

MSc. Daniel Prochowicz  
Faculty of Chemistry  
Warsaw University of Technology

Doctoral Thesis Summary

## **Chosen zinc and copper complexes as building units in the construction of coordination polymers**

Supervisor: Professor Janusz Lewiński

The rapid evolution of a new class of porous inorganic-organic materials known as metal-organic frameworks (MOFs) is stimulating research in crystal engineering, chemistry, and materials science. MOFs intriguing molecular topologies, combined with novel chemical and physical properties, make these functional materials potentially useful for a wide variety of applications, such as hydrogen storage, selective gas separation, nonlinear optics, and highly selective heterogeneous catalysis. The conceptual approach for MOF engineering is based on the self-assembly of cationic systems acting as nodes with polytopic organic ligands acting as linkers. This strategy relies upon the use of SBU allows the design of specific nanometer-scale framework geometries with particular pore structures. MOFs take advantage of the versatile coordination chemistry and polytopic linkers, which makes it possible to design an almost infinite variety of MOF structure. Among them, Zn-MOF materials based on secondary building unit (SBU)  $\{Zn_4O\}^{6+}$  and the organic carboxylate linker are particularly intensely investigated. MOF synthesis is traditionally dominated by solvothermal solution-based methods requiring elevated temperatures and pressures. However, in these processes, large volumes of solvent are required to produce bulk quantities of the MOF materials for industrial use, which is environmentally unfavourable and makes the products costly. To overcome this problem, much effort has been made to develop alternative preparation methods. In this regard, the mechanochemical synthesis is now becoming an increasingly important strategy in materials synthesis and provides a faster, cleaner and less expensive alternative to the preparation of MOFs.

This dissertation aims at synthesis and characterization of building units based on Zn and Cu metal complexes of multifunctional organic ligands, and further evaluation of their utilities as precursors of hybrid organic-inorganic microporous materials with desired functionalities. The important objectives are to develop novel advantageous methods of materials fabrication by self-assembly processes in liquid or solid state.

The first part of the dissertation presents a novel effective and mild methodology for the synthesis of a series of oxozinc carboxylates involving well-defined alkylzinc precursor and water. The more detailed structural analysis revealed that these discrete oxozinc clusters self-assemble through specific noncovalent interactions to produce diverse types of noncovalent porous materials. Moreover, the unique adducts of an oxozinc carboxylate cluster with Lewis bases were isolated and structurally characterized.

In the next part of the presented work has been demonstrated a novel and effective strategy for generation of MOF material through utilization of mechanochemical grinding. On the basis of the presented results it has been shown that mechanochemical reactions in the presence of well-defined oxozinc cluster lead to the formation model MOF-5 material. Moreover, the studies clearly indicate that the acid-base equilibrium play a crucial role for reaction yield of reported mechanochemical processes. Thermogravimetric analysis (TGA) and gas sorption studies show that such synthesized MOF-5 material is stable and possess permanent porosity. Moreover, the solvothermal approach for the synthesis a new microporous material based on 2,5-diperfluoroterephthalic acid has been demonstrated.

In the last part of this dissertation results concerning the mechanochemical methods for the construction of homochiral coordination polymers and metalloligands based on copper (I) halide salts with quinine. A novel and very interesting 1D homochiral coordination polymer incorporating two different types of molecular building unit in alternating 1:2 sequence was isolated and structurally characterized. It was shown that van der Waals interactions between adjacent 1D polymer chains lead to an extended quasi-honeycomb homochiral pillared 3D network with solvent-free 1D channels. Moreover, the oxygenation process of the resulting CuX/quinine systems involving either of solvothermal or mechanochemical approach affords novel chiral N,N-ditopic metalloligands.