Research program of the Institute of Inorganic Chemistry of the Czech Academy of Sciences in 2018-2022

The research conducted at the Institute of Inorganic Chemistry (IIC) is oriented to the preparation and structural elucidation of novel inorganic molecules and materials and full experimental and theoretical analyses of their properties and functionalities.

The researchers of the Institute are committed to:

- Maintain the high standard of their explorative scientific activities
- Enhance their global visibility and impact on science
- Apply their chemical knowledge to the needs of society
- Maintain the ethical standards of their scientific work
- Educate students and public

To fulfill our mission we focus our research on the following areas:

- **Light-responsive inorganic molecules and materials**
- **Chemistry of boron compounds**
- **New materials for a sustainable environment**
- **Conservation and cultural heritage science**
- **Geochemical analysis of sediments**
- **Applied research**

This program is based on core research competencies in established areas of IIC expertise, but is flexible to the changing trends in modern science, national and international grant funding priorities, and mobility of scientific staff. The fulfillment of this research program is discussed by the Institution's board at the end of each year.

Light-responsive molecules and materials

This research domain seeks to discover and develop novel molecules, nanostructured materials, and (nano)materials with inherent luminescent (fluorescence, phosphorescence, oxygen- or temperature-dependent luminescence) and photosensitizing properties. The focus will be on systems that satisfy critical parameters such as stability in water, photostability, transparency, and non-toxicity, and that display useful interaction with surrounding components, gas or ion diffusivity, and bio-compatibility.

These novel molecules and materials will be investigated in their pure solid form, as solutions and dispersions, embedded in polymers (fabrics, films, nanoparticles, coatings), or incorporated into organic or inorganic nanoparticles that provide additional functionalities (e.g., antenna effect, covalent bonding with a matrix, host-guest interaction, ion-responsive luminescence).

Studied types of photoactive entities:

Transition metal (e.g., Mo, W, Re, Cu) cluster complexes and porphyrinoids. The aim here is to develop new cluster complexes as biomaterials with photodynamic and radiosensitizing properties. IIC scientists were the first to propose that such cluster complexes constitute versatile theranostic tools with desirable features such as high luminescence quantum yields, production of singlet oxygen, and high radio-opacity making them useful as contrast agents, and radioluminescent properties attractive for X-ray luminescence computed tomography or X-ray induced photodynamic therapy of cancer. In this respect, we propose to synthetically tune these cluster complex biomaterials for efficient *in-vitro* and *in-vivo* singlet oxygen photosensitization and radiosensitization with a special attention to specific cancer cell targeting. We envisage a promising future for these materials in antimicrobial coatings, for use in photodynamic therapy, and in oxygen sensing, due to their high photostability that enables their application over long periods and gives efficient production of cytotoxic singlet oxygen.

Organized assemblies of porphyrin units. Here the proposed materials belong to the family of porphyrin-based covalent organic frameworks and metal-organic frameworks. Porphyrin units, which have the ability to produce singlet oxygen upon visible light irradiation, will serve as building blocks for biomaterials with novel functional entities designed to enhance specific photophysical and photochemical properties. The variability of the joining moieties will enable the control of the surroundings of the porphyrin units and prevent their close contacts, *i.e.*, providing structural control that, in turn, enables the tailoring for photophysical applications. These materials will be developed for application in areas such as photodynamic antimicrobial coatings, photodynamic therapy (especially in the form of nanoparticles), and site-specific oxygen sensing.

Luminescent borane molecules. We have shown recently that solutions of the macropolyhedral borane *anti*-$B_{18}H_{22}$ show laser emission with a good efficiency and an outstanding resistance to photodegradation when compared to commercial organic laser dyes; making it the first laser borane. We hope to expand on these promising beginnings and delineate a full understanding of the potential and limitations of this and other new luminescent borane molecules at a fundamental level with an aim to maximize laser efficiency and photostability, and offer emission at tunable wavelengths. The successful completion of these aims will introduce the boranes as novel and competitive alternatives to present organic laser dyes. In addition, our intention is to prepare and study polymer systems as thin film matrices for newly synthesized luminescent boranes, probe and investigate the behavior of the borane/polymer thin films in an electric field, and determine the relationship between the structure and properties of the luminescent borane compound and the polymer in which it is embedded at a fundamental level with the ultimate aim to create electroluminescent devices.

Chemistry of boron compounds

The study of boron hydride chemistry belongs to a core competency of the IIC. The IIC boron group has undergone a diversification from its traditional focus on new types of boron hydride clusters to include a spectrum of potential outlets for the chemistry, such as in biomedicine, surface chemistry, weakly coordinating anions, extraction agents for radionuclides and optics.

Systematic synthetic chemistry of carboranes and metallacarboranes. During last years, the very stable cobalt bis(dicarbollide) anion has become an increasingly important structural motif for the design of new biologically active compounds and materials. Our ambition is to find new pathways for direct substitution in various, still inaccessible, geometric positions of the cage by groups enabling easy interconnections with other fragments and, thus, tuning three-dimensional interactions. We shall also strive develop synthetic routes to asymmetric substitutions with two different groups: (i) with high reactivity (e.g., amines, carboxyls, hydroxyls, thiols), (ii) providing additional biochemical interactions (e.g., with an enzyme cavity, immobilization to surfaces).

We also plan to extend alkylation strategies into the area of 10-vertex dicarbaborane and 11-vertex tricarbollide skeletons with the aim of constructing organized globular molecules. Thorough understanding of the chirality of carboranes and metallacarboranes, and its consequences for medicine and asymmetric catalysis, remains a bottle-neck to further development of the field. We plan to focus on the synthesis of racemic boron cluster compounds, develop methods of their enantioseparation, and study their interactions with model chiral hosts. In particular, our ambition is to understand chiral phenomena in respect of the contemporary development of boron drugs.

Biologically active compounds. Carbonic Anhydrase-IX (CA-IX) is a target enzyme for the anti-metastatic treatment of hypoxic tumors. Recently, we designed (metalla)carboranes which serve as specific and selective inhibitors of the CA-IX isoenzyme. Looking forward, we intend to focus on further optimizations of inhibitor structures, design and synthesis of CA-IX-selective diagnostic probes for radioimaging and MRI methods, and structural modifications enabling specific targeting of CA-VII, the isoform associated with brain diseases.

We discovered (in collaboration with IMTM Olomouc) that some boron compounds cross gastrointestinal and/or blood brain barriers. We anticipate the continuation of this study, *i.e.*, the syntheses of modified (car)boranes designed for several newly selected targets and the exploration of their pharmacology. In particular, we plan to investigate structural factors that enable compounds to cross the biological membranes/barriers, identify putative transporters responsible for active transport, and to employ this knowledge in designing drugs potentially useful for the treatment of multidrug resistant CNS infections and/or brain cancer.

Boron cluster molecules for self-organized nanosystems. This research theme targets mainly two-dimensional surface-supported and self-organized structures and patterns of borane and carborane constituents. The interest will be focused on the functionalization of the rigid carborane cores, its impact on their lateral interactions, and their interactions with the outer environment. Special attention will be paid to the translation of single constituent inherent properties to collective properties of the respective two-dimensional assemblies, and thus to our better understanding of self-assembly principles and driving forces. The obtained knowledge will be applied to building blocks design towards functional nanosystems applicable in areas that range from electronic devices, molecular recognition systems, and anti-corrosive surface treatment to sensing and responsive materials in biology.

Theoretical chemistry of polyhedral boron compounds. We intend to evaluate paramagnetic ^{11}B NMR spectroscopic parameters of metal-containing borane clusters at the high computational level. Previously, the development of the chemistry of these compounds has been limited due to the difficulty of their NMR characterization. Another aim is the analysis of electronic structure in boron clusters and the prediction of molecular sites for possible substitutions. Further theoretical and experimental investigations of chalcogen and pnictogen bonding are intended, mainly in relation to the mechanism of inhibition of various enzymes. Various heteroboranes will be tackled by means of gas-phase electron diffraction, where the resulting structure is determined unambiguously, the corresponding internal coordinates can test the reliability of various computational protocols.

Chemistry of main group metal heterocyles. This chemistry is focused on the synthesis of the new family of heterohelicenes built from fused siloles with up to 20-30 condensed heterocycles, the longest helicene known so far. We are expecting to obtain new types of saturated and unsaturated (poly)heterocyclic compounds containing B, Si, Ge, Sn, O, S, and N in various combinations. These compounds are potentially useful for molecular electronics and capacitors.

New materials for a sustainable environment

A growing global population dramatically increases the level of pollution in all components of the environment, the atmosphere, water and soil. This research activity will focus on searching for new materials, and on optimizing the properties of known types of materials, for environmental applications and use under real conditions.

Photocatalytic materials. We have already introduced many new catalysts for the photodegradation of pollutants. The most promising are composite materials, which we intend to investigate further, in particular with respect to the optimization of their synthesis, photocatalytic activity, stability, specificity, and adsorption rate, kinetics and degradation mechanisms of various pollutants. Composites with graphene, nanodiamonds, carboneus or other quantum dots can bring substantial progress in developing highly active photocatalytic materials.

Despite the enormous effort to find alternatives, nanostructured TiO_2 remains the most promising material for photocatalytic applications in the environment. Here, our research will focus on the optimization of its properties with regard to applications in photocatalytic coatings and building materials. We also anticipate the development of a "floating photocatalyst" that combines sorption and photocatalytic properties and could be used to purify surface waters from low concentrations of stable aromatic pollutants, including biphenyls and dioxins.

Reactive sorbents. We have developed reactive sorbents with high activity towards organophosphorus pesticides and chemical warfare agents. These materials are useful for protection and decontamination purposes in military and civilian areas. The stability of sorbents in various matrices, solvents, or thin films is crucial for practical applications. To achieve these interests, we are planning to continue in cooperation with the Military Research Institute in Brno and our industrial partners in developing applicable forms of reactive sorbents. In this regard, thin layers seem to be a very promising area, therefore we intend to investigate various binder systems that have a high permeability for gases, which can be then used, for example, for protective paints. We will focus on the description of their degradation mechanisms and the effects of various reaction conditions. We will elucidate also degradation of cytostatic drug on these materials, especially the kinetics and mechanism of their decomposition on nanoparticle surfaces.

Layered materials. We will investigate exfoliation techniques to produce graphene or other two-dimensional materials in good quality and high quantity (e.g., methodology based on new ultrasonic reactor with cascatrode instead of sonotrode). We are aiming at the production of graphene stabilized in various solvents and matrices and the fabrication of new graphene-polymer composites with applicable mechanical or electronic properties. In addition, graphene-based composites with a high sorption capacity for radionuclides (^{137}Cs, ^{85}Sr, etc.) will be fabricated and investigated.

We will pursue the removal of cytostatic drugs using these nanomaterials. Our preliminary results showed their very good sorption capacity. Therefore, we are planning to develop a cleaning sorbent for accidental contamination by these hazardous compounds. We will study the toxicity and behavior of graphene or related nanomaterials in living cells. The stability and non-toxicity of graphene will allow us to investigate their medical applications, for example their use as nanocarriers for drugs and composites with organometallic species.

Two-dimensional materials (graphene, layered double hydroxides, etc.) will also be used for the fabrication of polymeric matrices with combined conductive, magnetic, or thermal properties. Interfacial interactions between these materials and polymers will be adjusted using ionic liquids in order to control the resulting structure from the nanometric scale upwards.

Other materials that we are interested in include MAX phases. We will focus on their preparation and investigation of the changes in mechanical properties and structure after neutron and high-energy-electron bombardment. These materials offer promising applications in the field of the surface treatment of the inner and/or external construction parts of nuclear reactors, or as mechanical and chemical protection for the surfaces of fuel cells.

Coordination polymers. Metal-organic frameworks (MOFs) are a class of crystalline porous polymers which combine inorganic nodes with organic linkers. We aim to investigate MOFs for degradation of organophosphorus pesticides and chemical warfare agents in order to specify degradation mechanisms and factors affecting the degradation efficiency. In addition, we are planning to develop novel MOF–polymer composites, with polymers embedded in the pores, for enhanced gas separation. For this purpose, we will employ already described MOFs with larger micropores or mesopores. We also propose new class of MOFs with very high thermal stability and stability in solvents, having potential applications in biology and gas storage.

Magnetic and thermoelectric materials. The main focus will be on the syntheses of multiferroic and thermoelectric materials and composites for energy-saving electronics. These materials will be studied in the form of thin films and ceramics. We will combine the Mössbauer spectroscopy with methods of structural analysis and magnetic properties in order to explore the potential use of magnetic (nano)materials in medicine.

Conservation and cultural heritage science

The preservation and interpretation of the European cultural heritage is an important challenge relevant to modern society. Considering this high societal impact, we will continue in performing interdisciplinary research, focusing on the application of inorganic chemistry to the advanced materials microanalysis of art objects and the study of chemical degradation processes of pigments in paints. Within a joint workplace of the IIC with the Academy of Fine Arts in Prague (ALMA) the results help in the evaluation of works of art in terms of their originality, age, provenance, and in implementing innovative conservation approaches.

Microanalysis of pigments. Modern non-invasive tools and techniques will be used for *in situ* studies of paintings. We plan to improve and evaluate the methodology of the microanalysis of less investigated paint components, e.g., clay pigments, using powder micro-XRD and supplementary methods (e.g., micro-ATR FTIR), and critically assess all the procedures for obtaining reliable results. Further tests will be focused on the detection of minor or trace elements accompanying mineral pigments as a part of provenance studies of historical paintings and related technologies (glazes, glass mosaics, etc.).

Degradation and alteration processes. We plan to perform an extensive study of saponification, which results from the interaction of metal elements (typically Pb, Zn) with fatty acids of oil-based binding media. Neo-formed metal soaps cause an increase in transparency of the affected layer and, finally, blistering and sloughing of the painting surface. The planned research aims to describe conditions promoting the formation, growth, and aggregation of metal soaps and to assess ways to stop or slow down the process. Furthermore, yet unexplored processes of salt corrosion in mural paintings will be investigated in order to rationalize color changes and other undesirable processes leading to, for instance, the formation of highly soluble arsenates.

Geochemical analysis of sediments

We plan to continue studies on polluted fluvial systems, in particular floodplains, in aim to reconstruct past chemical pollution, characterize pollution hotspots, predict the future fates of pollutants retained in fluvial sediments, and contribute to the knowledge on fluvial deposition/erosion processes. The main strategic partners are the Faculty of Environment, University in J. E. Purkyně in Ústí nad Labem, Faculty of Science in Palacký University in Olomouc, and the Institute of Geology of the CAS.

We will continue study on the fossil-barren lacustrine sediments of the Most Basin using chemo-, cyclo-, and magneto-stratigraphy with an aim to reconstruct climate changes around the Miocene Climatic Optimum (after 17 million years before the present). The geochemical information we generate will be interpreted in terms of the paleoenvironment, and thus contribute to the broader global picture of climate changes under unstable polar ice sheets. The main strategic partners are the North Bohemian Mines, Ltd. and the Institute of Geology of the CAS.

In addition, we will continue to collaborate with researchers of other institutions, who are interested in use the know-how in chemical analysis of sediments, which we have gathered in the last 10 years.

Applied research

We will continue to cooperate with private subjects to fully utilize the potential of the compounds and materials developed within the IIC.

Construction materials

- Realization of the pilot scale production of inorganic agents for remediation of facades suffering with green algae and molds; the optimization of photocatalytic SiO_2-TiO_2 composites for self-cleaning surfaces.
- New inorganic matrices for reparation of concrete surfaces in nuclear industry and the development of a new generation of materials shielding neutron and gamma radiation with increased ballistic properties.
- Environmentally friendly types of concrete with new ecological binders for reconstructions of roads by cold recycling technology "*in situ*".
- New technology of 3D printing based on original inorganic systems enabling printing of artifacts for art design, ceramic-like and artificial sandstones.

Boron compounds. Salts of $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ ions and their derivatives are widely applied as solid electrolytes for batteries, in drug design, boron neutron capture therapy, catalysis, and in automotive industry. We developed new technologies for the production of $B_{10}H_{10}^{2-}$ and anhydrous $M_2B_{12}H_{12}^{2-}$ or $MB_{12}H_{12}$ (M= Li^+, etc.). These technologies will be subject of larger scale verifications and licensing. We will participate in a process development for the separation of minor actinides from radioactive wastes using liquid-liquid extraction technology (under EU Project GENIORS 2017-2020). Our tasks are directed to elucidations of the stability and degradation pathways of organic ligands and solvents under high doses of ionizing radiation.

Inorganic sorbents. Recently, we described a new form of metatitanic acid with the high adsorption capacity for radionuclides and heavy metals. We anticipate the development of the technology for the production of this material.

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