MS33 Supramolecular recognition

MS33-04
Crystal engineering of supramolecular assemblies of bowl-shaped host molecules
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Abstract
Small-molecule supramolecular chemists are inspired by large, supramolecular assemblies, such as viruses, produced by nature.[1] However, large, synthetic, multi-component (n > 3) supramolecular assemblies which enclose chemical space are still relatively rare phenomena in the field of small-molecule, supramolecular chemistry. Atwood and MacGillivray reported the first example of such an assembly by showing that the bowl-shaped host molecule *C*-methylcalix[4]resorcinarene **1** can spontaneously assemble in a nitrobenzene solution to form a large, chiral, supramolecular assembly consisting of 6 molecules of 1 and 8 water molecules, the latter 'stitching' molecules of **1** into a hexameric assembly, $\mathbf{1}_6$•$(H_2O)_8$ via O-H•••O hydrogen bonds.[2] Despite >140 structures reported since this discovery containing **1** co-crystallised with various guest and/or solvent molecules, only one similar hexameric assembly of **1** was reported by Holman et al. where 6 of the 8 water molecules were replaced by 2-ethylhexanol molecules.[3] Here we present a crystallisation of **1** from a number of alcohols, which yielded similar hexameric assemblies to that of the MacGillivray-Atwood and Ugono-Holman hexamers. However, interesting differences were found, including the first case where two unique multi-component assemblies are found within the same crystal structure for these types of structures.[4] In addition, we report the hexameric assembly of **1** with 1-propanol as the solvent, increases the interior cavity size by simultaneous insertion of water and 1-propanol as the 'stitching' molecules, indicating a possible means of engineering the size of these cavities.[5]

References
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