

Assembly-by-Design: Polyhedral metal complexes as molecular building blocks of functional supramolecular assemblies (FunSup)

The development of highly complex chemical systems, self-assembled by the donor-acceptor and/or noncovalent interactions, lays at the core of supramolecular chemistry. Continuously growing demand for innovative solutions stimulates the chemistry world, i.e., to design and develop new molecular building units or to perform rational syntheses of materials with desired functionalities.

Multinuclear metal complexes with proper geometric requirements can act as linkers and secondary building units (SBUs) of a vast range of metal-organic frameworks (MOFs). They can also form diverse noncovalent supramolecular networks ranging from structures representing zeolitic topologies to soft porous materials. A more in-depth understanding of the reactivity of molecular complexes featuring the mentioned above units towards small inorganic and organic molecules is particularly crucial for the design and post-synthetic modifications of MOFs.

The rational design and synthesis of molecular metal complexes and their transformation through noncovalent-driven self-assembly are becoming a fascinating research topic in the recent decade. Specifically, noncovalent porous materials (NPMs) or molecular porous crystals (MPCs) assembled from organic molecules or molecular metal complexes are the examples of such efforts, becoming an emerging class of metal-organic materials targeted for various applications. Achieving control over secondary sphere geometries and self-assembly processes of metal complexes as molecular building units remains an ongoing challenge. In this view, the character of the metal centres, as well as the composition of the organic ligand backbone, can play a crucial role providing control over weak noncovalent interactions, which govern the packing of molecules in the crystals. Moreover, the supramolecular structure of molecular crystals can easily be tailored by subtle modifications of the organic skeleton or co-crystallization of various molecular building blocks. This allows to tune the multiple functionalities of designed solid-state materials. Therefore, a comprehensive understanding of the intermolecular interactions is thus essential for the design of new building blocks and, ultimately, supramolecular networks.

Based on our long-term experience and achievements in the field, the overall goal of the proposed project is focused on advancing the basic knowledge on supramolecular chemistry and materials science. To this aim, we will utilize pre-designed metal complexes with the prototypical oxo $[M_4O]^{6+}$ and paddle-wheel $[M_2]^{4+}$ cores ($M = Cr, Mn, Fe, Co, Ni, Cu, Zn$) as the model molecular building blocks of supramolecular assemblies, which will enable us to probe the influence of various structural factors on the self-assembly processes. We strongly believe that enquired in-depth understanding of the multifaceted chemistry of selected molecular metal complexes will provide strong bases for further development of new supramolecular functional materials.