1. PHD PROJECT DESCRIPTION (4000 characters max., including the aims and work plan, all in English)

Project title:

Porosity and dynamics in crystals of macrocyclic compounds

1.1. Project goals

The project is aimed at rationalising the synthesis of porous crystalline materials based on macrocyclic compounds (calixarenes) by studying intra- and intermolecular interactions present in their crystal structures. Its realisation should shed some light on the relationship between structure and sorption properties, as well as the mechanisms governing dynamics taking place in single-crystals of the host-guest systems studied.

1.2. Outline

The synthetic pathways, as well as the behaviour of calixarenes in solution, have been studied for many years.[1] However, studies performed on the solid state, especially those concerning their conformational flexibility, are not progressed at all.[2] The idea of the project is to focus on the crystalline form of these macrocyclic compounds and, by carefully studying the intra- and intermolecular interactions (present in the obtained compounds as well as in crystal structures of compounds reported till now), gaining knowledge needed to design crystals containing voids or channels. The porosity properties of these would be further studied, as well as the influence of macrocycles' modifications on the size/shape of the formed voids. As initially the space available in crystal structures of macrocycles is usually taken up by solvent, the removal of which can lead to either sustain the space or cause its collapse, triggered single-crystal-to-single-crystal transformations will be an important part of the research. They will allow to follow the dynamics taking place in monocrystals, which is only recently emerging as a subject of studies and hopefully will help to uncover some mechanisms standing behind this process.[3] As the realisation of this proposal falls under the framework of an ongoing SONATA BIS project funded by the National Science Centre, entitled: "The role of non-covalent interactions in the formation of supramolecular assemblies and the phenomenon of single-crystal-to-single-crystal transformations", the work of the PhD student would be additionally (on top of the base remuneration) funded through the grant.

1.3. Work plan

The work is planned for 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 Cambridge Structural Database and programs needed for visualisation and analysis of crystal structures, as well as synthetic lab techniques. The first year should finish with the synthesis of some macrocyclic compounds, their full basic characterisation (NMR, MS, IR, elemental analysis, and melting point determination studies) and their crystallisation under different conditions. 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, which will be performed at UMK and/or at Warsaw University, 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), and synthetic work to modulate the obtained porous properties. This will be further supported by extended solid-state studies, as well as actuating and studying single-crystal-to-single-crystal transformations.

1.4. Literature

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.

1.5. Required initial knowledge and skills of the PhD candidate

The candidate should have a passion for lab work (which forms a big part of the project) 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).

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

As the proposed study is on the border of synthesis/crystallography and solid-state science, the candidate after its finalisation 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 and how to study the sorption properties of the porous materials. The techniques to perform single-crystal-to-single-crystal transformations are still being developed, which has been also performed by the mentor of this proposal. Moreover, the candidate will have the opportunity to get to know other lab environments, e.g. at Warsaw University and KU Leuven (Belgium) and really feel part of the research community by participating in conferences and/or workshops as well as writing papers and grant proposals.