**Poster Presentation**

MS43.P32

Towards computer-guided tuning of the crystal packing of porous organic cages

A. Pulido[1], M. Liu[2], P. Reiss[2], A. Slater[2], S. Chong[2], M. Little[2], T. Hasell[2], M. Briggs[2], A. Cooper[2], G. Day[1]

[1]University of Southampton, School of Chemistry, Southampton, United Kingdom, [2]University of Liverpool, Liverpool, United Kingdom

Among microporous materials, there has been an increasing recent interest in porous organic cage (POC) crystals, which can display permanent intrinsic (molecular) and extrinsic (crystal network) porosity. These materials can be used as molecular sieves for gas separation and potential applications as enzyme mimics have been suggested since they exhibit structural response toward guest molecules[1]. Small structural modifications of the initial building blocks of the porous organic molecules can lead to quite different molecular assembly[1]. Moreover, the crystal packing of POCs is based on weak molecular interactions and is less predictable that other porous materials such as MOFs or zeolites.[2]   In this contribution, we show that computational techniques -molecular conformational searches and crystal structure prediction- can be successfully used to understand POC crystal packing preferences. Computational results will be presented for a series of closely related tetrahedral imine- and amine-linked porous molecules, formed by [4+6] condensation of aromatic aldehydes and cyclohexyl linked diamines. While the basic cage is known to have one strongly preferred crystal structure, the presence of small alkyl groups on the POC modifies its crystal packing preferences, leading to extensive polymorphism. Calculations were able to successfully identify these trends as well as to predict the structures obtained experimentally, demonstrating the potential for computational pre-screening in the design of POCs within targeted crystal structures. Moreover, the need of accurate molecular (ab initio calculations) and crystal (based on atom-atom potential lattice energy minimization) modelling for computer-guided crystal engineering will be discussed.

[1] J. T. A. Jones, D. Holden, T. Mitra, et. al, Angew. Chem. Int. Ed. 2011, 50, 749-753., [2] T. Tozawa, J. T. A. Jones, S. I. Swamy, et. al, Nature Materials, 2009, 8, 973-978.
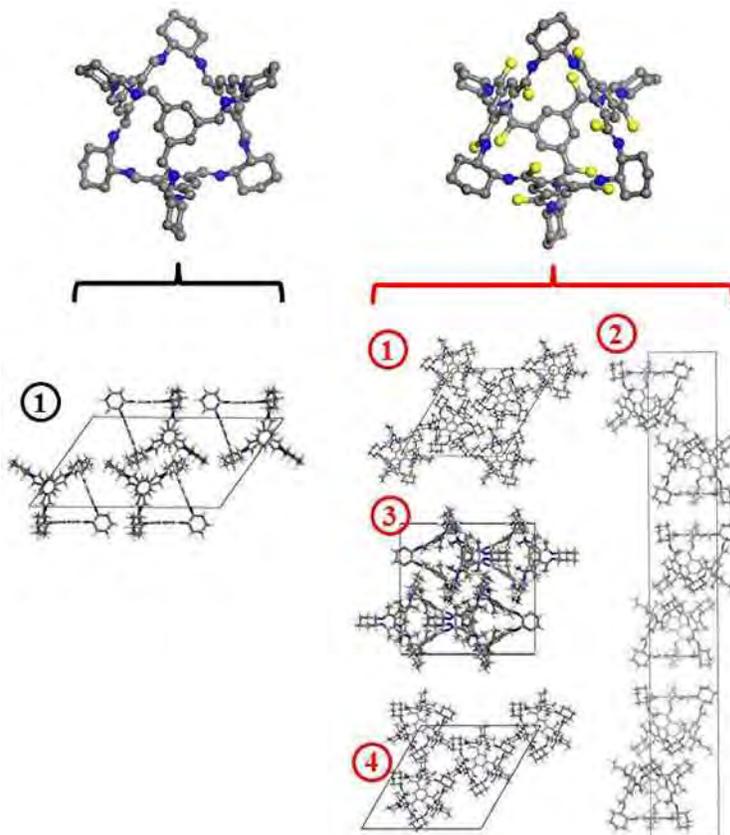
Keywords: Crystal Structure Prediction, Computational Chemistry, Crystal Engineering