CHAPTER 13

Executive Summary and Conclusions

Structurally authenticated complexes based on *p*-sulfonatocalix[4]arene and a diverse range of imidazolium based cations demonstrates the preferential binding of calixarene towards these components rather than towards selected phosphonium cations (*mono*- or *bis*-). The inclusion complexes are drawn into the calixarene cavity and assembled through weak supramolecular interactions, notably π···π and C-H···π interactions, and hydrogen bonding. Multi-component solid state structures involving conformationally restricted cone-shaped *p*-sulfonatocalix[4]arene and other organic cations (imidazolium and phosphonium) are consistently self arranged into 'up–down' antiparallel bilayer arrangements, with the lower rim hydroxyl groups arranged in a back-to-back manner at the van der Waals limit or possibly with the phenolic groups involved in H-bonding.

Structural features involving a common 'molecular capsule' or skewed 'molecular capsule' motif based on two *p*-sulfonatocalix[4]arene moieties surrounding one or two imidazolium cations, in a way depending on the choice of unsymmetrical imidazolium cations, have been demonstrated. This type of 'capsule' arrangement is readily formed with the inclusion of disc-shaped crown ether molecules or amino acids, shrouded by two calixarenes. It is also noteworthy that *p*-sulfonatocalix[4]arene has flexibility in its conformation, with subtle changes in forming pinched cones, and it is also versatile in taking on a 4- or 5- charge for each 'molecular capsule' in achieving electrical neutrality in the solid, which arises from the loss of one of the phenolic -OH protons from the lower rim of the cavitand. The formation of the 'molecular capsule' can involve aquated rare earth metal species which they can be either present as homoleptic species or bound to one or more oxygen fragments of sulfonate groups with the coordination sphere satisfied by water molecules. The coordination of the rare earth metal species or otherwise results in different inter bilayer thicknesses, with a more compact arrangement of 'molecular capsules' when the metal ion is directly bound to the sulfonate groups of the calixarenes. This is related to a shorter lanthanide–O distance for the sulfonate groups bound directly to the O-atom relative to than the distance when the sulfonate groups are part of secondary coordination sphere of the metal ions.

A series of imidazolium based cations bearing different alkyl chain lengths at one of the terminis show the flexibility of inclusion in the calixarene being accommodated in the cavity in different ways. The important characteristics for the complexation of *p*-sulfonatocalix[4]arene and imidazolium cations are the length of the terminal alkyl chains and electrostatic effects. Imidazolium cations with short chain lengths, 1-*n*-ethyl-3-methylimidazolium and 1-*n*-butyl-3-methylimidazolium, reside in the hydrophobic cavity of the calixarene, through either the methyl termini or the ethyl/*n*-butyl termini, with additional hydrogen bonding arising between the anchoring points of the sulfonate groups and the imidazolium aromatic ring hydrogen atoms. Two such imidazolium cations can be confined in a ‘molecular capsule’ motif based on two calixarenes. In addition, one imidazolium cation in different orientations, as well as disordered solvent molecules can be accommodated in the ‘molecular capsule’. The nature of the ‘molecular capsule’ arrangement depends on how the metal centres interact with the calixarene, *i.e.* covalent bond versus hydrogen bonding formation. Formation of skewed ‘molecular capsule’ prevails when the longer *n*-butyl alkyl chain in 1-*n*-butyl-3-methylimidazolium snugly fits in the calixarene cavity in a V-shape, with the other cavity most likely occupied by disordered solvent molecules. The calixarenes are arranged in a head-to-head manner normal to the cavities, in the form of ‘molecular capsules’.

The interplay of imidazolium cations with longer alkyl chains in 1-*n*-hexyl-3-methylimidazolium**,** 1-*n*-octyl-3-methylimidazolium**,** and 1-*n*-octyl-2,3-dimethylimidazolium, is rather similar, where the charged head group resides in the calixarene cavity; however the hydrophobic tail is directed away from the upper rim of *p*-sulfonatocalix[4]arene**.** Sciotto *et al.* reported the inclusion of linear alcohols with different alkyl chains, showing that the binding mode is similar to the inclusion of imidazolium cations in *p*-sulfonatocalix[4]arene, with shorter alkyl chain for the alcohols almost completely residing in the calixarene cavity, but not so for longer alkyl chains, which is expected on the amount of space available in the cavity.

Incorporating *n*-octyl chain, in 1-*n*-octyl-3-methylimidazolium, results in new organic bilayer arrangements where the long alkyl chain penetrates an adjacent calixarene bilayer. Incorporating a C-methyl group on the imidazolium cation, 1-*n*-octyl-2,3-dimethylimidazolium, also results in the terminal *n*-octyl chain penetrating the adjacent bilayer, similar to the same alkyl chain in 1-*n*-octyl-3-methylimidazolium, as well as a different arrangement again, with the cation confined in ‘molecular capsule’. The extra methyl group residing in the π-rich cavity offers additional weak H-bond interaction between the H-atoms and the O-atoms of the calixarene sulfonate groups. *N*-butyl-*N*-methylpyrrolidinium cation, also has similar inclusion properties with the multi-component system with the head group residing in the hydrophobic cavity and the butyl chain directed away from the sulfonate groups.

Supermolecules based on two geometrically opposed *bis*-imidazolium cations with methyl or butyl termini, and *p*-sulfonatocalix[4]arene results in end capping each *bis*-imidazolium cation. This effectively creates ‘molecular capsules’ where the cation spans two calixarenes. The ‘molecular capsule’ confining 1,1’-[1,4-phenylenebis(methylene)]bis(3-methyl-1H-imidazolium-1-yl) can be either skewed with the included cation having methyl termini in the *trans*-configuration, or having a mirror plane bisecting the calixarenes with ,1’-[1,4-phenylenebis(methylene)]bis(3-methyl-1H-imidazolium-1-yl) taking on an eclipsed *cis*-configuration. For *bis*-imidazolium cation with butyl chain at the termini, 1,1’-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl), the cation can be crystallographically imposed with the ‘molecular capsule’ or interact with the cavities of two adjacent *p*-sulfonatocalix[4]arene, in either

90^o or 180^o with respect to each other. Similarly the host-guest interplay involving 1,10-phenanthrolinium ion and *p*-sulfonatocalix[4]arene, reported by Liu *et al.*, results in of ‘*bis*-molecular capsules’. It is also noteworthy that when 1,1’-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl) is end capped by two *p*-sulfonatocalix[4]arene at 90^o relative to each other, a polymeric chain/array linked by aquated gadolinium (III) metal ions prevails, and the chains are packed in an orthogonal manner creating layers of *p*-sulfonatocalix[4]arene polymers.

The interactions between the imidazolium based and pyrrolidinium based cations and *p*-sulfonatocalix[4]arene, in solution have also been established using ^{1}H NMR spectroscopy, including ROESY experiments. The results support the inclusion phenomena as found for solid structures where the terminal polar groups of the guests are directed into the cavity, while the apolar aliphatic chain of longer analogues of imidazolium cations are directed away from the polar sulfonate groups of the calixarenes.

The addition of large phosphonium cations, tetraphenylphosphonium, (3-methoxyphenyl)triphenylphosphonium or benzyltriphenyl phosphonium cations into the multi-component complexes results in thicker calixarene bilayers in which these cations are embedded in between the bilayers and extend the hydrophobic layer where they assemble in the common multiple phenyl embraces between molecules into infinite networks, consisting of chains, nets or layers with the bilayer thicknesses ranging from 13 to 15 Å. Generally the phosphonium cations are involved in C–H···π interaction between themselves or with *p*-sulfonatocalix[4]arene, as well as weak H-bonding with the oxygen containing fragments of the calixarene. Tetraphenylphosphonium cation commonly self assembles in between the bilayers of *p*-sulfonatocalix[4]arene forming infinite chain networks in the extended structure, while (3-methoxyphenyl)triphenylphosphonium cation forms nets or grid-like layers, and benzyltriphenyl phosphonium cation forms compact layers, where these cations interact through the established phenyl embrace between molecules.

Incorporating 1,4-bis(triphenylphosphoniomethyl)benzene cation into multi-component systems with *p*-sulfonatocalix[4]arene results in a range of remarkable structural types; 1,4-*bis*(triphenylphosphoniomethyl)benzene cation can be embedded (i) in between a head-to-head arrangement of calixarenes, and (ii) in between the back-to-back lower rim arrangement of calixarenes. The methylene bridges in *p*-sulfonatocalix[4]arene intertwine with sulfonate groups of the calixarenes through H-bonds, and are directed away from the sulfonate groups with the central aromatic rings being involved in π···π interactions. For arrangement (ii), 1,4-bis(triphenylphosphoniomethyl)benzene cation shrouds *p*-sulfonatocalix[4]arene in the same plane with the methylene bridges of the calixarene involved in close C–H···π interactions with the pendant arms of 1,4-*bis*(triphenylphosphoniomethyl)benzene cation. The interplay between 1,4-*bis*(triphenylphosphoniomethyl)benzene and *p*-sulfonatocalix[4]arene is flexible in being maintained in some form while the calixarene bind imidazolium cations in their cavities, albeit with different orientations of calixarenes. Indeed the plane of the calixarene can tilt in sequentially binding 1-*n*-ethyl-3-methylimidazolium to 1-*n*-hexyl-3-methylimidazolium, with the induced tilt angles ranging from 7.2 to 65.5^{o}.

The interplay of 1,4-*bis*(triphenylphosphoniomethyl)benzene with *p*-sulfonatocalix[4]arene in can also result in complex multi-component structures, besides the conventional ‘up–down’ antiparallel bilayer arrangement. The interlocking of 1,4-*bis*(triphenylphosphoniomethyl)benzene methylene bridges with sulfonate groups of the calixarenes introduces a different bilayer arrangement, with the calixarenes arranged with their cavities aligned in opposite directions, with the upper rim sulfonate groups being in close proximity to adjacent calixarenes, effectively creating a plane of such polar groups. Another striking feature the interplay of 1,4-*bis*(triphenylphosphoniomethyl)benzene and *p*-sulfonatocalix[4]arene is the formation of hydrophobic scaffold network where the pockets can constrict ‘molecular capsules’ and water molecules. The rigid 1,4-*bis*(triphenylphosphoniomethyl)benzene scaffold network in the solid state can also have weak H-bonding of the methylene bridges of 1,4-*bis*(triphenylphosphoniomethyl)benzene to *p*-sulfonatocalix[4]arene sulfonate groups.

The previous discussion gives some insight into the use of trivalent lanthanide ion in building up solid state structures in general. The presence of trivalent lanthanide ion appears to template the crystallisation, but which, despite the well-documented complexation of the lanthanide ions by sulfonated calixarenes, is not included in the final product. This was first established for the *p*-sulfonatocalix[4]arene/tetraphenylphosphonium system which requires the presence of trivalent lanthanide ions, but yet they are not necessarily included up in the final complex. Similar findings have now been noted for 1,4-*bis*(triphenylphosphoniomethyl)benzene where in the absence of lanthanide ions poorly diffracting crystals were obtained and structure determination was not possible. Thus, the presence of the lanthanide ions in forming stable solid complexes is important in controlling the organisation of the other species, yet it is not taken up in the final lattice.

A level of predictability has been achieved with respect to multi-component solid state structures between *p*-sulfonatocalix[4]arene, ionic liquid based cations, large phosphonium cations and lanthanide metal cation. These complexes may prove useful in supramolecular chemistry in future studies. The self assembly strategies involving multi components in building complex structures is valuable in the applications of functional materials, such as designing porous material for gas or small molecule separations as well as for biological receptors.

Carbon rich nanomaterials such as SWCNTs and fullerenes can be solubilised in water by mechanical grinding the tubes or balls with *p*-sulfonatocalix[4]arene and/or sulfonato-imidazolium component, followed by sonication in water. The composite material has nano-particles of the calixarene randomly arranged on the surface of the carbon nanotube and fullerene or calixarene/sulfonato-imidazolium supermolecules randomly arranged on the surface of the fullerene. This approach has possibilities in using other amphiphiles in solubilising carbon nanotubes and may also be applicable to stabilise and solubilising other forms of carbon including carbon quantum dots, and composites of different forms of carbon.