Unconventional ligands pave way towards unusual oxidation states for metal-organic frameworks

Metal-organic frameworks are a versatile class of materials. Possibilities to introduce various classes of organic linkers, mainly carboxylates, as well as to combine them with a wide range of d- and f- metals leads to an ability to finely tune coordination polymers to introduce desired properties. The combination of the metal nodes with organic linkers allows for the formation of polymers of different dimensionality and topologies. This allows for coordination polymers to find a plethora of applications in catalysis [1], adsorption and storage of gases and hazardous chemicals [2], drug delivery [3], etc.

For uranium, the most abundant and environmentally significant of 5f-elements, the chemistry of coordination polymers containing uranyl(VI) ions is comparatively developed [4]. However, the positioning of oxo atoms in the axial plane of uranyl(VI) ion leads to a prevalence of 1D or 2D coordination polymers. Lower-valence U MOFs are significantly less studied, however, but could be interesting due to their unique redox and environmental properties.[5] The use of unconventional organic linkers, such as OH-based (catechols, phenolates) or N-based (imidazolates, tetrAZolates) could allow for frameworks with unusual oxidation states which are appealing from both fundamental and practical points.

The proposed project has the objective of synthesis and characterization of uranium-based coordination polymers, in particular, highly reactive multidimensional extended frameworks, employing solvothermal synthesis, post-synthetic modification, and in situ techniques (red/ox and exchange processes). Particular attention will be devoted to exploring their capacity in the storage of industrially significant gases such as nitrogen, carbon dioxide as well as potential reactivity of frameworks towards small molecules. The subject proposed involves the study of the obtained materials using different techniques. The structure will be determined by single-crystal X-ray diffraction studies and supported by XRPD, IR, TGA. The properties will be studied by means of gas adsorption, luminescence, and reactivity experiments.