₅(DMF)₃]²⁺ (right). Tert-butyl groups of thiolates are omitted for clarity. Silver is green, sulfur – yellow, O- red, N- blue.

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Supramolecular polyhalogen-halometalates

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Ability of halide complexes (hetero- or, more commonly, homoleptic) to form inclusion compounds with di- or polyhalogens via halogen bonding (XB) was noticed decades ago. Surprisingly, this feature was not systematically studied for years; after a long pause, this area experiences revival nowadays.

The talk covers the results obtained by our group¹⁻⁷ within the last few years: the family of structurally diverse polyhalide-halometalates of bismuth, antimony, tellurium, tin, lead and some other elements, as well as their physical properties relevant to modern materials science.

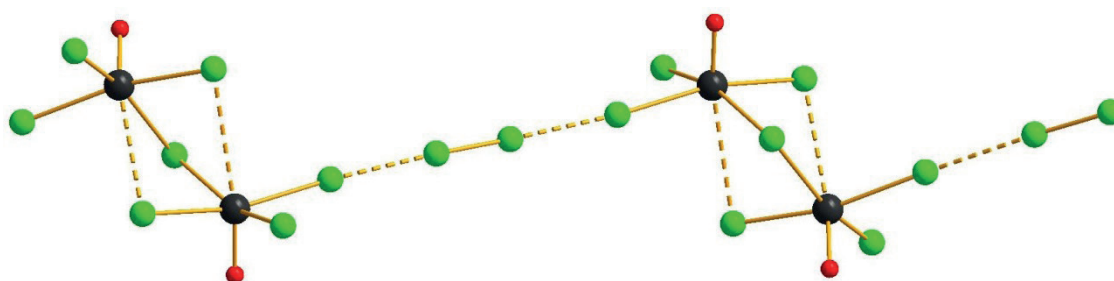


Figure 1. Example of polyhalogen-halometalate: {[Se₂O₂Cl₇](Cl₂)}

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Can we merge the covalent and tetrel bonds (TtB)?

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We used the orbital-free quantum crystallography approach to reveal the role of electrostatic, $u_{es}(r)$, and exchange correlation, $u_x(r)$, components of the total static one-electron potential, $u_{st}(r)$, for the weak and strong bonds between tetrel atoms Tt = C, Si, Ge, Sn, Pb in tetrahedral molecules and halide anions Hal⁻ = F⁻, Cl⁻, Br⁻. This allowed disclosing the quantitative trends in electronic features for bonds of different strength.¹ In all studied complexes Y–TtX₃...Hal⁻, the Tt atom provides its local electrophilic region for bonding. This fact is a reason to call such interactions as typical tetrel bonds. However, for the strong interactions between Tt and Hal atoms, the question arises: could we categorize such interactions as the covalent bonds?

The analysis of $u_{st}(r) = -u_{es}(r) + u_x(r)$ along the interatomic line between Tt and Hal atoms, in combination with kinetic Pauli potential, $u_p(r)$, which reflects the spin-dependent electron-motion features, indicates the change in type of bonding at the splice of weak and strong interactions. The gap between positions of extremes in $u_{es}(r)$ and $u_{st}(r)$, Δ_{st-es} (Fig.1), along the line linking the Tt and Hal⁻ is wide for weak bonds and narrow for strong ones. It is in very good agreement with the number of minima in $u_p(r)$ between bounded atoms. This gap exponentially correlates with $u_x(r)$ in various series with fixed nucleophilic fragment. Thus, a criterion for categorizing the noncovalent tetrel bonds (TtB) based on the potentials features was suggested.²

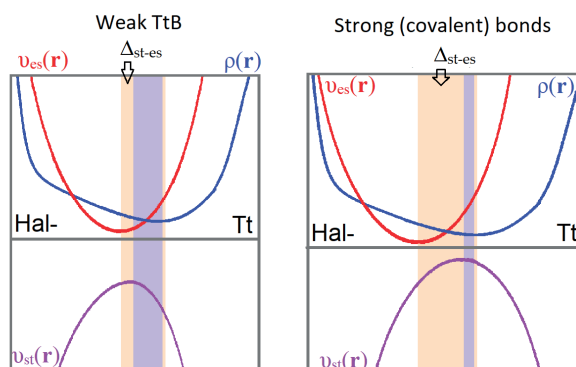


Figure 1. The gap width between positions of electrostatic potential minimum and static potential maximum along interatomic line Hal⁻...Tt in Y–TtX₃...Hal⁻ complexes.

Acknowledgements

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The intriguing world of noncovalent interactions

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Noncovalent interactions are widespread in nature and contribute to the bonding of chemical systems. Compared to covalent bonds, intra- and intermolecular noncovalent interactions are usually weak and have much lower energy and directionality, which is reflected in the term “noncovalent”. Due to the active development of these topics during recent years, most achievements in chemistry in the 21st century already is and will continue to be largely determined by noncovalent interactions.

Our achievements in this area include diverse acid-base interactions of transition metal and main group element hydrides, which ultimately determine their activity in stoichiometric and catalytic processes such as (de)hydrogenation, dehydrocoupling, alkene isomerization, and could be used for fine-tuning of metal hydride properties¹⁻⁴.

The fine-tuning option of noncovalent interactions opens ways to design ligands and metal complexes with predictable structures and predetermined properties, as demonstrated by the example of pyrazolate complexes of Group 11 metals. Those include metal interaction with diverse bases (regium bonds) that has primary impact on the luminescence properties of group 11 metal pyrazolates⁵⁻⁶.

It will be a fascinating journey into an intriguing world of noncovalent interactions.

Acknowledgements

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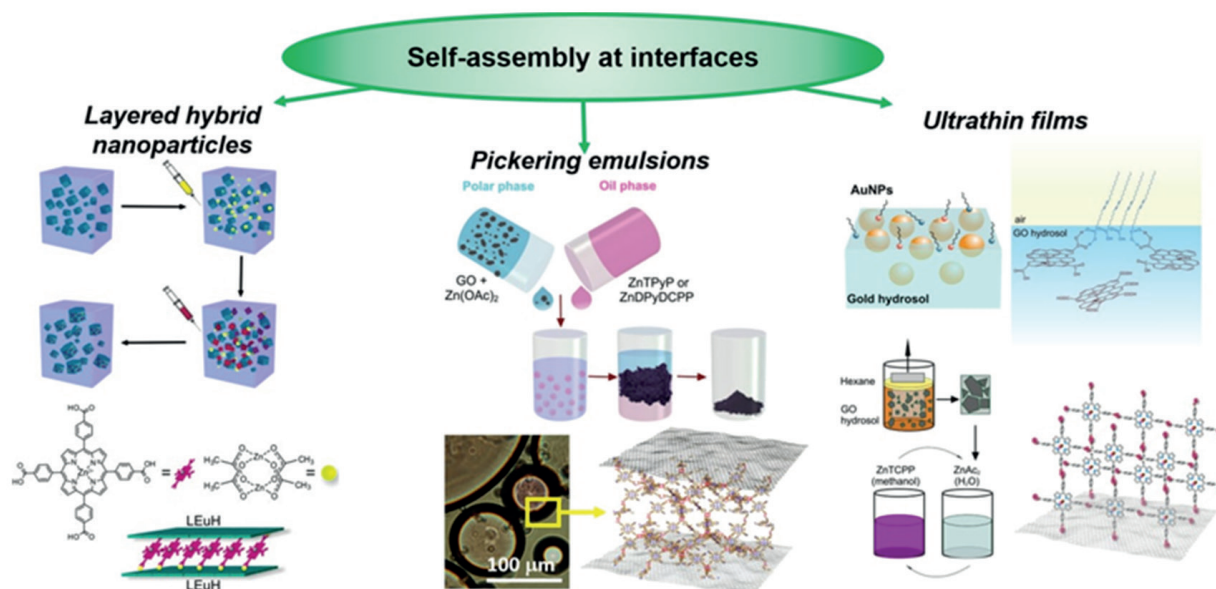
Noncovalent self-assembly of supramolecular hybrids

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Supramolecular self-assembly at interfaces is a powerful tool for integrating organic and inorganic compounds into hybrid nanostructures for a number of potentially useful applications such as sensing membranes, photoactive surface coatings, charge transferring layers, catalysis and photocatalysis.¹ The synergy of interactions between organic and inorganic components at the nanoscale due to the charge/energy exchange processes may lead to the enhancement of properties or even to the emergence of new physical and chemical effects in these materials.

Several strategies exploiting interfacial self-assembly for rationalizing the design of planar and porous dispersed nanohybrids will be discussed. One-step integration at the air-water interface as well as liquid-in-interface epitaxy method are applied for fabrication of multifunctional ultrathin planar hybrids and surface-attached SUROMFs for photovoltaic applications (see Figure). Colloidal synthesis in hydrosols and Pickering emulsions is a tool for structuring new hybrid catalysts comprising potent chromophores such as porphyrins. Integration of zinc porphyrins with layered rare earth hydroxides gives symbiotic (i.e., mimicking symbiotic behavior) catalysts as artificial enzymes², whereas their hybrids with graphene oxide exhibit the ambivalent photocatalytic properties in aqueous media. These strategies are broadly useful for advancing fabrication of hybrid nanomaterials toward ecology friendly and resource-saving technologies.



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Molecular Recognition via Chemo- and Biosensing of Novel Luminescent Complexes Based on Cyclic Phosphines

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Within the last decade a wide range of luminescent bi-, tetra- and hexa-, homo- and heteronuclear complexes of gold (I) and copper (I) based on heterocyclic phosphine scaffold has been designed.^[1] Cyclic nature of the phosphine ligands is responsible for supramolecular host-behavior of the complexes. For instance, dinuclear Au(I) complex with cyclic PN-ligands, could be regarded as a “host” molecule with two binding sites, “upper” and “lower”. The “upper” binding site is nucleophilic, while the “lower” one is electrophilic due to positive partial charges of hydrogen atoms of P–CH₂–N moieties.^{2,3}

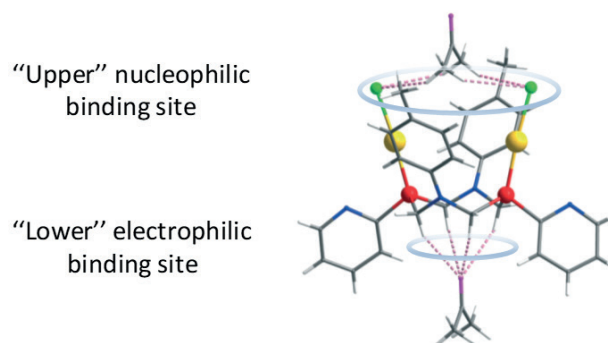


Figure 1. “Upper” and “lower” binding sites of dinuclear Au(I) complex

Unique structure of complexes on a scaffold of the hybrid cyclic P,N-ligands favors the stimuli-induced structural reorganizations followed by stimuli-responsive luminescence. For these compounds, phosphorescence is observed in a wide range of wavelengths, including the infrared range⁴ and a rare two-band white emission.^{5,6} The possibility of using both the complexes themselves and materials created by immobilization of their nano-sized colloids on a polyelectrolyte matrix as sensors for pH, temperature,^{7,8} the presence of organic solvents,⁹ biothiols,¹⁰ as well as for illuminating cell organelles has been demonstrated by confocal microscopy.^{11,12} So, the complexes are versatile building blocks for bottom-up design of smart nanomaterials for analytical and biomedical applications.

Acknowledgements

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Noncovalent Interactions in Crystal Engineering of Charge-transfer Complexes of Polyaromatic Donors and Quinone-type Acceptors

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Charge transfer single crystals are attracting more and more attention owing to their multiple applications in molecular electronics. The supramolecular arrangement of donor and molecular components is the crucial factor which determines the electronic properties of charge-transfer cocrystals. The fundamental difference between cocrystals composed of segregated and alternating donor-acceptor stacks manifests in their drastically different conducting properties. However, even slight changes of crystal structure may result in different nature of conductivity in semiconductors.

In this talk I will overview our results on charge transfer single crystals, their crystal structure and properties. The donor molecules include polycyclic aromatic hydrocarbons and their substituted derivatives, such as anthracene, tetracene, chrysene, benzanthracene, coronene, metal phthalocyanines. The quinone derivatives including TCNQ and its fluorine substituted compounds, as well as halogen containing benzoquinones, are used as acceptors. The following issues will be discussed:

- Intermolecular interactions, which determine the crystal structure, their strength and directionality
- The role of the size and topology of donor molecules
- The role of substituents effects
- The interplay among the components, crystal structure, charge transfer, optical and electrochemical properties.

Considering available data, it can be concluded that, though face-to-face π - π interactions are responsible for formation of charge transfer cocrystals, side-on weak interactions, such as hydrogen bonding, F...H, N...H and F...F, can significantly modify the structure and properties of these materials and interfere with direct correlation between the donor and acceptor strength of components on one side and charge transfer and conductivity of cocrystals on the other side.

Acknowledgements

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Non-covalent interactions polymer-solvent: from a “small nuisance” to structural-molecular plasticization

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Works on organic, inorganic and organometallic synthesis, catalysis, obtaining crystals and biomaterials make the main contribution to the modern vision of the role of non-covalent interactions. At the same time, such a vast field of knowledge as polymer materials science has turned out to be practically out of sight, despite the fact that non-covalent interactions in polymer objects are important for understanding the mechanism of many processes (from relaxation in films to thermochemical reactions) and for controlling these processes.

We started by studying the reason for the change in the physicochemical properties of amorphous glassy homopolymers films containing residual solvent. Even a small (up to 5-8% wt.) content of the residual solvent dramatically changed, for example, the membrane properties of films, sharply increasing the selectivity of gas separation while maintaining permeability. Next, we focused on non-covalent interactions in the “polymer-solvent” system, expanding the range of objects of study to rubbers, partially crystalline polymers and copolymers.

We have found a “transitional point” between the term “structural plasticization” (for thermodynamically incompatible systems) and “molecular plasticization” (for thermodynamically compatible systems) and established its mechanism. In a thermodynamically compatible system, the solvent, through non-covalent interactions with the less energetically favorable conformers of the elementary unit, initiates the transition to the most energetically favorable conformers. That increases the probability of the existence of more energetically favorable conformations in the elementary unit and leads to conformational ordering in the macromolecule, forming a short-range order in the polymer matrix. These changes remain in the film/coating, including after solvent desorption, and determine the morphology (packing) of macromolecules. We have shown that the structural-molecular plasticizer affects the structure and properties of the polymer at the stages: synthesis of a macromolecular compound, in the course of obtaining films from solutions and during the course of thermochemical transformations in polymers, which makes it possible to control the functional properties of the material.

We justified the combination of theoretical (quantum chemical modeling) and experimental methods of vibrational spectroscopy, including FTIR-ATR spectroscopy, to study changes in the conformational structure of macromolecular compounds. We have shown that not only the methods of FTIR absorption spectroscopy, in which the basic law of light absorption is satisfied, but also FTIR-ATR spectroscopy can serve as a reliable tool for the quantitative description of fine structural changes important in the study of the structure–property relationship. We established the fact of data correlations obtained by ATR spectroscopy and wetting methods and substantiated the structural criteria that correlate with the physicochemical characteristics of polymer objects: the ratio of optical densities of polar bond vibrations.

Silver Nanoclusters

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Over recent years, research on the ligand-protected silver clusters have gained significant interest owing to their unique potential applications in catalysis, organic optoelectronics, and luminescent materials. However, the synthesis of structurally precise silver nanoclusters and their assembly mechanism are still challenging and become one of the prime interests of chemists. The controllable synthesis of high-nuclearity silver nanoclusters involves the ingenious use of capping ligands or/and templating agents. Thereinto, the main role of the templating agents is to promote the order arrangement of silver ions around them to form discrete molecules. Our lab has performed comprehensive studies on the ligand-protected silver clusters including silver(I) clusters and silver(I/0) clusters in the past eight years.¹ Furthermore, some interesting photo- and electrochemical properties revealed by silver clusters including luminescent thermochromism and electrical conductivity are quite interesting.²

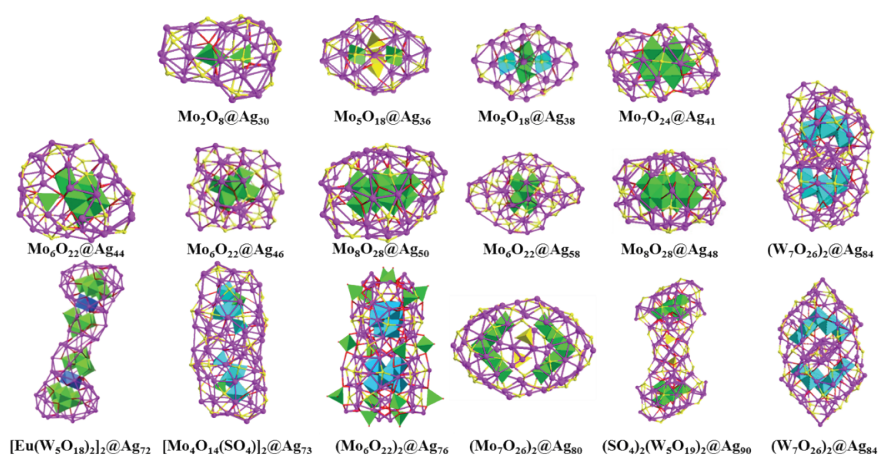


Figure 1. The family of POMs templated silver nanoclusters

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Donor-acceptor origin of Noncovalent Interactions

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Atoms are unhappy alone and, with the exception of noble gases, readily form chemical bonds with each other. All molecules, in turn, have both occupied and vacant orbitals, which allow them forming donor-acceptor (DA) complexes, which are widespread in modern chemistry and find applications in catalysis, stabilization of reactive and activation of unreactive molecules.

Due to the different chemical nature of Lewis acids and Lewis bases, DA bonds range in energy from 2.5 to more than 200 kJ mol⁻¹. In the present report, structures of antimony halide complexes with acetonitrile and pyridine will be presented.¹⁻⁵ In particular, the nature of weak interactions will be discussed based on the determined structural features in the solid state and quantum chemical computations. Sb-halogen interactions can be described as $n\sigma$ complexes in the framework of DA bonding model.⁶ In such complexes, the lone pair of LB donates the electron density to the σ^* antibonding orbital of LA. All so called halogen, chalcogen, pnictogen, tetrel, triel, aerogen and other named and yet unnamed “elemental” bonds are all fit into the class of $n\sigma$ DA complexes. Even when the value of the charge transfer is very small and bond is quite long and weak, it is the orbital features of the interacting components that determine directionality of the bonding and are responsible for the non-uniformity of the electron density. Thus, all “elemental” bonds may be successfully described using simple DA model.

A simple structural parameter, non-covalence criterion (NCC), defined as a ratio of the atom-atom distance to the linear combination of sums of covalent and van der Waals radii, was proposed.³ NCC correlates with E(2) values for Sb-N, Sb-Cl and Sb-Br bonds, and appears to be useful criterion for a preliminary evaluation of the bonding situation.

Acknowledgements

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NMR study of hydrogen and halogen bonds with P=O and POOH groups

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In this work we test if and how ³¹P NMR chemical shifts could be used to establish geometry and energy of hydrogen and halogen bonds formed with participation of P=O and POOH groups. We discuss experimental and computational challenges of obtaining non-averaged values of NMR chemical shifts and interpreting them in terms of intermolecular distances and complexation energies, which was attempted by us in a series of recent publications.¹⁻⁶

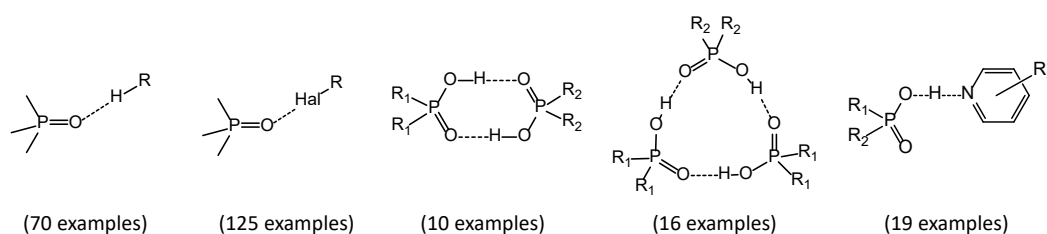


Figure 1. Left: hydrogen- and halogen-bonded complexes of phosphine oxides; right: self-associates of phosphinic and phosphoric acids and their complexes with pyridines.

Figure 1 shows general structures of the studied complexes, where R₁ could be equal to R₂ or not. Considering sets of complexes allowed us to generalize and propose several correlational dependencies which could be of practical value. Figure 2 shows three individual complexes of *tert*-butylphosphonic acid, which helped us to identify H-bonding patterns exhibited and preferred by this acid.

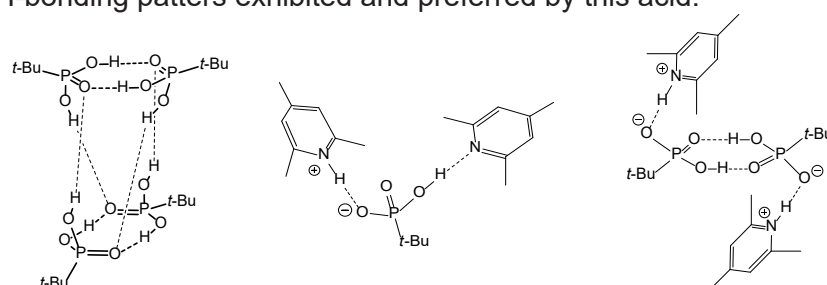


Figure 2. Self-associates of *tert*-Butylphosphonic acid and its complexes with pyridines.

Acknowledgements

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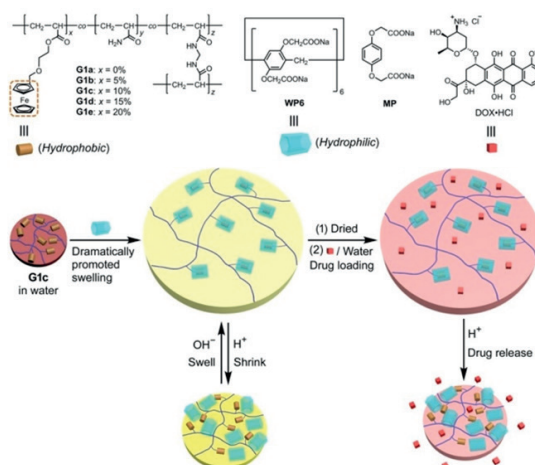
The Orthogonal Self-Assembly of Supramolecular Materials

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Focusing on the challenge of controllable self-assembly in the construction of supramolecular complexes, our group has been developing several types of supramolecular complexes constructed by orthogonal self-assembly through the incorporation of more types of non-interfering non-covalent interactions.¹) A variety of stimuli-responsive supramolecular vesicles have been constructed by host-guest complexation of water-soluble pillar[6]arene (WP6) and different guest molecules for drug delivery, showing pH-, photo-, calcium ion-, or thermal-responsiveness;² 2) A smart hydrogel with ferrocene groups on pendant of polymer networks was fabricated. The hydrogel was dramatically swollen, which was an approximately 11-fold promotion in weight compared with that in pure water, due to the formation of the inclusion complexes between WP6 and ferrocene groups in the hydrogel. Meanwhile, potential application of such a smart hydrogel in pH-responsive drug release and smart windows was demonstrated as well;^{3,4}

We believe that this orthogonal integration strategy of different properties might provide a new direction for design and development of novel functional materials, such as the fabrication of a novel artificial light-harvesting system.⁵⁻⁷



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The image features a solid blue background. In the top-left and bottom-right corners, there are decorative geometric patterns composed of overlapping, semi-transparent triangles in various shades of blue, creating a layered, architectural effect.

INVITED LECTURES

Homogeneous Organocatalysis Provided by the σ -Hole Donors

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Noncovalent organocatalysis involving hydrogen (HB), halogen (XB), chalcogen (ChB), and pnictogen (PnB) bonding between a catalyst and reaction substrates has attracted great interest over the last decade, since organic catalysts typically exhibit negligible sensitivity to air and moisture, and demonstrate a lower environmental footprint than metal-containing species. Although many efficient HB donating organocatalysts are well-explored, the fundamental principles of catalysts providing other types of noncovalent interactions are still under extensive study.

In this report, the latest experimental and computational data on the catalytic activity of the σ -hole donating organocatalysts will be discussed.¹⁻⁵ The relative activity among PnB-, ChB-, XB-, and AeB-donating species, as well as influence of total charge of the species and their formal oxidation state will be considered to highlight general directions of rational design on new environmentally benign and efficient organocatalysts.

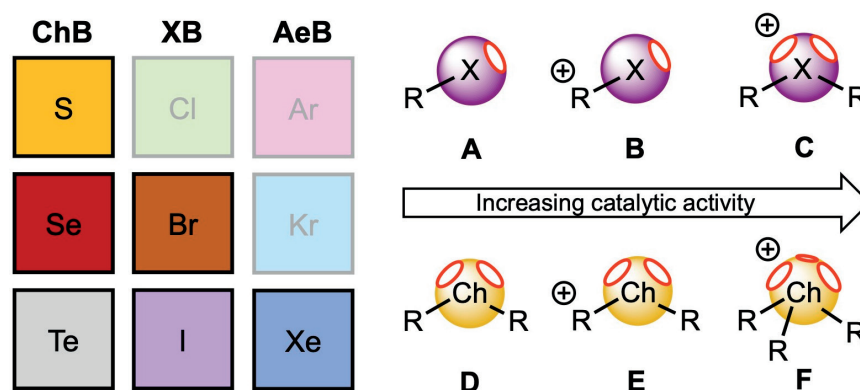


Figure 1. Abundant types of the σ -hole donating organocatalysts.

Acknowledgements

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Non-covalent interactions in the design of luminophores based on transition metal complexes

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Transition metal complexes that demonstrate photoemission in the visible and NIR range are an extremely interesting class of functional compounds, so called luminophores, which are widely used in many practical fields related to light conversion and generation. Furthermore, the study of the properties of luminophores in the solid phase is an area of growing interest for the design of highly organized luminescent molecular materials.

A wide range of non-covalent interactions (metallophilic interactions, π -stacking, halogen bonds, hydrogen bonds) and their combinations related to the composition and structure of the ligand environment of complexes, are responsible for the luminescent properties of the solid state that are different from the properties of molecules in the solution. Thus, it is the non-covalent interactions that play a crucial role in the processes of supramolecular self-assembly and crystal engineering of luminescent molecular materials.¹⁻⁴

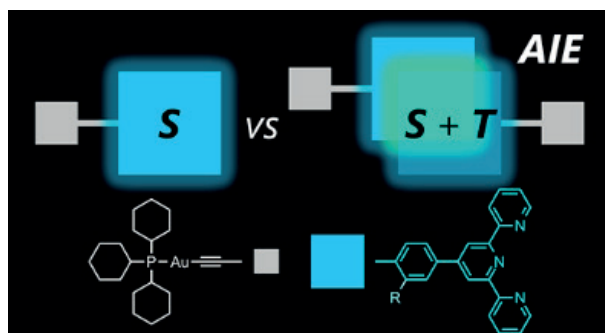


Figure 1. Schematic representation of the aggregation-induced emission of Au(I) complexes in the solid state¹

Acknowledgements

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Metal iodide as I-centered Lewis acid

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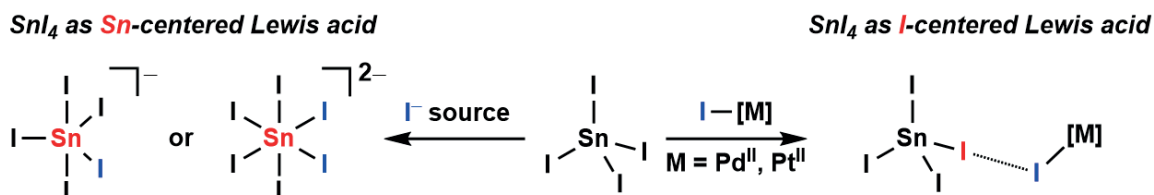
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Iodine as electronegative halogen in most of its inorganic compounds serves as Lewis base iodide. However, in elementary form iodine is well-known Lewis acid, which is able to form so-called halogen bonds.¹

Careful inspection of p-element iodide chemistry allows to find intriguing examples of I-centered acidity including nonmetal iodides NI₃ and PI₃, and metalloid iodides AsI₃, SbI₃ and GeI₄. The latter compound was reported to form the Ge–I⋯I[−] interactions instead of Ge-centered iodide complexation.²

Tin(IV) iodide is well-known precursor for Sn(IV) complexes. The reactions with iodide sources give [SnI₅][−] and [SnI₆]^{2−} complexes.^{3,4} However, we found the palladium(II) and platinum(II) isocyanide and platinum(II) dialkylcyanamide iodide complexes as kinetically inert compounds form the Sn–I⋯I–M (M = Pd, Pt) interactions instead of expected Sn-centered complexation during the cocrystallization process with SnI₄ (Scheme 1). The isomorphous cocrystals were grown with GeI₄ and CBr₄ instead of SnI₄ with the same or homologous complexes, confirming the same halogen-centered Lewis acidic role of SnI₄, GeI₄, and CBr₄ toward iodide Pd^{II} and Pt^{II} complexes. Numerous theoretical calculation with different methodologies also confirmed the I-centered acidity of tin(IV) iodide.



Scheme 1. Previously reported Sn-centered Lewis acidity (left panel) toward iodides and the established I-centered Lewis acidity of SnI₄ (right panel).

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The role of non-covalent interactions in the stability and spectroscopic properties of organoelement compounds: From phenylated pnictogen derivatives to sandwich complexes of 3d metals

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Organometallics occupy a special place in the world of non-covalent interactions (NCI). On the one hand, NCI can provide a large contribution to the metal-ligand bonds, which affects many physical and chemical properties, including spectroscopic parameters and reactivity. On the other hand, intra- and inter-molecular NCI are responsible for countless structural features observed in crystals of metal complexes as well as for fine thermodynamic and kinetic effects in organometallic reactions. In this work, representative examples of the NCI influence on the dissociation energies and structural transformations of organoelement systems are discussed.

Lewis pair complexes bearing a BR_3 acid and a R'_3E base ($E = P, As, Sb$; R, R' – organic ligands) play key roles in modern chemistry and technology, their properties being strongly related to catalysis and material science. The donor acceptor complexes $Ph_3EB(C_6F_5)_3$ attract special interest due to the elongated E-B bond. In depth theoretical studies of the $Ph_3EB(C_6F_5)_3$ systems presented in this work provide new insights into the electronic structures of these molecules. Analyses of molecular geometries, orbitals, dissociation energies and electron density distributions reveal crucial influence of NCI on the $Ph_3EB(C_6F_5)_3$ stability.

Transition-metal sandwich compounds form one of the most important classes of organometallics. They are relevant to various fields of modern fundamental and applied chemistry. Many of their unique spectroscopic and physicochemical properties arise from their low ionization energies. Valuable information on the structural changes accompanying the excitation or detachment of an electron from sandwich molecules can be obtained from the gas-phase UV absorption or threshold ionization spectra. In combination with DFT calculations, spectroscopic experiments reveal surprisingly different structural transformations of 3d sandwich complexes. The interplay between the covalent and non-covalent metal-ligand interactions appears to be responsible for these amazing effects.

Acknowledgements

DFT studies of the 3d metal sandwich compounds were supported by the Russian Science Foundation (Project 18-13-00356).

Metal-Involving Noncovalent Interaction in Palladium(II) and Platinum(II) Isocyanide Complexes

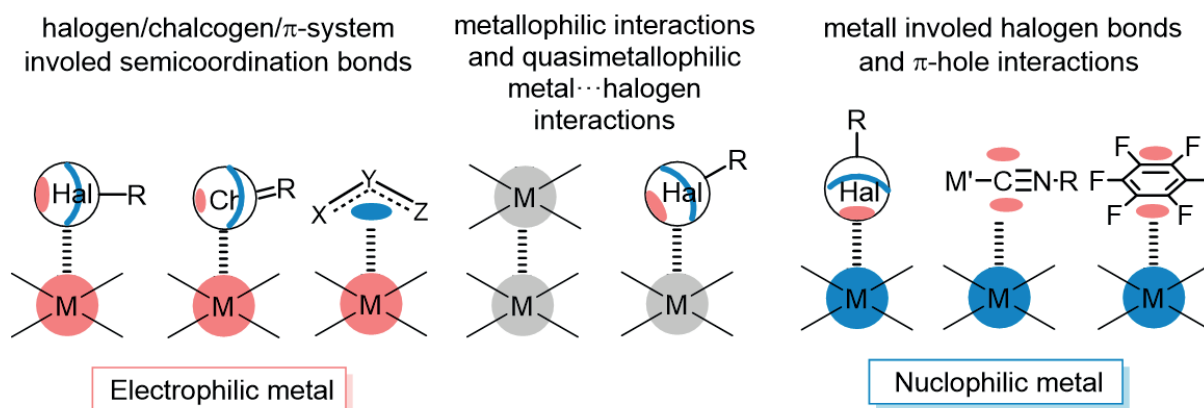
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Scientific interest in non-covalent interactions (NCIs) has grown exponentially during the past decade in light of emerging evidence that these interactions can control structures and properties of supramolecular systems and thus play key roles in various chemical, physical, and biochemical processes. Compared to purely organic compounds, metal complexes bear additional sites capable of forming several types of non-covalent interactions such as metallophilic interactions, anagostic and agostic interactions, semicoordination bonds, metal involved hydrogen bonds, halogen bonds, chalcogen bonds, metal $\cdots\pi$ and metal $\cdots\pi$ -hole interactions.

Exploring isocyanide complexes it was recognized that the platinum group metal centers can act as donors (electrophilic component) of NCIs or as acceptors (nucleophilic component) of NCIs. It was observed, that the solid-state luminescence of isocyanide platinum(II) complexes depend on the aggregation motives.^{1,2,3} Based on our data and the previous observations, we hypothesized that the metallophilic interactions are accompanied by the reduction of vibrational relaxation due to the formation of a rigid supramolecular structure and responsible for increase in the phosphorescence EQYs between polymorphs with presence and absence of Pt \cdots Pt interactions.¹ Details of these studies will be discussed.



Types of metal-involving noncovalent interaction recognized in [M]-CNRs (M= Pd^{II}, Pt^{II}) species.

Acknowledgements

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Functionalised Chalcogenadiazoles and their Coordination Compounds: Intermolecular Contacts in the Crystals

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Intermolecular chalcogen-nitrogen interaction (ICNI) plays an essential role in the formation of crystal packing of 2,1,3-benzochalcogenadiazoles (Scheme 1) and related compounds. The structure forming influence of ICNI is growing in the row S–Se–Te leading to an almost covalent bonding between Te and N.^{1,2}

Introduction of functional groups to the benzene part of the 2,1,3-benzochalcogenadiazoles as well as their participation in coordination to metals lead to a competition between ICNI and other interactions: π - π stacking, hydrogen bonds, etc. Nevertheless, even in these cases the trend to ICNI persists.

This report is focused on the discussion of intermolecular interactions observed in the structures of the functionalized 2,1,3-benzochalcogenadiazoles and their metal complexes synthesized recently by our team.³⁻⁵

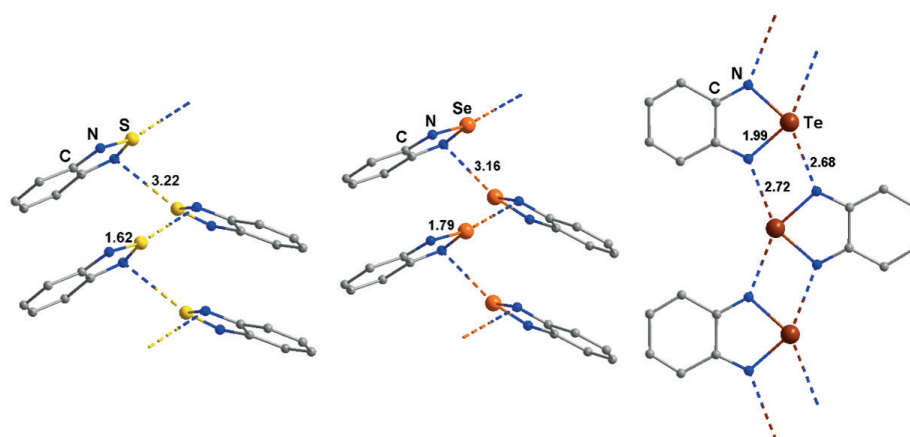


Figure 1. The short Q–N (Q = S, Se, Te) contacts in the structures of 2,1,3-benzochalcogenadiazoles. Hydrogen atoms are omitted, the distances are given in Å.

Acknowledgements

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Chiral Non-Classical Metal-Templated Hydrogen Bond Donor Catalysts

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Chiral organocatalysts have proven to be green, readily available, and cheap catalytic systems for various asymmetric transformations. However, one of the main problems in this case is the requirement of large catalyst loadings (up to 50 mol.%) in order to achieve a high asymmetric induction. Recently, as an alternative to classical organocatalysts, a new class of stereochemically inert transition metal complexes has been proposed.¹ These metal template complexes showed high catalytic activity and enantiocontrol even at a loading of 0.001 mol% (ppm).¹

We herein have developed a new class of octahedral cobalt(III) complexes of Λ - and Δ -configurations based on commercially available (1*R*,2*R*)-cyclohexanediamine or (1*R*,2*R*)-diphenylethylenediamine and different salicyl aldehydes (Figure).² In the presented complexes, the amino groups become efficient hydrogen bond donors (or Brønsted acids) due to coordination with the metal ion. The obtained chiral complexes efficiently catalyzed various asymmetric reactions with enantioselectivity up to 96% ee.²⁻⁶

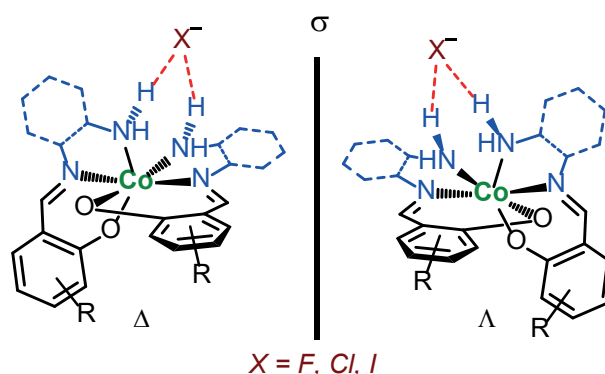


Figure. Structures of octahedral Co(III) complexes

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This work has been supported by the Russian Science Foundation (RSF grant No. 20-13-00155).

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Structure, optical and magnetic properties of sandwich lanthanide phthalocyaninates as a function of solvation

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Double- and triple-decker lanthanide phthalocyaninates exhibit unique physical-chemical properties, particularly single-molecule magnetism. Among other factors, the magnetic properties of these sandwiches depend on their conformational state, which is determined via the skew angle of the phthalocyanine ligands.

In the present work we report a comprehensive conformational study of heteroleptic trisphthalocyaninates, $[(15C5)_4Pc]M^*[(BuO)_8Pc]M[(BuO)_8Pc]$ or $[M^*,M]$ for brevity, where M^* and $M = Y$ and/or Tb . We demonstrated that metal centres M and M^* adapt distorted prismatic (DP) or antiprismatic (AP) coordination surrounding depending both on the substituents in corresponding Pc ligands and solvation factors. Thus, replacement of aromatic solvents (C_6H_6 or $PhCH_3$) with CH_2Cl_2 or $CHCl_3$ switches the M centre polyhedron from AP to DP, while the M^* surrounding remains AP, regardless of the nature of the solvent. The AP/DP switching has profound influence on the optical properties of complexes, moreover, it causes a strong increase of the axial component of the magnetic susceptibility tensor as evidenced by NMR spectroscopy. Crystallization of $[Y^*,Y]$ from CH_2Cl_2 or $PhCH_3$ allowed to characterize both conformers by X-ray diffraction and identify noncovalent interactions which stabilize certain conformations.

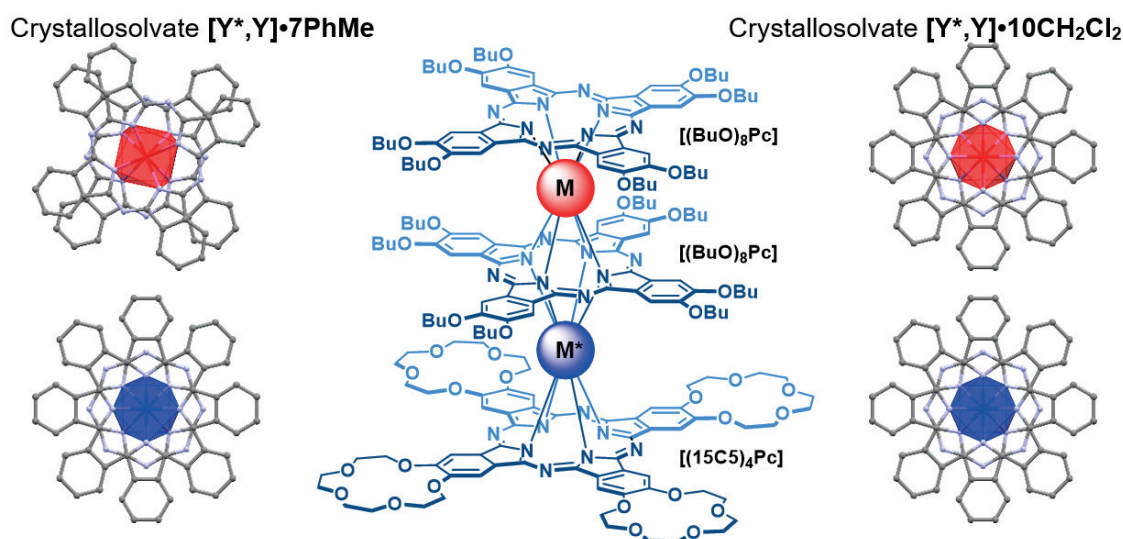


Figure 1. Symmetry of coordination surrounding of metal centres in heteroleptic complexes $[(15C5)_4Pc]M^*[(BuO)_8Pc]M[(BuO)_8Pc]$

Acknowledgements

This work was supported by Russian Science Foundation (project 18-73-10174-P).

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Novel fluorescent chemosensors for the detection of metal ions in aqueous solutions and in living cells

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Heavy and transition metals contamination of the environment causes serious health problems to humans. In this respect, development of selective and sensitive fluorescent probes in water and in biological samples is currently in a great demand.¹ Herein, dyad compound **NI-SP** bearing 1,8-naphthalimide (NI) and styrylpyridine (SP) photoactive units, in which *N*-phenylazadithia-15-crown-5 ether receptor is linked with energy donor NI chromophore, has been evaluated as a ratiometric fluorescent RET-chemosensor for mercury (II) ions in living cells. In aqueous solution, **NI-SP** selectively responds to the presence of Hg²⁺ via the enhancement in the emission intensity of NI. At the same time, the fluorescence band of SP arising as a result of resonance energy transfer (RET) from the excited NI unit appears to be virtually unchanged upon Hg²⁺ binding. This allows self-calibration of optical response. Bio-imaging studies showed that the ratio of fluorescence intensity in the 440 – 510 nm spectral region to that in the 590 – 650 nm region increases when cells are exposed to increasing concentration of Hg²⁺, thus enabling detection of intracellular Hg²⁺ ions and their quantitative analysis in the 0.04–1.65 μM concentration range. It was also demonstrated that monochromophoric 1,8-naphthalimide derivatives bearing *N*-phenylazadithia-15-crown-5 ether receptor can also be used as fluorescent chemosensors for Hg²⁺ and Ag⁺ cations in pure aqueous solutions.^{2,3}

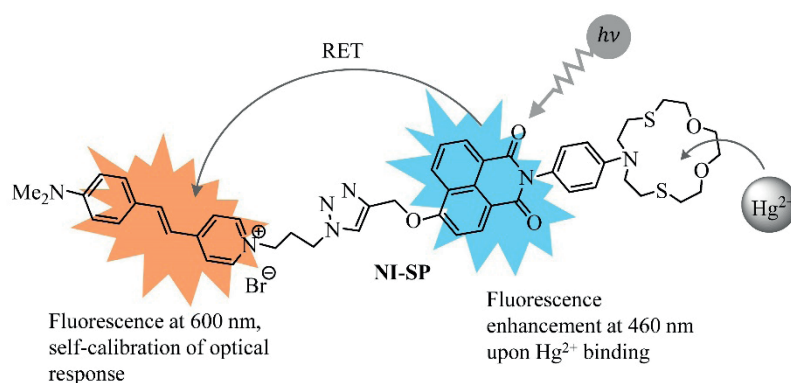


Figure 1. Chemical structure and mechanism of optical response of probe **NI-SP**

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Structure-directing Role of Hydrogen Bonds of Hydroperoxo Groups in Crystalline Adducts of Organic and Inorganic Hydroperoxides

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We show the strong similarity between hydrogen bonding of hydroperoxo functionality in organic hydroperoxide crystalline adducts (HPCA) and the much larger group of crystalline peroxosolvates with the following common features: i) The hydroperoxo groups play a dominant structure-directing role in the crystal structure of HPCA; ii) Organic hydroperoxides always form one hydrogen bond (per OOH group) as a proton donor (HB-D) in cocrystals; iii) A basic or amphoteric nature of the coformers is a requirement to obtain HPCA. Three new cocrystals of potassium salts of organic hydroperoxides with molecular hydroperoxides were synthesized. SCXRD revealed strong charge-assisted ROO⁻...HOOR hydrogen bonds (Figure 1). The energies/enthalpies of H-bonds and K...O interactions in HPCA were estimated for the first time using solid-state DFT computations and periodic electron density analysis. The calculated energy values of the ordinary intermolecular HB-D are lower than those of the charge-assisted bonds. Considering only the unique interactions, the total value of H-bond energies is almost twice as high as the total value of K...O coordination bond energies in one of the synthesized HPCA.

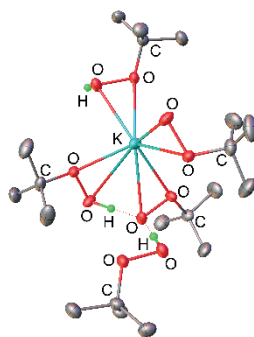


Figure 1. Noncovalent interactions in crystalline adduct of *tert*-butyl hydroperoxide and its potassium salt. H-bonds are shown as dashed lines.

Acknowledgements

This study was supported by the Russian Science Foundation (grant no. 22-13-00426, <https://rscf.ru/en/project/22-13-00426/>).

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Phosphorescent complexes of $\{\text{Mo}_6\text{I}_8\}^{4+}$ and $\{\text{W}_6\text{I}_8\}^{4+}$ with perfluorinated aryl thiolates featuring unusual molecular structures

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A series of novel cluster complexes $(\text{Bu}_4\text{N})_2[\text{M}_6\text{I}_8(\text{SAr}^f)_6]$ ($\text{M} = \text{Mo}$ or W ; $\text{SAr}^f = \text{p-SC}_6\text{F}_4\text{-C}_6\text{F}_5$, $\text{p-SC}_6\text{F}_4\text{Cl}$, or $\text{p-SC}_6\text{F}_4\text{CF}_3$) was prepared by exchange reactions between $(\text{Bu}_4\text{N})_2[\text{M}_6\text{I}_{14}]$ and AgSR^f . In the crystal structures all the thiolate ligands adopt an idiosyncratic orientation along one of the idealized three-fold axes passing through two opposite $\mu_3\text{-I}$ ligands and the centers of two opposite faces of the M_6 octahedra. This leads to shortened intramolecular $\text{C}\cdots\text{I}$ distances inside the cluster, about 3.4 Å, being noticeably less than the sum of van der Waals radii (3.68 Å). In order to confirm or disprove the existence of intramolecular noncovalent interactions $\text{C}\cdots\text{I}$, DFT calculations followed by the topological analysis of the electron density distribution within the QTAIM approach were carried out at the $\omega\text{B97XD/DZP-DKH}$ level of theory. The clusters exhibit red photoluminescence with relatively high quantum yield, up to 0.42 in the case of $(\text{Bu}_4\text{N})_2[\text{W}_6\text{I}_8(\text{SC}_6\text{F}_4\text{CF}_3)_6]$. A development of this work might be in the direction of materials science using the cylindrically shaped cluster anions as building blocks. Particularly, in the case of $\text{SAr}^f = \text{p-SC}_6\text{F}_4\text{-C}_6\text{F}_5$, the resulting cluster anions $[\text{M}_6\text{I}_8(\text{SAr}^f)_6]^{2-}$ assume the shape of nanosized cylinders (ca. 2.3 x 1.1 nm, Fig. 1) which makes them attractive candidates for design of red-emitting liquid crystals.¹

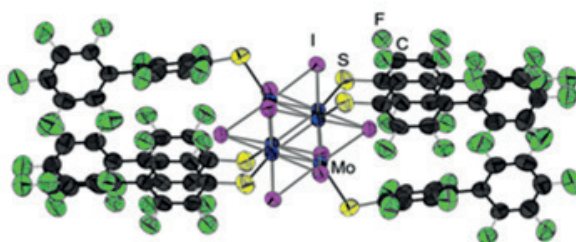


Figure 1. View of $[\text{Mo}_6\text{I}_8(\text{p-SC}_6\text{F}_4\text{-C}_6\text{F}_5)_6]^{2-}$

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Diaryliodonium sulfonates as tecton for crystal engineering

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In the last years, diaryliodonium salts are actively used as double σ -holes halogen bond (XB) donors^[1–3] for the crystal engineering, catalysis and organic synthesis. However, currently study of supramolecular pattern displays essential issue for the design of new materials based on iodonium compounds.

In this work we propose utilization of new types iodonium salts as zwitterionic (4-aryliodonio)benzenesulfonates and iodonium naphthalenedisulfonates for the crystal engineering of 1D, 2D and 3D-supramolecular architectures (Figure 1).

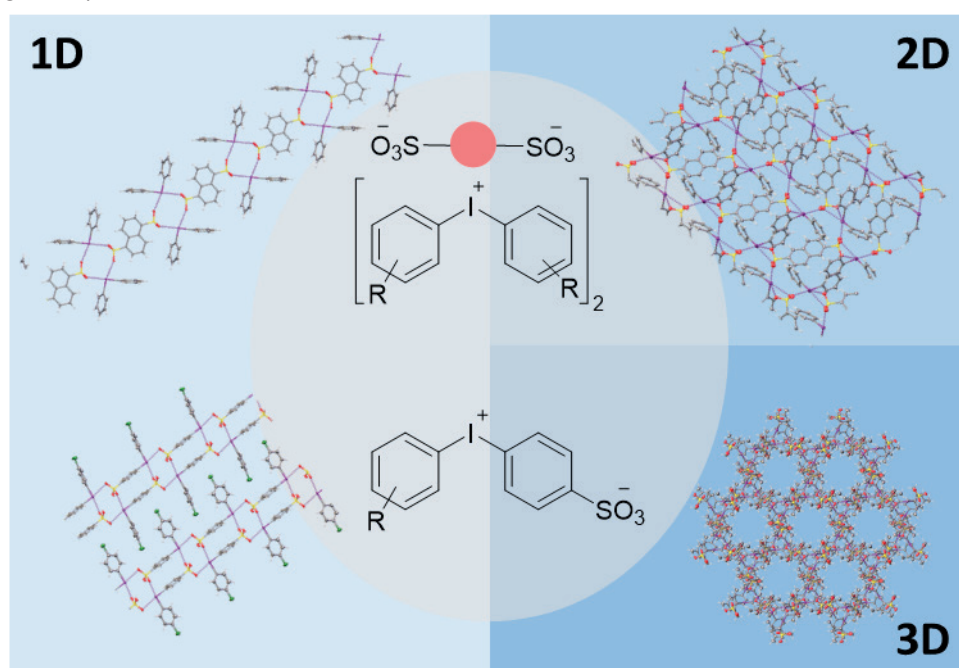


Figure 1. Supramolecular architecture of diaryliodonium sulfonates

Acknowledgements

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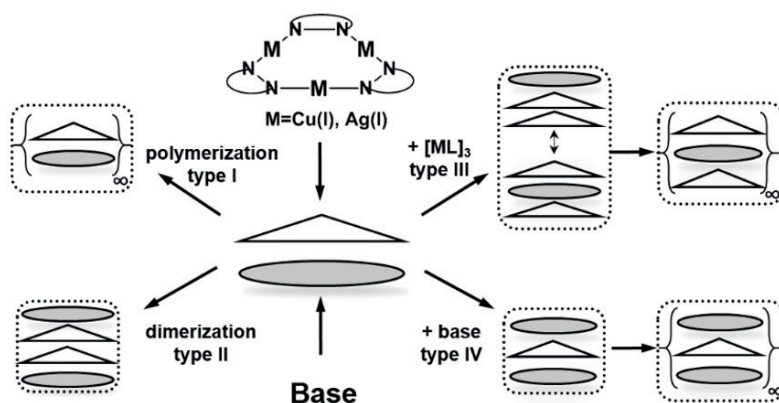
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Role of Intermolecular Interactions in the Chemistry of Cyclic d¹⁰ Metal Pyrazolates

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Intermolecular non-covalent interactions play an important role in coordination chemistry. Hydrogen, halogen bonding, and π - π stacking interactions lead to the formation of supramolecular aggregates of organic compounds determining their properties. Metal complexes with organic ligands allow the formation of other types of intermolecular forces such as metal-metal (M-M) or metal- π (M- π) interactions. Designin complexes based on metal-involved interactions are of constant interest in the past decades. Their ability to form coordination/supramolecular aggregates determines the properties and practical applications such as catalysis, gas sensing, molecule recognition, and photoluminescence. Group 11 metals form macrocyclic compounds with pyrazole of general formula $[MPz]_n$, where n depends on the type of substituents in the pyrazolate ligand and on a metal atom. Copper(I) and silver(I) form with pyrazole di-, tri-, and tetranuclear complexes or polymers. Cyclic trinuclear d¹⁰ metal pyrazolates are of the main interest because their planar structure determines the ability to form supramolecular aggregates (Scheme 1).¹



Scheme 1. Possible pathways of macrocycles complexes supramolecular aggregations.

Herein we present our results on the investigation of the intermolecular interaction of trinuclear macrocyclic pyrazolates with bases of different natures and structures such as carbonyl compounds, π -electronic systems, and diimines.

Acknowledgements

The work is supported by RSF (project № 19-73-20262)

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Photonics in Superbasic Environment

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The ground-state chemistry in superbasic media is marked by striking and unexpected results of both mechanistic and synthetic value.¹ The present work is aimed at elucidation of the peculiarities of the processes occurring in a superbasic environment involving electronic excitation. The model studies reported herein refer to a detailed investigation of the environmental effects and the influence of the specific noncovalent interactions on the spectral properties of curcumin and its derivatives in alkaline DMSO,²⁻⁴ as well as on the chemiluminescence of luminol under the same conditions.⁵ Visually, solutions of curcumin in alkaline DMSO exhibit contrasting color transitions of its deprotonated forms (Figure 1, *at the left*), which is not observed in aqueous media. Also noteworthy is the astonishing persistence of curcumin towards photo- and autoxidation under superbasic conditions. The observed inertness of curcumin towards oxidation in a superbasic environment is accounted for by the coordination interactions with alkali metal cations. The same interactions also account for the phenomenon of cationochromism observed in the curcumin fluorescence (Figure 1, *at the right*). These findings may be effectively used in developing the new spectral analytical techniques.⁴

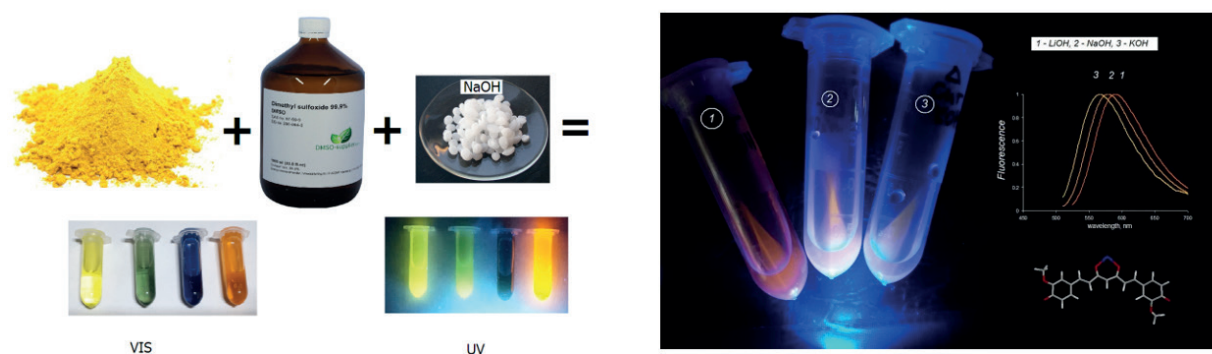


Figure 1. Graphical abstracts in the work² (*at the left*) and in the work³ (*at the right*).

Deprotonation of luminol is an important step in its chemiluminescence, and a superbasic medium (e.g., alkaline DMSO) is necessary to convert luminol into a doubly deprotonated form. Using alkaline DMSO enabled us to determine the conditions and ways for inhibiting, quenching and subsequent reactivation of the luminol chemiluminescence using hydrogen peroxide and, for the first time, to establish a detailed mechanism of such a process, whose key stage pertains to the electron transfer from luminol dianion to oxygen during autoxidation.⁵

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The background is a solid medium green color. In the top-left and bottom-right corners, there are decorative geometric patterns consisting of overlapping, semi-transparent triangles in various shades of green, creating a layered, mountain-like effect.

ORAL COMMUNICATIONS

Inhomogeneity of electron density in a central potential: more insights into the localization phenomenon

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When considering new types or new geometries of noncovalent interactions, chemists commonly face two principal questions. Is this interaction of bonding character (or, what atoms are bonded in the first place)? How does this interaction formed (what nature does it have)?

While the first question is nowadays answered by using so-called real space methods, such as the “Atoms in Molecules” theory,¹ the second question is often considered in the light of electrophile/nucleophile formalism. It is a common practice to support this simple and often ambiguous treatment by electronic structure calculations. In this respect, a number of real space methods were developed to get insights into the electron localization phenomenon for various interatomic interactions, including noncovalent ones.²⁻⁵

Any of these methods has its own advantages and shortcomings, but all of them suffer from the inconsistency problem: the localization phenomenon is studied to understand peculiarities of bonding but there is no relation between bonding and any of these localization metrics.

In this work, a measure of inhomogeneity of electron density in a central potential is suggested. Based on this new function the relationship connecting the localization of electrons with the strength of bonding interaction between topological atoms is obtained. The localization phenomenon is finally discussed on the basis of several examples calculated by means of *ab initio* methods.

Acknowledgements

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Steric Effects in The Synthesis, Structure and Reactivity of Lithioanilines

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Noncovalent Li \cdots H interaction facilitates the second metalation of 4-lithio-1,8-bis(dimethylamino)naphthalene with selectivity up to 100% and yields up to 90%. Steric hindrance in amines, bearing a bulky substituent next to the NMe₂ group, stabilizes the conformation that suppresses the DOM effect and thereby activates the direct *meta*-metalation (Figure 1).

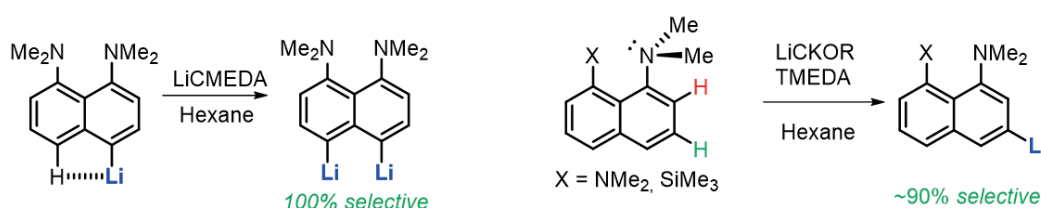


Figure 1. Selective unconventional lithiation of strained naphthylamines

While most α - and β -monolithionaphthalenes exist in solution in THF as an equilibrating mixture of monomers and dimers, sterically hindered 2-lithio-1,8-bis(dimethylamino)naphthalene exists exclusively as monomer. Similarly, α -dilithionaphthalenes exist in solution exclusively as monomers with each lithium atom coordinated to both *peri*-positions (Figure 2).

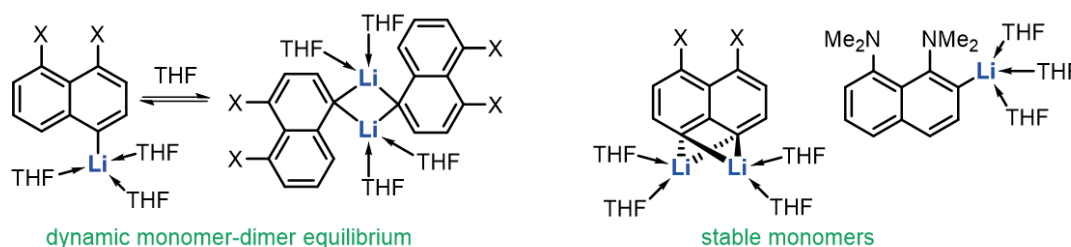


Figure 2. Steric control of self-association

Sterically promoted interaction of *peri*-dilithionaphthalenes with nitriles leads to the formation of benzo[*de*]isoquinolines. Upon treatment with nitriles 2-lithio-1,8-bis(dimethylamino)naphthalene undergoes sterically facilitated intramolecular substitution of the 1-NMe₂ with the formation of benzo[*h*]quinazolines (Figure 3).

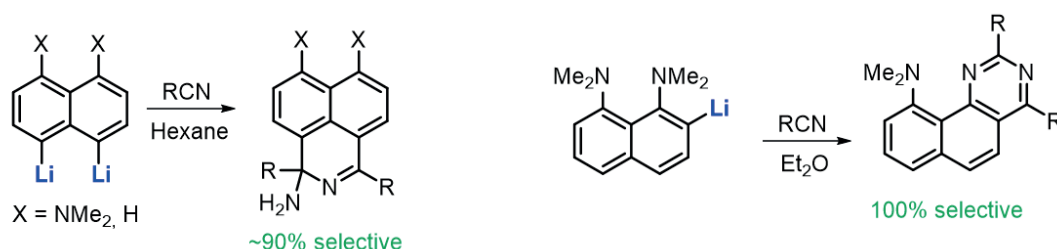


Figure 3. Steric promotion of heterocyclisations

Acknowledgements

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Self-association of Dimethylarsinic Acid: Optical, NMR, and Calculation Study of Solid State and Solutions

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Dimethylarsinic acid (Me₂AsPOOH, DMA) also known under trivial name Cacodylic acid has two centers capable of forming Hydrogen bond: AsOH can act as a proton donor and As=O can play role of a proton acceptor. Thus, DMA can form H-bond associates like at was found for different carboxylic and phosphinic acids. In crystals, the latter can form cyclic dimers or infinite chains depend on the substituents. However, crystals of DMA growing from protic or aprotic solvents form either cyclic dimers (polymorph I) or infinite chains (polymorph II). These polymorphs were studied by X-ray diffraction analysis, IR and Raman spectroscopy. The parameters of the unit cell and intermolecular distances were obtained. The results of DFT calculations with periodical boundary conditions performed for both polymorphs are closed to the experimental values. Attenuated total reflection (ATR) spectra of polymorphs I and II recorded in the range of 4000 – 550 cm⁻¹ are rather similar to each other. Particular the broad ABC structure of the ν(OH) band is observed in these spectra. This is typical for the spectra of systems with very strong hydrogen bond. Despite similarity there is some region that allows one to discern the polymorphs by spectrum. The Raman spectra of DMA crystals were obtained in the region of 4000 – 100 cm⁻¹. The intrigues feature of these spectra is weak but well distinguishable ABC-like ν(OH) band. DMA is rare example were such a band was recorded in Raman spectra of the system with the strong hydrogen bond. Again, the Raman spectra of both types of DMA crystals are similar at high frequency shift region, however, at shifts below 500 cm⁻¹, they are differ markedly.

NMR spectra of the solution of partially deuterated DMA in a mixture of liquefied freonic gasses (CDF₃/CDF₂Cl) were recorded at temperature of T = 100 K. It was found that DMA under such conditions forms only cyclic dimers. IR spectra of the solution of DMA in different aprotic solvents were obtained at room temperature at concentrations 2.5·10⁻² – 5·10⁻⁴ mol/L. The spectra have signature of the strong hydrogen bond. In the mentioned concentration range, the spectra are the same for each solution. It is indicating that self-associates exist in solution even at quite low concentrations and the equilibrium does not shift to monomers. These results have been recently published.¹

Acknowledgements

This work was financially supported by the Russian Science Foundation (Project RSF 18-13-00050). Analytical measurements and calculations were performed using the facilities of St. Petersburg State University Research Park: optical spectra were obtained at the Center for Geo-Environmental Research and Modeling (GEOMODEL), NMR spectra were recorded at the Center for Magnetic Resonance, X-Ray studies were performed at the Center for X-ray Diffraction Studies, quantum-chemical calculations were conducted at the Computing Center of St. Petersburg State University (<http://cc.spbu.ru>).

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Noncovalent Interactions in Transition Metal Complexes

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Supramolecular assembly involving metal complexes is used in various fields of science, from catalysis to materials science, medicinal and bioorganic chemistry. Compared to organic compounds, metal complexes usually have a larger number of centers capable to form noncovalent interactions. The presence of several interaction centers complicates the control over the formation of supramolecular aggregates, but at the same time, this diversity opens up broader opportunities for fine tuning the target structures and, ultimately, properties.

Non-covalent interactions involving metal complexes include those involving metal atoms as centers of noncovalent interactions or atoms or groups of non-metal atoms from the ligands. The variety of noncovalent contacts in the structures of transition metal complexes leads to their mutual influence, competition or cooperation, and determines the supramolecular structure of the complexes. This report will discuss structural features of transition metal complexes and their adducts with various halogen bond donors. The halogen bond, which is a type of attractive non-covalent interaction between the electrophilic region of the halogen atom (σ -hole) and the nucleophilic region of the same or another molecule, has been chosen for consideration as a non-covalent interaction that has been actively studied in recent decades. The following aspects will be considered: the purposeful choice of complexes for creating unusual types of halogen bonds; the influence of the structure of the complex on the possibility of the appearance of certain noncovalent interactions; co-existence and mutual influence of halogen bonding and other types of non-covalent interactions, such as a semicoordination bonding.

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Peroxosolvates of biologically active compounds

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During the 20th century peroxosolvates (crystalline adducts of hydrogen peroxide) were subject of recurrent studies as perspective solid sources of H₂O₂. It was found that stability of peroxosolvates were determined by the number, strength and topological organization of hydrogen bonds formed by H₂O₂ molecules. Recently peroxosolvates of active pharmaceutical ingredients attracted renew research interest due to their enhanced biological activity.¹

Furacin is an antimicrobial agent belonging to the nitrofuran class. We examined its possibility to form peroxosolvates. Crystallization of furacin from 96%, 50%, and 20% hydrogen peroxide led to three solvates C₆H₆N₄O₄•H₂O₂ (**1**), C₆H₆N₄O₄•1.5(H₂O₂) (**2**), and C₆H₆N₄O₄•3.5(H₂O₂) (**3**), respectively. Surprisingly, more rich in hydrogen peroxide solvatomorphs crystallized from more diluted H₂O₂ solutions. These compounds represent the second example of solvatomorphism (peroxomorphism) among crystalline hydrogen peroxide adducts.² All three structures contain 1:1 supramolecular synthon with strong unprecedent bifurcate donor hydrogen bond HOOH...2(O). Compound **3** is the first example of the structure containing 2D hydrogen peroxide layers.

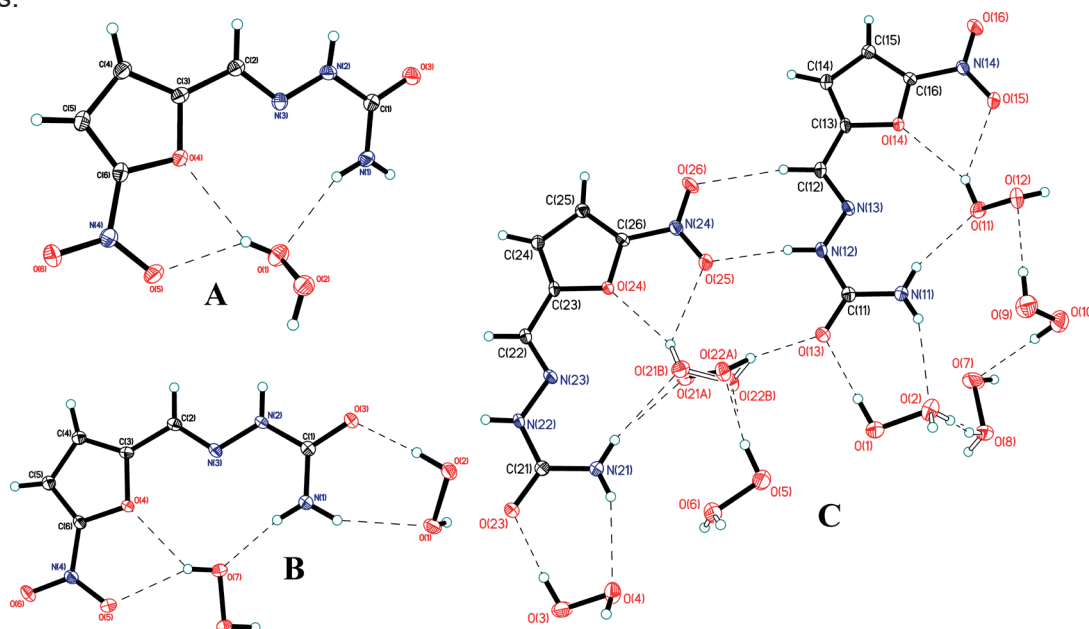


Figure 1. Asymmetric units for **1**, **2**, and **3**.

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Supramolecular organization and electronic structure of 4*H*[1,2,3]Triazolo[4,5-*c*][1,2,5]oxadiazole 5-oxide and its salts

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A big challenge in the design of materials with desired properties is to combine dissimilar and sometimes unrelated performance characteristics in a single compound or crystalline sample. One of the possible approaches is the synthesis and crystallization of multi-component structures, such as co-crystals, crystal solvates, and salts, where fine-tuning of properties can be achieved by modification of one of the components.

This work considers the supramolecular organization of a series of 4*H*[1,2,3]triazolo[4,5-*c*][1,2,5]oxadiazole 5-oxide (TODO) salts with inorganic and organic cations¹. The parent compound, being a fairly strong acid, easily forms salts both with classical alkali metal and nitrogen-containing cations as well as with hydroxonium cation, including mixed salts. Although many hydrogen-containing cations participate in hydrogen bonds, none of these bonds are strong, which lead to high density of crystalline samples.

An interesting feature of the salts work are numerous anion⋯anion and, in many cases, cation⋯cation interactions. Such bonding interactions have been identified and characterized based on topological analysis of the experimental and theoretical electron density distribution. An attempt is made to interrelate electronic structure of anions and cations, geometrical features and physical properties of the bulk samples.

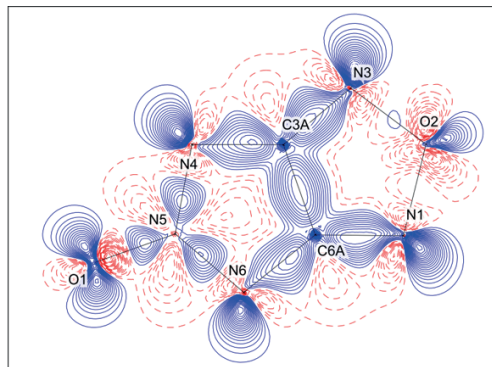


Figure 1. Deformation electron density distribution in the TODO anion (Na salt)

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Noncovalent interaction-driven stabilization of octahedral coordination in molybdenum disulfide sheets alternating with organic interlayers

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Molybdenum disulfide is a remarkable 2D material attracting tremendous and increasing attention, mainly due to fascinating electron transporting, photothermal and catalytic properties of its metastable polymorph modification (1T) distinguished by octahedral Mo-S coordination. Stabilization of 1T-MoS₂ is thus highly demanded to facilitate its application.

Towards this purpose, we synthesized and studied layered compounds containing regularly alternating monolayers of negatively charged 1T-MoS₂ and organic cationic guest molecules. The guests differing in chemical structure, capability of noncovalent bonding with sulfide layers, position and hybridization of their nitrogen cationic centers were used in the study including alkylammonium cations, diamines, aromatic and non-aromatic heterocycles.

The structure of the compounds was determined using the combined approach, which includes modeling of XRD powder patterns with K. Ufer's supercell and quantum chemical optimization of structural models.¹⁻² The obtained structural information allowed us to identify and characterize different types of host-guest noncovalent interactions occurred in these systems (NH⁺···S, CH⁺···S, π···S), evaluate their strength and contribution to stabilization of octahedrally coordinated MoS₂ network.¹⁻⁶

An influence of noncovalent interactions in the studied MoS₂-organic compounds on thermal behavior, spectral and electrocatalytic properties of their host 1T-MoS₂ layers is discussed.⁶

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New self-cross-linkable hydrogels based on natural and synthetic polyacids

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New materials formed by non-covalent interaction possess a great potential for use in medicine and biotechnology, including drug delivery, due to the ability to undergo reversible transformations under changing of the external factors. Composite hydrogels based on polymer mixtures, networks of which are formed by hydrogen, ionic, or hydrophobic bonds, could be considered as an example of similar non-covalent cross-linked systems. Owing to its biocompatibility, biodegradability, antimicrobial activity, and low toxicity, natural polysaccharide sodium alginate (**Alg**) find a wide application in medicine and pharmacology as a drug and gene carrier, wound dressing, scaffold for tissue engineering. The most common form of application of Alg are hydrogels - polymer networks cross-linked with various type bonds and capable of swelling in aqueous media. Ionotropic Alg-based gels formed upon interaction with multivalent cations are not homogeneous and stable enough. Methods for obtaining stable covalently cross-linked gels are complicated by preliminary modification of polymers, using multifunctional cross-linkers, and further purification of product. Preparing mixed hydrogels based on Alg and other polymers allows avoiding the disadvantages of the both mentioned above methods, being simpler and more promising method. In our recent work¹, this approach was successfully used for obtaining the mixed hydrogels from Alg and the copolymer of methyl vinyl ether and maleic anhydride.

The present study was aimed at the investigation of the effect of the synthetic polyacid structure on the formation and properties of their interpolymer complexes with Alg. The hydrogels based on the complexes was shown to be predominantly formed due to hydrogen bonds, the type of which depends on the polyacid structure and bound water contribution to H-binding. The study of the hydrogel behavior in water and phosphate buffer with pH 7.2 revealed that the ratio of components and the treatment temperature determine properties of the hydrogels, along with the polyacid structure. The possibility of using hydrogels as the basis for drug delivery systems was performed using the drug lidocaine as a model.

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Three-dimensional Crystalline Organic Framework Linked by Hydrogen bonds and Additionally Stabilized by the Opposite Charges of the Components as Heterogeneous Acid Catalyst and a Media Stabilizing Metal Nanoparticles

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A new, self-assembled and self-healing class of recyclable heterogeneous Brønsted acid catalysts have been developed by mixing an aqueous solution of tetrasodium salt of tetraphenylmethane-tetrasulphonate (TPSM) and a salt of tetrakis(4-aminophenyl)methane. As a result, three-dimensional crystalline organic framework (**F-2**) was obtained, linked by hydrogen bonds and additionally stabilized by the opposite charges of the components (Fig. 1). The materials functioned as a new type of catalytically active Brønsted acid in a series of reactions, including the ring opening of epoxides and acetal formation reactions in organic solvents. **F-2** was also proved to be an efficient media for stabilizing metal nanoparticles. For example, **Pd@F2 (A-2)** was simply made by mixing an aqueous solution of tetrasodium salt of tetraphenylmethane-tetrasulphonate (TPSM) and PdCl₄ salt of protonated tetrakis(4-aminophenyl)methane under H₂ in water to give the black powder of **A-2**. The material contained 17-20% of Pd and was not pyrophoric. **A-2** could be used as an efficient heterogeneous catalyst of acetylene derivatives reductions with its activity similar to that of Pd/C. **A-2** reduced the aldehyde and epoxide groups very slowly and allowed the reduction of the acetylene groups to be hydrogenated selectively in the presence of the aldehyde groups. The behavior contrasts with that of Pd/C which reduces both aldehyde and acetylene groups simultaneously. A rationale for the behaviour was put forward.

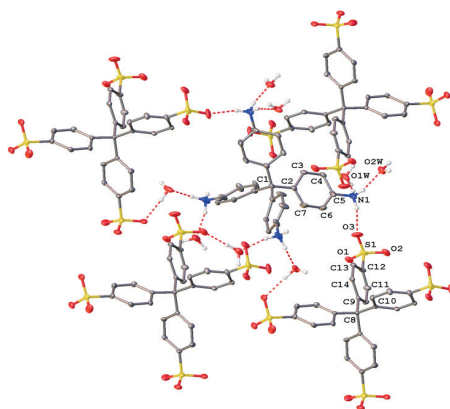


Figure 1. X-ray structure of a crystal of F-2

Acknowledgements.

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The first examples of acetylene complexes of Ca and Ln(II) based on 1,8-bis(ethynyl)carbazoles

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The hydrofunctionalization of acetylenes is an efficient and atom-economical approach to the formation of carbon-heteroelement bonds based on the addition of E–H substrates to C≡C triple bonds. One of the key stages of these reactions is the coordination of the C≡C bond on the metal center and its further activation due to electrostatic polarization in the coordination sphere of electropositive ions of alkaline earth (AE) and rare earth (RE) metals.¹ Despite the fact that organometallic derivatives of AE and RE metals are effective catalysts for these reactions, only a few examples of acetylene complexes Mg²⁺ and Yb²⁺ are known to date.^{2,3} In this regard, the synthesis of new types of acetylene complexes, the study of their structure and reactivity is an important task, both from practical and fundamental points of view.

We have demonstrated that application of bis(ethynyl)substituted carbazoles, 3,6-tBu₂-1,8-(RC≡C)₂Carb₂H (Carb = carbazolyl; R = Ph, SiMe₃) allowed to synthesize the series of low-coordination complexes [3,6-tBu₂-1,8-(RC≡C)₂Carb]₂M(THF)_n (M = Ca^{II}, Yb^{II}, Sm^{II}; Fig. 1), in which the interaction between M²⁺ and C≡C bond are realized. The presence of M···C≡C interactions was proved by X-Ray study, IR spectroscopy along with theoretical calculations.

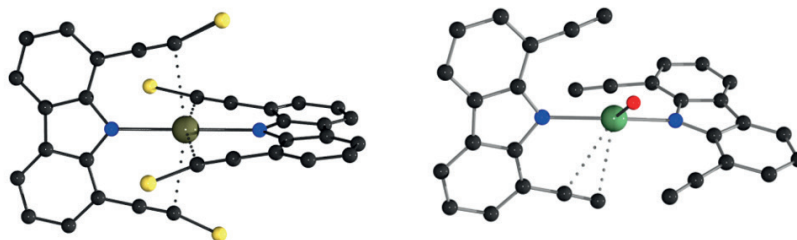


Figure 1. Molecular structures of [3,6-tBu₂-1,8-(Me₃SiC≡C)₂Carb]₂M (M = Ca, Yb, Sm) and [3,6-tBu₂-1,8-(PhC≡C)₂Carb]₂Ca(THF).

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This work has been carried out in the framework of the Russian state assignment.

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Noncovalent interactions in crystalline hydroperoxo complexes of p-block elements

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Hydroperoxo complexes have been attracting research attention in the last decades partly due to the growing interest in enzymatic mechanisms. Based on the CSD and ICSD databases there are only 4 hydroperoxocomplexes of p-block elements and only 2 of these structures were reported with localized protons.

Triphenylsilicon and germanium hydroperoxo complexes were crystallized and characterized by single crystal X-ray diffraction and vibrational spectroscopy revealing what seems to be a common motif for p-block element hydroperoxo ligands, hydroperoxo double hydrogen bonding (Figure 1). Solid state DFT computations agree well with the X-ray resolved crystal structure and reveal that the energy of hydroperoxo double hydrogen bond is >60 kJ mol⁻¹.

In crystalline triphenyllead hydroperoxide the hydroperoxo ligand acts as a proton donor, forming an O–H...C hydrogen bond with the adjacent aromatic ring of the same 1D coordination chain.

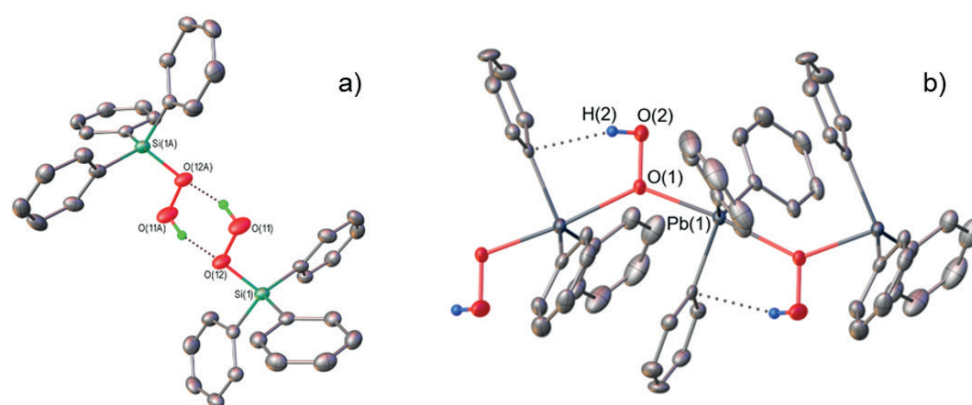


Figure 1. Hydroperoxo double hydrogen bond in the structure of Ph₃SiOOH (a).
Hydrogen bond in the crystal structure of Ph₃PbOOH (b).

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Bimetallic ionic pairs (^tBuPXCYP)Pd(μ -OC)M(CO)₂L in catalytic dehydrogenation

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Hydrogen is an environmentally friendly source of energy and reagent in the chemical and oil refining industries. In this context, promising hydrogen storage techniques are based on solid and liquid-phase chemical hydrogen storage materials, in particular, borohydrides, ammonia borane, hydrazine, hydrazine borane, formic acid etc. The use of these materials for hydrogen storage provides a high weight and volume density of hydrogen, safety and low costs, since it greatly facilitates transportation. Development of new catalytic dehydrogenation systems gives the ability to control the rate and amount of hydrogen released, as well as the selectivity of the resulting products.

Recently, we have shown that the bimetallic systems [LW(CO)₂(μ -CO)···Pd(PCP)], formed as a result of the reaction of two hydrides - basic [(PCP)Pd(H)] and acidic [LWH(CO)₃] (L = Cp, Tp)^{1,2}, are bifunctional catalysts for the dehydrogenation of amine-boranes.³ The presence of acidic and basic metal centers triggers the cooperative BH/NH bonds activation. Herein we have extended the application to the dehydrogenation of formic acid catalyzed by the bifunctional bimetallic complexes (Figure 1). The data acquired by volumetric and spectroscopic (IR, NMR) methods allowed us to identify the rate-determining step of the process, estimate the TOFs and propose the catalytic reaction mechanism.

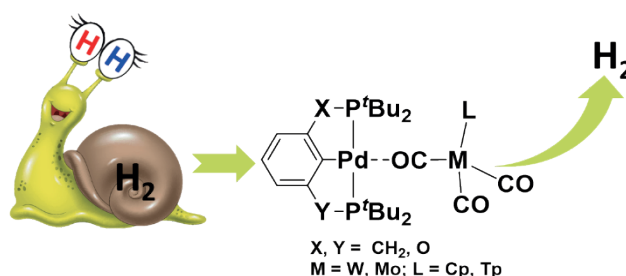


Figure 1.

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Stable radicals as tectones in design of magnetic materials

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Last few decades investigation of single molecular magnets (SMM) is one of the hot topics in field of stable organic radicals. In point of view of SMM design inter- and intramolecular channels of spin-spin interactions play a pivotal role influenced on bulky magnetic properties. Non-covalent interactions attract attention of researchers due to ability of control of crystal packing and, as a result, spin-spin interactions using tecton exchanging without necessity of chemical transformations. Among all non-covalent interactions halogen bonding is of the utmost interest due to predictable selective coordination between σ -hole of halogen and atoms with high electron density. As unpaired electrons in stable radicals could be halogen-bonding acceptors we focused on nitronyl-nitroxides as building blocks in design of self-assembled organic magnetic materials.

In our research meta- and para- isomers of pyridyl-containing nitronyl-nitroxides were crystalized with 1,4-diiodotetrafluorobenzene in different molar ratio (**Aggregates 1 – 5**, Figure 1 left). All **Aggregates 1 – 5** shown significantly vary crystal packing including ring-closed structures (Figure 1 right) with short contacts between iodine atoms and oxygen atoms in nitroxide moiety or nitrogen atoms of pyridine cycle.

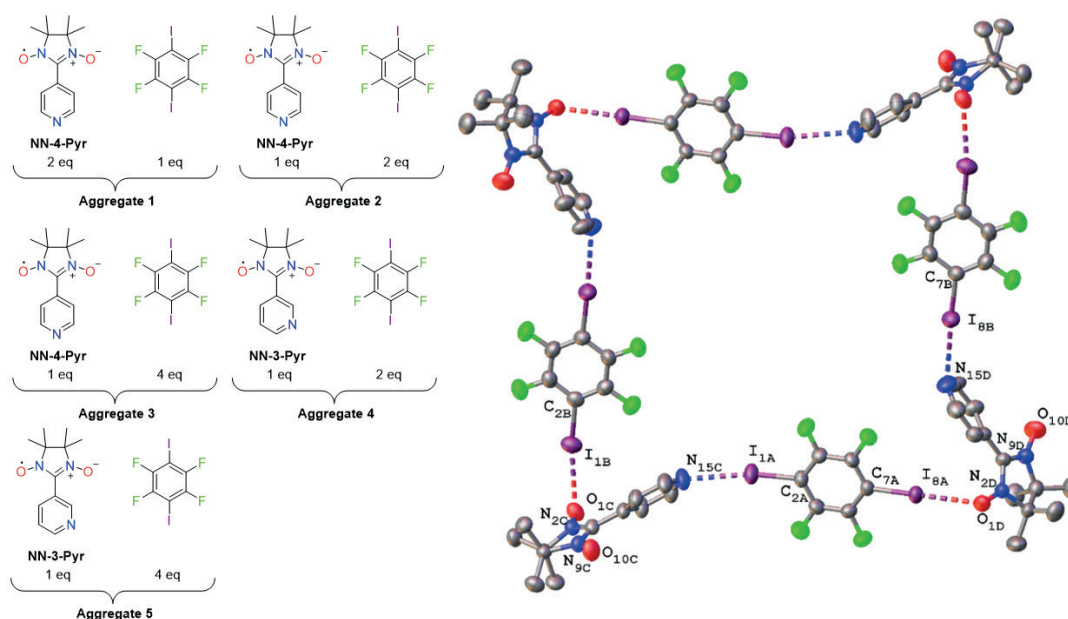


Figure 1. Investigated supramolecular **Aggregates 1 – 5** (left) and example of crystal packing of **Aggregate 4** (right).

Further experiments will connect with decreasing of interspin distance and measurements of magnetic properties of prepared materials.

Acknowledgements

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1,2,5-chalcogenadiazoles – donors of chalcogen bonding for molecular recognition and sensorics

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1,2,5-chalcogenadiazoles – a class of heterocyclic compounds with interesting set of inherent properties, most notably the π -acceptor properties due to the electron deficiency of the heterocyclic system. As π -acceptors these compounds are used for the preparation of radical-anion salts, charge transfer complexes and building blocks for polyconjugated organic semiconductor materials.¹

At the same time these compounds display σ -acceptor properties, forming supramolecular complexes with Lewis bases (LB), which are coordinated to the chalcogen atom via chalcogen bonding – a secondary bonding interaction between lone electron pair of LB and a region of depleted electron density with a local positive electrostatic potential – a σ -hole.² Figure 1 depicts a scheme of the complex formation, as well as an example of such a complex together with the molecular electrostatic potential map of the 1,2,5-selenadiazole derivative. Upon complexation a new long wave-length charge transfer band appears in the electronic absorption spectra. Complexes have a wide range of formation constants depending on the nature of the heterocycle and LB. This contribution discusses synthesis, structure, thermodynamic and optical properties of these complexes relevant for the possible applications of chalcogenadiazoles as receptors and sensors.

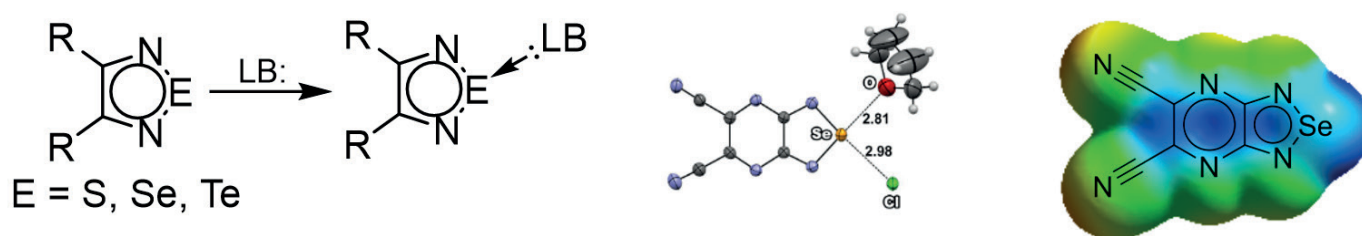


Figure 1. Left: Scheme of the supramolecular complex formation.

Center: XRD structure of the complex of 5,6-dicyano[1,2,5]selenadiazolo[3,4-*b*]pyrazine with chloride ion and thf. Right: a map of the molecular electrostatic potential on its isoelectronic surface ($r = 0.001$ a.u.).

Color code: blue – positive potential; green – 0; yellow, red – negative potential.

Acknowledgements

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Influence of noncovalent interactions on the structure and luminescent properties of Cd(II) and Ln(III) fluorobenzoate complexes

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The development of novel design methods of complexes for creating compounds with predefined properties set, that can serve as components for various materials is the object of many modern studies. Using of penta- and tetrafluorobenzoic acids along with various aromatic N-donor ligands make possible directly influence both molecular and crystal structures of metal complexes and their properties via control of non-covalent interactions [1-2].

In case of pentafluorobenzoic complexes Cd-Ln (Ln(III) = Eu, Tb, Gd, Dy) with 1,10-phenanthroline (phen), a considerable effect of the crystallization temperature on the composition and structure of the resulting products is observed. It was recorded for the first time, that crystallization from identical solutions at room temperature leads to formation of the coordination polymer $\{Cd_2Ln_2(phen)_2(C_6F_5COO)_{10}\}_n$ (1), while crystallization on heating (at constant 75°C) leads to the formation of the molecular complex $[Cd_2Tb_2(phen)_2(C_6F_5COO)_{10}]$ (2) [2].

The combination of pentafluorobenzoic anions with various aromatic monocarboxylic acid anions leads to the obtainment of a several heteroanionic carboxylate complexes of the following composition $[Ln_2(phen)_2(C_6H_5COO)_2(C_6F_5COO)_4]$ (3, Ln(III) = Eu, Tb, Er) and $[Cd_2Eu_2(phen)_2(C_6H_5COO)_2(C_6F_5COO)_4]$ (4). Herewith, the most important structure-forming factor in synthesized compounds 1-4 is molecules stabilization due to a number of non-covalent interactions between the substituting groups of pentafluorophenyl and phenyl (π - π , C-F- π , C-H-F, F- π , etc.).

It was found that for polymeric compound 1(Tb) and molecular 2 the values of luminescence quantum yields differ greatly (63% for 1(Tb), 33% for 2 and 45% for 3). Studies of heteroanionic complex 3 showed that the values of quantum yields and luminescence effectiveness with the introduction of second type of anion increase by 1,5-2 times compared with homoanionic analogues and reach 79% and 92%, respectively [3].

Acknowledgements

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Aggregation-induced emission of non-symmetric C^N*N^AC-cyclometallated platinum(II) complexes

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Square-planar platinum(II) complexes are known to be prone to axial π - π and d_{z^2} - d_{z^2} intermolecular interactions, which lead to the alteration of their photophysical properties, e.g. appearance of aggregation-induced emission (AIE) bands. We report a series of square-planar platinum(II) complexes **Pt1-Pt5** with non-symmetric tetradentate C^N*N^AC-cyclometallated ligands (Figure 1A).¹ The complexes exhibit efficient luminescence with a quantum yield of up to 47% and bands' maxima ranging from 560 to 690 nm in degassed solution. Complexes **Pt1**, **Pt2**, and **Pt4** show mechanochromism in the solid state. Upon rapid injection of their THF solution in water, these complexes form nanosized particles with red-shifted AIE, indicating a change in the excited state. TD DFT computational analysis allowed assigning the observed AIE to ³MMLCT excited states of Pt-Pt bonded aggregates of these complexes (Figure 1B). For complex **Pt2**, we stabilized these aggregates inside micellar nanocarrier providing a new approach for near-infrared biosensors (Figure 1C).²

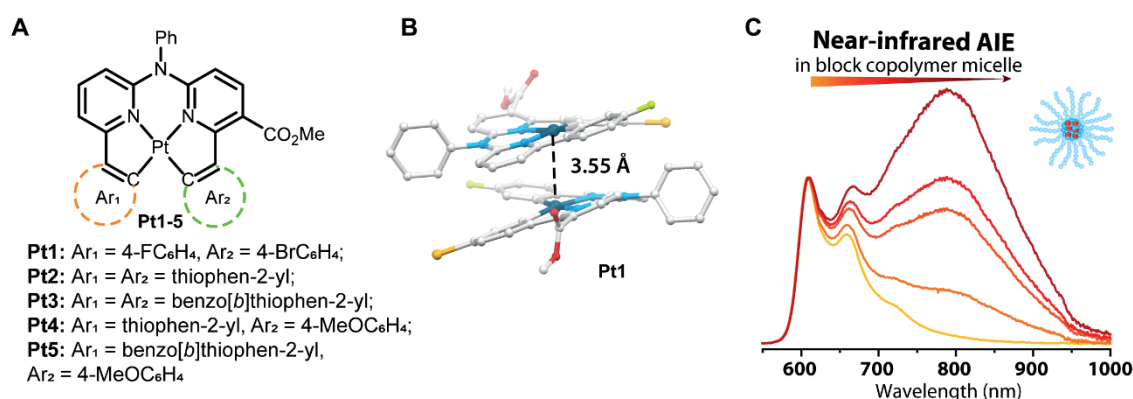


Figure 1. A. Simplified structure of **Pt1-Pt5** complexes; B. Optimized geometry of dimer of complex **Pt1** with short Pt-Pt contact; C. NIR-emission of copolymer micelles loaded with different wt. % of complex **Pt2**.

Acknowledgements

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Crystal Structure Control of Perylene Single Crystals by Additive-Assisted Crystallization

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Additive-assisted crystallization is a powerful tool for crystal engineering. The presence of even minute amounts of impurities may affect the kinetic and thermodynamic parameters of a crystallization process¹. Whereas kinetic factors are responsible for crystal nucleation, growth and dissolution the exact mechanism of the phenomenon on the molecular level is still not clear. There are also no systematic studies of the additives' effect on crystallization of small conjugated materials in organic optoelectronics.

In this work we studied additive-assisted crystallization of perylene (PRN). Anthracene, rubrene, pyrene and 9,10-diphenylanthracene (DPA) were used as additives. The addition of these materials (up to 20 %mol) leads to a control of the balance between α -PRN and β -PRN polymorphs. Increasing the concentration of DPA-additive leads to a β -form nucleation. The mechanism of DPA-additive action was suggested based on the crystal structure of PRN-DPA co-crystal. The addition of DPA results in stabilization of herringbone (HB) packing of β -perylene via C-H $\cdots\pi$ interactions between DPA and perylene molecular layers (Fig. 1).

The PRN-DPA co-crystal demonstrated photoluminescence with PL QY of 29% and semiconducting properties with hole mobility of 10^{-2} cm²V⁻¹s⁻¹.

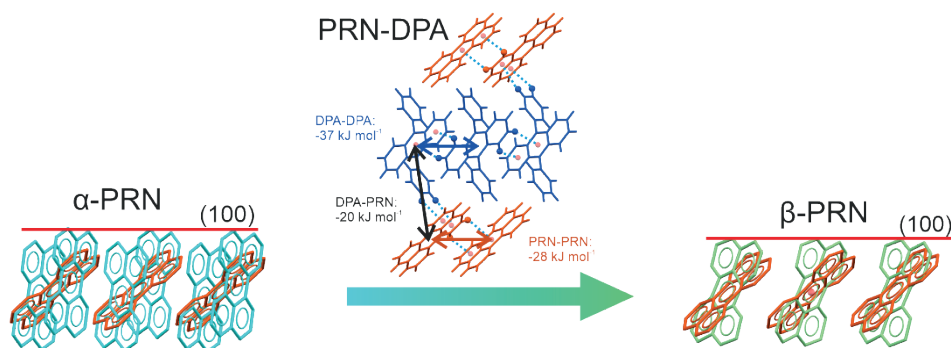


Figure 1. Crystal structure fragments of α -PRN (cyan, sandwich HB packing) and β -PRN (green, HB packing) in comparison of perylene arrangement in PRN-DPA co-crystal. The structure of co-crystal with interaction energies is illustrated above the arrow.

Acknowledgements

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Theoretical insights on non-covalent interactions in functional materials

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Non-covalent interactions (NCI) are playing a major role in the creation of functional materials in various fields ranging from hybrid organic-inorganic systems to polymer composites. In particular, halogen and pnictogen bonds are crucial for the crystallization and self-assembly of various materials. In this talk, the role of non-covalent interactions in the formation of the hybrid 2D lead halide perovskites and their interfaces with 3D counterparts is analyzed using theoretical modeling. The topological descriptors of the electron density are employed for the visualization and quantification of the NCI in these compounds. The relationships between the NCI descriptors, the crystal structure and the interaction energies within these compounds are investigated. This analysis provides useful insights on the mechanisms and trends in the formation of the hybrid 2D perovskites and their interfaces, needed for the design of novel perovskite-based materials for optoelectronics and photovoltaics.

Acknowledgements

The research is carried out using the equipment of the shared research facilities of HPC computing resources at Lomonosov Moscow State University. The Siberian Branch of the Russian Academy of Sciences (SB RAS) Siberian Supercomputer Center is gratefully acknowledged for providing supercomputer facilities.

Non-covalent interactions in the active center of the antioxidant enzyme glutathione peroxidase

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This work is devoted to a quantum-chemical investigation of the mechanism of catalytic reduction of peroxides involving glutathione peroxidase. This enzyme protects biomolecules from oxidative damage and prevents the development of cardiovascular and neurodegenerative diseases. The relevance of this research is determined by challenges of modern biochemistry, in particular by the need of new targeted low molecular weight antioxidant drugs.

At the first stage of the work an investigation of $\text{CH}_3\text{Se}(-)\cdots(\text{H}_2\text{O})_n$ clusters, (which represent a simplified model of the antioxidant enzyme glutathione peroxidase active center in a physiological environment), and their hydrogen bonding was carried out.^{1,2} It is shown that in spite of the relative weakness of hydrogen bonds $\text{OH}\cdots\text{Se}(-)$ (<6 kcal/mol), the external electron shell of selenium atom experiences critical changes during formation of each hydrogen bond. In this case, the hydrogen bonds $\text{OH}\cdots\text{Se}(-)$ are anticooperative, i.e. the addition of each water molecule reduces the strength of the already formed hydrogen bonds.

Further, a quantum mechanical investigation of the structure of the real active center of glutathione peroxidase (for three forms of selenocysteine fragment $-\text{SeH}$, $-\text{SeOH}$ and $-\text{Se}(\text{O})\text{OH}$, which correspond to the products and reactants of the first two reactions along the catalytic cycle) was carried out.³ Non-covalent interactions formed by the selenocysteine fragment and water/peroxide molecules among themselves and with other amino acid residues were studied in detail, their role in peroxide reduction reactions is discussed. The presence of σ -hole interactions (chalcogenic, tetrel and pnictogenic bonds) in the active center of glutathione peroxidase has been shown for the first time.

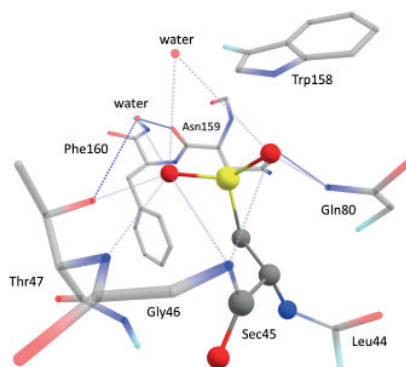


Figure 1. The active center of the enzyme glutathione peroxidase.

Acknowledgements

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Calculations of the energy of non-covalent interactions in organic crystals. Comparison of periodic and non-periodic models

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The identification and quantitative description of intermolecular interactions in crystals is a non-trivial task, both experimentally and theoretically. An exception are molecular crystals in which the sublimation enthalpy/lattice energy is determined by one type of intermolecular (noncovalent) interactions, such as H₂O, CF₄ etc. In most cases, empirical approaches are used that relate the energy of the intermolecular interaction with one or another parameter of the electron density at the bond critical point.¹ These approaches are often used to evaluate intermolecular interactions of different natures in various crystals, which gives rise to well-founded criticism.² Possible reasons for this criticism include the following. 1) The identification of a non-covalent interaction is based solely on the presence of the bond critical point. 2) The limits of applicability of these approaches are not clear. 3) The dependence of the theoretical values of the electron density parameters at the bond critical point on the approximations used in the calculations by the DFT method has not been studied. These issues have recently been resolved.³ When comparing the periodic and non-periodic approaches to the calculation of non-covalent interactions in molecular crystals, another problem arises. In calculations of non-periodic systems, hybrid functionals (B3LYP, M06-2X, etc.) and Gaussian basis sets are usually used. In solid-state physics, the PBE (PBE-D3) functional with plane wave basis sets is most often used.⁴ A systematic comparison of the properties of molecular crystals calculated using the above approaches has not been carried out. This is due to a number of difficulties, which are discussed in detail in the presentation.

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Voronoi molecular surface for analysis of noncovalent interactions

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The identification of differences and similarities in noncovalent interactions of molecules in closely related solids (polymorphs, solvates, homologues, isostructural series, and others) allows revealing the role of molecular functional groups and crystal field effect for crystal engineering. The molecular Voronoi surfaces give qualitative, quantitative and visual representation of all types of intra- and intermolecular noncovalent interactions in crystals of inorganic, organic and macromolecular compounds (Fig. 1) from unified positions.

Using this approach we analyzed conformation polymorphs of photochromic N-salicylideneanilines, and (2',4'-dinitrobenzyl)pyridine derivatives. Interplay of hydrogen and halogen bonds was studied for polymorphs of alkylboron-capped iron(II) and cobalt(II) hexachloroclatrochelates, and for a series of polybromide salts. The effect of crystalline environment on molecular conformations of a flexible imatinib molecule, tryptophanate-anion and on a photoinitiated solid-state reaction of eicosaborate isomerization were studied. Noncovalent interactions of imatinib, abirateron and bicalutamide in their polymorphs, solvates, salts and ligand-receptor complexes were compared. The molecular Voronoi surfaces were proved to be suitable for understanding of the interplay between intermolecular strong and weak interactions, effect of a particular contact on molecular geometry and material properties, and were found to be applicable to a large number of objects.

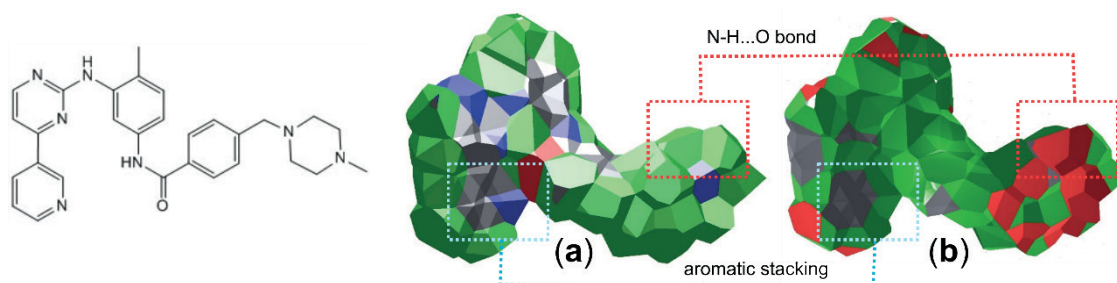


Figure 1. Molecular Voronoi polyhedron of imatinib in complex with the quinone oxidoreductase NQO2 (PDB code 3FW1) colored in accord with the nature of (a) inner, imatinib and (b) outer, receptor atoms.

Color code: C-gray, H-green, N-blue, O-red. The aromatic stacking in the region of pyrid-3-yl and the O...H interactions in the region of piperidine rings are additionally marked.

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Application of lattice sums of non-covalent interaction energies in pharmaceutical crystal engineering

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Crystal engineering is one of the most widely used routes for obtaining solid forms of active pharmaceutical ingredients with altered physicochemical properties¹ such as solubility, tableability or photostability. The need of reliable building blocks for structure design led to a rise of the heterosynthion approach, in which the cocrystallization was reduced to formation of one or few stronger hydrogen bonds.² However, a number of later publications have shown that side interactions also play a critical role in the crystal packing and formation of multicomponent crystals.³ The quantification of various contributions from different packing motifs and interaction types allows one to range the synthons from the strongest to the weakest to facilitate the virtual screening for new crystal forms. Such quantitative analysis can be performed by theoretical methods that consider the lattice energy E_{latt} as a sum of pair interaction energies, in contrast to more widely used DFT-D based schemes.

The present work illustrates the use of lattice sum approaches in non-covalent interaction analysis and lattice energy calculations for crystalline forms of drugs and related compounds studied in our lab for the last few years. For a family of 23 structurally relative adamantane-substituted sulfonamides, a good agreement was observed between the experimental sublimation enthalpies and the lattice summation of interaction energies derived from QTAIM-based descriptors.⁴ The impact of the level of theory on computed E_{latt} values was studied in the polymorphic system of nilutamide, where Gavezzotti's PIXEL approach was found to outperform some of more sophisticated periodic DFT-D methods.⁵ The interplay between the conformation, packing type and relative stability of crystal phases has been observed for the multicomponent crystals of antifungal isavuconazole, antibacterial nitrofurantoin, antiandrogenic compound apalutamide, tricyclic antidepressant amitriptyline etc.⁶ Computed values were found to correlate well with observed trends in thermophysical properties. The division of molecules into individual fragments combined with packing similarity analysis were used to provide insight on the contribution of different functional groups into the crystal structure stabilization. For fluoroquinolone antibacterials, an important role of side alkyl fragments on the columnar packing of molecules was established.

Acknowledgements

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The case of cocrystals of group 10 metal dithiocarbamates with electrondeficient arenes: the first example of Ni(II) reverse sandwich structure

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Cocrystallization of the dithiocarbamate complexes $[M(S_2CNEt_2)_2]$ ($M = Ni$ **1**, Pd **2**, Pt **3**) and X-substituted perfluoroarenes ($X = I, Br$; 1,2-dibromoperfluoro-benzene FBB and 1,2-diiodoperfluorobenzene FIB) gives isomorphous cocrystals of $(1-3) \cdot 2(FBB)$ and $1 \cdot 2(FIB)$, correspondingly, whose structures were studied by single-crystal X-ray diffractometry. The crystal structures demonstrate similar intermolecular contact types: short arene $MS_4 \cdots \pi$ -hole stacking contacts, $X \cdots S$ halogen bonds, $C-H \cdots X$ ($X = Br, I$) bonds and $C-H \cdots F$ hydrogen bonds. In these structures, the $\{dz^2-ML_n\}$ moiety functions as an integrated five-center acceptor (that includes a metal dz^2 -orbital, **even** for a poorly dz^2 -nucleophilic Ni^{II} center) toward the π -hole of an X-substituted perfluoroarene. This interaction provides stacking of inorganic and organic units furnishing the reverse sandwich structures. Density functional theory (DFT) calculations, in combination with quantum theory of atoms-in-molecules (QTAIM) and noncovalent interaction plot (NCIplot) analyses, supported the structure-defining role of the $\{MS_4\} \cdots \pi$ -hole contacts. The nucleophilicity of the $\{MS_4\}$ cores toward electron deficient π -holes was verified from the molecular electrostatic potential surface (MEP) and electron density/electrostatic potential (ED/ESP) profiles, and atoms-in-molecules (AIM) charge analysis.

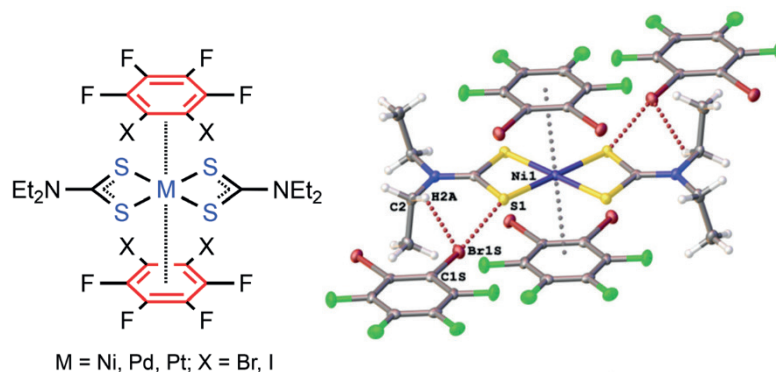


Figure 1. $\{dz^2-ML_n\} \cdots$ arene contacts of $(1-3) \cdot 2(FBB)$ and $1 \cdot 2(FIB)$ (left) and a view of the molecular structure of $1 \cdot 2(FBB)$ Short contacts are given by dotted lines and thermal ellipsoids are shown with a 50% probability.

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One-Step Self-assembly of Graphene Oxide and Organic Chromophores into Multicomponent ultrathin films for Organic Electronics

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One-step fabrication of multicomponent hybrid films arranged at nanoscale is among major challenges for organic electronics. Interfacial self-assembly of ultrathin hybrids makes it possible to combine organic and inorganic components with different solubilities as well as to control molecular packing in the ordered films.

We developed a new supramolecular strategy for interfacial self-assembly of graphene oxide (GO), glutamine-substituted perylene diimide (PDI-glu), 10,12-pentacosadiynoic acid (PCDA) and zinc acetate through hydrogen and coordination bonding into three- and four-component hybrid nanofilms. We showed that the hybrids assembled through H-bonds can maintain the light-induced Förster energy transfer from the PDI-glu to polymerized PCDA (PDA) and then to GO leading to the fluorescence quenching. In the hybrids assembled through coordination bonding with zinc ions, the energy transfer proceeds only from PDI-glu to the PDA. An important characteristic of these ultrathin hybrids is their stability with respect to photobleaching of chromophores due to the acceptor properties of GO. The zinc-containing hybrids integrated with a hole transport layer exhibited photodiodes properties. The device based on four-component hybrid comprising both PDI-glu and PDA showed photocurrent/dark current ratio almost an order higher that of the three-component hybrid assembled with a single light absorber PDA.

We believe that our results can be adapted for a wide variety of organic chromophores and polymerizable surfactants to develop high-efficient functional GO-based nanohybrids for organic electronics.

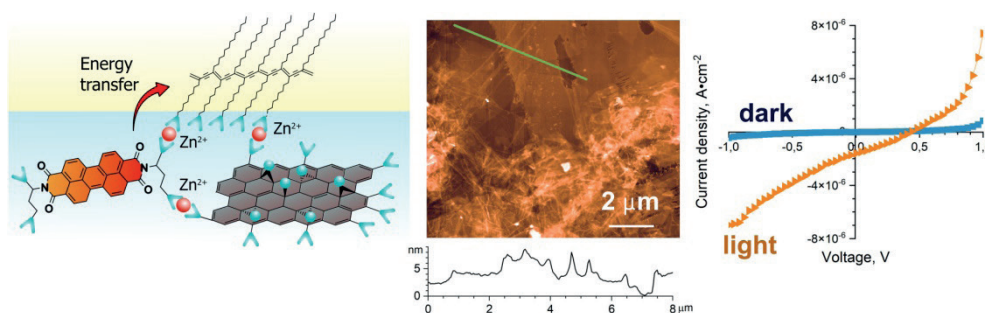


Figure 1. Schematically illustrated process of self-assembly of ultrathin hybrid film at air-water interface, AFM image of hybrid transferred onto solids and current-voltage curves of photovoltaic device based on the hybrid measured in dark and under visible light irradiation.

Acknowledgements

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The distance between minima of electron density and electrostatic potential as a measure of halogen bond strength

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Halogen bond (XB) belongs to the class of so-called σ -hole interactions. In Bader's Quantum Theory of Atoms in Molecules approach¹ the topological analysis of XB's electron density (ED) yields bond path which follows the maximal gradient of ED between two interacting atoms through the (3; -1) critical point. Along the bond path both ED and molecular electrostatic potential (ESP) go through minima. It was shown that the ED minimum is located closer to the electrophile atom, while ESP minimum – to the electron-rich nucleophile atom.^{2,3}

In this work we investigated how the distance between ED and ESP minima (Δd) changes upon strengthening of a XB (Figure 1). Considering an extensive set of complexes formed by various fluorine-, chlorine-, bromine- and iodine-containing compounds with trimethylphosphine oxide enabled us to determine a correlation of the Δd on local electron kinetic energy density at the bond critical point, which tends to a common limiting value for the strongest halogen bond⁴.

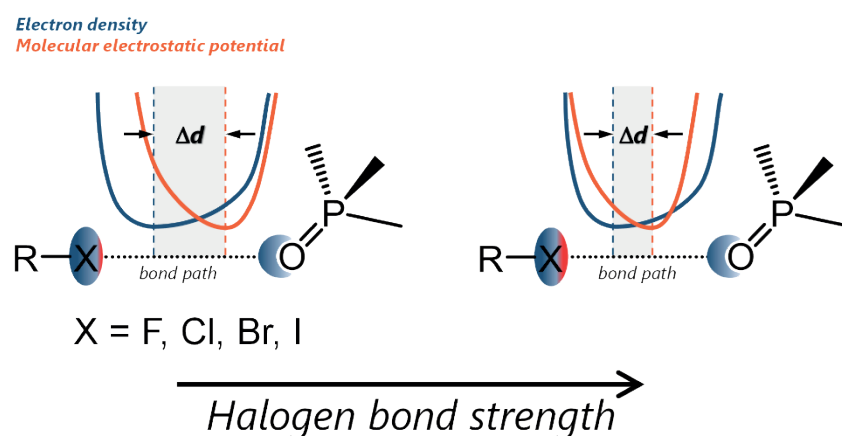


Figure 1. Schematic representation of the distance between minima positions of the electron density and molecular electrostatic potential distributions along the X...O halogen bond.

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Crystallization cocktails for X-ray diffraction analysis of liquids

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X-ray diffraction is an indispensable tool for characterizing new chemical compounds. Unfortunately, its main requirement – a good single crystal – is not always easy to meet, especially for substances that are liquid at room temperature. Those can be grown directly on an X-ray diffractometer [1]; however, it is a rather tedious and often serendipitous task to identify the proper crystallization conditions. An alternative approach relies on the use of ‘chaperones’ able to produce co-crystals with liquid substances. Among them, organic guanidinium sulfonates are the most promising [2], as their flexible network of hydrogen bonds can adapt to various organic compounds. However, they need to be first synthesized from commercial salts and then dissolved in a solution of a compound of interest to produce a co-crystal.

To take this approach to another level, we propose ‘crystallization cocktails’ made from ‘on-the-shelf’ amines and sulfonic acids that allow obtaining – by a simple mixing in a suitable solvent (Figure 1) – high-quality co-crystals of liquid substances for single-crystal X-ray diffraction. Those have been successfully tested on a series of liquid phenols that were yet to be structurally characterized.

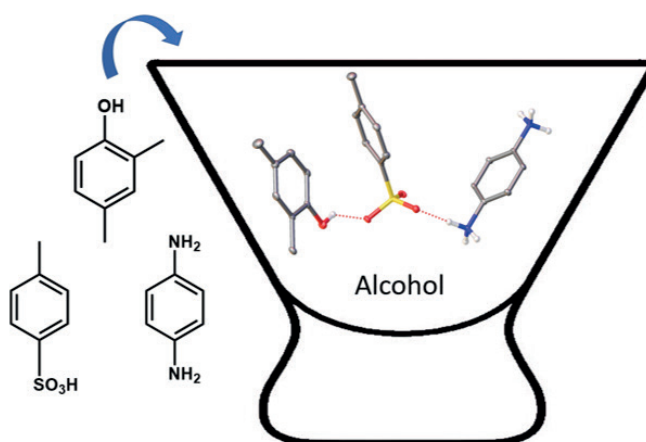


Figure 1. A concept of ‘crystallization cocktails’.

Such ‘cocktails’ can be potentially tailored to any molecular compound by a proper choice of the ingredients, thereby paving the way towards structure determination of poorly crystallizing substances, including those that are liquids at room temperature or generated *in situ*.

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Metal-involving Noncovalent Interactions in Dithiocarbamate and Dithiocarbonate Pt(II) and Pd(II) Complexes

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In the past five years, the demand for square-planar d^8 -metal complexes as sterically accessible sites involved in diverse noncovalent interactions has increased dramatically. Despite their positive charges, these centers can function as d_{z^2} -orbital centered nucleophiles (hereinafter d_{z^2} -nucleophiles) toward various σ - and π -hole donors. According to our previous experience¹ a substantial increase of d_{z^2} -nucleophilicity can be achieved by employing strong electron-donating dithiocarbamate ligands. This study stimulated our further interest in relevant systems and for the continuation of our project we addressed the metal(II) dithiocarbamates $[M(S_2CNET_2)_2]$ ($M = Pd, Pt$) and dithiocarbonates $[Pt(S_2COR)_2]$ ($R = Et, iPr$) and studied their co-crystallization with X-substituted perfluoroarenes $\{Ar^FX; X = I, Br; 1,2\text{-dibromoperfluorobenzene (1,2FBB)}, 1,4\text{-dibromoperfluorobenzene (1,4FBB)}, 1,4\text{-diiodotetrafluorobenzene (1,4FIB)}, \text{ and } 1,3,5\text{-triiodotrifluorobenzene (1,3,5FIB)}\}$.

Co-crystallization of the complexes and Ar^FX gives crystalline adducts, whose structures were studied by single-crystal X-ray diffractometry (XRD). Upon analysis of noncovalent interactions in the XRD structures of the obtained co-crystals, we identified various intermolecular contact types: short arene $MS_4 \cdots \pi$ -hole stacking contacts, $X \cdots S$ and $I \cdots M$ halogen bonds, $C-H \cdots X$ ($X = Br, I$) bonds and $C-H \cdots F$ hydrogen bonds. In the case of the adducts $[M(S_2CNET_2)_2] \cdot 2(1,2FBB)$ and $[Pt(S_2CO^iPr)_2] \cdot 1,4FIB$ we found that the $\{d_{z^2}-M^II S_4\}$ moiety could function as an efficient integrated five-center nucleophile (that includes a metal d_{z^2} -orbital) toward the π -holes of electron-deficient arenes to form reverse sandwich structures exhibiting $d_{z^2}-M \cdots \pi$ -hole contacts.² DFT calculations in combination with QTAIM, NCIPLOT analyses, ED/ESP profiles and AIM charge calculations supported the structure-defining role of $\{MS_4\} \cdots \pi$ -hole contacts in the co-crystals.

Acknowledgements

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Preparation of PET@UiO-66 Functional Materials for Selective Binding of Chlorobenzenes Via Halogen Bonding: From Design to Application

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Here, we propose the development of a functional hybrid material prepared from waste polyethylene terephthalate (PET) with a nanolayered metal-organic framework (UiO-66) on PET (Figure 1). This material selectively binds and removes hazardous chlorine-containing aromatic impurities (CBs) through the formation of halogen bonds (HaB). CBs are dangerous substances of high risk to human and environmental health¹.

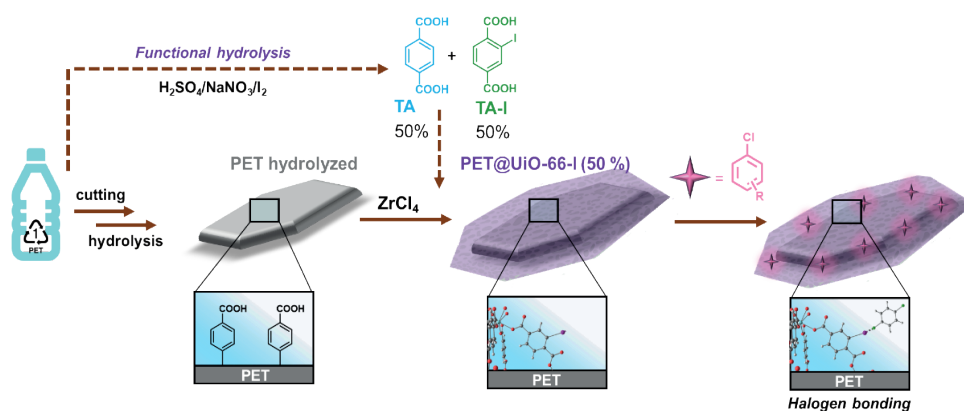


Figure 1. Artwork picturing the binding of 1,4-dichlorobenzene (DCB, a prototypal CBs) by UiO-66-I via the HaB based I...Cl supramolecular synthon

The introduction of HaB recognition unit into the structure UiO-66 enables to construction functional material for selective separation and removal of CBs. We found that 50% presence of 2-iodoterephthalic acid (I-TA) in the UiO-66-I is a perfect balance of porosity and the number of HaB donor sites giving UiO-66-I (50%). This I-TA content provides unprecedented selectivity in CBs adsorption over non-chlorinated aromatic analogs. The formation of halogen bonding between UiO-66-I (50%) and CBs was firstly theoretically shown by DFT calculations and later experimentally verified by UV-Vis, Raman and X-ray spectroscopy. The prepared PET@UiO-66-I (50%) showed high adsorption capacity for CBs related to the number of available HaB sites due to the chemical nature of adsorption. The high adsorption capacity was accompanied by unprecedented selectivity in the separation of CBs from non-chlorinated aromatic compounds due to the formation of I...Cl HaB between I in the structure of UiO-66 and CBs.

Acknowledgements

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Tricarbonyl manganese(I) hydrides as donors of proton or hydride ion

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In modern homogeneous catalysis complexes of noble metals are most often used, but nowadays there is an active search for alternative systems based on 3d metals¹. It has recently been shown that manganese(I) complexes are not inferior in efficiency to many catalysts for (de)hydrogenation reactions^{2,3}. The key stages of the catalytic (de)hydrogenation reaction are the processes of proton and hydride ion transfer with the formation of non-covalent bonded adducts and metal hydrides as intermediates.

In this report we present the results of the study of the hydride and proton donor ability of manganese(I) tricarbonyl complexes $L_2Mn(CO)_3H$ with phosphite, phosphine and NHC ligands (NHC = N-heterocyclic carbene) (Figure 1). The interaction of manganese hydrides with Lewis acids and bases of various strengths and nature was studied using IR (ν_{CO}) and NMR (1H , ^{13}C , $^{31}P\{^1H\}$) spectroscopy in a wide temperature range (160 - 298 K). We have established the possibility of the Mn-H bond repolarization caused by intermolecular interactions. The thermodynamic and kinetic parameters of proton and hydride ion transfer processes are obtained. For hydride complexes with bidentate ligands, using *fac*(dppm) $Mn(CO)_3H$ as an example, it was shown that the mechanism of hydride ion transfer includes the formation of meridional isomers with higher hydricity of hydrogen atom⁴.

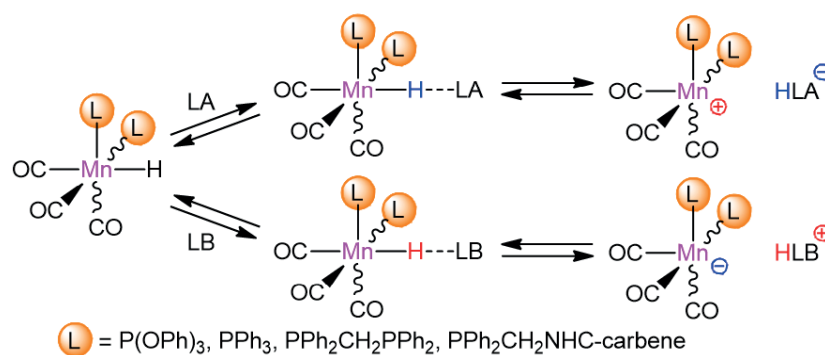


Figure 1.

Acknowledgements

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Estimation of the strength and geometry of hydrogen bonds in complexes with phosphine oxides by IR and NMR spectroscopy

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In this work we evaluate the possibility of using IR and NMR spectral characteristics of the P=O group to estimate the strength and geometry of hydrogen bonds in complexes. We present the result of study the set of hydrogen-bonded 1:1 complexes formed by triphenylphosphine oxide and substituted phenols. We discuss changes of ³¹P NMR chemical shift and the position of stretching vibration band of P=O group in IR spectra upon complexation. Figure 1 shows the general structure of the studied complexes.

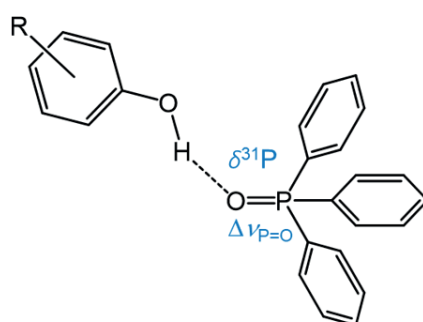


Figure 1. General structure of 1:1 complexes formed by triphenylphosphine oxide and phenols, as well as spectroscopic parameters considered in this work.

As the result we propose the set of simple correlations for estimating the geometry and strength of hydrogen bonds, which are often used for describing of hydrogen bond properties^{1,2}. Moreover, we consider complexes with multiple hydrogen bonds between phosphine oxide and phenols. Figure 2 shows the structure of 1:2 complex with two phenol molecules as an example.

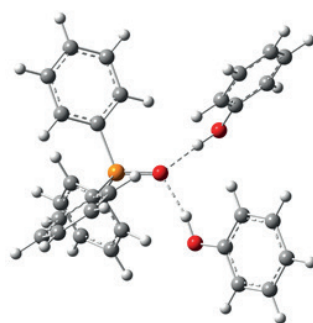


Figure 2. The structure of 1:2 complexes formed by triphenylphosphine oxide and phenols.

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Electrophoretic NMR is a tool for studying ionic compounds

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Electrophoretic NMR is a technique that allows the identification of ionic compounds and also determine some parameters such as electrophoretic mobility, transference numbers, charge, etc.¹ There are a number of examples of the application of the method to the study of various objects: supramolecular compounds, polymers, ionic liquids.

The possibility of using electrophoretic NMR to study chemical reactions involving charged molecules was shown. We studied the evolution of Pd/NHC complex in Mizoroki-Heck reaction. NHC ligand can enter various coupling reactions.² The formation of an azolium salt indicates bond disruption and is a sign of the formation of a nanoscale catalytic system. The specific shape of some signals in the ¹H eNMR spectrum indicates that they are related to an ionic compound.³

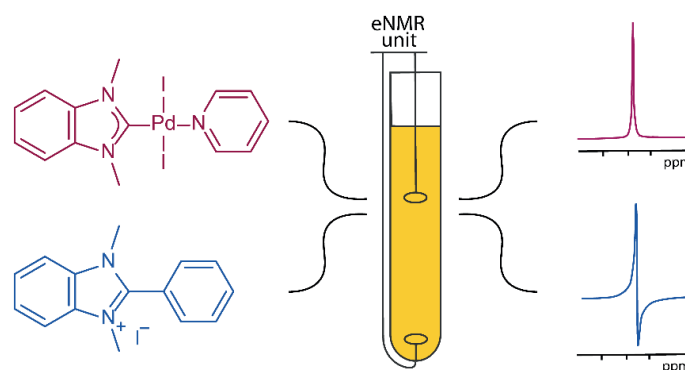


Figure 1. Phase modulation in the ¹H eNMR spectrum indicates a charged compound

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Hydrazinosolvates: unusual isomorphism and isomorphous substitution

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An unusual isomorphism of 18-crown-6 hydrazine disolvate $C_{12}H_{24}O_6 \cdot 2N_2H_4$ (**1**) and 18-crown-6 tetrahydrate (**2**) is observed. The isomorphous substitution of hydrazine by water molecules is found for the first time in the structures of tetrabutylammonium acetate hydrazine solvates hydrous $Bu_4N^+AcO^- \cdot 0.9(N_2H_4) \cdot 0.1(H_2O)$ (**3**) and anhydrous $Bu_4N^+AcO^- \cdot N_2H_4$ (**4**). [1] Surprisingly, the nature of these isomorphous relationships is completely different from the well-known isostructurality of organic hydrogen peroxide/water solvates. The asymmetric unit in the structure of **1** contains one crown ether cofomer and two solvent hydrazine molecules (Fig. 1) Both hydrazine molecules form four hydrogen bonds: four donors for N(1)N(2) and three donors and one acceptor for N(3)N(4). It should be noted that the maximal possible number of hydrogen bonds (four donors and two acceptors) were observed for N_2H_4 in the structures of the methanol and ethanol adducts $4MeOH \cdot N_2H_4$ and $2EtOH \cdot N_2H_4$. [2,3]

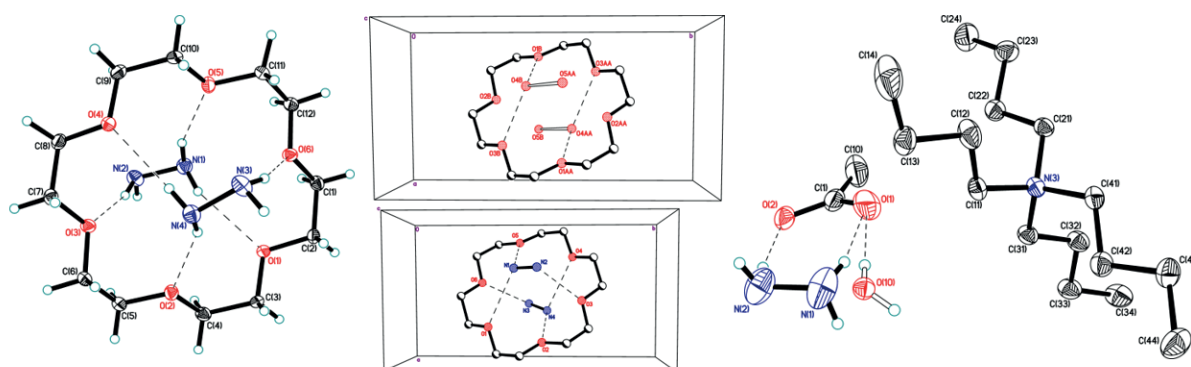


Figure 1. The asymmetric unit in the structure of **1** (left) and mutual arrangement of molecules in the structures of **1** (below) and **2** (above) (atomic coordinates taken from REGRAW01 [4]). View along the *c*-axis. Water···water hydrogen bonds are shown by open lines; others are denoted by dashed lines (middle). The asymmetric unit in the structure of **3** (right). The admixed water molecule is depicted with open lines. Displacement ellipsoids are shown at the 50% probability level. Hydrogen bonds are drawn with dashed lines.

Acknowledgements

The authors thank the Russian Foundation for Basic Research for financial support (*grant № 20-03-00449*).

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Plasmon resonance-enhanced absorption of visible light in ultrathin films of organic dyes and gold nanoparticles

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Plasmon resonance enhanced absorption (PREA) occurs due to the ability of gold nanoparticles (AuNP) to generate a strong electromagnetic field near the surface under light radiation because of the excitation of surface plasmon. Therefore, optical properties of organic molecules trapped within this field can be boosted. However, the enhancement can be only observed in ultrathin films due to a fast decay of the plasmon in a condensed phase.

Herein, we report a novel strategy for direct observations of the enhancement of visible light absorption in ultrathin hybrid films based on perylene and diacetylene derivatives by using the 2D gold plasmonic antennas with tunable optical properties. Two types of organic layers were used. First system represents a layer of nanowires assembled from disubstituted pentacosadiynoic perylene diimide. Perylene and diacetylene parts are covalently bonded in it. Second one contains glutamic diimide perylene and 10,12-pentacosadiynoic acid which are combined into an ultrathin film due to the adsorption on graphene oxide (GO) sheets. Diacetylene was polymerized to PDA under UV irradiation in both systems. Colloid-induced condensation of the cation-anion surfactant mixture onto the surface of gold hydrosol was used to assemble plasmonic antennas with spectral characteristics tuned in a range of 520-660 nm. This method permits to realize the general principle of resonance effects: overlapping of absorption maxima of the nanoparticle ensemble and the organic film. Hybrid systems were obtained by transferring plasmonic antennas with appropriate spectrum onto a support coated with organic films. Comparison of experimental absorption spectrum with the model one showed that PREA-effect was realized only in the GO/perylen/PDA system at the absorption band of the perylene. Systems containing both types of organic films and plasmonic antennas with optical properties matched to PDA absorption exhibited additive optical behavior. We believe that the geometry of contact between the gold nanoparticles and the chromophore film controls the propagation of the plasmon field into the organic phase and, thereby, the occurrence of PREA-effect at the organic-coated interface. When AuNPs lay on top of nanowires and PDA crystallites the plasmon field doesn't trap into the organic layers. In GO/perylen/PDA system contact area between AuNPs and loose GO sheets with adsorbed perylene molecules is increased. Hence, the plasmon field spreads within the layer and the plasmon enhanced absorption occurs.

We believe that our strategy can be successfully used to design novel function ultrathin materials for various technically relevant applications in organic optoelectronics and photocatalysis.

Acknowledgements

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Self-Assembly of Hybrid Photocatalysts Based on Porphyrin SURMOFs and Graphene Oxide

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In this work, we report a new method for the self-assembly synthesis of hybrid photocatalysts comprising graphene oxide (GO) and porphyrin-based surface-attached metal organic frameworks (SURMOFs). To obtain the SURMOF/GO hybrids in a powdered form, we developed a one-pot synthesis of these materials in the GO-stabilized oil-in-water Pickering emulsions.

The results of experimental studies involving X-ray diffraction, UV-vis spectroscopy, BET nitrogen absorption, gas chromatography-mass-spectrometry and MALDI-TOF spectroscopy. The catalytic activity of these mesoporous SURMOF/GO hybrids was investigated in photocatalytic degradation reactions of model organic compounds such as rhodamine 6G (Rh6G) and 1,5-dihydroxynaphtalene (DHN) with different molecule sizes, 1.12 nm and 0.34 nm, respectively. In the presence of oxygen, the substrates are oxidized due to photoinduced generation of singlet oxygen at porphyrin centers. Under anaerobic conditions, the photocatalysts can promote reduction by a direct electron transfer to the substrate in the pores of SURMOF. The size of micropores determines the efficiency of the anaerobic process. SURMOF/GO with a pore size of 1.6 nm can transform both substrates (Fig. 1), while the material with a pore size of 1.1 nm is active only with DHN molecules. The results provide a rational basis for substrate-selective hybrid photocatalysts integrated with tunable porosity of SURMOF components.¹

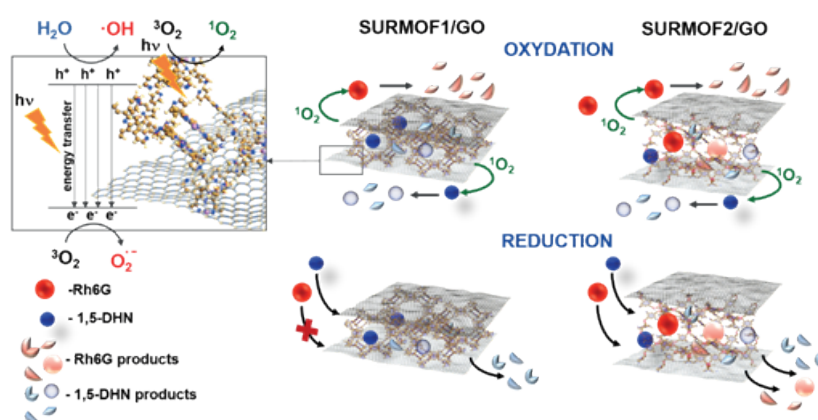


Figure 1. Schematic illustration of the proposed size-selective mechanism of photodestruction of Rh6G and DHN in the presence of the SURMOF1/GO and SURMOF2/GO under aerobic and anaerobic conditions.

Acknowledgements

This work was supported by the Russian Science Foundation (project No 20-13-00279).

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Hydrosilylation reaction catalyzed by platinum on carbon support: heterogeneous or dynamic?

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In the field of transition metal catalysis, the idea of “cocktail” or dynamic catalytic systems is developing into a mechanistic concept.¹ This involves equilibrating metal complexes, and metal nanoparticles, and clusters formed during a reaction. In order to characterize and identify species involved in dynamic catalytic systems, different analytical methods can be used.²

There are many applications of the hydrosilylation reaction in research and industry. Therefore, it is of great importance to reveal the nature of the catalytic system. The dynamic nature of alkene and alkyne hydrosilylation reaction catalyzed by Pt/MWCNT (multi-walled carbon nanotubes) was discussed.³

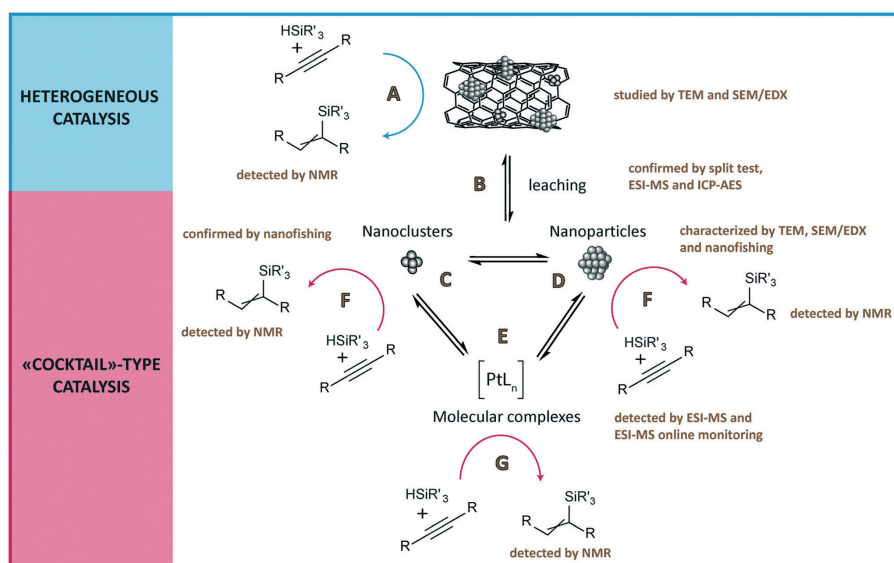


Figure 1. The investigation of platinum catalysed hydrosilylation reaction and methods involved³

First, using a combination of methods, it was shown that platinum nanoparticles, and molecular complexes are washed out into the solution, possibly, giving rise to another catalytic cycles in the solution. Second, an analysis of the selectivity of the reaction on a number of substrates also showed the formation of an α -isomer resulting from the catalytic activity of platinum clusters formed. Thus, the dynamic type of catalysis of hydrosilylation reaction catalyzed by platinum on carbon support is an important point to address in details.

Acknowledgements

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Study of the effect of the electron-withdrawing substituents on the catalytic capabilities of Pd/NHC complexes

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The use of Pd/NHC complexes has become an attractive practice in catalytic reactions due to their wide catalytic capabilities in synthesis methodologies, which stimulates the development of modifications of Pd/NHC complexes. However, a small number of Pd/NHC complexes with acceptor substituents have been presented so far. The introduction of F into the Pd/NHC has only a slight effect on the complex properties.¹ In this work, a number of new Pd/NHC complexes with F, Cl, Br, and CF₃ substituents were obtained. Catalytic activity in Heck and Buchwald-Hartwig reactions was studied for the synthesized complexes.

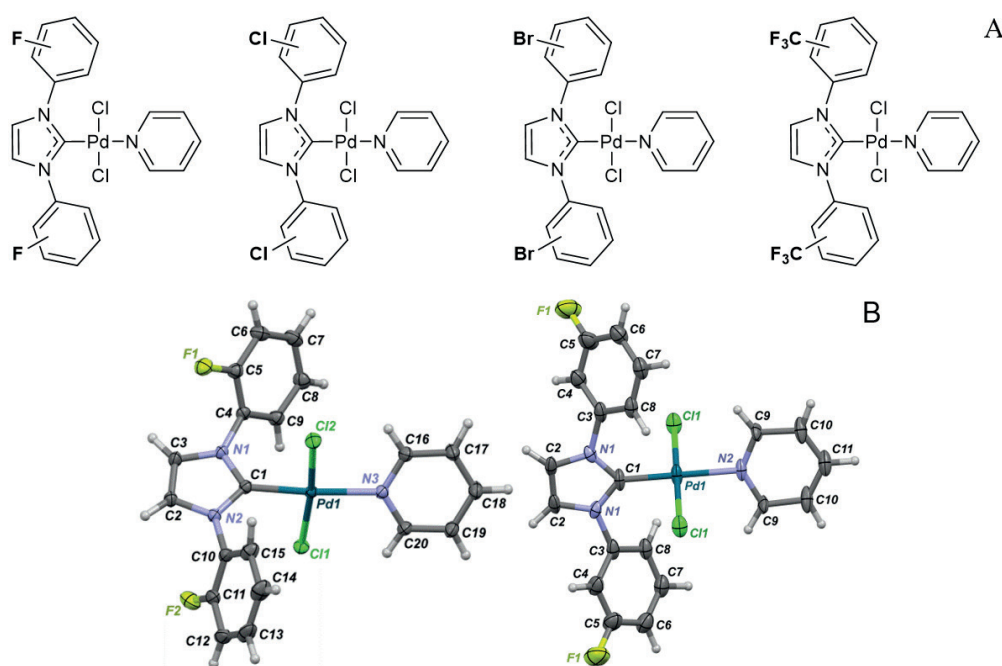


Figure 1. General structure of the resulting complexes (A). X-Ray for Pd/NHC_F complexes (B).

Acknowledgments

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Structure of hydrogen-bonded complexes of compounds containing As=O group

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In this work we study hydrogen-bonded complexes in which proton acceptor is triphenylarsine oxide and a set of phenols acts as proton donors.

Complexes formed in solid state were determined by X-ray diffraction analysis. Figure 1 shows hydrogen-bonded complex of triphenylarsine oxide and 2-chloro-4-nitrophenol. The result of complexation with unsubstituted phenol: one and a half molecule of phenol per one oxide molecule. The same result was obtained by Apperley, D.C.1 in the course of studying the complexation of phosphine oxide with phenol.

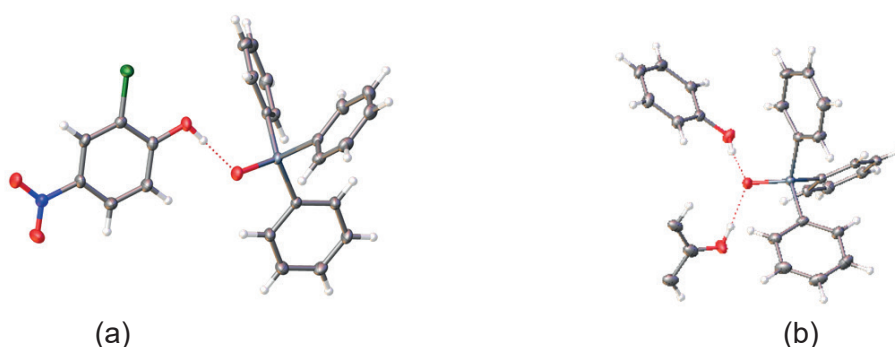


Figure 1. Hydrogen-bonded complexes of triphenylarsine oxide with (a) 2-chloro-4-nitrophenol and (b) phenol.

Complexation in solution was studied by NMR spectroscopy. To record the spectra of intermolecular complexes we use a unique technique: low temperature NMR spectroscopy. The spectra were recorded at a temperature of 100 K, the solvent is a liquefied mixture of deuterated freon gases. The stoichiometry of complexes and the type of mutual influence of hydrogen bonds were determined by analyzing spectra of partial deuterated solutions. Figure 2 presents the low-field part of the ¹H NMR spectrum of partially deuterated solution of triphenylarsine oxide and phenol. As a result, two different types of complexes are formed: 1:1 and 2:1, where there are two molecules of phenol per one oxide molecule.

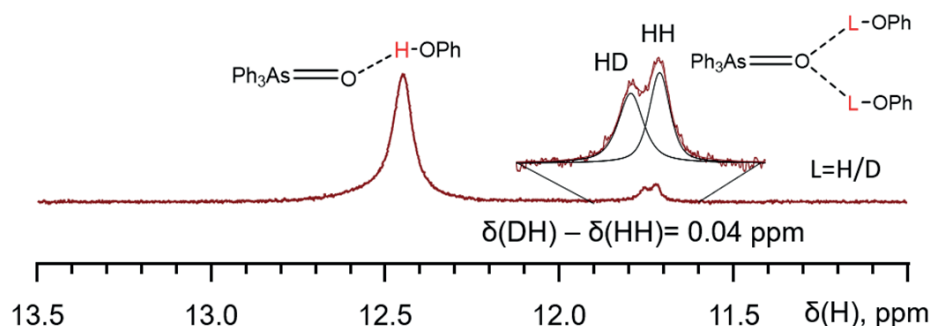


Figure 2. The low-field part of the ¹H NMR spectra of deuterated solution (50% D) of Ph₃AsO and phenol in a mixture of CDF₃/CDF₂Cl at 100 K.

Acknowledgements

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Non-covalent interactions of cyclometallated diketonate platinum(II) complexes with anticrown

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The moderately phosphorescent platinum(II) complexes [Pt(ppy)(acac)] (**1**; ppyH = 2-phenylpyridine, acacH = acetylacetone), [Pt(ppy)(hd)] (**2**; hdH = heptanedione-3,5), [Pt(ppy)(tmhd)] (**3**; tmhdH = 2,2,6,6-tetramethylheptanedione-3,5), [Pt(dfppy)(acac)] (**4**; dfppyH = 2-(2',4'-difluorophenyl)pyridine), and [Pt(dfppy)(tmhd)] (**5**) were precipitated on cocrystallization with the anticrown $\text{Hg}_3(1,2\text{-C}_6\text{F}_4)_3$ (**Hg₃**) to give the $\text{Hg}^{\text{II}}\text{-Pt}^{\text{II}}$ stacked heteroplanar architectures (**1–3**)·**Hg₃** and (**4–5**)·**Hg₃**· Me_2CO . Synchrotron X-ray diffraction studies of these cocrystals along with in-depth theoretical density functional theory (DFT; PBE0-D3BJ) calculations, employing a set of computational tools (QTAIM, ELF, IGMH, MEP, CDF, ETS-NOCV, and SAPT methods), allowed the recognition of the *spodium bonds* $\text{Hg}\cdots\text{Pt}$ and $\text{Hg}\cdots\text{C}$ (the former is significantly stronger than the latter) as the stacking-directing contacts. The major part (57%) of the total interaction energy between **3** and **Hg₃** (–32.9 kcal/mol), as a model system, comes from the $\text{Hg}\cdots\text{Pt}$ bonding. The heteroplanar stacking is mostly controlled by dispersion and electrostatic forces, but the $d_{22}(\text{Pt})\rightarrow\sigma^*(\text{Hg}-\text{C})$ charge transfer also provide a noticeable contribution; Hg^{II} functions as an electrophilic component of the $\text{Hg}\cdots\text{Pt}$ and $\text{Hg}\cdots\text{C}$ contacts. The spodium bond-driven supramolecular integration provides enhanced phosphorescence lifetimes and up to 6-fold solid-state quantum yield enhancement for all cocrystals compared to the parent Pt^{II} species. Appropriate DFT studies along with the analysis of calculated radiative and nonradiative decay rate constants indicate that the heteroplanar stacking reduces the population of the ^3MC state thus increasing the quantum yield.

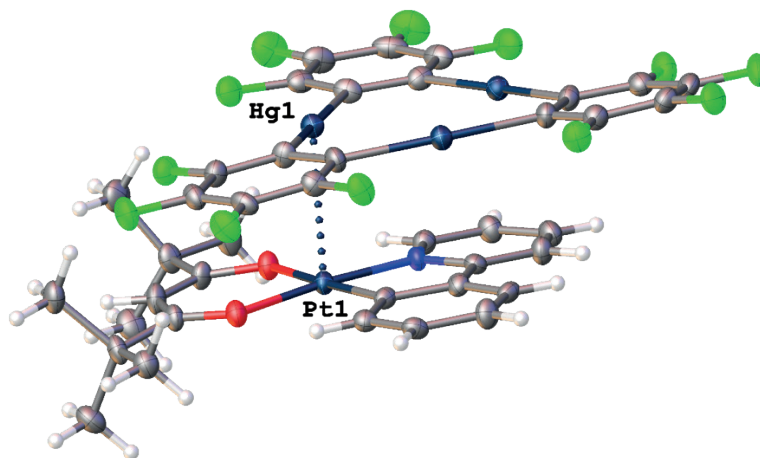


Figure 1. View of the molecular structure of **3**·**Hg₃**; thermal ellipsoids are shown with the 50% probability.

Acknowledgements

This work was supported by Russian Science Foundation (project No 21-73-10030).

Study of the interaction of benzo[d]thiazolo[3,2-a]quinolin-10-ium derivatives with DNA and antitumor activity *in vitro*

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Benzothiazole derivatives have the status of a versatile heterocyclic backbone due to their pharmacological applications to affect several biological enzymes, receptors, dyes, and cancer cell imaging.

Based on previous results and in continuation of our previous research on the development and synthesis of new intercalating agents, we report the development and synthesis of a new series of benzo[d]thiazolo[3,2-a]quinoline-10-ium derivatives (Fig. 1).

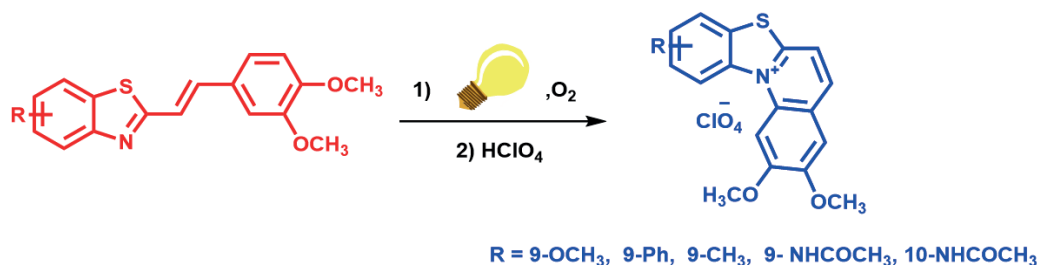


Figure 1. The reaction of obtaining a number of derivatives of benzo[d]thiazolo[3,2-a]quinoline-10-ium

The proposed structures are promising DNA intercalators. They have important structural features, namely, a planar polyaromatic system and cationic particles that enhance interaction with the negatively charged sugar-phosphate DNA fragment.

The variability of substituents in the benzothiazole fragment allowed us to study their binding to DNA, anticancer activity against four groups of cell lines using MTT analysis, and to perform molecular dynamics calculations.

Acknowledgements

The work was supported by the Russian Science Foundation (grant № 19-73-20187)

Noncovalent interactions as the driving force for building of molecular magnets based on nitronyl-nitroxide radicals

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Due to the possibility of the fine control of stable radicals' structures such molecules can be utilized as the base of new organic magnetic materials. These organic magnets have some advantages over inorganic ones and can be used in fields of quantum computing and smart materials.¹

Magnetic properties of an isolated nitronyl-nitroxide radical molecule are not enough so we propose application of the halogen bonding as the link between stable radicals.²

Previously we had shown the possibility of the formation of such interaction between pyridyl-containing nitronyl-nitroxide radicals and 1,4-diiodotetrafluorobenzene. Now we have focused on the distance decrease between radical centers. The well-known procedure³ were adopted for the synthesis of new 4-(4-iodoethynylphenyl)-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide which were crystallized in dichloromethane/heptane (1/1) mixture. The resulting crystal were investigated by XRD. The short contact is formed between iodine atom and oxygen atom as it shown in the illustration ($d(I\cdots O) = 2.878(3) \text{ \AA}$, $N_c = 0.81$, $\angle C-I\cdots D = 168.17(14)^\circ$).

Thus, we have demonstrated the short contact formation between iodine and oxygen atoms of the radical. An ordered infinite structure of the crystal lattice with a linear motif is also a noticeable feature of the radical.

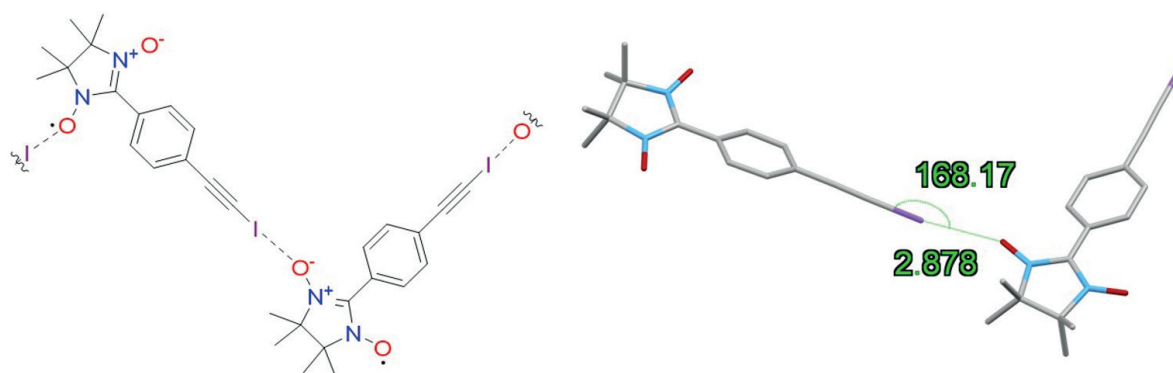


Figure 1. The formation of the halogen bond in the crystal lattice

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Study of the complexing properties of ligands with picolinate chelating groups

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Nitrogen-containing complexones are widely used as components of diagnostic and therapeutic agents, chemosensors, and in other areas due to the possibility of binding metal cations. Practically significant complexones are divided into two large classes: macrocyclic and acyclic compounds.

In this work, we studied the complexing properties of macrocyclic and acyclic nitrogen-containing ligands of various sizes with chelating picolinate groups (Fig.1).

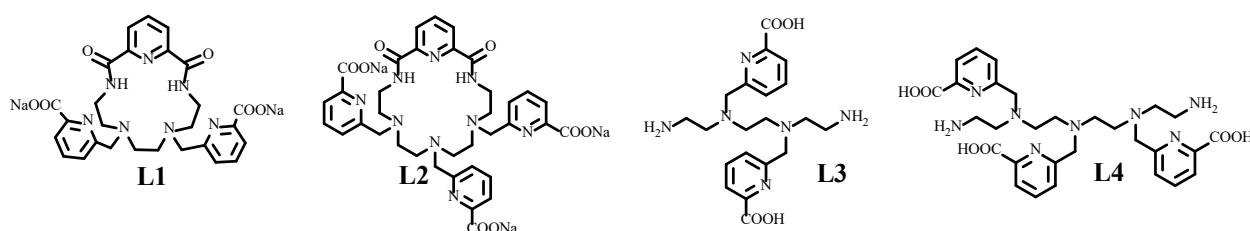


Figure 1. Studied ligands

Using potentiometric titration, it was found that $\text{Cu}^{2+}:\text{L}=1:1$ particles are formed and their hydroxyl and protonated forms. Acyclic ligands without bisamide moieties being a much more basic form of the complexes with higher stability constants. Complex formation with metals Cu^{2+} , Bi^{3+} , Ga^{3+} , Zr^{4+} was studied using NMR, ESI-MS and potentiometric titration. According to the X-ray analysis, the formation of polynuclear complexes with Cu^{2+} appears more likely. The structure of the Cu_2L_2 complex contains two water molecules coordinated to one of the metal atoms. In the structure of the aggregate $\text{Cu}_4(\text{L}_3)_2$ the most basic terminal aminogroups appear not to participate in cation's coordination whereas one oxygen of carboxylic group does (Fig.2).¹

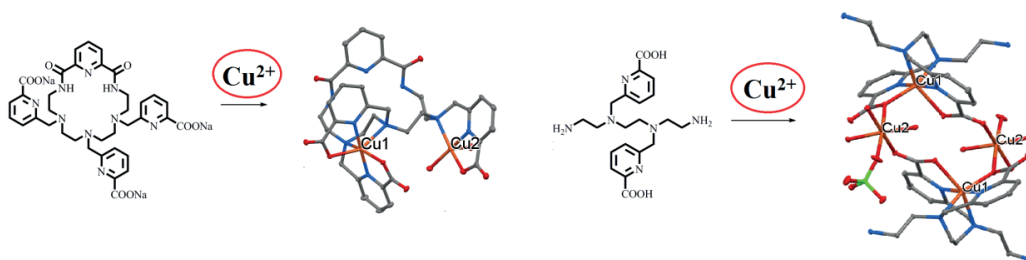


Figure 1. X-Ray Diffraction Data for copper complexes of L2 and L3 ligands

Acknowledgements

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Self-assembly of porphyrin-based metal-organic framework in layered europium hydroxide: a symbiotic hybrid material

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Porphyrin-based metal-organic frameworks (MOF) are the coordination polymers widely used in gas separation, sensorics, heterogeneous and photocatalysis due to coordination chemistry and optical properties of porphyrin complexes and porosity of metal-organic ordered structure. Nevertheless, these structures should be chemically and mechanically stabilized because of weak coordination bonding between porphyrin molecules and metal-clusters. A possible strategy for solving this problem is the assembly of MOFs on the solid surface of planar inorganic particles. This approach makes it possible to integrate the functional properties of porphyrin MOFs with those of supporting inorganic solids in a single hybrid structure. 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 layered europium (III) hydroxychloride (LEuH) as planar inorganic matrix with anion-exchange, coordination and luminescent properties.¹

We studied the catalytic activity of the material in a course of the hydrolysis of bis(4-nitrophenyl) phosphate as a model reaction for DNA phosphodiesterase and its artificial analogues. By studying the kinetics of the catalyzed hydrolysis with the UV-vis absorption spectroscopy, we showed that the intercalated hybrid exhibits synergetic catalytic effect on the process when compared to the activity of the non-intercalated LEuH matrix and ZnTCPP-based MOF. The changes in the structure and chemistry of the catalyst were studied by using Raman, FTIR and UV-vis spectroscopies, MALDI-TOF spectrometry and the X-ray diffraction.

The obtained results suggest that the hybrid material showed symbiotic properties, that is, mimicking the behavior of biological symbionts, due to the mutual stabilization of the components in the reaction media. The mutual stabilization of the components provides the catalytic synergy of the hybrid material since only mutually integrated porphyrin MOF and LEuH can efficiently catalyze the hydrolysis of organic phosphates. We believe that this strategy opens new routes for rational design of efficient hybrid materials on planar solids.

Acknowledgements

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Noncovalent DNA/RNA labeling with asymmetric bis(styryl) dyes

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Small fluorescent molecules are indispensable tools for chemical biology, being ubiquitous as biomolecular labels, environmental indicators and cellular stains.¹ Among the fluorescent dyes used for imaging in biology, noncovalent probes are important. Although the interactions resulting from noncovalent labeling are substantially less stable than covalent linkages, they occur at a faster rate and at a physiological pH range.²

In the present work, we propose two new noncovalent probes for ds-DNA or ss-RNA based on bis(styryl) derivatives **1**, **2** (Fig.1). The fluorescent quantum yield of styryl dyes in the free state is rather low, but when bound with a biomolecule, as a rule, their fluorescence increases its intensity many times over (Fig.1). The two proposed asymmetric bis(styryl) ligands have in their structure two different chromophores linked to each other by an aliphatic (dye **1**) or triazole (dye **2**) linker. Also, the suggested system can demonstrate the energy transfer (FRET) between the styryl components in the bis(styryl) dye, which helps to avoid errors in the fluorescence spectra associated with the effects of self-quenching and backscattering, which is very important for the visualization of biological objects.

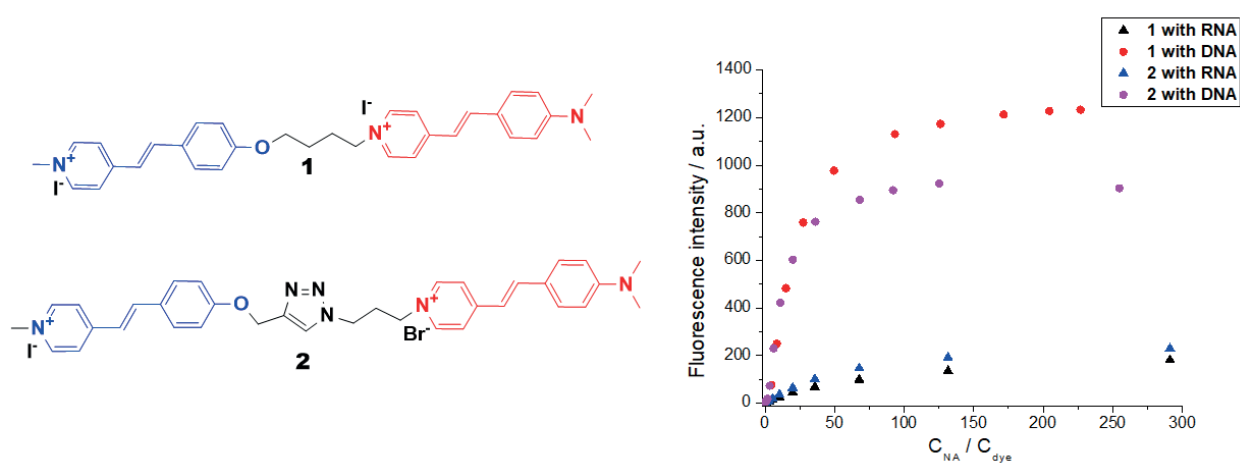


Figure 1. Structure of bis(styryl)s **1** and **2**. Comparative plot of emission intensity changes of dyes **1** and **2** with increasing concentration of NA.

Acknowledgements

This study was done with financial support from the Russian Science Foundation (project no. 21-73-20158).

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Various Approaches to Studying the Phase Transition in an Octamethylcyclotetrasiloxane Crystal: From X-Ray Structural Analysis to Metadynamics

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The octamethylcyclotetrasiloxane (D4, $[\text{Me}_2\text{SiO}]_4$) attracted our interest due to its molecular flexibility and great importance in the industry of various commercial products, including polymeric materials and lubricants. The compound has a crystal-crystal phase transition at $-16.3\text{ }^\circ\text{C}$, but structure of high-temperature phase was not established. To determine the crystal structure of the high-temperature phase and gain an insight into the mechanism of phase transition, we carried out the X-ray and differential scanning calorimetry (DSC) study of D4¹.

The combination of X-ray diffraction analysis and computational methods allow us to establish energy parameters and the pathway of phase transition. According to PBE0/6-311G(d,p) calculation of isolated D4, such conformation changes are characterized by a low barrier (0.07 kcal/mol). The character of molecular thermal motion and the path of phase transition were established with combination of periodic DFT calculations, including molecular dynamics and metadynamics. The effect of crystal field led to an increase in the calculated phase transition barrier (4.27 kcal/mol from low- to high-temperature phase and 3.20 kcal/mol in opposite direction, Figure 1).

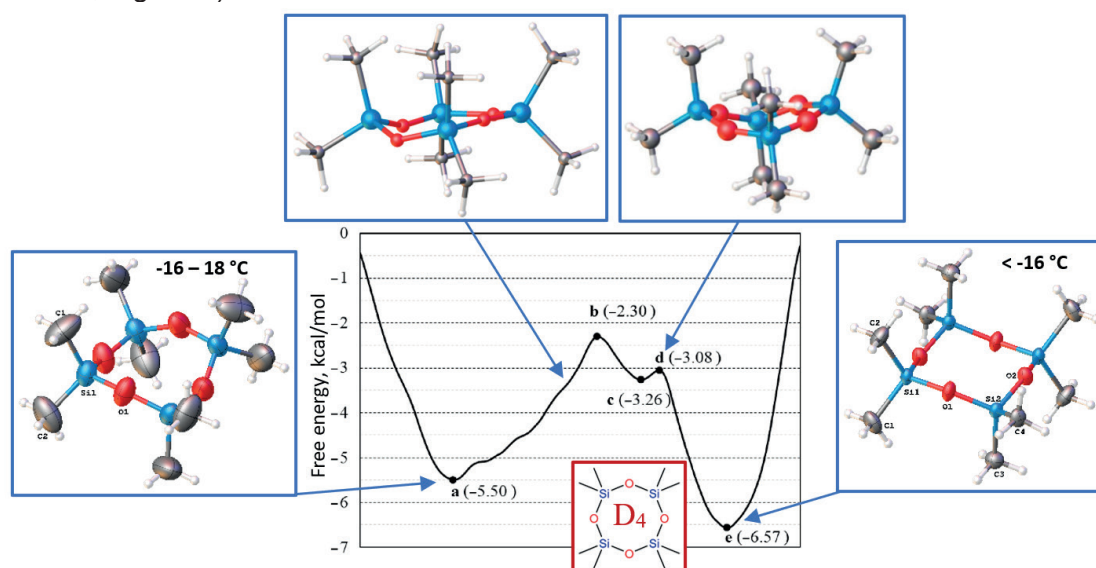


Figure 1. Dependence of Helmholtz free energy by phase transition process coordinate.

Acknowledgements

The work was supported by the Russian Foundation for Basic Research (project 19-33-90196).

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Supramolecular Hybrids Based on Ru(II) Porphyrin and Isonicotinate end-Decorated Octahedral Mo(II) Iodide Cluster

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Metalloporphyrins are attractive photoactive building blocks for supramolecular organization. Unlike Zn(II) derivatives forming labile supramolecular complexes via metal-directed coordination bonds,¹ Ru(II)CO porphyrins can strongly bind nitrogen ligands and form kinetically inert and thermodynamically stable assemblies in solution.

Herein we report a general approach to the design and synthesis of new stable supramolecular cluster-porphyrin (CP_n) hybrids with 5,15-bis[(p-tolyl)porphyrinato(2-)]ruthenium(carbonyl)(aqua) RuDToIP(CO)H₂O and Mo(II) iodide cluster (Bu₄N)₂{[Mo₆I₈](OOC-C₅H₄N)₆} PyMoC (Figure 1). The stepwise formation of discrete kinetically inert CP_n (n=1-6) adducts, including geometrical isomers for CP₂, CP₃, and CP₄ species, via Ru-N_{py} coordination bonds has been observed in solution by ¹H NMR and 2D ¹H-¹H COSY, ¹H-¹⁵N HMBC and DOSY techniques. It was shown that distribution of the resulting hybrid species in solution depends on the component ratio. Using a double equivalent amount of porphyrin relative to the cluster (C:P = 1:12) affords porphyrin-rich CP₅ and CP₆ species with molar ratio 1:3, while single crystals of only coordinatively saturated CP₆ complex can be isolated from this system and characterized by single crystal XRD. Varying cluster-porphyrin ratio, and the nature of the solvents, it is also possible to crystallize a more complex architecture where the CP₆ assembly incorporates two additional porphyrin molecules bound to the cluster core by hydrogen bonds.

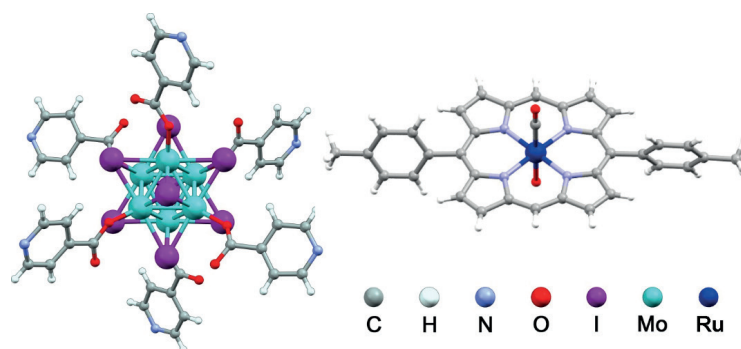


Figure 1. Structures of the PyMoC (left) and RuDToIP(CO)H₂O (right).

Acknowledgements

This work is supported by Russian Science Foundation (grant 21-73-00284).

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Noncovalent interactions in fluorinated bis(benzofuro)benzenes and their influence on the physical properties

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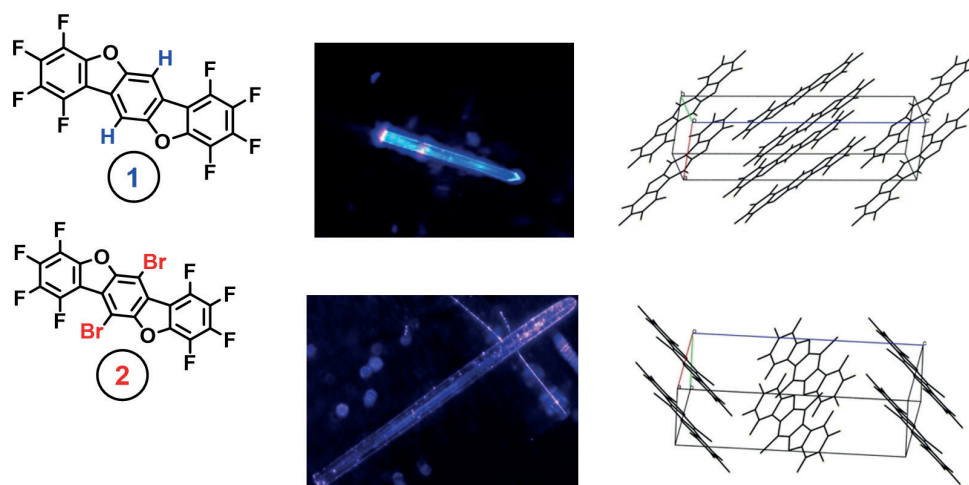


Figure 1. Chemical structure, appearance and crystal packing of **1** (top) and **2** (bottom).

Fluorinated benzannulated furans are promising compounds for organic optoelectronics due to their unique combination of emissive and semiconducting properties. We have developed a novel synthetic approach to the bis(benzofuro)benzenes **1**¹ and **2**² – promising building blocks for high-performance optoelectronic devices. The crystals of compounds **1** and **2** were grown using physical vapor transport with argon as a carrier gas. Interestingly, crystals of **1** show strong blue emission. Moreover, several mm long needle crystals of **1** not only show strong blue emission and great waveguide features, but also excellent flexibility, indicating the potential application of the crystals in flexible optoelectronic devices. Single-crystal X-ray data of **1** demonstrate that crystals have severe disorder and multiple weak electrostatic interactions. The molecules fit into infinite chains formed by neighboring π - π stacked dimers. The maximum hole mobility for **1** was theoretically estimated by the value $0.22 \text{ cm}^2\text{V}^{-1}\text{c}^{-1}$ and main charge transport direction along the **a** axis. Dissimilar characteristics were observed for dibromide **2**, however it provides with sites for further functionalization to tune optoelectronic properties.

Acknowledgements

The work has been carried out with support from the Ministry of Science and Higher Education of the Russian Federation, the project № FSUS-2021-0014.

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Noncovalent interactions in the aminohydroximate metallamacrocycles bearing alkali and rare earth ions

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Hydroxamic acids and their derivatives are water-soluble compounds of biological importance which can chelate efficiently the radioactive rare earth isotopes. The C_5 -symmetric aminohydroximate metallamacrocycles^{1,2} can be considered as a perspective platform for design and development of new ⁹⁰Y radiotherapy drugs. That demands upgrade of the synthesis methodology and deeper insight into the electronic structure of the coordination compounds suggested. In present work, the heterometallic Y(III)–Cu(II) macrocycle based on the alaninehydroximate (Alaha) ligands (Figure 1) and analogous K(I)–Cu(II) complex were investigated at the PCM(H₂O)-M06/def2-TZVP level of DFT. QTAIM analysis of the DFT optimized structures revealed the Y–O(oxime) (2.369–2.394 Å) and K–O(oxime) (2.670–2.674 Å) central bonds to be ionic “closed-shell” interactions, their energies being estimated as 14.4–15.7 and 5.0 kcal/mol, respectively. The Cu(II) bonds are characterized by higher covalent contribution (the “intermediate” type) and energy values of 37.0–61.5 kcal/mol. These results allow to suggest a new synthesis of the $\{Y[15-MC_{Cu(II)Alaha}^{-5}]\}^{3+}$ complex by replacement of the alkali ion in $\{K[15-MC_{Cu(II)Alaha}^{-5}]\}^{+}$ by Y^{3+} .

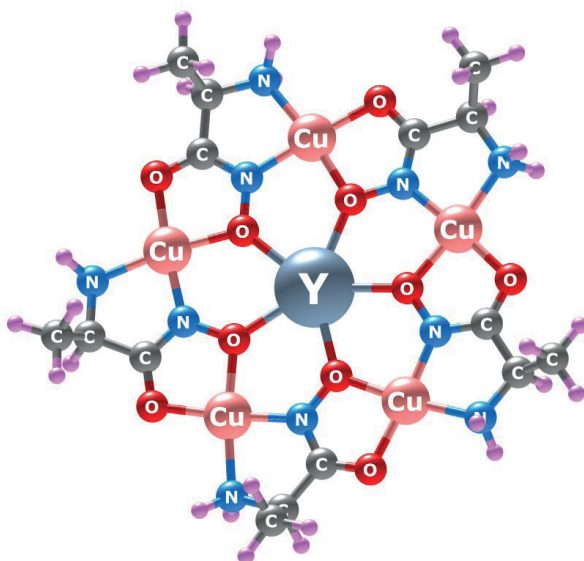


Figure 1. DFT optimized structure of the high-spin sextet $\{Y[15-MC_{Cu(II)Alaha}^{-5}]\}^{3+}$ complex. Interatomic distances, Å: Y–O(oxime) 2.369–2.394; Cu–O(oxime) 1.945–1.948; Cu–O(carbonyl) 1.923–1.926; Cu–N(imine) 1.890–1.892; Cu–N(amine) 2.022–2.026.

Acknowledgements

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POSTER SESSION



Bioderived C₆ furanics in cycloaddition reactions

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The Diels-Alder reaction is the first important step in the transition process from biobased furans to functionalized aromatic compounds (F2A process).¹ For a detailed representation of the HMF-based reaction space, a systematic study of the interaction of furans with DMAD was carried out. Active furans react with DMAD, producing 7-oxanorbornadienes in excellent yields. Furthermore, the aromatization methods leading to benzenes and phenols were studied.²

We have developed a new approach to transform HMF derivatives using dimeric furanic substrates as dienes and alkynes as dienophiles. Under thermodynamic control conditions, a cascade reaction was realized with exceptional regio- and diastereoselectivity, giving rapid access to a previously unachieved level of molecular complexity.

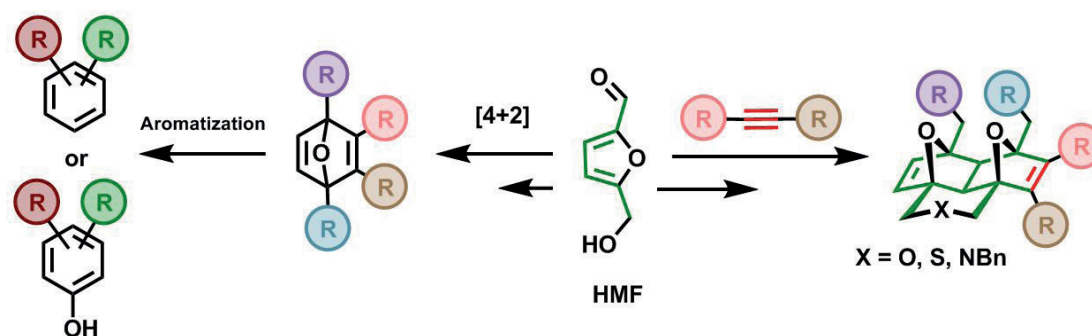


Figure 1. Cycloaddition reactions of HMF derivatives with alkynes.

Acknowledgments

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Application of the Morse Approximation for the Study of Noncovalent Interactions

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Despite a very rough approximation, the Morse model potential $M(r)$ ¹ is widely used in different fields of physical chemistry including the studies of intermolecular interactions (hydrogen bonding, properties of crystals, adsorption, etc.). The features of its practical use are presented based on articles;²⁻⁴ the distortions are described which are determined by the approximation of the original electronic term $U(r)$; the anharmonicity function is introduced, which is important for optimization of the problem statement; several examples of recent papers highlighting the effectiveness of the approach are given.

The difference $\delta(r) \equiv U(r) - M(r)$ as a function of the vibrational quantum number ν is used to evaluate the distortions. Based on the literature data, two types of the Morse potential were calculated for a number of diatomic molecules according the article¹ for two sets of initial parameters: $r_e, \omega_e, \omega_e x_e$ ($M1$) and r_e, ω_e, D_e ($M2$). The empirical function of anharmonicity $\omega x(\nu)$ is introduced as a progression of energy differences of adjacent vibrational levels. This function characterizes the anharmonicity at the certain region of the potential well $U(r)$ near the level ν and shows the deviation of Morse models $M1$ and $M2$ from initial term $U(r)$. The form of the functions $\delta(r)$ and $\omega x(\nu)$ for several molecules are presented and some generalizations are made.

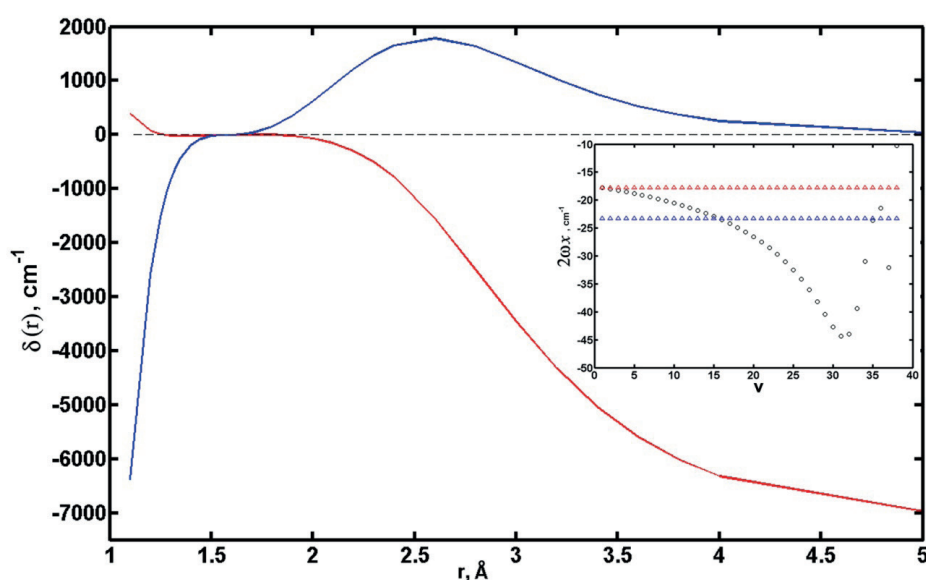


Figure 1. Deviations of Morse models $M1$ (red) and $M2$ (blue) from initial term $X^1\Sigma_g^+$ for B_2 molecule. Inset – anharmonicities for $U(r)$ (black), $M1$ (red) and $M2$ (blue)

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Tin(IV) iodide as a halogen bond donor

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Halogen bonds (XBs) are noncovalent intermolecular interactions, which are used in various domain¹: crystal engineering, medicine, stabilization of explosives, supramolecular chemistry, etc. In XBs, halogen atoms are electrophilic sites.

Tin(IV) iodide are a heavy analogue of halomethanes, which are well-known in XB studies. But SnI₄ was studied only as starting material for complexes with higher Sn coordination numbers, for example, [SnI₄(C₅H₅NO)₂]² i.e., as a Sn-centered electrophile.

In this work we have shown tin(IV) iodide can be a halogen bond donor, or an I-centered electrophile toward iodide ligands. SnI₄ was cocrystallized with *trans*-[PtI₂(NCN(CH₂)₄)₂], *trans*-[PdI₂(CN^tBu)₂], *trans*-[PtI₂(CN^tBu)₂] complexes with the formation of 1:1 molecular adducts. X-ray diffraction analysis showed Sn–I⋯I–M (M = Pd, Pt) intermolecular contacts (**Figure 1**), which can be interpreted as XBs accordingly to their geometrical parameters. Further theoretical periodic and cluster calculations confirmed noncovalent nature of the interactions using QTAIM analysis, NCI, WBI, and vertical dimerization energies. The philicity of the participants was determined by ESP surfaces, ELF projections, ED/ESP profiles, sums of natural charges, and superimposed orbitals.

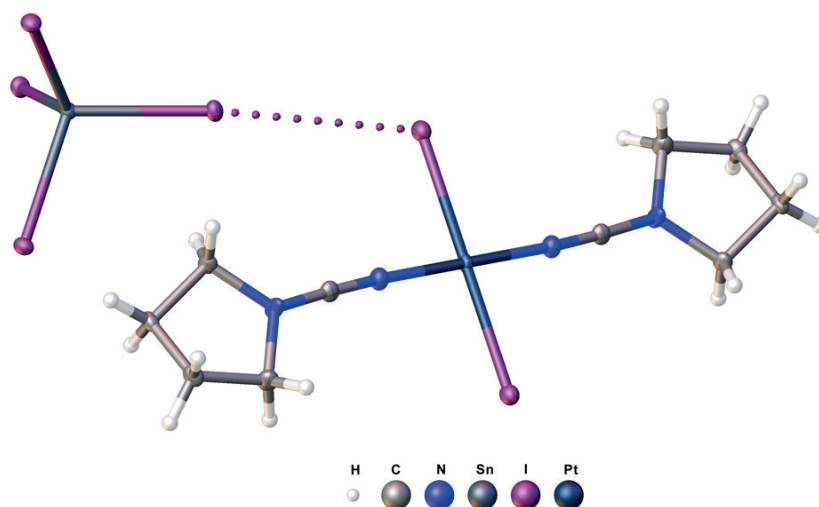


Figure 1. The Sn–I⋯I–Pt interaction in *trans*-[PtI₂(NCN(CH₂)₄)₂] \cdot SnI₄.

Acknowledgements

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Nucleophilic Ring Opening of Donor-Acceptor Cyclopropanes Catalyzed by Iodonium Salts

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The halogen-bond (XB), which forms between an electron-deficient halogen atom and a Lewis base (LB), has been considered to be a unique non-covalent interaction in recent decades. Halogen-bond donors have been used as effective non-covalent organocatalysts in a series of model processes, though the scope of reactions explored remains very scarce. In this study we report on the catalytic activity of cyclic iodonium salts in transformations of donor-acceptor cyclopropanes.

Using dimethyl (3,4-dimethoxyphenyl)cyclopropane-1,1-dicarboxylate and 1,3,5-trimethoxybenzene as model substrates, we found optimal conditions for ring opening reaction, which proceeds with the formation of arylated product in high yield. The use of less soluble diphenyleneiodonium catalysts (such as halide or trifluoromethanesulfonate salts) and coordinating solvents proved to be ineffective.

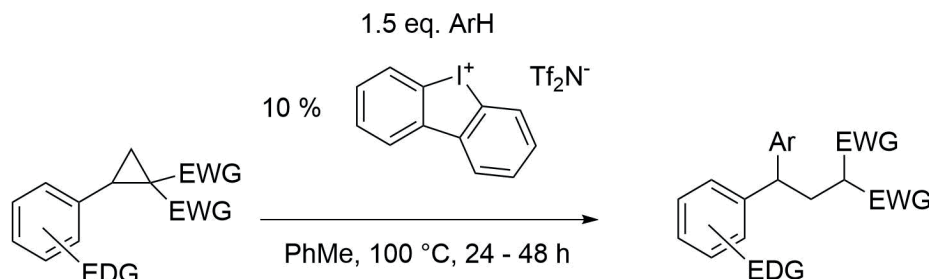


Figure 1. Optimal ring opening reaction conditions.

Next, we studied the scope of the disclosed reaction employing a series of donor-acceptor cyclopropanes and aromatic nucleophiles. In most cases products of ring opening were formed in high yields, though the use of less reactive nucleophiles or some donor-acceptor cyclopropanes with exceptionally strong electron-donating substituents led to formation of a desired product in low yield due to occurrence of side reactions.

Acknowledgements

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Styryl dyes for noncovalent labeling

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There are methods of covalent and noncovalent labeling to incorporate a fluorescent reporter into a biomolecule. Noncovalent labeling is possible due to the formation of strong hydrophobic and/or ionic interactions between the fluorescent marker and the biopolymer. Compared to the methods of covalent labeling based on chemical reactions, the noncovalent incorporation of a fluorophore has lower impact on the activity of a biomolecule¹.

In this study, we synthesized a series of styryl dyes with varying donor and acceptor fragments (Fig.1).

We studied the photophysical properties of dyes in free form in various solvents and in combination with biomolecules: a solution of albumin and calf thymus ds-DNA. All derivatives have a large Stokes shift and weak fluorescence in non-viscous media.

The results of spectrophotometric titration with ds-DNA showed the possibility of using styryl dyes for noncovalent labeling of DNA: the fluorescence signal of the dye increases after the addition of a biomolecule (Fig.1). The mechanism of dye binding to DNA was studied using circular dichroism spectroscopy and determination of the melting point of the complexes.

Experiments on noncovalent labeling of cancer cells in vitro were carried out. The localization of charged styryl dyes in mitochondria has been established.

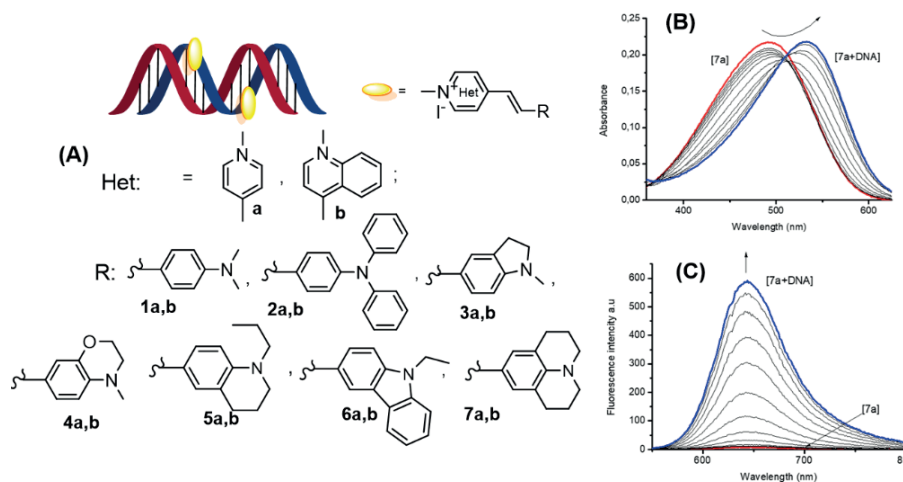


Figure 1. (A) Structures of styryl dyes; Spectrophotometric (B) and fluorimetric (C) titration of dye 7a with calf thymus DNA solution

Acknowledgements

This work has been supported by the grants the Russian Science Foundation, RSF №21-73-20158

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Molecular interactions in racemic and enantiopure thioureas

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New racemic and enantiopure thioureas bearing chiral 1-phenylethyl, 1,2,3,4-tetrahydro-1-naphthyl and 1-(1-naphthyl)ethyl groups were synthesized. The crystal structure of this series of thioureas is the result of fine balance of intramolecular and intermolecular interactions involving thiourea fragment and the energetic proximity of two conformations that differ by the orientation of N-H bonds (Fig. 1).

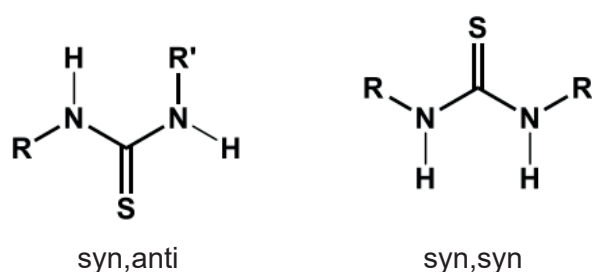


Figure 1. Two possible conformations of thioureas.

The formation of (*syn,anti*)-conformation is observed within a centrosymmetric In hydrogen-bonded dimer in most racemic crystals or pseudo-centrosymmetric dimer in enantiopure crystals, while there is (*syn,syn*)-conformation that results in a homochiral chain in enantiopure crystals or heterochiral chain via a glide plane in racemic compounds.

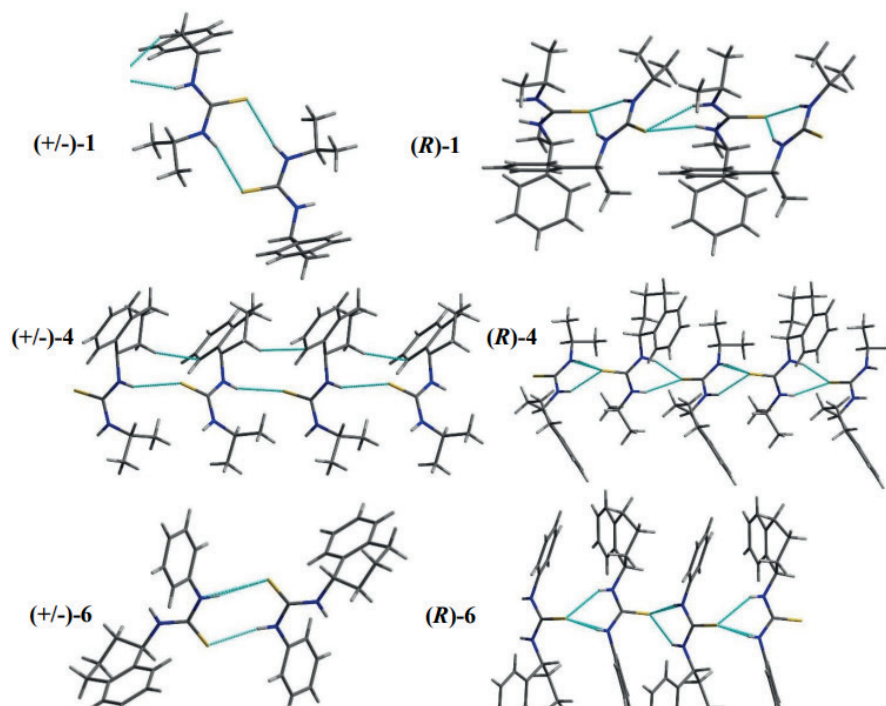


Figure 2. Supramolecular fragments in crystals of some thioureas.

Acknowledgements

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Diaryliodonium iodides and polyiodides

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Hypervalent iodine compounds are currently widely used in organic synthesis due to their high reactivity and low toxicity [1]. In synthetic chemistry, such compounds are used as mild oxidants, and in as atom- or group-transfer reagents to functionalized carbonyl compounds or alkenes [2].

Diaryliodonium salts are in a row of iodine(III) derivatives that form close ion pairs, including $Ar^1-I^+-Ar^2$ cations grouped with various counteranions. Diaryliodonium cations are well-known I-centered electrophiles, demonstrating two σ -holes, so they can form two halogen bonds [3].

There has been no systematic study of halogen bonds between diaryliodonium salts and iodides and polyiodides. Diphenyliodonium iodide and triiodide are the simplest studied representatives of this class of compounds. The central idea of this work was to investigate a series of diaryliodonium polyiodides with various substituents to the aromatic structure.

The general formula of counterions is signified as $Ar^1/Ar^2 = Ph/Ph, Ph/Mes, Mes/Mes$. Iodide derivatives were obtained as a result of exchange reactions of diaryliodonium trifluoroacetates and potassium iodide. Triiodide derivatives were synthesized from iodides by adding molecular iodine in a ratio of 1:1, according to the method described in the article [4]. The obtained compounds were characterized by a number of physical and chemical analysis methods, including single-crystal X-ray diffraction analysis. The nature of intermolecular bonds and the nature of bonds within anions were further investigated using density functional theory calculations.

Acknowledgements

The measurements were performed at the Center for X-ray diffraction Studies, Center for Magnetic Resonance, and Center for Chemical Analysis and Materials Research (Saint-Petersburg State University).

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Relationship between the configuration lability of nitrogen and sulfur atoms of sulfonamides of the thiazine series during the formation of crystal-forming motifs

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The crystal structure of thiazine sulfonamides contains two interesting stereochemical moments: firstly, the nitrogen atom in such a system usually acquires a pyramidal configuration, either conditionally direct or conditionally inverted. Secondly, the presence of two oxygen atoms in the sulfone group, carrying a close charge value and having approximately equal steric accessibility, but having different stereochemical identifiers (*pro-S* and *pro-R*), can lead to the participation of both one and the other oxygen atom in hydrogen bonding, which corresponds to different relative supramolecular configurations of the sulfur atom.¹

In the crystals of sulfonamides **1–5**, various packing motifs were identified, formed by classical N–H···O=S hydrogen bonds involving various diastereomeric forms.

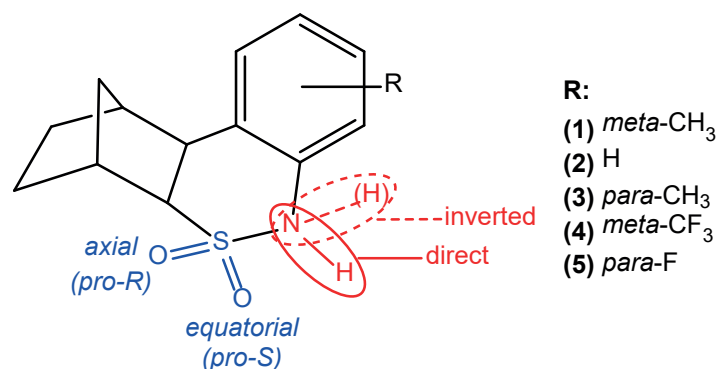


Figure 1. The general scheme of the studied of sulfonamides **1–5**.

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Supramolecular Assembly Of Binuclear Metal Complexes Via Metal-Involving Chalcogen Bonds

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In this work the supramolecular assembly of binuclear cyclometallated complexes $[\text{Pt}(\text{C}^{\wedge}\text{N})(\mu\text{-N}^{\wedge}\text{S})]_2$ ($\text{C}^{\wedge}\text{N}$ - 2-phenylbenzothiazole derivatives, $\text{N}^{\wedge}\text{S}$ - 2-mercaptopyridine, 1-methyl-1H-imidazole-2-thioland, 2-mercaptobenzimidazole derivatives) adducts with 1,2,5-chalcogenadiazoles (ChDA) (1,2,5-selenadiazole-3,4-dicarbonitrile and 1,2,5-telluradiazole-3,4-dicarbonitrile) via a chalcogen bond was demonstrated. According to DFT and SAPT calculations, the interaction energy $\text{Ch}(\text{Se}, \text{Te}) \cdots \text{dz}^2 [\text{PtII}]$ is estimated from -20 to -16 kcal/mol, indicating moderately strong chalcogen bonds. The orbital interaction ($\text{dz}^2(\text{Pt}) \rightarrow \pi^*(\text{ChDA})$), playing a leading role in the formation of the $\text{Ch} \cdots \text{Pt}$ bond, is also favorable for such structural orientation of ChDA and binuclear complex, and the back $\text{Ch} \rightarrow \text{Pt}$ charge transfer additionally stabilizes this geometry. In the same time, dispersion forces provide the principal contribution in the $\text{Ch} \cdots \text{Pt}$ bonding. The computational results indicate that the $\text{Ch} \cdots \text{Pt}$ bonding in adducts its geometrical features exhibit quite complex charact. Thus, here we have the case of a $\text{Ch} \cdots \text{Pt}$ chalcogen bond which mimics a semicoordination bonding.

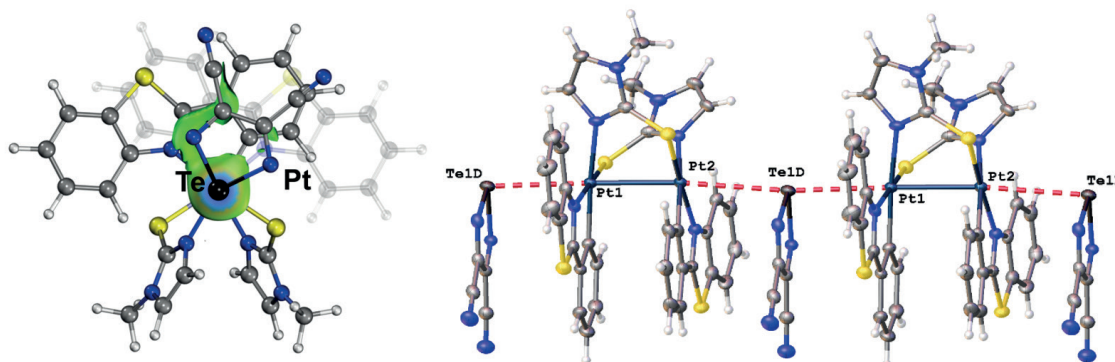


Figure 1. The $\text{sign}(\lambda_2)\rho(r)$ function mapped on the δg_{inter} isosurface for the $\text{Ch} \cdots \text{Pt}$ interaction ($\delta g_{\text{inter}} = 0.008$ au and blue-cyan-green-yellow-red color scale $-0.05 < \text{sign}(\lambda_2)\rho(r) < 0.05$).

Acknowledgements

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Study of the structural features of aqueous solutions of monoethanolamine of various compositions by experimental and theoretical methods of vibrational spectroscopy

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Aqueous solutions of monoethanolamine (MEA) are widely used in technologies for purifying various gas mixtures from acid gases, including carbon dioxide. Previously, it was suggested that the complex structure of aqueous solutions of MEA, both initial and saturated with CO₂, form various types of associates, which causes a decrease in the absorption capacity of MEA and the need to regenerate the absorbent during operation, and leads to significant economic losses^{1,2}.

In this work, a study was carried out using experimental and theoretical methods of vibrational spectroscopy, including methods of high-temperature IR spectroscopy and quantum chemical calculations with an analysis of theoretical vibrational spectra and structural electronic and energy characteristics of model objects. A high tendency of MEA to form associates to various compositions and structures with water molecules has been established. The possibility of interaction of carbon dioxide with MEA-H₂O associates of different compositions was studied. The structure of models of MEA-H₂O associates, which are capable of easily absorbing and desorbing carbon dioxide, is considered. The conditions for the formation in aqueous carbonized MEA solutions of ion pairs of the composition ammonium cations - carbamate anions, as well as supramolecular structures based on them, such as clusters, are established. The presence of such structures in carbonized MEA solutions reduces their absorption capacity and leads to the need to use high (≥110 °C) temperatures at the stage of CO₂ desorption, which in turn leads to MEA losses due to thermal and thermo-oxidative degradation reactions.

Acknowledgements

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Forming Stereochemically Challenging $Z' > 1$ Motifs in Organic Crystals through Various Non-Covalent Interactions

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Currently, there is a development of dynamic supramolecular stereochemistry, the main subject of study of which is the stereochemical features of binding molecules into supramolecular associates through classical hydrogen bonds or weaker interactions. In our works, we draw attention to the method of realizing the donor/acceptor potential of a prostereogenic grouping: sulfonic, methylene, oxygen atom of a chiral molecule in the process of forming a supramolecular associate through the formation of certain interactions. Historically, the concept of prochirality, the concept of prostereogenic grouping and the corresponding descriptors of prostereoisomerism have been used in classical organic chemistry to explain the spatial features of the course of chemical reactions and the predominant formation of one of the possible stereoisomers. However, the same thing happens during the formation of any supramolecular associate formed by classical hydrogen bonds, or a wide range of other intermolecular interactions – the prochiral group interacts with one of the chemically identical but stereochemically non-equivalent atoms, lone electron pairs or sides of a multiple bond, and thus acquires the status of a newly formed chiral center supramolecular level. By means of such transformation, supramolecular diastereomers can be formed in crystals with several independent molecules ($Z' > 1$) and in polymorphic modifications of the same substance.¹

The report will present examples of associates constructed by molecules of supramolecular diastereomers through classical and non-classical hydrogen bonds.

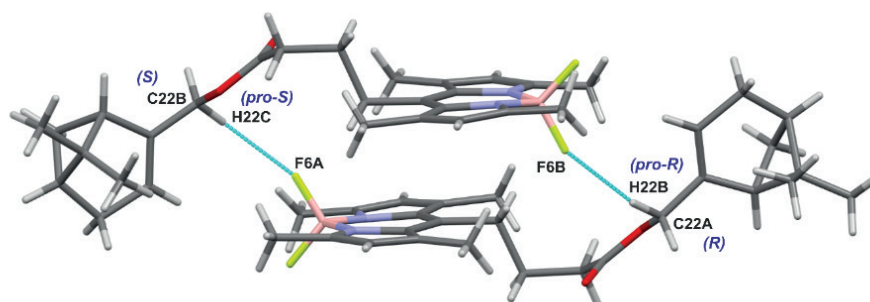


Figure 1. $Z'=2$ dimer in the BODIPY derivative crystal.

Acknowledgements

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Short contacts in nitroxide radicals' crystals with adamantyl and perfluorophenyl substituents

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Nitroxide radicals and their complexes have been intensively studied for many years, leading to key discoveries in the field of molecular magnetism, such as the preparation of pure organic ferromagnets and ferromagnets, complexes of transition metals with nitroxides showing magnetic ordering effects, and copper–nitroxide complexes with unusual spin-crossover behavior. This situation has stimulated the subsequent active developments in the chemistry of this class of paramagnetic compounds with an emphasis on the synthesis of their polyfunctional derivatives. Although, to date, a huge number of different nitroxides have been successfully obtained, there are still poorly studied but interesting types of organic radicals within this class ^[1].

Since nitroxide radicals rarely form significant short contacts even in the crystalline phase, it is of great interest to study the existing contacts and their effect on the crystal packing. Within the framework of this work, packings of several organic nitroxide radicals were studied and short contacts formed by radical fragments were identified and described.

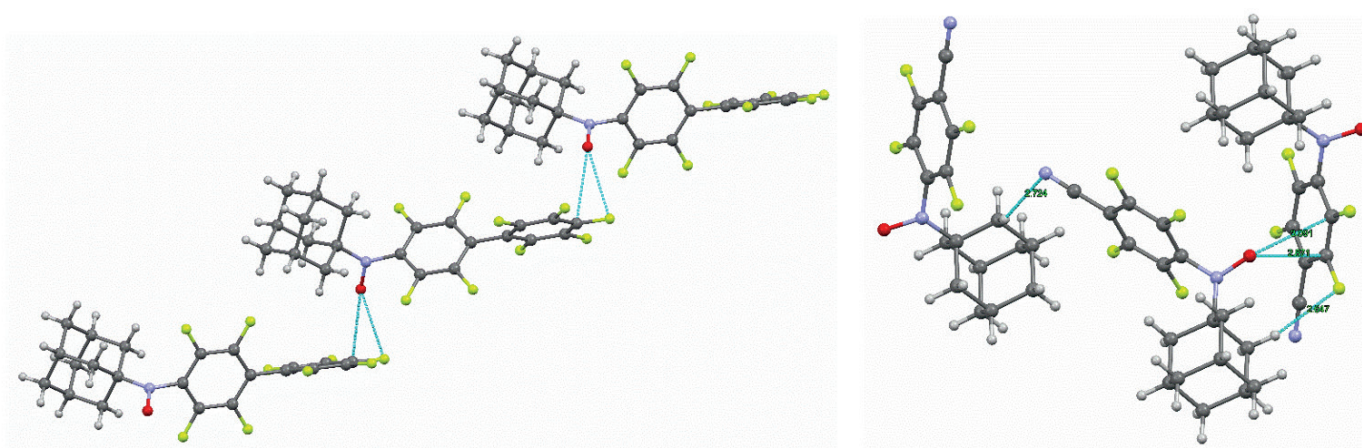


Figure 1. Short contacts of radical fragments

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Quantification of Pd/NHC evolution products in the Heck, Sonogashira, and transfer hydrogenation reactions

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Transition-metal-catalyzed reactions of C-C and C-heteroatom bonds formation are attractive in the field of fine organic synthesis and in industry. The most common catalysts used in the process are Pd-containing complexes, including Pd/NHC systems. The studies of reaction mechanisms and catalyst transformations have always been the point of interest for researchers. Investigation of decomposition pathways of Pd/NHC complexes is of much importance for developing more effective catalytic systems.^{1,2}

In this work, we have made an attempt to study the pathways of Pd/NHC evolution and quantify major products of Pd/NHC transformation such as H-NHC, O-NHC and Ph-NHC couplings in the Heck, Sonogashira and transfer hydrogenation reactions by using ¹H NMR spectroscopy and high-resolution electrospray ionization mass spectrometry (ESI-MS).

The O-NHC coupling leads to the main product of the complexes' evolution in the transfer hydrogenation reaction. In the Heck and Sonogashira reactions, all the target compounds were detected, where the Ph-NHC product is with the dependence of NHC ligand BIME>IMes>IPr.

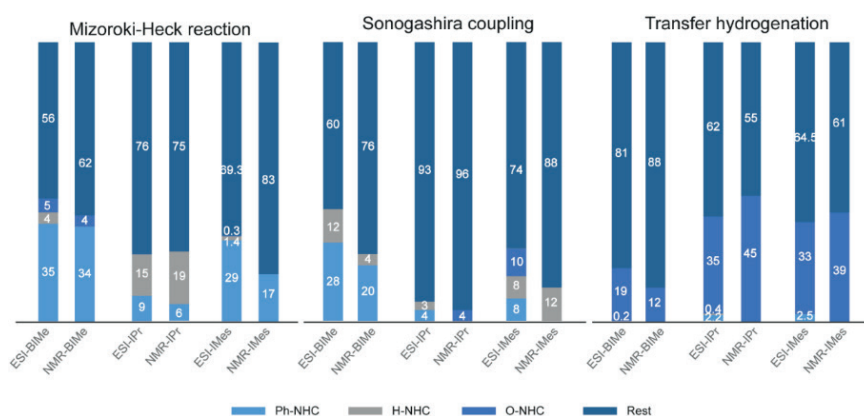


Figure 1. Determination of X-NHC yields by ESI-MS and ¹H NMR for all studied reactions.

Acknowledgments

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Analysis of Noncovalent Interactions in the Polymorphic Structures of N-(3-Chloro-2-methylphenyl)anthranilic Acid

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The aim of the investigation was to analyze noncovalent interactions in the structures of N-(3-chloro-2-methylphenyl)anthranilic acid by means of molecular Voronoi-Dirichlet polyhedra.¹ The substance was selected because its nine crystal structures had been solved. Every of them contains a unique conformation of the molecule allowing to define these structures as conformational polymorphs. Such systems are the proper forum for exploring the relationship between crystal structure and its properties.

In the course of analysis, all noncovalent interactions without exceptions were identified using the method of molecular Voronoi-Dirichlet polyhedra. According to $k\text{-}\Phi$ criterion, based on the differences of intramolecular contacts, all the studied modifications are conformational polymorphs, indeed.² The structures involve fifteen types of intermolecular contacts, nine of which were found in each of the nine modifications. For assessment of contacts participation in crystal structure formation the surface area of Voronoi-Dirichlet polyhedron is used. In the modifications of the title substance H/H, H/C, H/O and H/Cl are the most contributing contacts. Form IV has the highest contribution of the H/C contact, which takes the responsibility for π -stacking. Thus, π -stacking calculated as the sum of contacts H/C and C/C has the largest value in the form IV.³ Conversely, the lowest value of π -stacking is observed in the form II with the lowest surface area of the H/C contact.

Analysis of trends of noncovalent contacts as a function of the angle between the aromatic ring planes can help to clarify which contacts are the most influential on the crystal structure formation: intramolecular noncovalent or intermolecular. The respective trends relating to the substance under consideration do not feature any monotonicity. This fact highlights the major impact of intermolecular contacts. In other words, the molecular geometry of the studied acid mostly depends on the crystal field and less on the flexibility of the molecule.

Acknowledgements

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Re-thinking the Role of Dimeric Species in Catalysis

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Palladium-catalyzed reactions for carbon-heteroatom and carbon-carbon bond formation are highly demanded synthetic methods. Several unique catalytic systems have been developed to synthesize different classes of compounds with high regio-, and chemo-selectivity in recent years.^{1,2} To date, many palladium complexes exist that could catalyze a wide range of organic reactions. However, after one loaded a palladium complex into the reaction mixture, the pre-catalyst undergoes many transformations until a catalytically active complex is formed. One of the main problems in the studies of transition-metal-catalyzed reactions is determining the nature of active catalytic centers. Without knowledge of the nature of active species, rational design of a new generation of catalysts and increase of reaction selectivity is hardly possible.

In this work, the role of palladium dimer complexes formed during the reaction was studied, using the reaction of hydrothiolations of alkynes as a model reaction. A generally accepted picture, suggesting that dimeric palladium complexes, in many cases, are not directly involved in catalytic processes and act as resting states, has been re-considered using experimental and theoretical approaches. The concept developed may be helpful in a series of catalytic processes since relationships between monomeric and dimeric forms of metal centers are ubiquitous in catalysis.

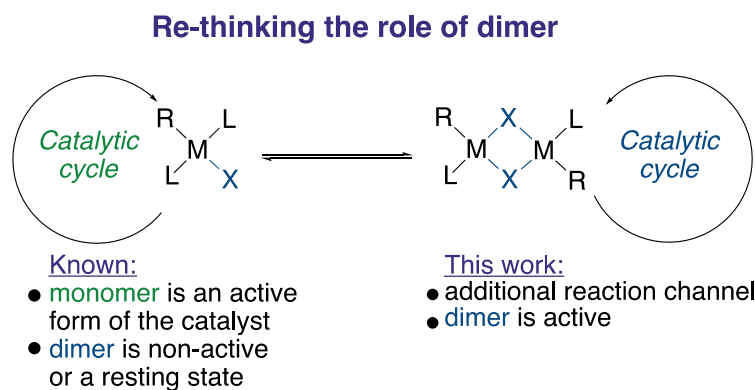


Figure 1. Re-thinking the role of dimer species in catalytic reactions

Acknowledgments

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XAS study of palladium catalyst changes in the Heck reaction

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Transition metal catalysts play an important role in organic synthesis, polymer science, the production of biologically active compounds and industry. In particular, heterogeneous carbon-supported metal catalysts (M/C) have found application in the fine chemical industry. Recent studies have shown that there are no clear boundaries between homogeneous and heterogeneous catalysis. The application of a heterogeneous catalyst often leads to the formation of soluble metal complexes, while the use of a homogeneous catalyst can result in the deposition of metal nanoparticles or precipitation of metal black.

In our study, we 3D printed two reactor compartments in which the Heck reaction took place. The printing was carried out with a material capable of withstanding the impact of the DMF solvent, and a temperature of 140 °C. In one compartment there was a heterogeneous catalyst precursor (5% wt. Pd / C) - compartment A. In the other compartment there was no catalyst - compartment B. Both parts were separated by filter paper. Then, XAS measurements were made on the compartment in which no catalyst was placed after the start of the reaction (compartment B). After 1 hour of the beginning of the Heck reaction, signals characterizing the presence of palladium in compartment B were recorded. As the reaction progressed, the XAS spectrum changed. Pd foil was filmed as a standard. One hour after the start of the Heck reaction, the spectra of the spectrum of palladium were recorded. These spectra were different from those taken for palladium foil. This is due to the fact that various palladium compounds, including monomolecular ones, accumulate at the initial moment of catalysis. Three hours after the start of the reaction, the presence of metallic palladium in the system could be detected in the spectra.

This experiment allows you to track the changes in the catalyst during the reaction and talk about the dynamic phenomena passing from palladium during the reaction. Thus, the formation of palladium in the metallic state from other precursors, such as molecular complexes during the Heck reaction, was recorded. This method allows the detection of the reprecipitation of catalytically active particles.

Acknowledgements

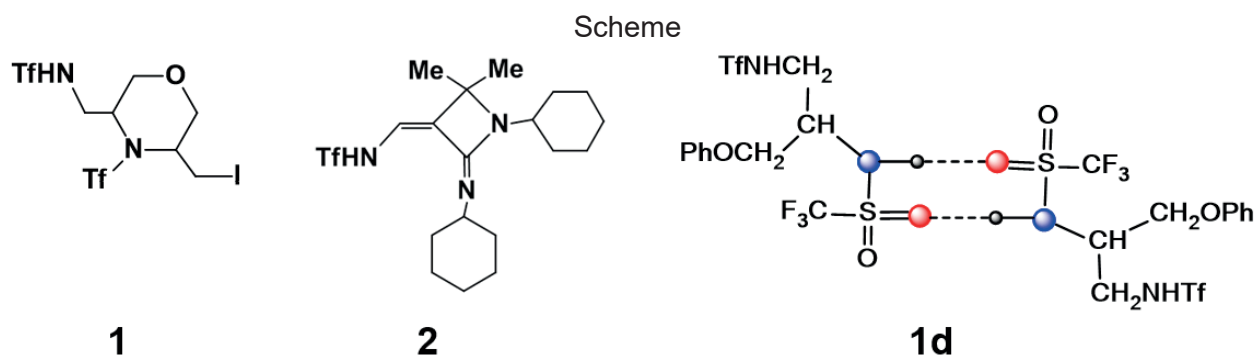
The authors thanks Russian Science Foundation (RSF Grant 19-73-20124) for the support.

Noncovalent Interactions in New Derivatives of Triflamide

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Noncovalent interactions in new derivatives of triflamide ($\text{CF}_3\text{SO}_2\text{NH}_2$) N-((5-iodomethyl-4-((trifluoromethyl)sulfonyl)morpholin-3-yl)methyl)triflamide **1** and N-[[2,2-dimethyl-1-cyclohexyl-4-(cyclohexylimino)azetidin-3-ylidene]methyl]-trifluoromethanesulfonamide **2** (Scheme) in the crystal and solution in inert media (CCl_4) were studied by X-ray analysis, FTIR spectroscopy and quantum chemistry calculations.



The crystal packing of **1** is formed by $\text{NH}\cdots\text{O}$ hydrogen bonding with the ethereal oxygen of the morpholine ring (Fig.1). In nonpolar CCl_4 , apart from the monomeric molecules of **1**, only $\text{NH}\cdots\text{O}=\text{S}$ -bonded cyclic associates having low dipole moment are present. According AIM analysis data energy of hydrogen bonds $\text{S}=\text{O}\cdots\text{H}-\text{N}$ in cyclic dimers **1d** (Scheme) consist 5.11 kcal/mol.

Likewise different types of self-associates in various phase states forms by molecules of amide **2**. According to X-ray analysis, the molecules of compound **2** in the crystal form 3D structure by weak $\text{S}=\text{O}\cdots\text{H}-\text{C}$ interactions (Fig.1), whereas the FTIR data are indicative of the presence of more stable self-associates with strong $\text{S}=\text{O}\cdots\text{H}-\text{N}$ hydrogen bonds both in the solid state and in solution. Calculated (B3LYP/6-311++G(d,p)) energy of hydrogen bonds $\text{S}=\text{O}\cdots\text{H}-\text{N}$ in cyclic dimers of compound **2** consist 6.13 kcal/mol whereas AIM analysis data shows that this energy is equal 5.44 kcal/mol.

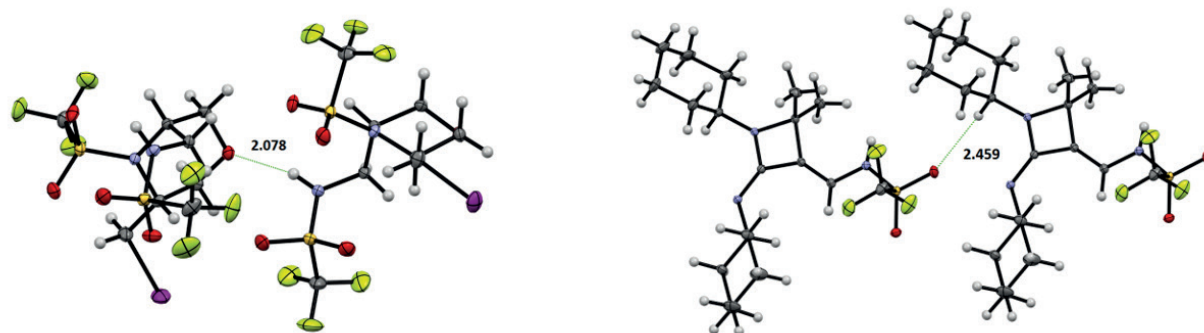


Figure 1. Hydrogen bonds $\text{NH}\cdots\text{O}$ and $\text{CH}\cdots\text{O}=\text{S}$ in the crystals of amides **1** and **2**

Acknowledgements

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Crystal Structure Control of Organic π -Conjugated molecules by Additive-Assisted Crystallization

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Linear π -conjugated small molecules are in strong demand for organic optoelectronics due to combination of high charge carrier mobility and efficient luminescence required for potential applications in light-emitting diodes, field-effect and light-emitting transistors and sensors. The optoelectronic properties of such materials strongly depend on the crystal packing and morphology. Therefore, the development of efficient tools for crystal structure and morphology control is in highly demand in organic optoelectronics. Additive-assisted crystallization is one of the powerful approaches used for this purpose¹.

In this work we studied additive-assisted crystallization of the benchmark semiconductor materials: pyrene, perylene (PRN), anthracene (Anth), 9,10-diphenylanthracene (DPA) and rubrene (Rub). The concentration of additives varied from 2 to 20 mol% in respect to the target material. We demonstrate additive-assisted crystallization effect on the series of perylene (which crystallizes in α - and β -polymorphic modifications depending on the concentration of additives), rubrene (which crystallizes in triclinic-I and orthorhombic polymorphs with DPA as an additive), and 9,10-diphenylanthracene (which crystallizes in three polymorphic modifications depending on the tetracene concentration) (Fig. 1). The effect of the additive on the crystal size and morphology is also discussed. The crystallization of tetracene and anthracene by additive-assisted methods did not lead to the targeted preparation of their polymorphic modifications.

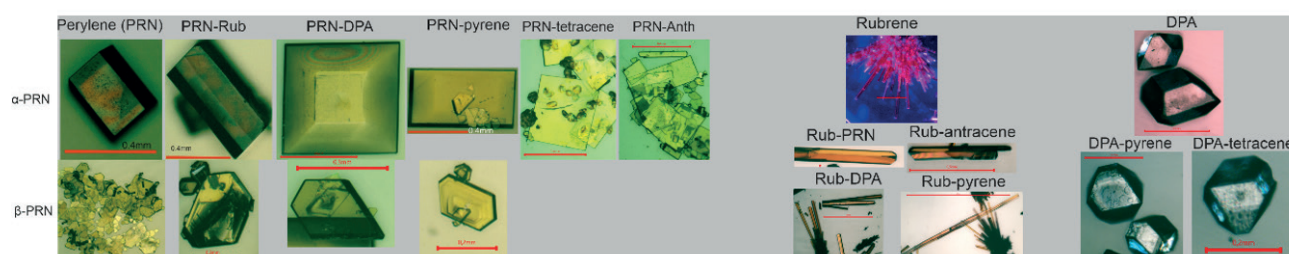


Figure 1. Optical images of studied semiconductor crystals obtained in the presence or absence of additives.

Acknowledgements

The work was supported by RSF project #21-73-00287. The powder X-Ray experiments was done using the equipment of the Research and Education Center of the Novosibirsk State University REC-008.

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Crystal engineering and magnetic properties of coordination polymers based on transition metal nitrate complexes with singly charged cations

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Nitrate complexes (NC) of transition metals are of great interest with their original crystal structure, due to the geometric features of the nitrate group, which can exhibit variable denticity in combination with various bridging functions. NC are capable of forming structures of various dimensions, which may contain both isolated anions and polynuclear coordination polymers (chains, ribbons, layers, or three-dimensional frameworks) (Fig. 1a, b). Among various systems studied in terms of low-dimensional magnetism [1], anhydrous transition metal nitrates stand out by peculiar properties stemming from the frustration of leading exchange interactions. In this paper, we present the results of a synthesis, structure investigation and physical properties of **10** new anionic layered NC with the general formula $A^i_x B^j_y [TM^l_z (NO_3)_{x+y+2z}]$ (A, B – alkali metal or pyridinium, TM – transition metal = Mn, Co, Ni, Cu). The crystal structure of the obtained compounds was established by X-ray diffraction analysis. In some cases, the nature of reversible structural phase transitions has been studied. Physical properties were investigated by measuring of T-dependence of magnetic susceptibility, magnetization and heat capacity.

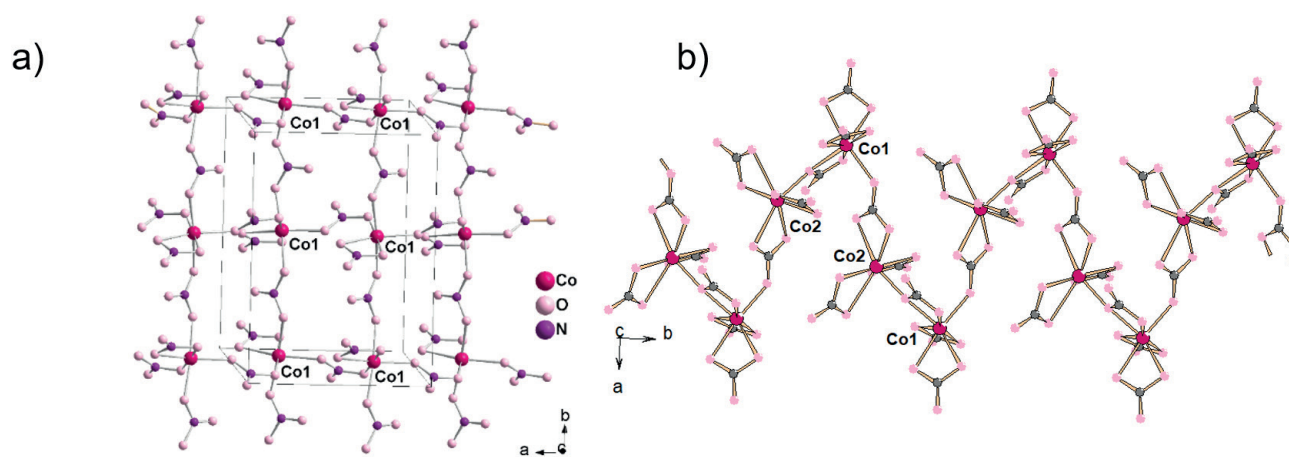


Figure 1. The crystal structure of layered anion in $(PyH)Cs[Co_2(NO_3)_6]$ (a) and chained anion in $(PyH)[Co(NO_3)_3]$ (b).

Acknowledgements

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Non-covalent interactions in organic precursors as a driving factor of coordination compounds structure

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It is known that non-covalent interactions play a decisive role in the molecular and electronic structures of compounds, determining the chemical and physical properties of compounds and materials. Previously^{1,2}, we described examples of the influence of stacking interaction between organic fragments on the structure of coordination compounds. The use of strong pi-donor systems as the second ligand in heteroligand fluoro-benzoate complexes leads to the formation of strong pi-pi interactions and the formation of coordination polymers, while less donor pi-systems form weaker stacking interactions or do not form them at all, and the resulting complexes have a molecular structure.

This present work presents a study of co-crystals of benzoic acid fluorine-substituted derivatives with aromatic compounds of various degrees of pi-donority - dinitrobenzoic acid, pyridine, quinoline, and phenanthroline derivatives, as well as the corresponding heteroligand coordination compounds. The analysis of the electronic, molecular and crystalline structures of the compounds was carried out, non-covalent interactions for each compound were identified and characterized. Correlations between interactions in organic systems and the structure of coordination compounds as well as its system of bonds are shown.

Acknowledgements

This work was supported by the Russian Science Foundation (project no. 22-73-10192).

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Stable reproducibility of a stereochemically complex three-dimensional motif of hydrogen bonds in various crystalline forms of 15-en-steviol and dihydrosteviol

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Progress in crystal engineering has led to the accumulation of a large amount of information about supramolecular associates formed in a complex way through classical hydrogen bonds or a wide range of other intermolecular interactions. Basic descriptors of stereochemistry (concepts of an asymmetric center, configuration) are not enough to describe such structures. Consideration of such systems urgently requires the use of concepts formed in classical dynamic stereochemistry to explain the special spatial aspects of chemical reaction behaviors and of the predominately forming one of possible stereoisomers - the concept of prohirality, the notion of prostereogenic grouping, and the corresponding prostereoisomerism descriptors.¹ This suggests the emergence of a new field - dynamic supramolecular stereochemistry.

In this work, the need for such an approach is demonstrated in the study of crystallization of 15-ene and dihydrosteviols. It is established that polymorphism is characteristic of these substances. The variety of crystal phases, as well as the transitions between them, were studied by DSC, single-crystal and powder XRD. It is shown that the same three-dimensional system of hydrogen bonds formed by supramolecular diastereomers molecules, the appearance of which is associated with the asymmetry of the hydroxyl oxygen atom, is steadily reproduced in the basic crystal forms of 15-en and dihydrosteviols.

Acknowledgements

The work was carried out with the financial support of the RSF (grant 22-13-00284)

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Application of Zn carboxylates in the synthesis of symmetrical nitrogen-containing derivatives of camphor

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Imines are important intermediates in the synthetic organic chemistry of pharmaceutical compounds. Previous studies have demonstrated the effectiveness of N,N'-(Hexan-1,6-diyl)bis(1,7,7-trimethylbicyclo[2,2,1]heptan-2-imine) as a new multifunctional additive for rubbers based on SKI-3. The use of this imine in the formulation of rubbers makes it possible to increase the strength characteristics, thermal-oxidative stability and provide the necessary vulcanization rate, in comparison with the vulcanizate, which includes a standard vulcanization accelerator - 2-mercaptobenzthiazole.

The synthesis of imines involves the condensation of a carbonyl compound with an amine. Depending on the activity of the starting materials, this reaction can proceed without a catalyst, or with the use of an acid type of catalysts: p-toluenesulfonic acid, $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Also, the condensation reaction between carbonyl compounds and amines is carried out in the presence of catalysts such as TiO_2 , $\text{CeCl}_3 \cdot \text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2$, $\text{Er}(\text{OTf})_3$, $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$, $\text{P}_2\text{O}_5/\text{SiO}_2$, $\text{Mg}(\text{ClO}_4)_2$, TiCl_4 , MgSO_4 –pyridinium p-toluenesulfonate, ZnCl_2 , $\text{Ti}(\text{OR})_4$, etc.

We have proposed the use of zinc carboxylates as catalysts. The objects of study were zinc salts of neodecanoic, 2-ethylhexanoic and octanoic acids. Zinc neodecanoate and zinc 2-ethylhexanoate are ionic liquids, which allows the reaction to be carried out under homogeneous catalysis conditions. Potential catalysts were used in the synthesis of N,N'-(Hexan-1,6-diyl)bis(1,7,7-trimethylbicyclo[2,2,1]heptan-2-imine) by the reaction of hexanediamine-1,6 with camphor.

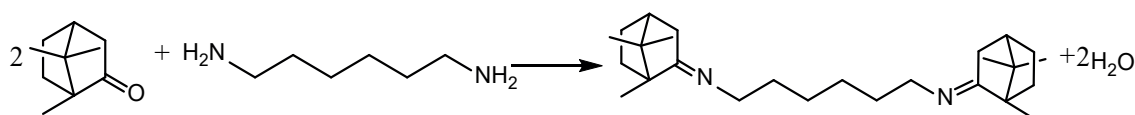


Figure 1. Interaction of hexamethylenediamine-1,6 with camphor

Condensation was carried out in toluene at a molar ratio of reagents (hexanediamine-1,6:camphor 1:2.6) with the removal of reaction water by azeotropic distillation in the presence of 5 mol% of the catalyst. The zinc salt of 2-ethylhexanoic acid showed the highest catalytic activity. Thus, within 15 hours of synthesis, complete conversion of hexamethylenediamine-1,6 to the corresponding diimine was achieved.

Acknowledgements

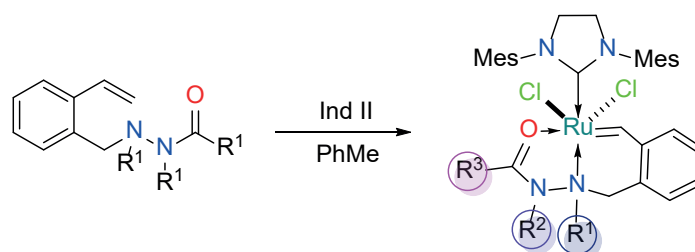
This work was supported by the Ministry of Science and Higher Education of the Russian Federation within the State Assignment (project FZUS-2021-0013).

Structure and properties of hydrazide-chelate of the Hoveyda-Grubbs type catalysts

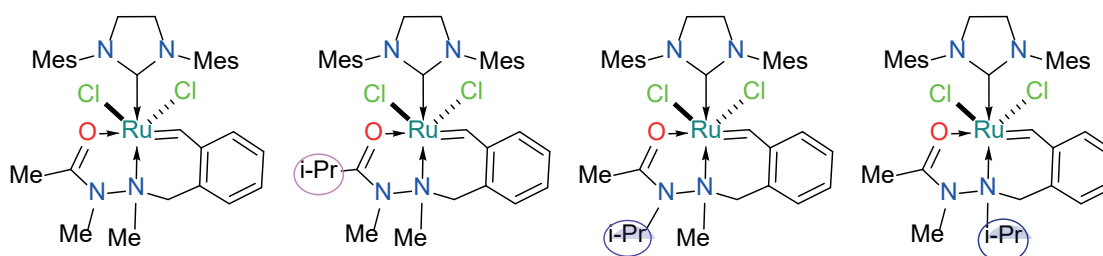
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This work is a continuation of our research team's study of new catalysts for olefin metathesis, which examines the effect of chelate ring expansion in Hoveyda-Grubbs-type catalysts. It is aimed at developing methods for obtaining new hydrazide-containing ligands with various substituents and target ruthenium complexes based on them, as well as studying their structure and properties, as well as revealing the dependence that describes the change in catalytic activity with varying substituents (R^1 , R^2 , R^3) at each of the modification sites present.



As a result of the work, hydrazide-containing benzylidene ligands and ruthenium complexes were obtained.



However, the most important quality of the complexes from commercially available catalysts is their almost complete tolerance to traces of moisture and even the absence of an inert atmosphere, which contrasts with the pronounced sensitivity of the second-generation Hoveyda-Grubbs-type catalyst to these factors.

Acknowledgements

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Stacking interactions: a supramolecular approach to upgrade weak halogen bond donors

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The cocrystallization of tetracyanobenzene (TCB) with aryl halogenides provided the series of new cocrystals TCB•ArX (ArX = PhCl, PhBr, PhI, 4-MeC₆H₄Cl, 4-MeC₆H₄Br, 4-MeOC₆H₄Cl, 1,2-Br₂C₆H₄). All cocrystals were studied by X-ray diffraction. In the obtained structures, we revealed the strong collective effect of $\pi\cdots\pi$ stacking and lone pair-(X) $\cdots\pi$ -hole interactions occurring between tetracyanobenzene and aryl halogenides on the strength of X \cdots N_{ciano} halogen bonding (HaB). Theoretical investigation demonstrated that the stacking interactions affect the σ -hole depth of the ArX, thus significantly boost their ability to act as HaB donors. According to the molecular electrostatic potential calculations, the σ -Cl-hole value (1.5 kcal/mol) in 4-chloroanisole increases significantly in the stacked trimer (TCB)₂•4-MeOC₆H₄Cl (12.5 kcal/mol). Theoretical DFT calculations showed the dramatic increase of X \cdots N_{ciano} HaB strength for stacked trimers in comparison with parent unstacked aryl halogenide.

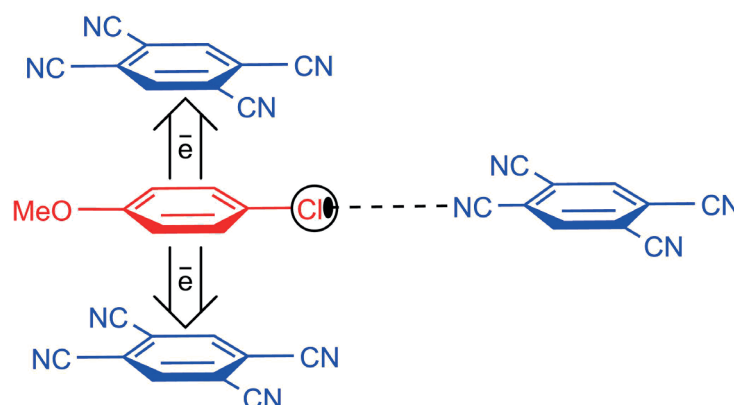


Figure 1. Model representation of the supramolecular organization of cocrystal TCB•MeOC₆H₄Cl.

Acknowledgements

This study was supported by the Russian Science Foundation (projects No 20-73-00038 and 22-73-10031; cocrystal growing and theoretical studies) and the Ministry of Science and Higher Education of Russian Federation in framework of the “Mega-grant” project (No 075-15-2021-585; crystal engineering). X-ray diffraction experiments were performed at the Center for X-ray Diffraction Studies of Saint Petersburg State University.

Synthesis of supramolecular complexes of beta-cyclodextrin with adamantane ureas - new series of encapsulated soluble epoxide hydrolase inhibitors

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A new generation of bioavailable water-soluble inhibitors of soluble epoxide hydrolase, which are supramolecular complexes of adamantane disubstituted ureas with cyclodextrins, was synthesized, and their physicochemical properties, inhibitory activity and metabolic stability were studied. The high lipophilicity of previously synthesized soluble epoxide hydrolase inhibitors ($IC_{50} < 1$ nM) made them a target of metabolic enzymes and adversely affected water solubility, which made their use *in vivo* difficult. In this case, the encapsulation of such highly active inhibitors by the formation of supramolecular complexes with β -cyclodextrin, is an urgent task.

A series of symmetric and non-symmetric ureas as well as symmetric diureas bearing adamantane moiety, promising when used as inhibitors of soluble epoxide hydrolase has been synthesized. For a number of 1,3-disubstituted ureas, complexes with α - and β -cyclodextrin were obtained (Figure 1). It was found that the most suitable method for the preparation of complexes consists in active mixing of stoichiometric amounts of 1,3-disubstituted urea and cyclodextrin in a mixture of ethanol: water (1:3) at a temperature of 80 °C. After evaporating by half, the solution was left to crystallize at a temperature of ~4 °C. The precipitated crystals were analyzed by NMR spectroscopy. Complex formation was determined in the NOESY experiment and by X-Ray crystallography.

Thus, the methods for the preparation of 12 adamantyl-containing and bicyclic isocyanates, and over 200 1,3-disubstituted ureas and diureas based on them were developed and optimized. Also obtained 30 complexes of 1,3-disubstituted ureas with cyclodextrins.

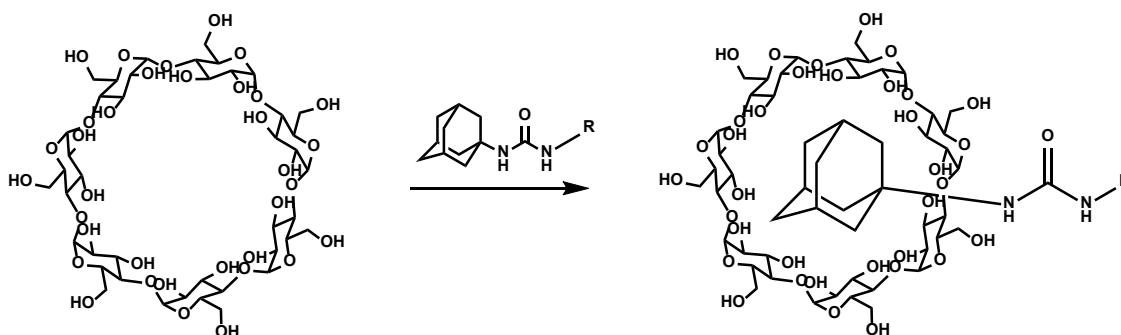


Figure 1. Formation of complexes with β -cyclodextrin

Acknowledgements

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Chalcogen-bonded donor–acceptor complexes of 1,2,5-selenadiazoles with halide ions

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1,2,5-Chalcogenadiazoles are of interest to the fundamental chemistry and its applications in materials science. Chalcogenadiazoles are mostly known for their π -acceptor character, utilized in polyconjugated organic electronic materials. However, they also exhibit σ -donor properties, e.g. in complexes with transition metals, due to the lone pairs of nitrogen atoms, as well as σ -acceptors properties due to the presence of the chalcogen-centered σ -holes capable of secondary bonding interactions (SBIs) / chalcogen bonding (ChB). Currently, such interactions / bondings attract enhanced interest due to their generality and potential applications, e.g. in anion recognition and transport, organocatalysis, supramolecular chemistry and crystal engineering, and materials chemistry.

This contribution presents the results of our study of the interaction of 5,6-dicyano[1,2,5]selenadiazolo[3,4-*b*]pyrazine **1** and 5,6-dicyano-2,1,3-benzoselenadiazole **2**, serving as a σ -hole donors, with halides X^- ($X = \text{Cl}, \text{Br}, \text{I}$), which are typical Lewis bases¹. The complexes isolated and characterized by X-ray analysis are new examples of a family of anionic complexes with chalcogen bonds previously isolated only for 3,4-dicyano-1,2,5-chalcogenadiazoles².

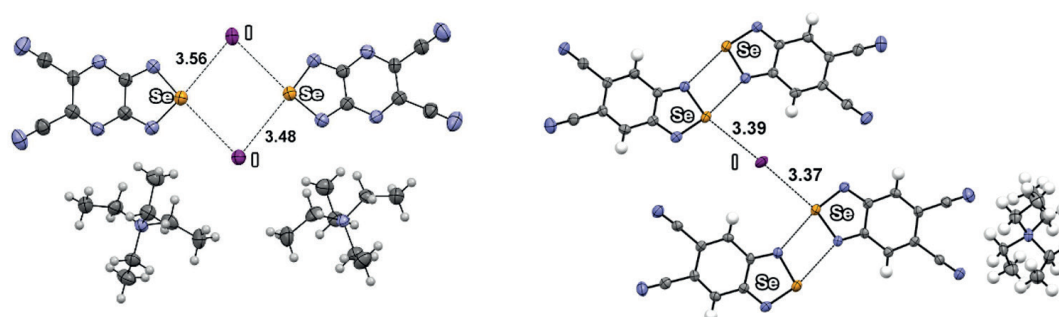


Figure 1. XRD structures of the synthesized complexes **1** (left) and **2** (right) with iodide-ion.

Acknowledgements

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Characterization of novel bimetallic complexes (^tBuPXCYP)Pd(μOC)M(CO)₂L and their reactivity toward HCOOH

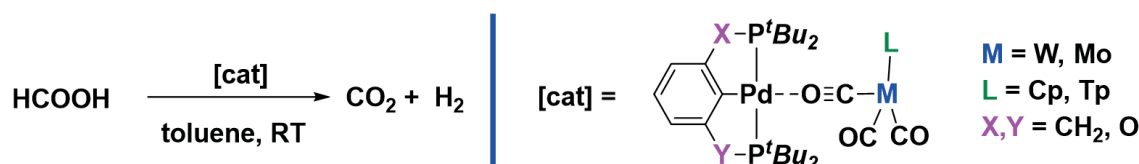
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Since the humanity is still concerned about the problem of finding clean energy sources, hydrogen energy is of considerable interest. However, due to the problems with the storage of gaseous H₂ and its low volumetric energy density, chemical hydrogen storage based on the reversible (de)hydrogenation is an attractive alternative. One option is to use formic acid (HCOOH) because it is a low-toxic liquid hydrogen storage system which contains 4.4 % H₂ by mass.¹ Bifunctional catalysts demonstrate good efficiencies in the processes of homogeneous catalytic dehydrogenation.² It was recently demonstrated that bimetallic complexes (^tBuPCP)Pd(μ-OC)W(CO)₂L³ (L = Cp, Tp) could effectively dehydrogenate amine-boranes (Me₂NBH₃, ^tBuNH₂BH₃).⁴

In this contribution we report the synthesis and characterization of the series of bimetallic complexes (^tBuPXCYP)Pd(μ-OC)M(CO)₂L (X,Y = CH₂, O; M = Mo, W; L = Cp, Tp) and the investigation of its catalytic activity in the formic acid dehydrogenation (Scheme 1). The study of the dehydrogenation process in stoichiometric conditions by IR (ν_{CO}) and NMR (¹H, ³¹P) spectroscopy allows us to find the reaction intermediates. As a result of volumetric studies we demonstrate the effect of ligands, metal atom and temperature on the rate of the catalytic reaction and estimate the TOFs.



Scheme 1.

Acknowledgements

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Alkoxide ligand environment for stabilization of reactive complexes of rare- and alkaline-earth metals

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The unique reactivity of alkyl complexes of rare earth metals and the ability to promote numerous thermodynamically unfavorable transformations, including the activation of inert CH-bonds and the functionalization of marginal hydrocarbons, causes increased interest in the development and design of such complexes. In most cases, in order to achieve the necessary reactivity, as well as to increase the speeds and selectivity of catalytic processes implemented on alkyl complexes of REE, the introduction of an auxiliary ligand environment into the structure of complexes is required, which gives the metal complex the desired steric-electronic load. The tertiary alkoxide anion R_3CO^- , due to its electron-donating nature and the possibility of rigid binding to an oxophilic metal center, can act as an effective, easily modifiable ligand system and meet the required requirements.

In this work, a series of tertiary carbinols was obtained and characterized: $[o-R_2NCH_2C_6H_4]_3COH$ ($R_2 = Me_2$ (**1**), $-(CH_2)_5$ (**2**)), $[o-NMe_2C_6H_4CH_2]_3COH$ (**3**), $[2,4(i-Pr)_2Ph]_3COH$ (**4**) - differing in steric-electron properties. It was also found that carbinols: $[o-R_2NCH_2C_6H_4]_3COH$ ($R_2 = Me_2$ (**1**), $-(CH_2)_5$ (**2**)), $[2,4-(i-Pr)_2Ph]_3COH$ have helical chirality and are represented in the crystalline state as two (P) and (M) enantiomers¹.

The coordination properties of carbinols **1** and **2** were investigated by the example of the formation of potassium alkoxide derivatives. It was found that K complexes easily give adducts with donor molecules – THF, Et_2O . The complexes are dimeric and contain one solvent molecule for each potassium ion in the crystal lattice. In the case of $[o-R_2NCH_2C_6H_4]_3COK$ ($R = -(CH_2)_5$ (**2**)), – none of the donor piperidine groups participates in binding to the metal ion, which makes it possible to obtain low-coordination complexes with coordinated π -aromatic ligands.

Bis(alkyl) complexes of scandium $[o-R_2NCH_2C_6H_4]_2COSc(CH_2SiMe_3)_2$ were synthesized and characterized ($R_2 = Me_2$ (**1**), $-(CH_2)_5$ (**2**)), stabilized by tertiary alkoxide ligands with NR_2 -donor groups. The complexes have sufficient thermal stability and can become excellent precursors for the synthesis of scandium imides, representing a highly reactive class of rare earth metal compounds.

Acknowledgements

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Alkali metal complexes with 1,8-bis(ethynyl)carbazolyl ligands

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Ligands based on substituted carbazoles are widely used in organometallic and coordination chemistry due to the simplicity of their synthesis and wide possibilities for modifying their steric and electronic properties by varying the nature of the substituents in the 1,8-positions of the carbazolyl fragment. The introduction of donor groups (pyrazolyl, PR₂, NHC-carbene) into 1,8-positions of carbazolyl skeleton provides rigid pin-cer-type coordination of these ligands with metal ions. On the other hand, the introduction of aryl substituents into the 1,8 positions makes it possible to obtain low-coordination complexes due to steric shielding of the metal center.

In our study, for the first time 1,8-bis(ethynyl)-substituted carbazoles 3,6-tBu₂-1,8-(RC≡C)₂CarbH were applied as anionic ligands. Novel phenylethynyl substituted carbazole 3,6-tBu₂-1,8-(PhC≡C)₂CarbH was prepared by Sonogashira cross-coupling reaction and along with previously known SiMe₃-containing analogue were used for the preparation of alkali metal complexes [3,6-tBu₂-1,8-(RC≡C)₂Carb]₂M(THF)₂ (M = Li, Na; R = Ph, SiMe₃; Fig. 1). According to X-Ray data and IR-spectroscopy in [3,6-tBu₂-1,8-(RC≡C)₂Carb]₂M(THF)₂ the interaction between M²⁺ and C≡C bond are realized what was proved by X-Ray study and IR-spectroscopy.

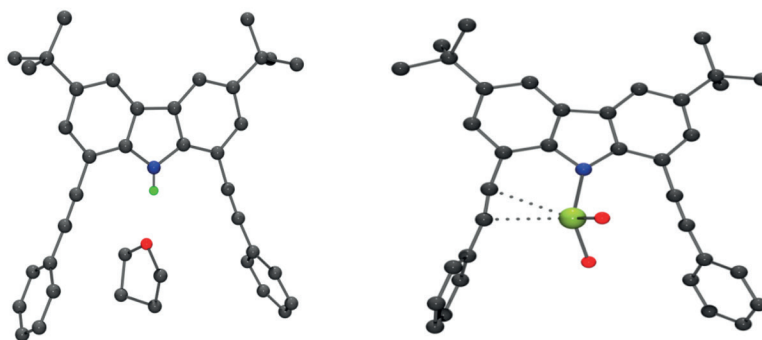


Figure 1. Molecular structures of 3,6-tBu₂-1,8-(PhC≡C)₂CarbH and [3,6-tBu₂-1,8-(Me₃SiC≡C)₂Carb]M(THF)₂ (M = Li, Na).

Acknowledgements

This work has been carried out in the framework of the Russian state assignment.

Synthesis of Adamantyl-containing hindered acids as promising precursors for 1,3-disubstituted ureas

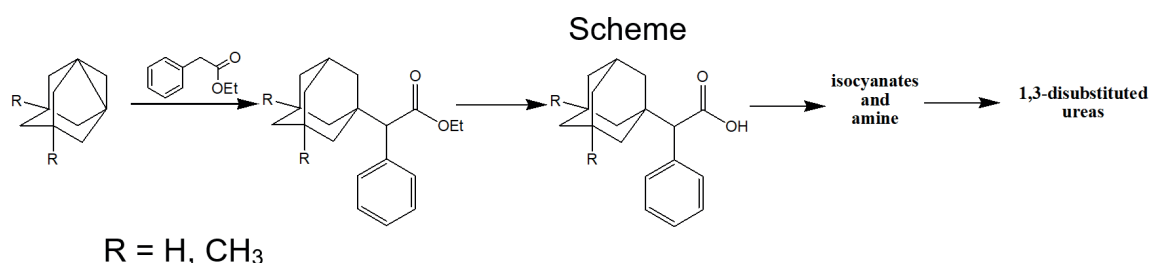
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Adamantyl-containing carboxylic acids, which have large sterically hindered bulky fragments in their structure, have been synthesized. Adamantyl acids are important intermediates for the production of amines and isocyanates, which, in turn, can be used to obtain 1,3-disubstituted ureas, inhibitors of human soluble epoxide hydrolase (sEH). The presence in the structure of molecules of 1,3-disubstituted ureas, closely spaced, bulky fragments of adamantyl (3,5-dimethyladamantyl) and phenyl, will make it possible to determine the possibility of using such structures as sEH inhibitors, since the catalytic center of the enzyme is a "tunnel" of limited size. In connection with this, we carried out a number of syntheses (scheme).



To obtain these acids containing bulky substituents, we carried out reactions of direct adamantylation of an phenylacetic acid ester using propellanes of the adamantane series (1,3-dehydroadamantane and 1,3-dehydro-5,7-dimethyladamantane). The obtained adamantyl-containing esters were subjected to alkaline hydrolysis using potassium hydroxide in ethylene glycol to obtain acids (55-67% yield). Due to steric hindrance, these ethers do not undergo hydrolysis in acidic and alkaline environments when using solvents such as ethyl alcohol, water, and their mixtures in various proportions. Moreover, heating to 100°C and using ultrasound also did not lead to hydrolysis. From the synthesized acids, isocyanates and amines were obtained, which were subsequently used for the synthesis of 1,3-disubstituted ureas in reactions with fluoro- and chloroanilines, fluoro- and chlorophenyl isocyanates, respectively.

Structure of 2-(adamantan-1-yl)-2-phenylacetic acid confirmed by X-ray diffraction. All obtained 1,3-disubstituted ureas are potential inhibitors of soluble epoxide hydrolase (sEH).

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