PHD PROJECT DESCRIPTION

Responsive molecular crystals based on organic macrocycles: toward sorption and sensing applications

1.1 Project goals: The project aims to unravel the mechanisms governing dynamic processes in crystalline supramolecular materials based on organic macrocycles, with particular emphasis on stimuli-responsive behaviour, host–guest interactions, and adaptive porosity. The research will focus on structural transformations induced by guest molecules and external stimuli (e.g. solvent, temperature, pressure), including single-crystal-to-single-crystal (SC–SC) transformations where possible. A key objective is to establish structure–property relationships linking macrocycle molecular structure, crystal packing, and host–guest interactions with sorption and sensing properties, enabling the rational design of functional materials for selective molecular recognition, separation, and detection.

1.2 Outline: Organic macrocycles (e.g. calixarenes, pillararenes, resorcinarenes, and related systems) represent a versatile platform for constructing functional porous materials. Their intrinsic cavities, combined with the ability to form supramolecular assemblies, make them attractive for host–guest chemistry, sorption, and sensing applications. Particularly interesting are systems that combine:

- well-defined molecular cavities,
- dynamic adaptability (conformational flexibility, guest-induced rearrangements),
- cooperative intermolecular interactions leading to porosity,
- stimuli-responsive optical or physicochemical properties.

Such systems can exhibit:

- selective binding of guest molecules (vapours, gases, VOCs),
- guest-induced structural transformations (including SC–SC processes),
- switchable porosity and gate-opening behaviour,
- detectable sensing responses.

The project will explore how macrocycle size and functionalization influence selectivity, as well as how crystal packing affects porosity, flexibility, and responsiveness. It will also investigate the role of external stimuli (guest molecules, temperature, solvent) in modulating host–guest interactions, structural transformations, and sorption behaviour. The long-term goal is to develop adaptive macrocyclic materials capable of selective guest recognition, and uptake with potential applications in environmental monitoring (e.g. VOC sensing), molecular separation, and chemical detection systems.

1.3 Work plan: The project is planned for 4 years and combines synthesis, supramolecular chemistry, 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 conclude with the synthesis and crystallization of selected organic macrocycles under various conditions, and the determination of their crystal structures. During the second year, the PhD student would spend some time (1-2 months) in the collaborative research group at KU Leuven, developing her/his synthetic skills. 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) C. D. Gutsche, L. J. Bauer, *Calixarenes. 13. The conformational properties of calix[4]arenes, calix[6]arenes, calix[8]arenes, and oxacalixarenes*, J. Am. Chem. Soc., 107, (1985), 6052-6059.

2) J. Thomas, G. Reekmans, P. Adriaensens, L. Van Meervelt, M. Smet, W. Maes, W. Dehaen, L. Dobrzańska, *Actuated conformational switching in a single crystal of a novel homodithiacalix[4]arene*, Angew. Chem. Int. Ed., 52, (2013), 10237-10240.

3) D. Luo, J. Tian, J. L. Sessler, X. Chi, *Nonporous Adaptive Calix[4]pyrrole Crystals for Polar Compound Separations*, *J. Am. Chem. Soc., 143*, (2021), 18849-18853.

4) X. Yang, C. Li, M. Giorgi, D. Siri, X. Bugaut, B. Chatelet, D. Gigmes, M. Yemloul, V. Hornebecq, A. Kermagoret, S. Brasselet, A. Martinez, D. Bardelang, *Energy-Efficient Iodine Uptake by a Molecular Host·Guest Crystal*, Angew. Chem. Int. Ed., (2022), e202214039.

5) X.-Y. Lou, S. Zhang, Y. Wang, Y.-W. Yang, *Smart organic materials based on macrocycle hosts*, Chem Soc Rev., 52, (2023), 6644-6663.

6) R. M. Losus, S. Bleus, V. Bon, S. Kaskel, W. Dehaen, L. Dobrzańska *Adaptive crystals of homothiacalix[4]arene capable of molecular recognition, with preferential uptake of benzene over cyclohexane,* Chem. Comm., 61, (2025), 19608-19611.

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 ($^{1}H/^{13}C$ 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 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.