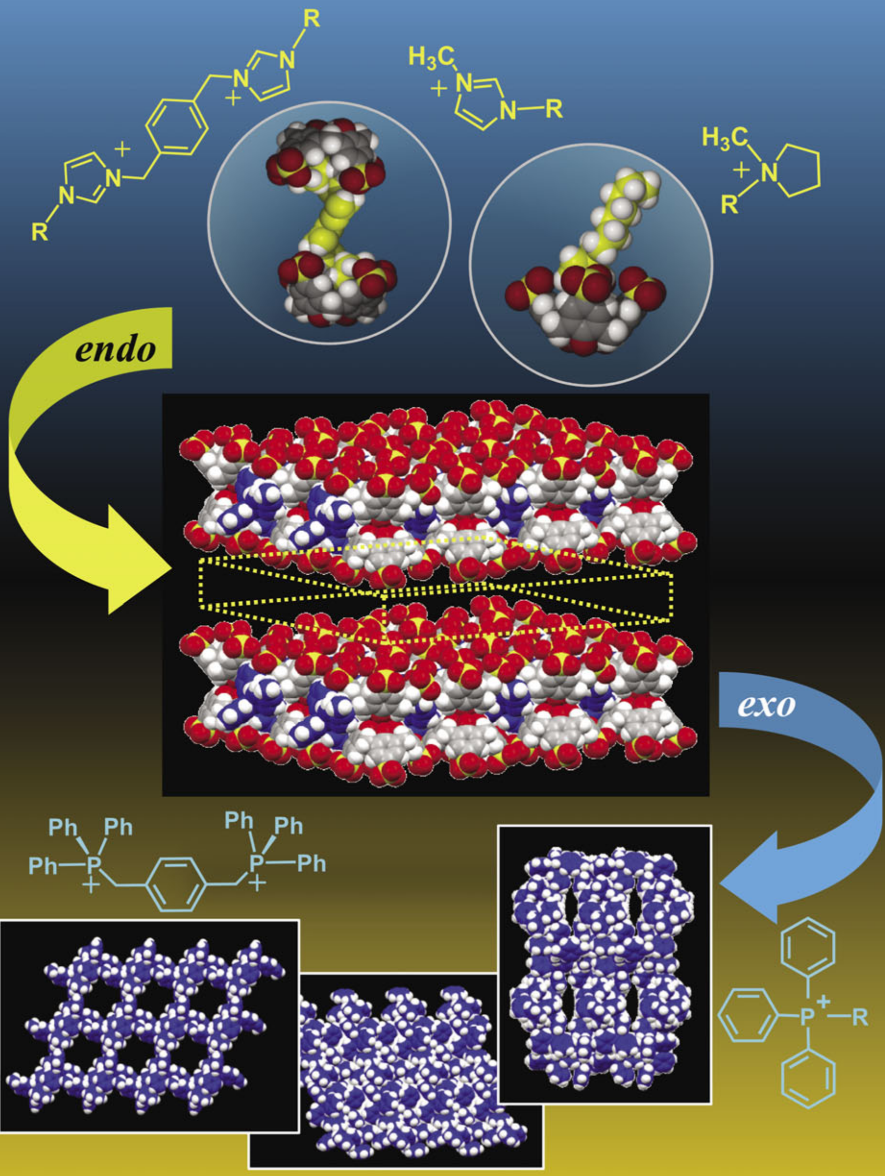
NJC

New Journal of Chemistry

An international journal of the chemical sciences

www.rsc.org/njc

Volume 34 | Number 9 | September 2010 | Pages 1785–2060



ISSN 1144-0546

RSC Publishing

PERSPECTIVE
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1144-0546(2010)34:9;1-J

Structural diversity of multi-component self-assembled systems incorporating *p*-sulfonatocalix[4]arene

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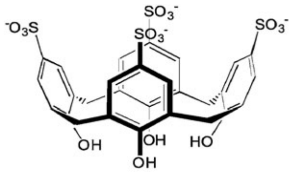
Received (in Victoria, Australia) 27th April 2010, Accepted 12th May 2010
DOI: 10.1039/c0nj00317d

Bowl shaped *p*-sulfonatocalix[4]arene is a versatile anion in building multi-component self-assembled materials, with a design strategy of incorporating small organic cations including imidazolium or pyrrolidinium cations within the cavity of the calixarene through their polar head groups, which is also established in solution for the two components. Another design strategy is the assembly of interlocking (embracing) large phosphonium cations around the outer (*exo*-) surface of the cavity of the calixarene. The selectivity of interplay of the different cations with the *endo*- and *exo*-surfaces of the calixarene requires the presence of aquated lanthanide(III) ions, but these ions are not necessarily incorporated into the extended structures.

Introduction

Self-assembly processes involve molecular recognition events between supramolecular tectons with some complementarity of inherently weak interactions.[1] Such processes provide access to complex and diverse architectures with a level of prediction of the structures depending on the design of the tectons. Calixarenes are a class of macrocycle which can be functionalised at the so called lower rim through the phenolic –OH groups, with the associated supramolecular chemistry being well documented.[2] They can also be functionalised through the upper rim at the *para*-positions relative to the –OH groups.[2] Calixarenes functionalized only at the upper rim with sulfonate groups are amphiphilic cavitands which have been extensively investigated as tectons in crystal engineering, and supramolecular chemistry in general. These cavitands have also been of interest because of their water solubility, with potential in mimicking biological processes,[3] and in gaining access to new materials using water as a benign reaction medium.[4,5]



p-Sulfonatocalix[4]arene in the cone conformation

The smaller ring size sulfonated calix[4,5]arenes commonly adopt the cone-shaped conformation which can bind a wide range of guest species in their cavities.[6] These 1 : 1 host–guest supermolecules can assemble into infinite networks through interactions between organic components and through primary and secondary coordination spheres of metal ions associated with the sulfonate groups.[5] The larger and readily accessible calix[6 and 8]arenes can adopt a plethora of different conformations, including double cone conformations which can also form host–guest complexes.[7] In general, the sulfonate

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groups in these calix[*n*]arenes can provide anchoring points for the complexation of organic and inorganic species, with lanthanide metal ions playing an important role in the formation, stability and overall cohesion of the structures through charge balance, hydrogen bonding, bridging, and templating effects.[8]

p-Sulfonatocalix[4]arene is the smallest oligomer in the series and can exist in four different conformations, however the rigid truncated cone conformation is more typical. Indeed there is only one exception to the cone conformation in the solid state which has one phenyl moiety in the opposite direction.[9] The cone conformer usually assembles in the solid state in the up–down anti-parallel bilayer arrangement,[10] Fig. 1, simultaneously creating hydrophilic and hydrophobic environments associated with the polar head groups and cavities respectively. Bilayer arrangements can serve as platforms in the construction of material that mimics the structure and properties of naturally occurring clays.[10] Sulfonated calix[5]-arene and calix[6]arene usually assemble in the cone and double cone conformations respectively, also usually in the up–down anti-parallel bilayer arrangements in the solid state.[11] It is noteworthy that the larger ring size calix[6,8]arenes can have conformational flexibility, with sixteen possible conformations for calix[8]arene (see below).[7c]

Two sulfonatocalix[4]arenes from adjacent bilayers can align in binding a common molecule or pairs of molecules, taking on the equivalent of a 'molecular capsule'. These self-assembled capsules can confine small diammonium guest molecules such as putrescine and cadaverine,[12] and large globular and disc-shaped guest molecules such as cryptand[13] and cyclam.[14] Here the bilayers can be considered as an assembly of 'molecular capsules'. However, the presence of the 'molecular capsule' arrangement for *p*-sulfonatocalix[4]arene in the solid state does not imply that it exists in solution prior to the crystallisation event. The 'molecular capsules' can also be slightly skewed/distorted in balancing the electrostatic interaction between the sulfonate groups and the poly-aquated lanthanide cations, and interactions with the included molecules.[15]

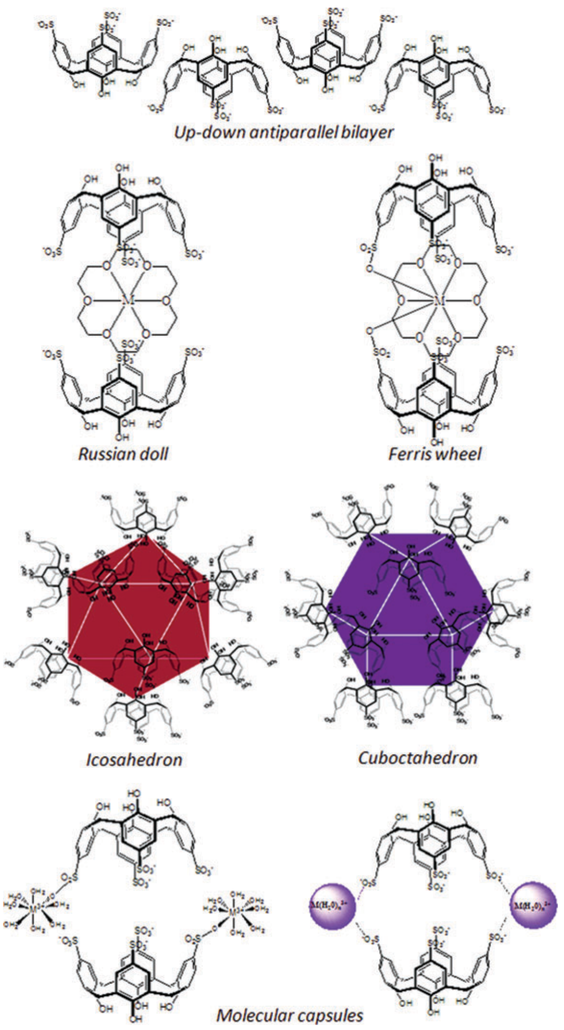

Fig. 1 Key structural types for the supramolecular chemistry of *p*-sulfonatocalix[4]arene.

p-Sulfonated calix[5,6]arenes can be regarded as forming 'molecular capsules' in the solid state even with the latter in the double cone conformation, in shrouding the diprotonated DABCO cation,[16] and 18-crown-6 molecules,[7a] or tetraphenylphosphonium cations.[7b] The counter ions for these larger calixarenes can also be included in the structure *exo*-relative to the interior of the capsules. Coleman *et al.*[7c] have reported the conformational extremities for *p*-sulfonatocalix[8]arene, with the macrocycle being in either an almost planar conformation in which all sulfonate groups are pointing out from the central pocket of the macrocycle, or in an 'inverted double partial cone' conformation where four adjacent sulfonate groups are pointing up and the other four are pointing down from the mean plane of the molecule. We have established that *p*-sulfonatocalix[8]arene can also adopt a 'pleated loop' conformation or can assemble into helical tubules in the solid state.[17]

The above bilayers containing 'molecular capsules' based on two *p*-sulfonatocalix[4]arenes can incorporate metal ions and

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organic molecules *exo*- with respect to the calixarene cavities, with the *endo*-space being versatile in binding a range of molecules of different sizes and shapes, as for the above larger calixarenes. In recent studies the presence of aquated lanthanide ions has been established as important in controlling the organisation of various multi-component bilayer arrangements, yet they are not necessarily taken up in the solid state.[7b,18]

Binding 18-crown-6 as its diaquo–sodium complex in the cavity of *p*-sulfonatocalix[4]arene results in the formation of 'Russian Dolls' with two calixarenes shrouding the disc-shaped guest molecule, which is sealed at the seam of the 'molecular capsule' *via* interactions of aquated lanthanide(III) ions, Fig. 1.[4] When a lanthanide ion is bound to the same crown ether and sulfonate groups simultaneously, a 'Ferris wheel' arrangement can form.[19] Departure from the bilayer arrangement, with and without the presence of 'molecular capsules' is possible, and includes the formation of spectacular icosahedral and cuboctahedral arrays of twelve calixarenes with their cavities directed away from the surfaces of the essentially spheroidal arrangement of calixarenes,[20] Fig. 1. Related to this is the formation of helical tubular arrays, with the dimples of the calixarenes also directed outwards.[20] The formation of the icosahedral arrangements is general for the lanthanide metals, while the formation of the cuboctahedral spheroids is limited to neodymium, praseodymium, and samarium(III) ions. These spheroidal species have recently been reviewed by Dalgarno *et al.*[21]

p-Sulfonatocalix[4]arene has many possibilities in binding a wide range of guest molecules including large organic cations, Fig. 2, for example the tetraphenylphosphonium cation, at least in the presence of an aquated trivalent lanthanide ion with the ratio of *p*-sulfonatocalix[4]arene and phosphonium cations at 1 : 3.[18] Here the phenyl arm of one phosphonium cation resides in the cavity of a *p*-sulfonatocalix[4]arene while the other two cations interlock through phenyl embraces. The phosphonium cations are also included in a bilayer arrangement of calixarenes, Fig. 1, which are in the usual up–down arrangement. This work has been extended to the binding of a range of large phosphonium cations under a variety of conditions using a combinatorial approach, in varying the ratio of the ions, pH and the ionic strength of the solutions.[22]

Expanded bilayers based on the assembly of *p*-sulfonatocalix[4]arene and tetraphenylphosphonium or benzyltriphenylphosphonium cations in the presence of lanthanide are also accessible where the cations intercalate between calixarenes, at the interface of the hydroxyl groups, Fig. 2.[22] Here a phenyl arm of tetraphenylphosphonium resides in the cavity of a calixarene, in between the bilayers. Subsequently this was extended to a bis-phosphonium cation, where one phenyl ring from the cation interacts *exo* and/or *endo* with respect to the cavity of *p*-sulfonatocalix[4]arene, which is in association with lanthanide ions, with the extended structure being porous.[23] A complex bilayer structure involving ytterbium cations and *p*-sulfonatocalix[8]arene has also been authenticated in the solid state, which is based on skewed 'molecular capsules' with the two calixarenes, in the pleated loop conformation effectively shrouding three tetraphenylphosphonium ions. In the extended structure the sulfonate groups are aligned on the surface of the capsules, creating a crisscrossed arrangement of large hydrophilic channels.[24]

This article focuses on the construction and structural diversity of complexes of *p*-sulfonatocalix[4]arene involving host–guest interactions between the calixarene and different imidazolium and pyrrolidinium cations in the presence of large phosphonium cations and lanthanide ions, Schemes 1 and 2. This is an area we recently developed, having its origins around exploiting the tuneable properties of imidazolium and pyrrolidinium cations, which feature extensively as components in ionic liquids, as a strategy for gaining control of the assembly of functionalised calixarenes through inclusion phenomena. These cations are available with a diverse range of combinations of different alkyl chain lengths, and it is noteworthy that long chains can result in long range ordering in ionic liquids,[25] which may translate to ordering in the solid state in multi-component systems herein. We find that by including these cations in the solid state there is also a tendency for the formation of 'molecular capsules' involving two calixarenes from adjacent bilayers. The article also develops a strategy of using large organic phosphonium cations in conjunction with the imidazolium and pyrrolidinium cations

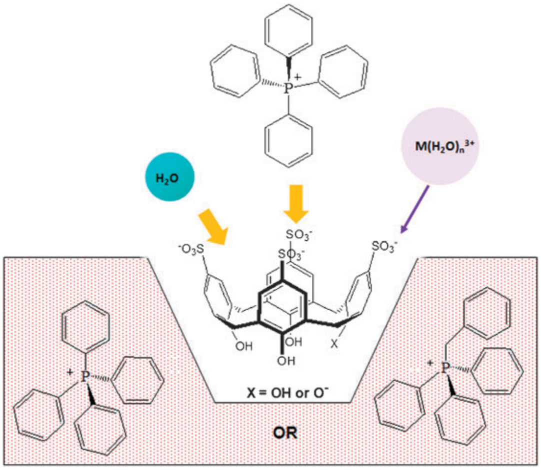
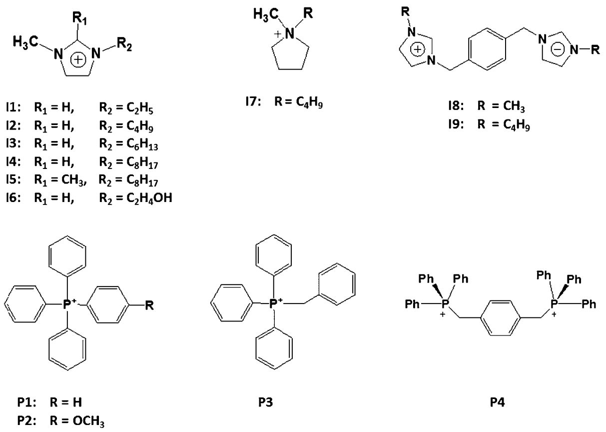
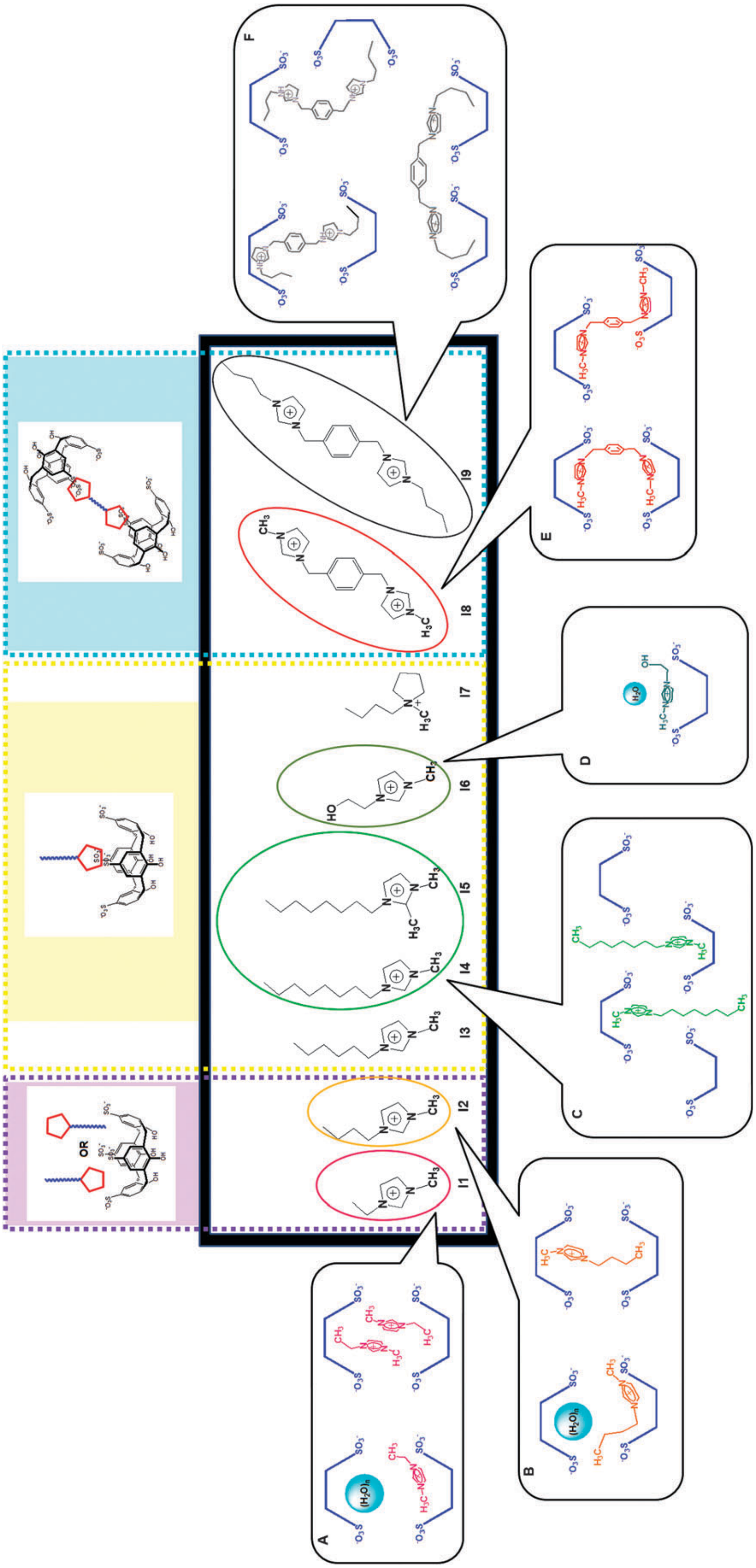


Fig. 2 Types of interactions of *p*-sulfonatocalix[4]arene with phosphonium cations.



Scheme 1 N-heterocycle and phosphonium cations which form multi-component materials with *p*-sulfonatocalix[4]arene.



Scheme 2 Different types of association of imidazolium cations (**I1** to **I9**) with *p*-sulfonatocalix[4]arene.

in constructing complex multi-component layered structures in the solid state. Other aspects of the supramolecular chemistry of *p*-sulfonatocalix[4]arene have been covered in review articles.[5,21]

Calixarene–guest molecular cation interactions

Structurally authenticated complexes based on *p*-sulfonatocalix[4]arene and a variety of imidazolium based cations demonstrate the preferential binding of calixarene towards these components rather than towards selected phosphonium cations (mono- or bis-) through one of the phenyl groups. Imidazolium cations bound in a calixarene cavity are involved in $\pi\cdots\pi$ and C–H$\cdots\pi$ interactions, and C–H$\cdots$O hydrogen bonding.[26–29] The calix[4]arene is consistently arranged in up–down antiparallel bilayer arrangements, as in Fig. 1, with the lower rim hydroxyl groups arranged in a back-to-back manner at the van der Waals limit or possibly through H-bonding involving the phenolic OH groups.

'Molecular capsule' or skewed 'molecular capsule' motifs based on two *p*-sulfonatocalix[4]arenes surrounding one or two imidazolium cations are formed, in a way depending on the structure of the unsymmetrical imidazolium cations.[29] Previously this type of 'molecular capsule' based on two *p*-sulfonatocalix[4]arenes has included disc-shaped crown ether molecules[21] or nucleic acid bases.[30] It is also important to note that *p*-sulfonatocalix[4]arene has flexibility in its cone conformation in forming pinched cones whereby two diagonally opposed 1,3-phenyl rings move closer together with the other two phenyl rings being splayed apart. In addition, the calixarenes in these systems are versatile in being able to take on a 4− or 5− charge within each 'molecular capsule' in achieving electrical neutrality within the solid. The 5− charged calixarene arises from the loss of one of the phenolic –OH protons from the lower rim of the cavitand.

The formation of 'molecular capsules' can involve interaction of the calixarenes with aquated rare earth metal species around the equatorial seam of the capsules. These species can be homoleptic in binding only to water molecules, where they interact with sulfonate groups through secondary coordination sphere hydrogen bonding. Alternatively the metal ions can be directly bound to one or more sulfonate O-centres, with the remainder of the coordination sphere being water molecules.[29] The nature of the interaction of the rare earth metal ions with the sulfonate groups effects the thicknesses of the bilayer, with thinner bilayers associated with a more compact arrangement of 'molecular capsules' involving direct metal to O-centres of sulfonate groups.

A series of imidazolium cations with different alkyl chain lengths attached to one N-centre while keeping the other a methyl group show flexibility of inclusion in the calixarene, being accommodated in the cavity in different ways,[27–29] Fig. 3. Important considerations associated with the complexation of *p*-sulfonatocalix[4]arene and imidazolium cations are the length of the alkyl chains and electrostatic effects. Imidazolium cations with short chain lengths,[29] **I1** (**A**) and **I2** (**B**), reside in the hydrophobic cavity of the calixarene, through either the methyl or the ethyl/*n*-butyl termini, with additional hydrogen bonding associated with 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, as can one imidazolium cation in different orientations along with disordered solvent molecules. The nature of the 'molecular capsule' arrangement can depend on how the metal centres interact with the calixarene, *i.e.* covalent bond *versus* hydrogen bonding formation (see above). Formation of skewed 'molecular capsule' where the calixarenes are slightly off centre in their head-to-head (upper rim-to-upper rim) prevails when the longer *n*-butyl alkyl chain in **I2** snugly fits in the calixarene cavity in a V-shape, with the other cavity most likely occupied by disordered solvent molecules.

The interplay of imidazolium cations with longer alkyl chains in **I3**, **I4**, and **I5** is rather similar, where the charged head groups reside in the calixarene cavity. However here the hydrophobic tail is directed away from the upper rim of the calixarene.[27,28,31] Ghoufi *et al.*[32] have reported relevant MD simulations on 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 chains for the alcohols almost completely residing in the calixarene cavity, but not so for longer alkyl

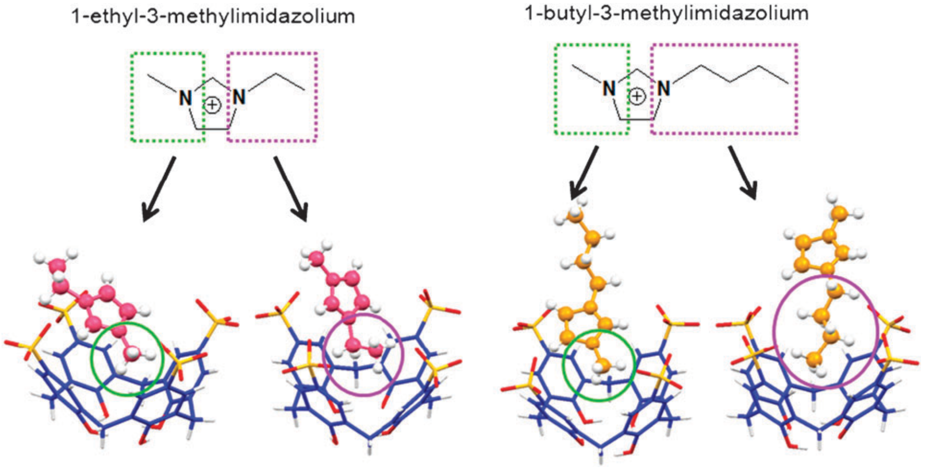


Fig. 3 Different modes of binding of imidazolium cations in the cavity of *p*-sulfonatocalix[4]arene.

chains, which is expected on consideration of the amount of space available in the cavity.

Incorporating an *n*-octyl chain in **I4** (**C**) results in a remarkably different organic bilayer where the long alkyl chain penetrates an adjacent calixarene bilayer, Fig. 4(a).[27] Incorporating a C-methyl group on the same imidazolium cation, **I5** (**C**), also results in the terminal *n*-octyl chain penetrating the adjacent bilayer, indeed in a way similar to the same alkyl chain in **I4**, as well as a different arrangement again, with the cation confined in 'molecular capsules', Fig. 4(b).[28] The extra methyl group residing in the π-rich cavity is involved in additional weak H-bond interactions between the H-atoms and the O-atoms of the calixarene sulfonate groups. For an imidazolium cation bearing a functional hydroxyl group, **I6** (**D**), the cation fits snugly into the calixarene cavity, with a water molecule essentially capping the [imidazolium $\cap$ calixarene] supermolecule through hydrogen bonding involving the *N*-hydroxyethyl group (Fig. 5). ^{1}H NMR spectroscopy demonstrates that this type of supermolecule persists in solution, with reduced conformational mobility of the calixarene relative to imidazolium cations devoid of *N*-hydroxyethyl functionality.[33] Pyrrolidinium cation, **I7**, also has similar inclusion properties within the multicomponent system, with the head group residing in the hydrophobic cavity and the butyl chain directed away from the sulfonate groups.[34]

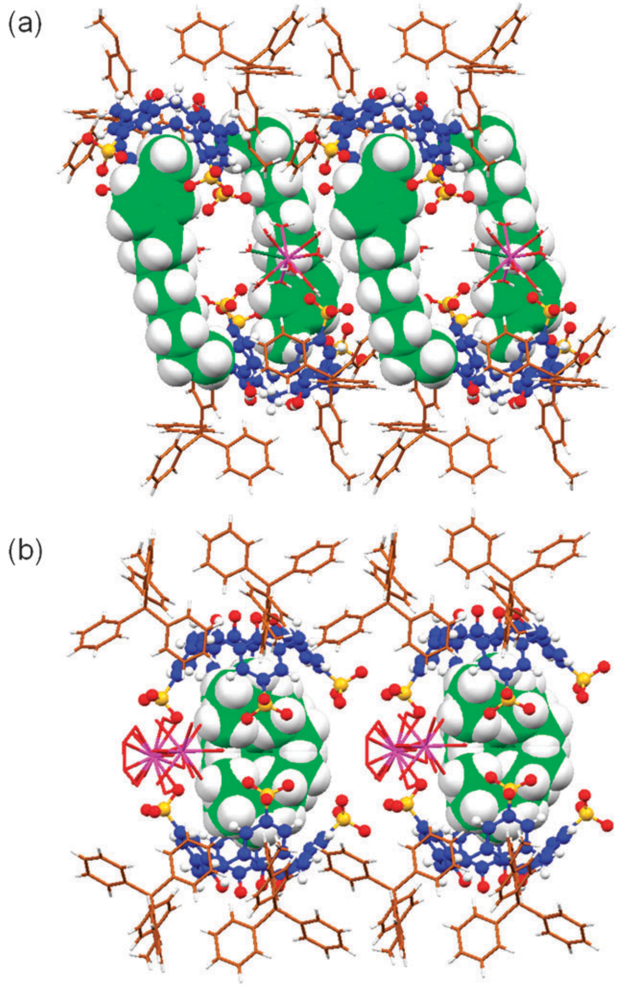


Fig. 4 Some space filling of the imidazolium molecules (green) confined in *p*-sulfonatocalix[4]arene, and layers of phosphonium cations (brown) in an extended bilayer showing (a) the penetration of the alkyl chain into an adjacent bilayer, and (b) formation of 'molecular capsules'.

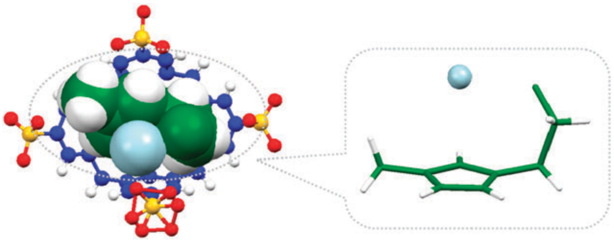


Fig. 5 Some space filling of **I6** in the calixarene cavity, with a water molecule in close proximity to **I6**.

Supermolecules based on two geometrically opposed bis-imidazolium cations with *N*-methyl or *N*-butyl termini, **I8** (**E**) or **I9** (**F**), and *p*-sulfonatocalix[4]arene result in end capping each bis-imidazolium cation, Fig. 6.[26] This effectively creates 'molecular capsules' where the cation spans two calixarenes. The 'molecular capsule' confining **I8** can be either skewed with the included cation having methyl termini in the *trans*-configuration, or have a mirror plane bisecting the calixarenes with **I8** taking on an eclipsed *cis*-configuration. For bis-imidazolium cations bearing *N*-butyl chains, **I9**, the cation can be confined within a 'molecular capsule', or interact with the cavities of two adjacent calixarenes within the same bilayer, orientated either 180° or 90° 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.*,[35] also results in a 'bis-molecular capsule'. It is also noteworthy that when **I9** is end capped by two calixarenes at 90° relative to each other, a polymeric chain/array linked by aquated gadolinium(III) metal ions prevails, and the chains are packed orthogonally, in the form of layers of connected calixarenes.[36]

The interactions between the imidazolium and pyrrolidinium cations with *p*-sulfonatocalix[4]arene have also been established in solution using ^{1}H NMR spectroscopy, including ROESY

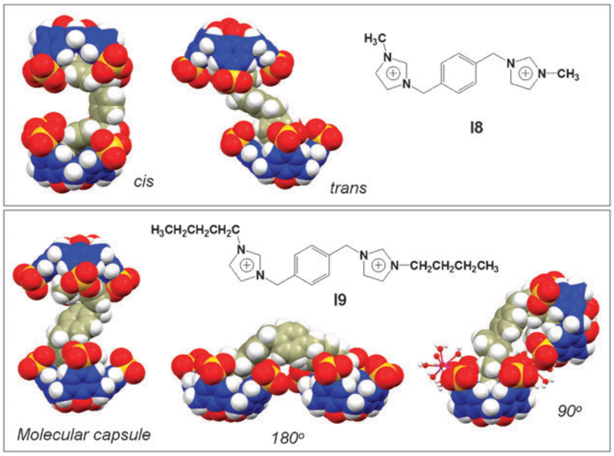


Fig. 6 Structural types for imidazolium cations **I8** and **I9** interacting with *p*-sulfonatocalix[4]arene.

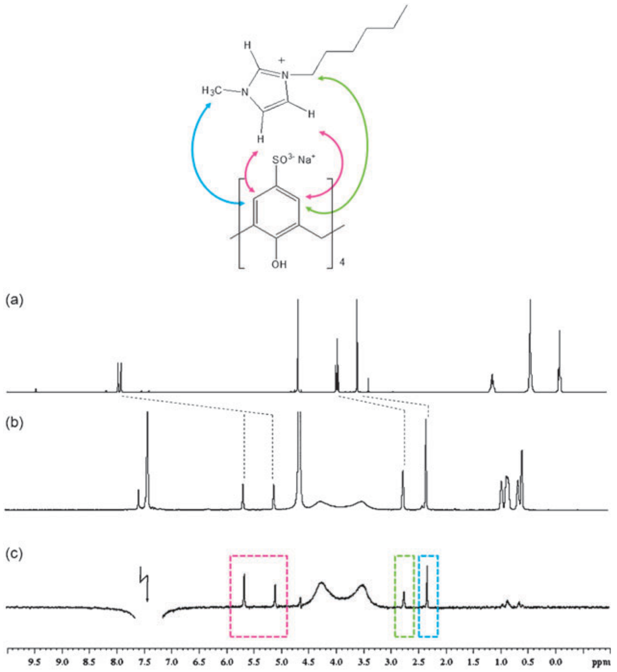


Fig. 7 Examples of ^{1}H NMR spectra for **I3** (a) and 1 : 1 mixture of **I3** and *p*-sulfonatocalix[4]arene (b). Selective irradiation of the calixarene aromatic protons in ROESY experiments showing strong NOEs between **I3** protons (c).

experiments (Fig. 7).[31,34] The results support the inclusion phenomena where the polar groups of the guests are directed into the cavity, while the termini of the *N*-aliphatic chains are directed away from the sulfonate groups of the calixarenes, as found in the solid structures. There is no evidence for forming 'molecular capsules' in solution which shroud one or two imidazolium or pyrrolidinium cations, at least in the absence of lanthanide ions and phosphonium cations.

Interlocking-phenyl embraced phosphonium cations

The concept of embracing molecules, especially those bearing phenyl or aryl groups organised on their surfaces, was developed by Dance and Scudder in 1995.[37] Embrace motifs can be bimolecular or multimolecular with individual phenyl groups engaged in edge-to-face (ef) and offset-face-to-face (off) attractive phenyl···phenyl interactions. Six fold and four fold phenyl embraces occur frequently in crystals containing Ph_4P^+ and terminal Ph_3P groups.[38]

The crystallization of *p*-sulfonatocalix[4]arene with large phosphonium cations, such as **P1**, **P2** or **P3**, results in the cations being embedded in bilayers, interposed between calixarenes.[27–29,34] Effectively these bilayers are expanded relative to the bilayer based purely on *p*-sulfonatocalix[4]arene, Fig. 8, with the thickness ranging from 13 to 15 Å. Within the bilayers the cations self-assemble through the common multiple phenyl embrace as part of infinite networks of chains, nets or layers, involving C–H···π interactions. They also have C–H···π interactions and SO···HC interactions with the calixarene. In general, within the bilayers **P1** self-assembles into infinite chains, whereas **P2** forms nets or grid-like layers,

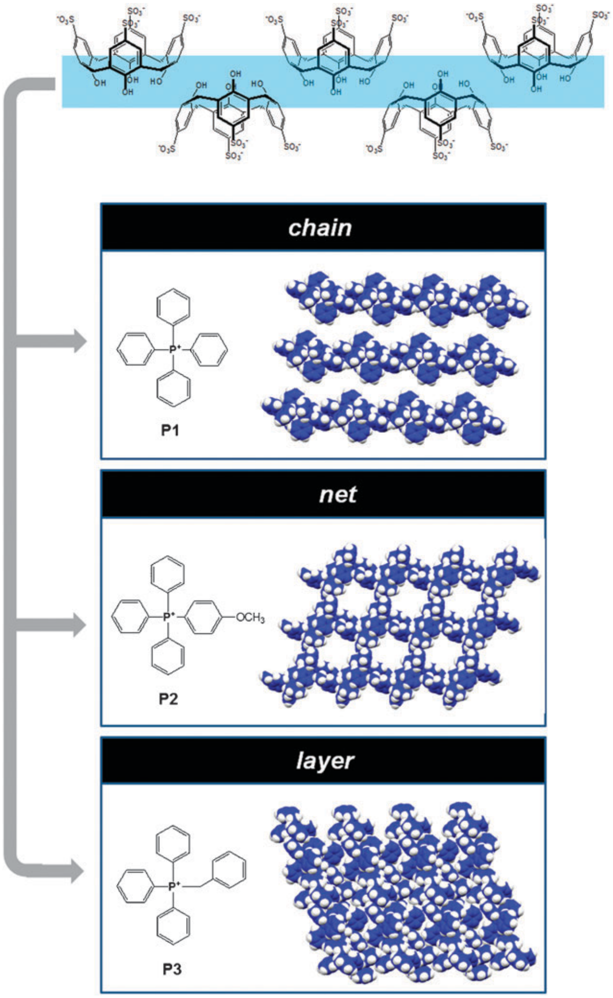


Fig. 8 Examples of phosphonium cation arrangements which are embedded in bilayers of *p*-sulfonatocalix[4]arene, as the blue band (top).

and **P3** forms more compact layers, with the cations interacting through inter-cation phenyl embraces, Fig. 8.

p-Sulfonatocalix[4]arene–phosphonium cation interplay

The self-assembly of *p*-sulfonatocalix[4]arenes and **P1** in the presence of ytterbium(III) metal ions can either form (i) columnar arrays where the cations are organised in a 3-D grid with the calixarenes arranged side-by-side in an up–down/zig-zag fashion, with channels present throughout the network;[18] (ii) multidirectional columns of **P1** cation pair as a scaffold network with the calixarenes encapsulated in pockets;[18] or (iii) a structure with back-to-back calixarenes at right-angles to each other and linked by the phosphonium cations which deviates from the common bilayer arrangement.[22] For (i) and (ii) the structures have a 1 : 3 ratio of *p*-sulfonatocalix[4]arene to **P1**, while for (iii) the ratio is 1 : 2 with the two components having close C–H···π interactions.[18,22]

The expanded calixarene bilayer arrangement is prevalent when imidazolium-based cations are introduced into the multicomponent systems involving calixarenes, phosphonium cations and trivalent lanthanide ions, now as aquated gadolinium(III). The calixarene cavity contains a small imidazolium cation rather than a rigid arm of a large phosphonium cation. The preferential binding of the imidazolium cation is consistent with electrostatic considerations, noting the charge for the phosphonium cations is expected to be more diffuse. It is also consistent with the greater complementarity of other interactions with the ability of the imidazolium cation to orientate itself in maximizing the interactions with the calixarene, for both interplay in solution and uptake in the solid state. For phosphonium cations there are steric limitations on the orientation of a phenyl ring in the calixarene cavity. The phosphonium cations **P1**, **P2** and **P3** take up space in the bilayer around the back-to-back stacked calixarenes involving C–H···π interactions and H-bonding between the two components. It is also noteworthy that this motif prevails in the absence of the imidazolium cations and in the presence of gadolinium(III) metal ion.[22]

Incorporating the bis-phosphonium cation **P4** into multi-component systems with *p*-sulfonatocalix[4]arene and imidazolium-based cations results in a range of remarkable structural types,[31] Fig. 9; **P4** can be (i) embedded in between a head-to-head arrangement of calixarenes, and (ii) embedded in between the back-to-back lower rim arrangement of calixarenes. The methylene bridges in **P4** intertwine with sulfonate groups of the calixarenes through SO···HC interactions, and are directed away from the sulfonate groups with the central aromatic rings being involved in π···π interactions. For arrangement (ii), **P4** shrouds *p*-sulfonatocalix[4]arene in the same plane with the methylene bridges of the calixarene involved in close C–H···π interactions involving the pendant arms of **P4**. The interplay between **P4** and *p*-sulfonatocalix[4]arene molecules is flexible in being maintained in the same form when the calixarenes bind imidazolium cations in their cavities, albeit with different orientations of calixarenes. Here the plane of the calixarene tilts sequentially in binding imidazolium cations **I1** to **I3**, with the tilt angles ranging from 7.2° to 65.5°.

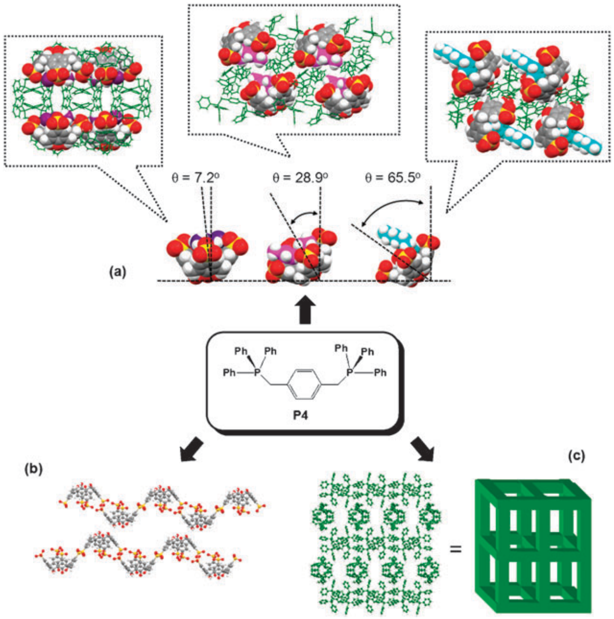


Fig. 9 Outcome of incorporating **P4** in building multi-component layered structures.

The interplay of **P4** with *p*-sulfonatocalix[4]arene can also result in complex multicomponent structures, besides the conventional 'up–down' antiparallel bilayer arrangement. The interlocking of **P4** methylene bridges with sulfonate groups of the calixarenes results in 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. This effectively creates a plane of such polar groups. Another striking feature of the interplay of **P4** and *p*-sulfonatocalix[4]arene is the formation of hydrophobic scaffold networks with pockets containing 'molecular capsules' and water molecules.[36] The rigid **P4** scaffold network in the solid state also has weak SO···HC interactions involving the methylene bridges of **P4** and the calixarene sulfonate groups.

Role of aquated lanthanide(III) ions

The previous discussion gives some insight into the use of trivalent lanthanide ion in building up solid state structures of the multi-component systems. The presence of trivalent lanthanide ions appears to template the self-assembly/crystallisation, but it is not always included in the final structure. This is despite the well-documented direct complexation of lanthanide ions by the sulfonate groups of the calixarenes. The lack of uptake of lanthanide ions for the multi-component materials herein was first established for the *p*-sulfonatocalix[4]arene/**P1** system, with no isolable discrete compound forming in its absence.[18] Subsequently similar findings were established for **P4** with the same calixarene.[31,36]

The contribution of trivalent lanthanide ions in the supramolecular assembly of water-soluble calixarene is significant as the cations can provide a wide range of metal coordination complexes which can result in different structural motifs in the solid state. Atwood *et al.*[39] reported the formation of a 2D coordination polymer *via* the addition of Ce and Pr(III) to *p*-sulfonatocalix[4]arene, while the addition of Gd, Tb and Tm(III) results in 2D hydrogen-bonded polymers. The incorporation of lanthanide ions also provides other variation of structural motifs, for example, 'Russian Doll' and 'Ferris wheel' arrangements.[21] Icosahedral arrays of 12 calixarenes form in the solid state for all the lanthanide metals, while the formation of the cuboctahedral arrays with the same number of calixarenes is limited to aquated Nd, Pr, and Sm(III) ions,[21] depending on the availability of 18-crown-6 molecules.

Conclusions and future prospects

The imidazolium and pyrrolidinium cations, which feature extensively as components in ionic liquids, can be incorporated in the cavity of *p*-sulfonatocalix[4]arene with some level of predictably, as a design strategy in building complex multi-component materials with this water soluble calix[4]arene, and a range of phosphonium cations and aquated gadolinium(III) ions. We have established that (a) the imidazolium or pyrrolidinium cation is selectively taken up into the cavities of *p*-sulfonatocalix[4]arene rather than the phosphonium cation, (b) the nature of the structure formed depends on the length of the *N*-alkyl chain attached to the imidazolium and pyrrolidinium cations, (c) the nature of the phosphonium cation influences the formation of multilayered components, and (d) the presence of lanthanide(III) ions is necessary to form the complexes, but they are not always incorporated into the structures.

A level of control has been achieved with respect to 'molecular capsule' formation involving *p*-sulfonatocalix[4]arenes and imidazolium cations bearing ethyl or *n*-butyl termini in the presence of lanthanide metal cations. The smaller imidazolium cations have a striking ability to assemble in different ways, where the cations can either have the charged head group or the *N*-alkyl chain residing in the hydrophobic cavity of the calixarene. Imidazolium cations with a longer *N*-alkyl chain (*n*-octyl) at the termini may either form 'molecular capsule' or can disrupt the usual bilayer arrangement with the alkyl chain penetrating the adjacent bilayer of calixarenes and phosphonium cations. End-capping of bis-imidazolium cation with two calixarenes is prominent where the two ends fit snugly into the calixarene cavity. The phosphonium cations assemble with calixarenes into bilayers, either as layers, grids or linear arrays. The formation of discrete complexes involving larger phosphonium cations is challenging, and the presence of lanthanide metal cations is important in assisting the formation of complexes but may not be incorporated in the structure. Bis-phosphonium cations can interlock with calixarenes, affording structures assembled in a distinctly different bilayer arrangement.

The self-assembly strategies involving multi-components in building complex structures are useful in developing the applications of functional materials, such as designing porous material for gas or small molecule separations. Moreover, incorporating charged magnetic material possessing hydrophobic surfaces and/or similarly charged molecules with novel opto-electronic properties into the structures is also possible in gaining access to functional material for device applications.

Acknowledgements

We thank the University of Malaya for financial support from Science Fund grant (03-001-03-SF0286), university research grant PS354/2009A, University of Malaya Centre for Ionic Liquids (TA021/2009A), the University of Western Australia, and the Australian Research Council for supporting this work. Thanks also to colleagues who contributed to the publications leading up to this article, especially Dr Alexandre N. Sobolev, Dr Lindsay T. Byrne and Dr Brian W. Skelton.

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