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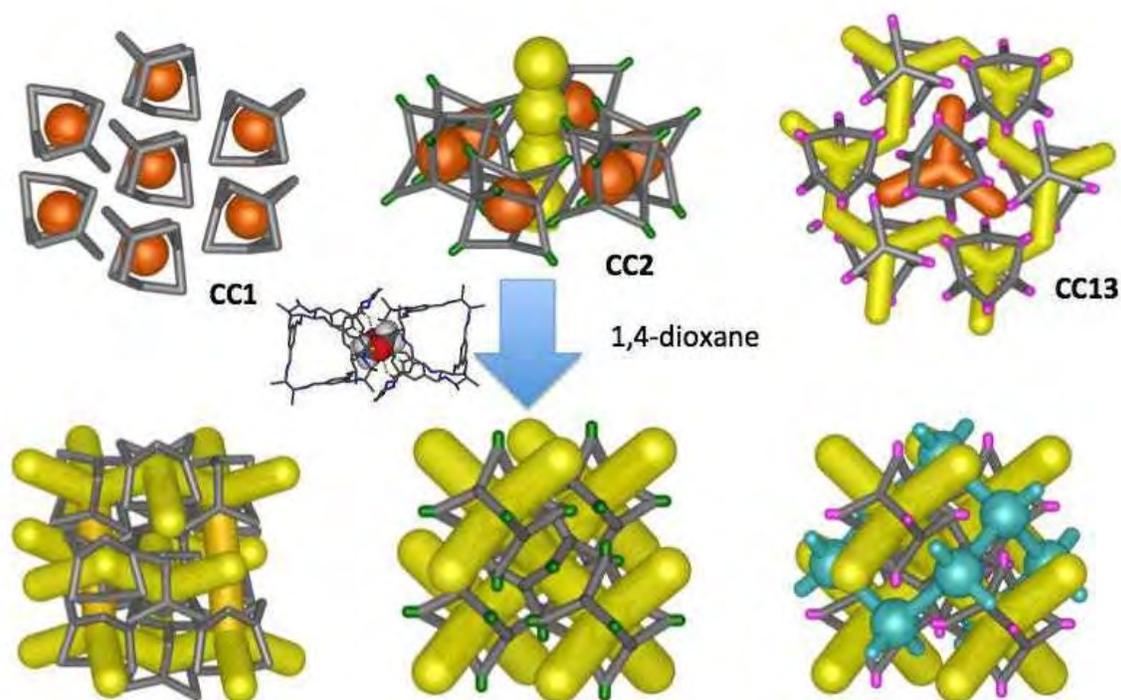
Exploiting weak supramolecular interactions to assemble organic cage materials

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Intensive research into microporous materials has been driven by potential applications in areas such as catalysis, gas separation, storage, and sensing. Recently, a new class of purely organic molecular cage materials has emerged, which can exhibit significant porosity arising from the internal molecular cavity as well as extrinsic porosity from packing in the crystal structure [1]. Unlike extended frameworks, porous molecular materials lack strongly directional interactions to drive their assembly, complicating the crystal engineering possible for isorecticular metal-organic frameworks [2], for example. Our work has focused on covalent imine-linked cages, which exhibit diverse crystal chemistry. The connectivity of the pore network is derived from the cage packing: Therefore, the crystal structure directly affects the observed porosity. The imine cages synthesised so far lack strongly hydrogen bonding groups. Thus, the solid state supramolecular assembly of cage molecules is governed by the aggregate of weak interactions, such as van der Waals forces. By identifying robust 'tectons', that is, regularly occurring supramolecular motifs, progress toward designing the crystal structure and therefore controlling the physical properties of organic cage materials becomes possible. Here, we report exploiting robust supramolecular motifs, comprising either cage modules or host and guest molecules to gain control over the porosity of the bulk material. We demonstrate how formation of a desired void network topology can be driven by hosting a specific guest in preferred sites which maximise weak host-guest interactions [3]. Subsequent guest removal can produce stable polymorphs, one of which exhibited double the Brunauer-Emmett-Teller surface area with respect to the originally observed polymorph. We also examine how the interaction between gas phase guests and cage host is important in the application of porous organic cages in rare gas separation.

[1] T. Tozawa, J. T. A. Jones, S. I. Swamy et al., *Nat. Mater.*, 2009, 8, 973–978., [2] M. Eddaoudi, J. Kim, N. Rosi et al., *Science*, 2002, 295, 469–472., [3] T. Hasell, J. L. Culshaw, S. Y. Chong et al., *J. Am. Chem. Soc.*, 2014, 136, 1438–1448.



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