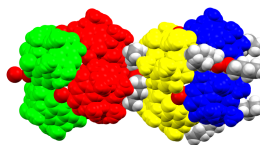


**MS29-P15** Large supramolecular assemblies of a bowl-shaped hostClive L. Oliver<sup>1</sup><sup>1</sup>. Department of Chemistry, University of Cape Town

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Nature is able to produce large, supramolecular assemblies of macromolecules with intricate complexities such as found in viruses and cellular membranes.<sup>1</sup> These complicated structures are held together by non-covalent interactions which are ultimately crucial in the functioning of these complex biological systems. Small-molecule supramolecular chemists are inspired by these complex supramolecular systems in nature, 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,  $I_6(H_2O)_8$  via O-H...O hydrogen bonds.<sup>2</sup> Despite the approximately 125 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.<sup>3</sup> Hexameric assemblies of pyrogallolarenes and dodecameric assemblies of sulfonatocalix[4]arenes have also been reported. It is notable that in all these assemblies only one type of assembly per crystal structure was isolated in the solid-state. Here we present a crystallisation of **1** from 1-butanol, which yielded two different types of hexameric assemblies within the same crystal structure. Furthermore, the two unique assemblies are linked part of the time into a heterodimer of hexameric assemblies which we entitle a supra-heterodimer, a 38-component assembly consisting of 129 hydrogen bonds. To the best of our knowledge, the isolation of two different large, supramolecular assemblies ( $n > 3$ ) within the same crystal structure has not been observed before and neither has identical large supramolecular assemblies been shown to link into discrete units. In addition, we report a hexameric assembly of 1-propanol with **1** which 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.



**Figure 1.** Space-filling representation of 38-component supra-heterodimer of **1**

**Keywords:** large supramolecular assemblies, supra-heterodimer