

Poster Presentations

[MS24-P33] Porous Organic Cage Tectonics.

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Crystalline microporous materials constructed with discrete organic molecules have received great interest driven by possible applications in the field of gas storage and molecular separation. [1-3] Organic cages are an extremely interesting class of such molecules owing to their rigid prefabricated intrinsic void which can be accessed by numerous guest molecules in the solid-state. [4,5] This property is directly influenced by the crystal packing of the cage units, which we have demonstrated can be switched in the solid-state by exposure to solvent vapour. [6] We have also recently demonstrated that the dimensions of the cage window, which limits the diameter of the resulting porous network, can control the uptake of a particular organic guest based on its size and shape. [7] A unique property of these porous organic crystals, over porous systems assembled through the formation of a chemically bound framework, is that the intrinsically porous cage units, from which they are assembled are solution processable. We have shown that this allows for the modulated assembly of porous materials consisting of two or three cage tectons which have tailored porosity to nitrogen. [8] However to accurately predict the crystal packing of these cages tectons in single or multi-component form remains to be one of the upmost challenges in this area of research. [9]

Here we present a detailed study as to the effect of solvent on the crystal packing of some of our organic cage tectons. For example, **CC3**, [4] tends to pack in a direct window-to-window fashion generating a interconnected diamondoid

network. However an interplay of host-guest and electrostatic interactions can be used to direct the crystal packing of the cage units. Subsequent solvent removal from these forms can either be accompanied by single-crystal-to-single-crystal transformations to network structures which are topologically similar to that of the solvate. Or the packing motif of the cage tectons can undergo significant rearrangement to a more energetically favourable form. This strategy has enabled enhancements in the apparent Brunauer-Emmett-Teller surface area of these crystalline materials. In addition if the solvated form is unstable to desolvation then analysis of its crystal structures can often provide valuable information as to why this is the case. Using this strategy we have been able to stabilise a particular packing motif of **CC3**, which was observed in a solvated structure but collapsed following solvent removal, by crystallising it in the presence of a second cage tecton. The second cage tecton essentially fill the solvent filled void in the analogous solvated phase and is our first example of crystallising two symmetrically and dimensionally different cage tectons. This cocrystal shows high thermal stability unlike its analogous single component solvate and demonstrates that cocrystallisation can be used as a design strategy for influencing the pore limiting diameter of the resulting network structure.

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