Functional molecular materials discovery underpinned by crystal structure prediction

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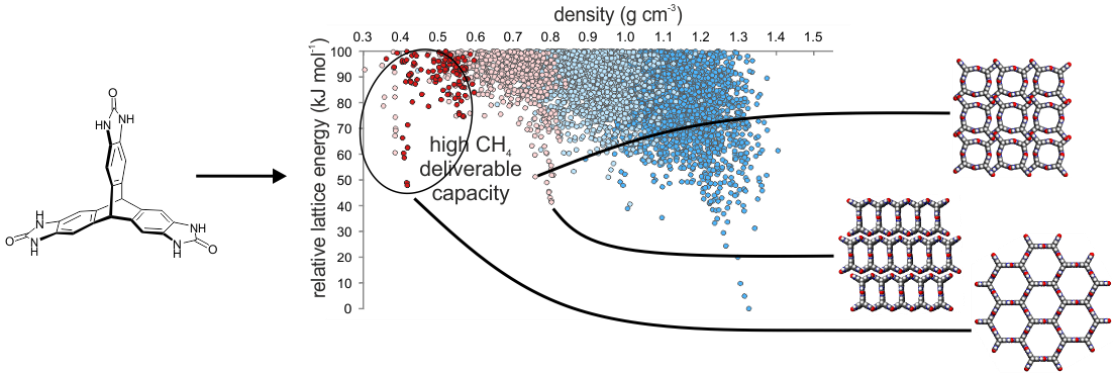
The design of molecular crystals with targeted properties is the goal of crystal engineering. However, our predictive understanding of how a crystal's properties relate to its structure, and how crystal structure in turn relates to molecular structure, are not yet sufficiently reliable to confidently design functional materials. One reason for this is that the crystal structure adopted by a molecule is rarely determined by a single, predictable structure-directing interaction, but typically results from a balance of many relatively weak intermolecular interactions. Therefore, it is common for a molecule to have many nearly equi-energetic possible crystal structures, with the best structure (the global lattice energy minimum) favoured by only a few kJ mol^{-1} or less over alternative structures that might have very different physical properties. This existence of competing low energy crystal structures is related to the prevalence of polymorphism in molecular crystals, as well as the observation that small changes to chemical structure can lead to dramatic changes in crystal packing.



Computational methods for crystal structure prediction (CSP) have been developed to help anticipate the crystal structure that a molecule will form. These methods are based on a global search of the lattice energy surface and a ranking of local energy minima according to their calculated relative stabilities. Each of the crystal structures in the resulting ensemble encodes a set of properties, many of which are calculable using computer simulations. This talk will discuss how the set of predicted structures, their calculated energies and simulated properties, which we present as an energy-structure-function (ESF) map, can be used to guide experimental programmes for materials discovery. The ESF mapping approach will be illustrated with its use in the discovery of unprecedented porous molecular crystals[1] and its application to organic semiconductors[2-4].

[1]. A. Pulido *et al*, *Nature* **2017**, 543, 657.
[2]. J. E. Campbell, J. Yang and G. M. Day, *J. Mat. Chem. C* **2017**, 5, 7574.
[3] F. Musil, S. De, J. Yang, J. E. Campbell, G. M. Day and M. Ceriotti. Chem. Sci. **2018**, 9, 1289-1300.
[4] J. Yang, S. De, J. E. Campbell, S. Li, M. Ceriotti, G. M. Day, *Chem. Mater.* **2018**, 30, 4361-4371.