

SUPRAMOLECULAR MULTIVALENT CALIXARENE SCAFFOLDS

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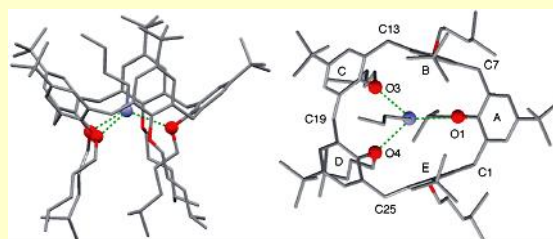


Fig. 1 Side (left) and top (right) views of the crystal structure of the $n\text{-BuNH}_3^+$ endo-cavity inclusion complex with a cone calix[5]arene penta-O-ether.

Calixarenes, three-dimensional molecular platforms of varying size and shape, are easily available in good yields by well-established procedures from cheap starting materials, and are currently being subjected to chemical alteration at their wide and/or narrow rims in the attempt of providing (i) highly preorganized permanent cavities, capable of selective inclusion within their hydrophobic cups of organic ammonium ions of biological relevance (see Fig. 1 for typical binding features of the complexes), and (ii) more complex systems (supramolecular assemblies) by exploiting the noncovalent interactions encoded in the covalent structure of complementary subunits (α,ω -alkanediammonium salts, porphyrins).

Keywords: Calixarenes, Molecular recognition, Self-assembly, Sensing, Supramolecular chemistry

1. Recent advances in calix[5]arene chemistry: from host-guest to supramolecular chemistry

As a result of their π -basic cavities, calix[5]arenes have a strong affinity for the linear alkylammonium ions. The mutual attraction between these two 'molecular modules' is based on a set of weak interactions (hydrogen bond, cation- π , CH- π and van der Waals) that, by acting in concert, provide an excellent tool for the construction of increasingly complex supramolecular systems. Earlier, we have prepared capsular assemblies composed of two calix[5]arene molecules held together by an α,ω -alkanediyl-diammonium dication. We then moved, by a natural conceptual evolution, to the development of oligo-/structures, virtually derived from the junction of capsular complexes. Along these lines, we have recently reported the formation of hetero- and homo-component supramolecular systems, reliant on the calix[5]arene/alkaneammonium recognition motif, via iterative inclusion events of calix[5]arene/alkaneammonium modules. For instance, bis-calix[5]arenes with divergent cavities, linked at their lower rim by *o*-, *m*- or *p*-xylyl spacers, have been shown to form, in the presence of alkanediammonium salts, hetero-component non-covalent (poly)capsular structures composed of pairs of complementary homoditopic monomers (i.e. AA/BB-type supramolecular polymers). The modular calix[5]arene/alkaneammonium system, however, is not only able to provide capsules and polycapsules, but, thanks to its versatility, allows the 'mixing of the components' as well. That is, the preparation (via covalent addition of a dodecylamine moiety at the lower rim of the calixarene) of monomeric heteroditopic precursors able to self-assemble into oligo/polymeric structures of AB-type as a result of variations of the pH. Because of the potential applications that such a type of non-covalent synthetic approach may provide in the emerging field of supramolecular polymers (adaptive materials, dynamers, liquid crystals and nanostructured assemblies with chiral memory, we are currently pursuing the design and study of hetero- and homo-component systems based on calixarene and alkane(di)ammonium ions or

porphyrins (*vide infra*).

2. Non-covalent synthesis of hetero-component modular systems

It is well-known that water-soluble anionic calix[4]arenes can promote, in the presence of cationic porphyrins, the formation of highly organized hetero-component aggregates with pre-defined stoichiometry and sequence. On the basis of this knowledge, we have recently succeeded in the synthesis of the second generation of these systems, based on water-soluble octacationic bis-calix[4]arenes and tetraanionic porphyrins. The results obtained have demonstrated that, owing to the presence of the two calix[4]arene divergent cavities, hierarchical self-assembly can be programmed and easily controlled, simply by adding the two modules in the correct sequence, giving rise to supramolecular systems growing first in a planar fashion and then in the third dimension. Research is now being directed to chiral hetero-component assemblies with porphyrins by employing chiral multi-calix[4]arene subunits (amplification of chirality). Furthermore, the noncovalent synthesis of more complex (star-type or tetrahedral) supramolecular architectures are underway by making use of polyamino surface-functionalized multi-cavity calixarenes (three or four units), covalently bound to pseudo-planar 'three-bladed cores' or to three-dimensional (e.g., 1,3-alternate calix[4]arene) platforms.

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Selected Publications

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