

PHD PROJECT DESCRIPTION

Responsive porous crystals based on 3d transition metal coordination compounds: toward sorption and sensing applications

1.1 Project goals: The project aims to unravel the mechanisms governing dynamic processes in crystalline coordination materials based on 3d transition metals and di-/tripodal N-donor ligands, with a particular focus on stimuli-responsive structural transformations and their impact on porosity, sorption, and sensing properties. The research will involve triggering and analysing single-crystal-to-single-crystal (SC–SC) transformations induced by external stimuli (e.g. guest molecules, temperature, pressure), combined with advanced structural and physicochemical characterization. A key objective is to establish structure–property relationships linking crystal dynamics with guest uptake or selective sorption enabling the rational design of functional materials for chemical sensing and molecular separation.

1.2 Outline: Responsive crystalline materials, derived from coordination compounds of 3d transition metals, represent a rapidly developing field at the intersection of coordination chemistry, crystal engineering and materials science. Particularly attractive are systems that combine: structural flexibility (breathing, gate-opening, phase transitions), accessible or switchable porosity, and stimuli-dependent optical responses. Such materials can exhibit: guest-induced structural transformations (SC–SC processes), selective sorption of small molecules (vapours, gases, VOCs), coupled sensing responses (e.g. colour changes). Synthetic strategies for preparing these materials range from traditional solution-based methods to more advanced techniques such as solvo-thermal synthesis. Structural characterization techniques such as X-ray crystallography, spectroscopy, and thermal analysis play crucial roles in elucidating the structure-property relationships and understanding the mechanisms underlying responsiveness in these materials. Their tunable responsiveness and multifunctionality make them promising candidates for addressing challenges in areas such as environmental monitoring, chemical sensing, molecular separation technologies. The project will explore how ligand design (di-/tripodal N-donors) controls: topology, flexibility, pore accessibility and how external stimuli (guest molecules, temperature, pressure) induce: reversible structural transformations and modulation of sorption properties. The long-term goal is to develop adaptive crystalline materials capable of selective guest recognition, and uptake.

1.3 Work plan: The work is planned for 4 years and combines synthesis, crystallography, and materials characterization. The first half of the year would be devoted to getting to know the subject, literature studies, getting familiar with the use of the Cambridge Structural Database and programs needed for the visualisation and analysis of crystal structures. The first year should finish with the synthesis of a range of metal complexes and their crystallisation under different conditions (synthesis and full characterisation of some of the heterocyclic ligands, if needed). Further studies can not be given a proper timeframe. Everything will depend in which direction the experiments will develop. However, they will embrace single-crystal X-ray diffraction analyses of the obtained crystalline products, solving and refining the obtained crystal structures, monitoring SC–SC transformations, systematic investigation of the factors that influence the formation of particular supramolecular architectures (e.g. crystallization conditions: the effects of altering solvent, temperature), analyses of intermolecular interactions, investigation of porosity and sorption properties, and synthetic work to modulate the revealed properties. The studies will be supported by comprehensive solid-state characterization using techniques such as PXRD, TGA, DSC, IR spectroscopy, and solid-state NMR.

1.4 Literature (*max. 7 listed, as a suggestion for a PhD candidate preliminary study*)

1) I. Senkowska, V. Bon, A. Mosberger, Y. Wang, S. Kaskel, Adsorption and Separation by Flexible MOFs, *Adv. Mater.* 2025, 2414724.

2) D. Saito, T. Galica, E. Nishibori, M. Yoshida, A. Kobayashi, M. Kato, Reversible and Stepwise Single-Crystal-to-Single-Crystal Transformation of a Platinum(II) Complex with Vapochromic Luminescence, *Chem. Eur. J.* 28, 2022, e202200703.

3) J. Alen, L. Van Meervelt, W. Dehaen, L. Dobrzańska, Solvent diffusion through a non-porous crystal ‘caught in the act’ and related single-crystal-to-single-crystal transformations in a cationic dinuclear Ag(I) complex, *CrystEngComm*, 17, 2015, 8957-8964.

4) L. Dobrzańska, G. 17, O. Lloyd, C. Esterhuysen, L. J. Barbour, Guest-induced conformational switching in a single crystal, *Angew. Chem. Int. Ed.*, 45, 2006, 5856-5859.

1.5 Required initial knowledge and skills of the PhD candidate

The candidate should have a passion for laboratory work and be familiar with standard synthetic laboratory equipment, as well as basic methods of compound characterization ($^1\text{H}/^{13}\text{C}$ NMR spectroscopy in solution, mass spectrometry, IR spectroscopy, and melting point determination). Familiarity with single-crystal X-ray diffraction (SCXRD), powder X-ray diffraction (PXRD), and thermal analysis (TGA/DSC) will be considered an advantage.

1.6 Expected development of the PhD candidate's knowledge and skills

Upon completion of the project, the candidate is expected to have a solid understanding of organic synthesis, metal complexation, and single-crystal X-ray diffraction analysis of small molecules. She/he will also gain expertise in solid-state characterization techniques, including powder X-ray diffraction, thermal analysis (TGA, DSC), and solid-state NMR, as well as methods for inducing and studying single-crystal-to-single-crystal transformations. Furthermore, the candidate will have the opportunity to actively engage with the research community through participation in conferences and/or workshops, as well as through the preparation of scientific publications and grant proposals.