Research Agenda of the Institute of Inorganic Chemistry of the Czech Academy of Sciences in 2023-2027

The scientific activity of the Institute of Inorganic Chemistry (IIC) is focused on various aspects of inorganic chemistry. Inorganic chemistry is developing dynamically and its influence is increasing to other areas of natural sciences, such as materials, physical, medicinal and environmental sciences, and others. The research conducted at the IIC is focused on preparation and structural elucidation of novel inorganic or organic-inorganic molecules and materials, and experimental and theoretical analyses of their properties and functionalities. In addition, the IIC is a home of two interdisciplinary laboratories developing approaches and methodologies on foundations of inorganic chemistry in cultural heritage science and environmental geochemistry. All these activities contribute to major national objectives and societal goals such as new medical practices, advanced materials for high-tech applications, sustainable environment, and the preservation of monuments and fine arts. This mission has evolved from core research competencies in the IIC, but remains flexible to the changing trends in modern science, national and international grant funding priorities, and the mobility of scientific staff.

The focus of the IIC is devoted to fundamental research, to which most projects and research efforts have been focused, original syntheses, and the delineation of functionalities using advanced techniques available at the IIC or through national and international collaborations. Importance of applied research is increasing, and with rare exceptions our collaborative work with companies is based on our unique know-how and evolves from our ideas and results of own fundamental research.

The research agenda is the continuation of the successful research in 2018 – 2022. The program is flexible to changing trends in modern science, national and international grant funding priorities, and mobility of scientific staff. The goal of the management is to systematically keep working conditions of the employees at high standards, including liberate conditions favorable to new multidisciplinary topics, which were enriched and diversified in last years to cover new inspiring ideas coming from medicine, surface chemistry, molecular biology, or environmental protection. The research agenda can be revisited and updated based on new achievements, endeavors, and progress.

The researchers of the Institute are committed to:

- Maintain the high standard of their 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.

Identified research priorities in the IIC:

- **Chemistry of Boron**
- **Photoactivatable Inorganic Molecules and Materials**
- **Advanced Sorption Materials for Environment**
- **Conservation and Cultural Heritage Science**
- **Environmental Geochemistry**
- **Applied Research**

1. Chemistry of Boron

Boron hydride chemistry is a core competency of the IIC with a rich history and worldwide reputation. The topic 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, catalysis, surface chemistry, extraction agents for radionuclides, and luminescence/optics.

Boranes in Medicinal Research. In 2019 we described that some metallacarboranes act as specific Carbonic Anhydrase IX enzyme (CA IX). Occurrence of this enzyme in cancer tissues is associated with development of metastases and poor patient prognosis, and its inhibition presents target for cancer therapy and diagnostics. We will continue in the development of anticancer drugs and advanced diagnostic tools based on this discovery. In addition, we will work on compounds for boron neutron capture therapy, boron proton capture therapy, the fight against bacteria and civilization diseases. To achieve these goals we will utilize methods of organic and boron cluster syntheses combined with methods of medicinal chemistry. Another aim is connected with electrochemical labelling of biopolymers with modified boron clusters. Indeed, we have shown that the clusters are promising new electrochemical labels of biomolecules with a tunable electrochemical response. Together with our partners we will search for specific bonding of newly designed boron clusters to fragments of DNA and peptides.

We will also focus on planar and axial chirality of boron clusters, which is still grossly underdeveloped area. We plan to prepare representative set of chiral ionic and neutral boron clusters and develop *semi*-preparative separation techniques for their enantioseparation. This research might result in new unconventional types of chiral molecules for applications in chiral recognition, medicinal chemistry, and enantioselective catalysis.

Boranes as Luminescent Materials. There is a demand in the fields of optoelectronic devices, energy conversion, luminescence sensing and bioimaging, and photodynamic therapy, for efficient luminescent materials. Here, there is renewed interest in the binary boron hydride cluster compound anti-$B_{18}H_{22}$ since our discovery of its utility as a new class of laser material. Future work will seek to establish new controlled synthetic routes to substituted macropolyhedral boranes via the fusion of more easily-synthesised, pre-substituted nonaborane and heterononaborane species. This will afford boranes with substituents that are not available by current techniques. We will thus delineate the effect cluster-fusion has on the mobility of substituted boron vertices, whilst generating a portfolio of novel macropolyhedral inorganic cluster compounds that are very likely to display extraordinary luminescence. From these efforts we anticipate a series of entirely novel, highly stable and efficient luminophores potentially useful in laser technology and a multitude of other areas requiring the efficient and stable conversion of UV radiation into visible light.

Boranes and Carboranes in Surface Science. We follow the line of investigating these building blocks as parts of molecular arrays to better understand the fundamental principles of self-assembly including the role of weak but long-range dipole-dipole forces or short-range van der Waals interactions. We will continue our synthetic work on designed cage molecules which allow us to systematically explore the relation between their properties and specific function of their molecular assemblies and exploit them as precursors for molecularly thin, self-supporting membranes with applications ranging from electronics to filters or catalysis. We will (i) proceed in mapping of dipole-driven patterns hidden within hexagonal arrangements of (car)borane molecules; (ii) investigate quasi-periodic 2D structures made of molecules with accentuated pentagonal symmetry in order to achieve tiling of the surface, and (iii) use chiral carboranes to investigate spin-selective electron transport through respective self-assembled monolayer barriers. Within cluster-flat surface analogy, we will further explore the area of hybrid clusters with metal core and boron-based shells, focusing mainly on bigger clusters. We anticipate a growing interest in these molecules and derived materials as well as their various applications.

Theoretical Chemistry of Polyhedral Boranes. We will continue our efforts in terms of evaluating paramagnetic and diamagnetic ^{11}B NMR spectroscopic parameters of metallaboranes at the high computational level. Further theoretical and experimental investigations of various types of bonding associated with this class of materials will be pursued. The point is that the concept of multicenter bonding appearing in boron clusters has not been so far researched explicitly. The recently tackled new era of boron-cluster-based cationic species will be expanded, both experimentally and computationally with an emphasis on the search of reaction mechanisms of their originations and possible applications in medicinal chemistry. In addition, supporting the efforts described in the previous paragraphs will be a theoretical/computational approach, enabling elucidations in structure and properties of newly made molecules.

Activated Borane – a Porous Borane Cluster Network. Activated borane is a new microporous material developed at the IIC. It is based on borane clusters and organic molecules bound together by B-B and B-C bonds. This new class of porous polymers has an unprecedented chemical nature and untapped application potential. We will develop the synthetic protocol for tuning the properties and provide characterization data on the structure. We foresee the broad application potential of Activated Boranes in the area of the adsorption of pollutants, in drug delivery and heterogeneous catalysis.

Boranes as a Fuel. Among the aneutronic reactions, the fusion of protons with boron atoms ($p + {}^{11}B \rightarrow 3\,{}^{4}He$) appears the most promising candidate, due to the relative abundance of boron as a fuel and the ease of its handling. Amongst the main unresolved question is better understanding of what the ideal fuel for p-^{11}B actually is. We are at the beginning of an interdisciplinary project seeking to investigate and possibly validate the use of molecular boranes as a viable ideal fuel for p-^{11}B fusion.

Borenium Salts for Sensors. Recently a new direction of research has focused on cationic boranes (borenium species) as strongly Lewis acidic compounds. We will use them as components for construction of Frustrated Lewis Pairs and later on for transition-metal free catalysis. Moreover, some of those molecules display luminescent properties that are tightly associated with their unquenched acidity. We will explore the opportunity to utilize them as molecular sensors. The present research brings new perspectives within the traditional areas of research – boron chemistry and development of photoactive materials.

2. Photoactivatable Inorganic Molecules and Materials

This research domain seeks to develop molecules and (nano)materials with inherent photo-induced properties as theranostic tools for photo/radiobiology, effective phosphors, scintillators, sensitizers for photodynamic therapy, bactericidal and virucidal surfaces, and photocatalysts. The entities involved are transition metal complexes, composite (nano)materials, nanostructured surfaces, and transition metal oxides. The research involves syntheses, understanding the mechanisms behind their functions, and optimization of their properties towards applications:

Transition Metal Cluster Complexes. This segment of coordination chemistry studies at the IIC includes predominantly Mo, W, Re, Cu, Au, Ag atoms. Especially, the octahedral cluster complexes $[\{M_6L^i_8\}L^a_6]^n$ (M = Mo, W, Re; L^i = I, S, etc.; L^a = organic/inorganic ligands) were identified as suitable photofunctional entities for medicinal, luminescent, radioluminescent, and materials applications. We will continue in the development of new cluster complexes and their assemblies with nanocarriers for photodynamic therapy, X-ray-induced photodynamic therapy, sensors, and photoantimicrobials. There are challenges to solve (i) the use of alternative sources of excitation with greater penetrability into tissues to produce reactive oxygen species in deeper locations (two-photon excitation, X-rays, etc.); (ii) exploration of the complexes as potential nanoscintillators for X-ray luminescence computed tomography or X-ray contrast agents; (iii) photo-induced antiviral activity; (iv) development of biomaterials composed of the complexes with a tailored shell of tumor-targeting moieties, ensuring prolonged circulation, negligible interaction with serum proteins, and superior tumor-specific accumulation.

Porphyrinoids. This research area involves porphyrins, phthalocyanines, subphthalocyanines, etc. as standalone molecules or their assemblies (e.g., metal-organic frameworks, nanoparticles, polymer-based nanotherapeutics). The construction of assemblies will enable control of the surroundings of the porphyrinic units and prevents their close contacts (aggregation), i.e., the structural control will allow for constructing materials with proton conductivity (mostly coordination polymers) and a number of biomaterials for light-induced applications such as photodynamic antimicrobial coatings, photodynamic therapy, polymer-based nanotherapeutics with activatable porphyrinoids for theranostics, and sensing.

Photocatalytic Materials. This agenda is based on our expertise in the area of photocatalytic materials for degradation of pollutants on the surfaces of nanosized metal oxides and their composites. In this respect, two-dimensional (2D) nanomaterials show a great promise. We will develop composite materials based on photocatalytic metal oxides (TiO_2, CeO_2, etc.) with 2D nanomaterials (e.g., metal diborides, carbon nanostructures) delaminated using the ultrasonic technology developed at the IIC. The photocatalysts, also in the form of floating photocatalysts, will be utilized for degradations of low concentrations of stable toxic pollutants in water such as pharmaceuticals, endocrine disruptors, pesticides, PCBs, dioxins, DDT, and nanoplastics in water supplies. The degradation mechanisms will be also investigated. In addition, we will utilize developed photocatalysts in electrochemistry, water splitting, and the design of bactericidal surfaces.

3. Advanced Sorption Materials for Environment

This research program capitalizes on our previous research on sorption materials oriented on removal/degradation of pollutants including endocrine disruptors, pesticides, organophosphates from environment.

Reactive Sorption Materials. Materials such as CeO_2 and its composites (e.g., with graphene oxide, aluminosilicates) are capable to remove and decompose chemical warfare agents, pesticides, endocrine disruptors, drugs, or VOC. In further research, we will focus on developing these smart materials with high degradation efficiency against multitude of pollutants, if possible accelerated by photocatalysis. We will tackle emerging pollutants such as perfluorinated chemicals and substances increasing resistance to antibiotics, and bio-pollutants (viruses and bacteria). Our intention is to develop durable, nontoxic sorption materials that can be regenerated and reused. The design of surface acidity/basicity of these materials should allow controlling the selectivity of sorption for various pollutants.

A new direction has emerged from our research of nanosized metal oxides, especially CeO_2 (called nanoceria), which shows multi-enzyme mimetic ability. We will further investigate phosphatase-like activity of nanoceria for cleavage of phosphodiester bonds in biomolecules (e.g., phospholipids, DNA) that can be utilized in therapeutics and biomedicine. We also intend to investigate antioxidant enzyme-like activities of nanoceria and its reactive oxygen species-generating properties for targeting cancer cells and bacteria, sterilization, disinfection, and preventing the formation of biofilms.

Coordination Polymers. Metal-organic frameworks (MOFs) are a class of crystalline porous polymers. We aim to investigate aqueous stability of MOFs (mostly zirconium-based MOFs) and to exploit possibilities to synthesize novel MOFs based on phosphinate coordination groups with high stability in aqueous dispersions and biological media. Elucidated functionalities will include sorption of emergent pollutants, proton conductivity, and semiconducting properties.

Inorganic Ion-Exchange Materials. The materials based on metatitanic acids, iron containing compounds, and graphene-zeolite composites will be developed for removal of radionuclides, heavy element ions, or other polluting ions (e.g., SeO_4^{2-}) from water supplies. We will focus on structural aspects of these materials and factors to affect their functionality. Some modifications are expected to endow these materials with antibacterial properties in addition to efficient sorption of pollution ions.

Two-Dimensional Materials. These materials (graphene, layered double hydroxides / alcoxides, etc.) will be investigated as sorbents of polluting ions. Some of them will be modified by various ionic liquids and utilized as heterogeneous catalysts for ring opening polymerization. The ionic liquids will be based on coordination complexes and organometallic compounds.

4. Conservation and Cultural Heritage Science

The preservation and interpretation of the European cultural heritage is an important challenge for modern society. Numerous risks leading to deterioration of monuments related to climate change or overtourism newly appeared. In this respect, we will continue with interdisciplinary research focused primarily on paintings, within the joint workplace of the IIC with the Academy of Fine Arts in Prague. Systematic research of painters' inorganic pigments will be focused on the search for their origin and on the processes of their interactions with organic components of paint layers and/or surroundings leading to color and mechanical degradation. The results will be applied in the evaluation of works of art in terms of their originality, age, provenance, and in the implementation of innovative procedures for their protection and restoration.

Provenance Research. The procedures of advanced non-invasive and non-destructive instrumental microanalysis of paints will be explored with emphasis on the phase and structural analyses of pigments. Together with advanced elemental analysis, e.g., trace element detection, it will be possible to differentiate their origins and to track and link the paths of the materials and technologies with the paths of the artists, which is very challenging and demanded task.

Degradation and Alteration Processes. Our motivation is not only to describe, but also explain mechanisms of numerous degradation processes occurring in paintings with the aim to prevent them. Within an extensive study of pigment-binder interactions, especially saponification (i.e., growth and migration of metal soaps in paint layers causing blistering and flaking of the painting surface), the mechanisms of crystallization of metal-organic species will be primarily studied, which can be a principal factor determining the riskiness of the entire process. The effects of light and climatic factors will be monitored as well, also for other degradation processes responsible for color changes in paintings (e.g., As, Cd, and Pb pigments' transformations).

5. Environmental Geochemistry

The program is focused on the integration of inorganic chemistry to holistic case studies on anthropogenically impacted fluvial and reservoir sediments and soils. The key study areas will involve contaminated floodplains, dam reservoirs, and soils in human-impacted landscapes. Chemistry expertise will be used for distinguishing anthropogenic contamination and geochemical anomalies in sediments and soils.

Contaminated Floodplains and Reservoirs. This topic will include evaluation of the spatial distributions of contaminants, in particular risk elements, in sedimentary bodies, i.e., in the floodplain architecture and reservoir sediment stratigraphy. Studies will be focused on risk elements, their subsurface/vertical migration, and uptake of risk elements by plants as a gate to the food web. Risks of risk element remobilization by human inherences to rivers and reservoirs will be evaluated including dating of sediments to reconstruct contamination history.

Distinguishing Anthropogenic and Natural Geochemical Anomalies in Soils. Concentrations of risk elements in sediments and soils reflect geology/geochemistry of parent rocks, pedogenic processes, element segregation by soil- and sediment transport, and possible anthropogenic contributions. Differentiation of anthropogenic contributions remains challenging in real landscapes, including analyzing impacts of soil acidification as specific anthropogenic effects. Works will be mainly performed in the north-western areas of the Czech Republic, with geological complexity and anthropogenic impacts much above what is common at the Central European scale. This complexity requires detailed and carefully planned geochemical mapping in selected areas. Geochemistry data mining will include advanced tools of compositional data analysis respecting mathematical properties of those datasets and inter-element relationships.

6. Applied Research

We will cooperate with private subjects to fully utilize the potential of the compounds and materials developed at the IIC especially in these areas:

New inorganic materials for higher safety in the nuclear industry – this area includes, e.g., core-catcher sacrificial materials; inorganic materials for shielding of ionizing radiation; high-stability concretes for nuclear industry.

Environmental applications - this area includes, e.g., remediation of biotically attacked plasters, facades, ceramics, wood, and concrete blocks; water stabilization and purification; eco-concretes; development of 3D printing technology for ecological materials; metal-free catalysts; advanced sorption materials for purification of water and removal of radionuclides, heavy metals, chemical warfare agents, and persistent organic compounds.

Projednáno na 128. jednání Rady Ústavu anorganické chemie AV ČR, v.v.i., které se konalo per rollam od 15.11. – 20.11.2022.