1. PHD PROJECT DESCRIPTION

Project title:

Responsive molecular crystals based on organic macrocycles

1.1. **Project goals:** The project aims at revealing the mechanisms standing behind the dynamics taking place in the crystal unity, based on studies performed on supramolecular systems containing organic macrocycles (calixarenes, pillararenes) by triggering single-crystal-to-single-crystal transformations, analyses of SCXRD data and performing solid-state supportive studies (PXRD, TGA, DSC, IR, solid-state NMR).

1.2. **Outline:** The synthetic pathways, as well as the behaviour of organic macrocycles in solution, have been studied for many years.[1] However, studies performed on the solid state, especially those concerning conformational flexibility, have hardly progressed at all.[2] The idea of the project is to focus on the crystalline forms of organic macrocyclic compounds and, by carefully studying the intra- and intermolecular interactions (present in the obtained compounds as well as in crystal structures of the compounds reported till now), uncover the mechanisms of externally triggered transformations taking place in the single-crystal unity. [3]

1.3. **Work plan:** The work is planned for a maximum 4 years. 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 determination of some crystal structures of macrocyclic compounds obtained from our partner institution (prof. W. Dehaen, synthetic chemist, KU Leuven, Belgium), crystallised under different conditions and familiarity with the methods used for supportive solid-state characterisation. During the second year, the PhD student would spend some time (2 months) in the collaborative research group at KU Leuven, developing her/his synthetic skills and progress her/his skills in crystal structures' refinement, especially modelling disorder. Further studies can not be given a proper timeframe. Everything will depend in which direction the experiments will develop. However, they will embrace the further synthesis of organic macrocycles, single-crystal X-ray diffraction analyses of the obtained crystalline products, solving and refining the obtained crystal structures, systematic investigation of the factors that influence the formation of particular supramolecular architectures (e.g. crystallization conditions: the effects of altering solvent, temperature). This will be further supported by extended solid-state studies by applying a range of methods such as PXRD, TGA, DSC, IR, solid-state NMR.

1.4. **Literature** *(max. 10 listed, as a suggestion for a PhD candidate)*

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) C. Fischer, T. Gruber, D. Eissmann, W. Seichter, E. Weber, *Unusual Behavior of a Calix[4]arene Featuring the Coexistence of Basic Cone and 1,2-Alternate Conformations in a Solvated Crystal*, Cryst. Growth Des., 11, (2011), 1989-1994.
3) 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.

4) 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.
5) X. Yang, C. Li, M. Giorgi, D. Siri, X. Bugaut, B. Chatelet, D. Gigmes, M. Yemloul, V. Hornebecq, A.
6) Kermagoret, S. Brasselet, A. Martinez, D. Bardelang, *Energy-Efficient Iodine Uptake by a Molecular Host·Guest Crystal*, Angew. Chem. Int. Ed., (2022), e202214039.
7) XY. Lou, S. Zhang, Y. Wang, YW. Yang, *Smart organic materials based on macrocycle hosts*, Chem Soc Rev., 52, (2023), 6644-6663.

1.5. Required initial knowledge and skills of the PhD candidate

The candidate should have a passion for lab work and be familiar with synthetic lab equipment, as well as with basic methods of compound characterisation ($^{1}H/^{13}C$ NMR in solution, MS, IR, melting point determination).

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

The candidate, after finalisation of this project, should be well familiar with organic synthetic methods, as well as with methods for single-crystal X-ray diffraction analysis of small molecules and techniques for solid-state characterisation: powder X-ray diffraction, thermal analysis (TGA, DSC), solid-state NMR as well as the techniques to trigger single-crystal-to-single-crystal transformations. Moreover, the candidate will have the opportunity to get to know other lab environments, e.g. at KU Leuven (Belgium) and feel part of the research community by participating in conferences and/or workshops as well as writing papers and grant proposals.