

Superbowls and CavitanDs - Guest Molecule Direction of Nano-Scale Self Assembled Systems

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Structure determination of the Superbowl¹ (a fused polycyclic pentacavitand, $MWt \approx 5000$) (fig.1) was preceded by determination of a set of eight structures of the precursor tetrabromo monocavitand compound (fig 2). These structures display a number of distinct and remarkable nano-scale self assembled arrangements. Each of the rigid internal cavitanD bowls whether in the monocavitand or the superbowl contains either (i) an alkyl group derived either from a neighbouring cavitanD molecule or from included solvent, or (ii) chlorinated solvent molecules. Crystal structures of all of the compounds also display inclusion of additional species in the non-rigid stem-like potential cavity lying outside the rigid bowl between the four pendant pentyl feet.

Evident highly selective inclusion of molecules of a solvent contaminant in the non-rigid external cavity of the terabromocavitand led to the systematic examination of crystals formed in the presence of a series of chemically related potential guests. The supramolecular crystal quality is observed to be strongly correlated with the identity of the guest molecule available for inclusion in the potential external cavity. A consequent reduction in disordering of the alkyl chains which is dependent on the identity of the external guest is observed, indeed in some instances the disorder is effectively eliminated.

For the Superbowl structure, intermolecular interactions from the four included deuteriochloroform molecules lying between the alkyl feet to adjacent superbowls delineate a 2 nm thick discrete layer of Superbowl assemblies. The presence of ethanolic alkyl groups in the wall cavitanD bowls and chloroform in the basal bowl exemplifies both types of internal inclusion which had originally been observed in the structures of the monomeric cavitanD solvates.

Structure determination for the Superbowl and for the disordered cavitanD structures provided significant crystallographic challenges, the resolution of which will also be discussed.

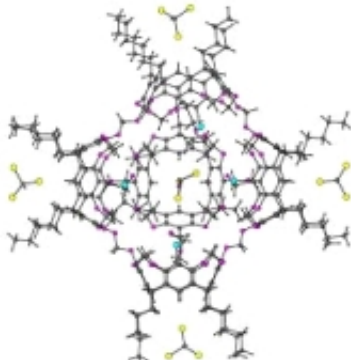


Fig. 1

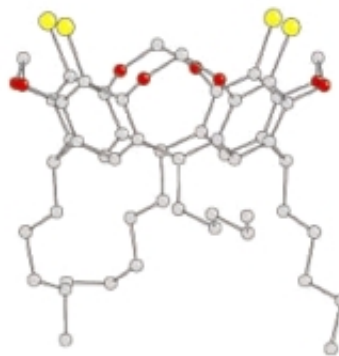


Fig. 2

- (1) Barrett, E.S., Irwin, J.L., Edwards, A.J., Sherburn, M.S. J.A.C.S., 2004, 16747-16749.