# Sulfonatocalixarenes: molecular capsule and 'Russian doll' arrays to structures mimicking viral geometry

Scott J. Dalgarno,*[a] Jerry L. Atwood*[a] and Colin L. Raston*[b]

*p*-Sulfonatocalix[4,5,6,8]arenes are versatile building blocks, able to assemble into 'molecular capsule' arrays based on two calixarenes, as well as a variety of other structural motifs, with the extended structures dominated by the formation of bilayers. For *p*-sulfonatocalix[4]arene, assembly into nanometre scale spheroids (of either icosahedral or cuboctahedral geometries) as well as nanotubules (all of which take on structural features akin to those of viruses) is possible, depending on the guest molecules and lanthanides present in solution.

## Introduction

Since the pioneering work concerning the synthesis of the parent calix[*n*]arenes by Gutsche and co-workers, the host–guest and supramolecular chemistry of these versatile molecules has flourished.[1–3] This development relates in part to the molecules possessing cavities or clefts which are capable of binding molecules with appropriate electronic and or steric complementarity. Specific properties of these molecules can be tailored by functionalising either the 'upper rim' or 'lower rim' of the calixarene framework.[1] In many cases, such modification is straightforward and this allows access to a virtually unbounded library of potential host molecules.

Of the large family of water-soluble calixarenes that have been synthesised in recent times, we have been interested in the solid state supramolecular chemistry of

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*p*-sulfonatocalix[*n*]arenes (where *n* = 4, 5, 6, 8, general notation herein SO$_3$[*n*]). Whilst not only offering the opportunity to employ water as a benign solvent for reaction or crystallisation, these calixarenes present hydrophobic cavities for guest inclusion of organic molecules, although the inclusion of water is also possible.[4,5] The 'upper rim' sulfonate groups are capable of interacting with a range of organic, charged organic, inorganic or hydrogen-bond donor species.[4] Furthermore, these water-soluble calixarenes also display interesting biological behaviour, a topic which was recently reviewed by Coleman *et al.*[6]

The smallest *p*-sulfonatocalixarene, SO$_3$[4], often adopts a cone conformation and assembles in up–down antiparallel bilayer arrangements, thereby mimicking the structures of organic clays in the solid state, Fig. 1.[5] Overall, the smaller calixarene has special features which relate to its supramolecular chemistry being significantly more developed than that of the larger analogues. These features include: (i) less problematic collection and refinement of single-crystal diffraction data for smaller systems, (ii) ease of synthesis of the calixarene relative to some of the larger calixarenes, (iii) limited torsion mobility and complications associated with alternative conformation, and (iv) the ease of complex crystallisation. Highly complex multi-component architectures based on SO$_3$[4] have been structurally authenticated. These include bilayer arrangements based on 2-D or 3-D coordination polymers, large coordination or host–guest complexes, and amino acid complexes.[4,7] Often the calixarenes are aligned so that the 'upper rim' of one SO$_3$[4] from one bilayer is facing the 'upper rim' of another, thus forming a common inclusion sphere. The two host molecules and their contents form molecular capsule arrangements that often take on the characteristics of 'Russian dolls', *i.e.* layers of self-assembled material around a central core. Under specific conditions, formation of the antiparallel bilayer packing of SO$_3$[4] can be circumvented, and the ensuing parallel packing of the cone-shaped calixarene can impart curvature on the resultant supramolecular structures. This is manifested in the formation of spectacular nanometre scale spheroids or tubules.[8]

The focus of this article is to map out some of the structural diversity of sulfonatocalix[*n*]arene complexes, particularly in relation to the formation of molecular capsules and 'Russian dolls', as well as nanospheroidal and tubular arrangements. Until recently, much of this work was based on *p*-sulfonatocalix[4]arene. Now, the corresponding calix[5, 6 and 8]arenes have been shown to form arrays based on molecular capsules that are also comprised of two 'upper rim aligned' hosts.[9] These assemblies offer themselves as alternative building blocks for the construction of larger and higher complexity nanoarrays.
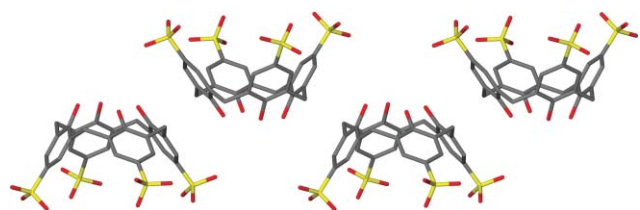


**Fig. 1** An example of the structural up–down antiparallel bilayer arrangement as formed by the self-assembly of *p*-sulfonatocalix[4]arene.[5]

## Molecular capsules and 'Russian dolls' based on *p*-sulfonatocalix[4]arene

Numerous multifaceted supramolecular arrangements based on *p*-sulfonatocalix[4]arene have been structurally authenticated through the use of single-crystal X-ray diffraction techniques. A survey of the Cambridge Structural Database (CSD) shows that of the 74 structural reports based on SO$_3$[4], a significant number have pairs of the calixarene arranged into molecular capsules.[10] The majority of these have crown ether or other related disc-shaped molecules shrouded by two SO$_3$[4] molecules. Charge balance is by (i) suitably charged *exo*-capsule organic/inorganic species that 'seal' the capsule and the contents within (hence the name 'Russian doll'),[4a,b,8b,11] (ii) variation in the degree of protonation of the sulfonate groups, or (iii) deprotonation of one of the phenolic moieties.

These 'Russian dolls' are readily formed by combining sodium *p*-sulfonatocalix[4]arene with 18-crown-6. A degree of structural versatility is associated with the inclusion of a sodium cation in the crown ether; sodium centres can have two *trans*-water molecules, or two *trans*-oxygen centres from sulfonate groups, one from each calixarene, Fig. 2.[11] These sealed 'Russian doll' superanions take on an overall 7− charge and their formation can be associated with selective retrieval of large polynuclear transition-metal aquo species or aluminium Keggin ions from polymeric metallic mixtures.[4b]

The rare earths have also been shown to form similar 'Russian dolls' with these superanions, as well as alternative 'Ferris wheels' or hybrids of both with SO$_3$[4]–18-crown-6 host–guest systems, Fig. 3.[12] The rare earths can be either (i) present as homoleptic aquated ions, (ii) be bound directly to one or more oxygen centres of sulfonate groups with the coordination sphere satisfied by water molecules, or (iii) be encapsulated as Ln–18-crown-6–H$_2$O complexes with the
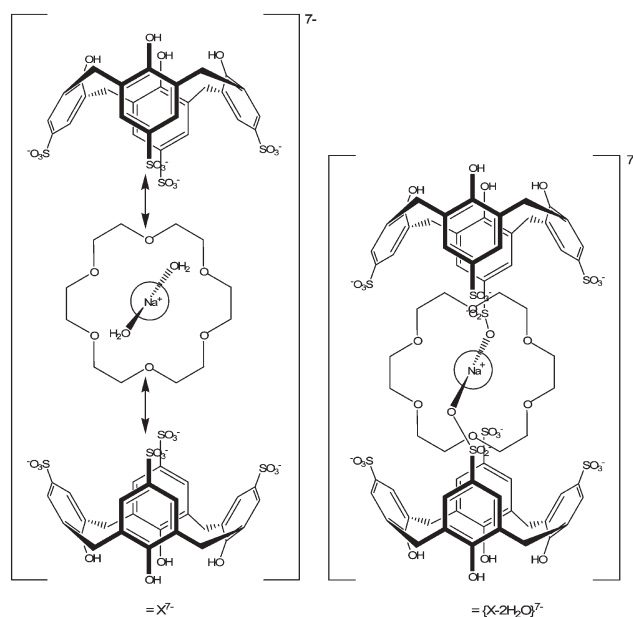


**Fig. 2** Superanionic capsules that selectively crystallise polynuclear hydrolytic transition-metal or aluminium Keggin ions from solution. The capsules are formed by addition of 18-crown-6 to an aqueous solution of sodium *p*-sulfonatocalix[4]arene.[4a,b,11]
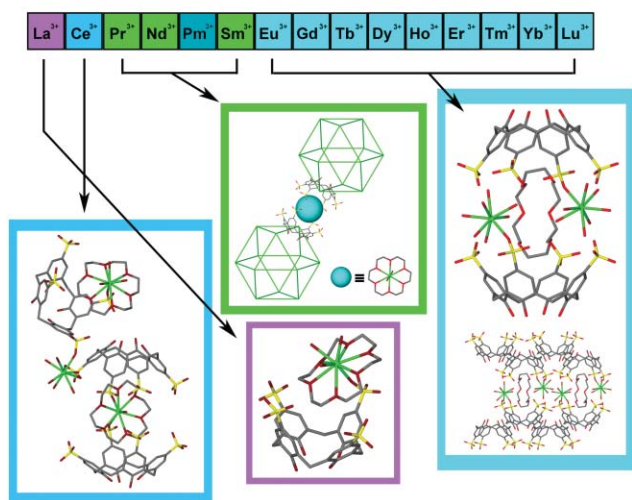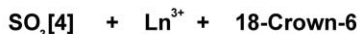
**Fig. 3** Structural diversity for lanthanide complexes of 18-crown-6 and sodium *p*-sulfonatocalix[4]arene.[4a,b,8b,11,12]

presence of additional *exo*-capsule lanthanide cations.

When (di-)cationic (bi-)cyclic (di-)aza-functionalised molecules are employed in place of 18-crown-6 in ternary SO$_3$[4]–guest–Ln(III) systems, the potential guest has less propensity for lanthanide metal complexation in aqueous solution. This therefore offers an increased level of control in the formation of the molecular capsule by forcing all lanthanide metal cations to be *exo* to the resultant superanion.

When the globular species [2H(2.2.2)cryptand]$^{2+}$ is employed, the guest is trapped in a molecular capsule arrangement as part of a 2-D lanthanide coordination polymer **A** (Fig. 4).[13] The Ln$^{3+}$ cations exactly match the charge

complex formation in such systems, assuming that an SO$_3$[4] molecule presents a 4− charge at a pH < 4–5; a capsule containing a dicationic guest would have an overall negative charge of 6–, ideal for crystallisation with two Ln$^{3+}$ counterions. Molecular capsule motifs, **B–D** (Fig. 4), are also found when [2H(diaza-18-crown-6)]$^{2+}$, [H(1-aza-18-crown-6)]$^+$ or [2H(diaza-15-crown-5)]$^{2+}$ are used as potential guest species, respectively.[14–16] In all four cases, single-crystal growth of the supramolecular complexes is rapid and occurs within 15 to 30 min for the charged cyclic guests, and overnight for [2H(2.2.2)cryptand]$^{2+}$. Surprisingly it is not possible to form >a crown ether containing molecular capsule with [H(1-aza-15-crown-5)]$^+$ under a variety of conditions, although a 'neodymium-sealed' capsule **E** (Fig. 4) is formed (structurally characterised) as part of a 2-D coordination polymer.[15]

For smaller (di-)cationic (bi-)cyclic aza-functionalised guests, the resultant supramolecular arrangements **F** and **G** (Fig. 4) have alternative host–guest bilayers consisting of 1 : 1 SO$_3$[4]–guest moieties.[16] When [2H(diaza-12-crown-4)]$^{2+}$ is employed as a potential guest, single-crystal growth is also rapid upon addition of the appropriate lanthanide metal salt.[16]

All of these results suggest that even when a dicationic guest is employed, the ability of the guest to bind two hosts (based on steric considerations) is more influential in the assembly of the supramolecular array, a fact to which the omission of protonated 1-aza-15-crown-5 may perhaps be attributable; 1-aza-15-crown-5 appears to have a size and charge mismatch for SO$_3$[4], thereby preventing complex formation with in either a capsule or bilayer motif in these lanthanide based systems.

The phenomenon of rapid crystallisation suggests calixarene and crown ether pre-association in solution prior to complexation of the lanthanide ions. A series of $^1$H NMR diffusion ordered spectroscopy (DOSY) experiments have been carried out to ascertain host–guest complexation, at least in the absence of Ln$^{3+}$ cations because of their paramagnetic
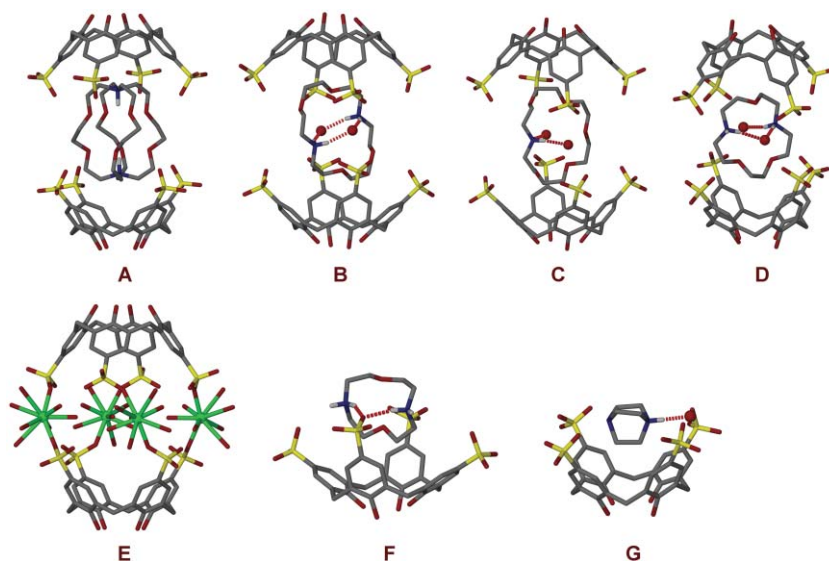


**Fig. 4** Molecular capsule (**A–D**), sealed coordination capsule (**E**), and alternative host–guest motifs (**F** and **G**) formed when (di)protonated (di)aza-functionalised guest molecules are involved and rapidly crystallised (with exception of **E** and **G**) with selected lanthanide metals and SO$_3$[4].[13–16] Lanthanide metal cations (except those in **E**), water molecules of crystallisation (except those shown in **B–D** and **G**) and hydrogen atoms (except NH) have been omitted for clarity.

**Table 1** Binding constants for the complexation of (di-)protonated aza-crown ethers with *p*-sulfonatocalix[4]arene in solution.[17]

| Guest | $K_a/M^{-1}$ |
|---|---|
| [2H(diaza-18-crown-6)]$^{2+}$ | $6.1(5) \times 10^3$ |
| [H(1-aza-18-crown-6)]$^+$ | $9.9 \times 10^5$ |
| [2H(diaza-15-crown-5)]$^{2+}$ | $2.5 \times 10^4$ |
| [H(1-aza-15-crown-5)]$^+$ | $5.1 \times 10^2$ |
| [2H(diaza-12-crown-4)]$^{2+}$ | $1.4 \times 10^5$ |

properties.[17] This established that SO$_3$[4] complexes the (di-) protonated aza-crown-ether guests in solution, and this most likely happens in solutions containing the lanthanide ions, prior to their addition and concomitant structural studies. In these DOSY experiments, for all but 1-aza-15-crown-5, the aforementioned protonated crown ethers bind either strongly or *very* strongly to *p*-sulfonatocalix[4]arene (Table 1).

The above complexation can also be used to purify diaza-18-crown-6 from a crude reaction mixture through crystallisation of a lanthanide based molecular capsule.[18] In this process, crystals of the complex are filtered off and washed with water. The complex is destroyed by the addition of dilute NaOH until the pH reaches ~8. The resulting mixture is neutralised with dilute HCl and the diaza-18-crown-6 recovered from the aqueous mixture by extraction with organic solvents.

## Nanometre scale spheroidal and tubular arrays based on *p*-sulfonatocalix[4]arene

The typical up–down antiparallel bilayer packing of SO$_3$[4], as shown in Fig. 1 and 3, can be circumvented under certain conditions.[8] When this occurs, the molecules can pack in a parallel manner and this in turn can enforce curvature on the resultant supramolecular arrays. When pentasodium *p*-sulfonatocalix[4]arene (Na$_5$SO$_3$[4]) is treated with pyridine *N*-oxide (PNO) and lanthanum nitrate in a 2 : 2 : 1 ratio, large single crystals grow over a several hour period.[8a] The molecular components assemble as C-shaped dimers based around a lanthanum(III) centre through Ln–O$_3$S coordination, Fig. 5. The extended structure has 12 molecules of SO$_3$[4] arranged at the vertices of near spheroidal, nanometre scale icosahedron. The central core of the icosahedral spheroid has a volume of around 975 Å$^3$, comprising two sodium ions and thirty water molecules. This is notably the most efficient and highly symmetrical way of arranging twelve entities at the vertices of
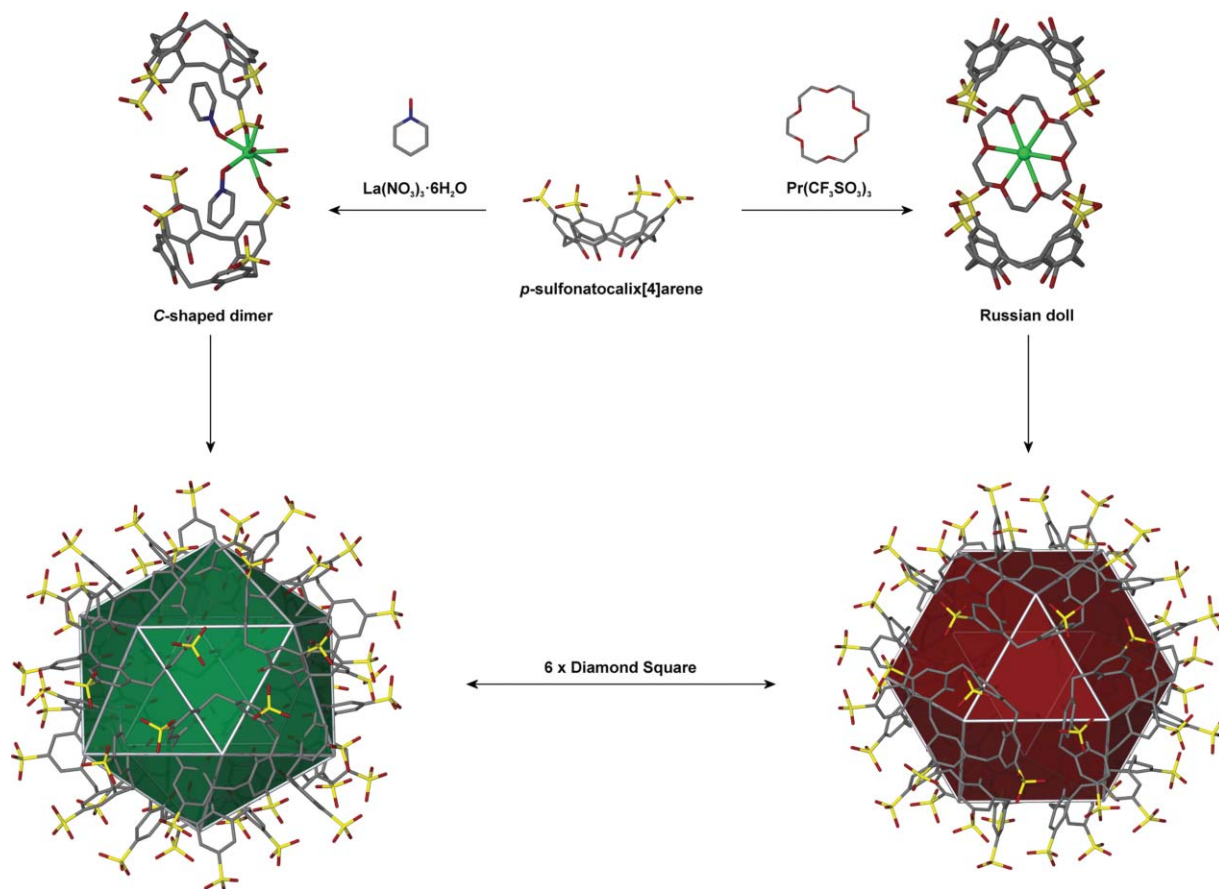


**Fig. 5** Schematic formation of nanometre scale spheroids based on *p*-sulfonatocalix[4]arene. In the left hand pathway, co-crystallisation of SO$_3$[4] with pyridine *N*-oxide and lanthanum nitrate results in the formation of a C-shaped dimer. The extended structure formed with the C-shaped dimer shows twelve SO$_3$[4] molecules to reside at the vertices of an icosahedron (shown by green faces within spheroid). In the right hand pathway, the use of 18-crown-6 as a guest and praseodymium triflate as a metal salt enforces the calixarenes to assemble in a 'upper rim' to 'upper rim' arrangement as molecular capsules. The extended structure based these capsules has twelve SO$_3$[4] molecules at the vertices of a cuboctahedron (shown by red faces within the spheroid). The icosahedron (Platonic) and the cuboctahedron (Archimedean) are dual solids and are related by a sextuple diamond square process.[8,19]

a Platonic solid, the result of which being that the 'spheroid shell' is tightly packed. Each individual icosahedron is linked to six neighbouring icosahedra through six pairs of C-shaped dimers in a trigonal antiprismatic fashion, *i.e.* edge-sharing icosahedra.

Exchanging 18-crown-6 for pyridine *N*-oxide, and praseodymium(III) (or neodymium(III) or samarium(III)) triflate for lanthanum nitrate in the ternary $SO_3[4]$–guest–Ln system described above, a second nanospheroid now based on a cuboctahedron is formed, Fig. 4.[8b] Praseodymium(III) ions are complexed by 18-crown-6 together with two *trans*-water molecules, and form the core of 'upper rim' to 'upper rim' molecular capsules, similar to the *trans*-aqua 18-crown-6 complex of sodium, Fig. 2 and 3. In the extended solid-state structure, these 'Russian dolls' are arranged in the form of cuboctahedra. A remarkable feature of the structure is that the change in $SO_3[4]$ packing, due to molecular capsule formation, results in the introduction of pores to the 'spheroid shell' which are occupied by disordered water molecules. The central core of each cuboctahedron is composed of six aquated homoleptic praseodymium ions and the metal centres reside at the vertices of an octahedron, the axes of which are directed towards the
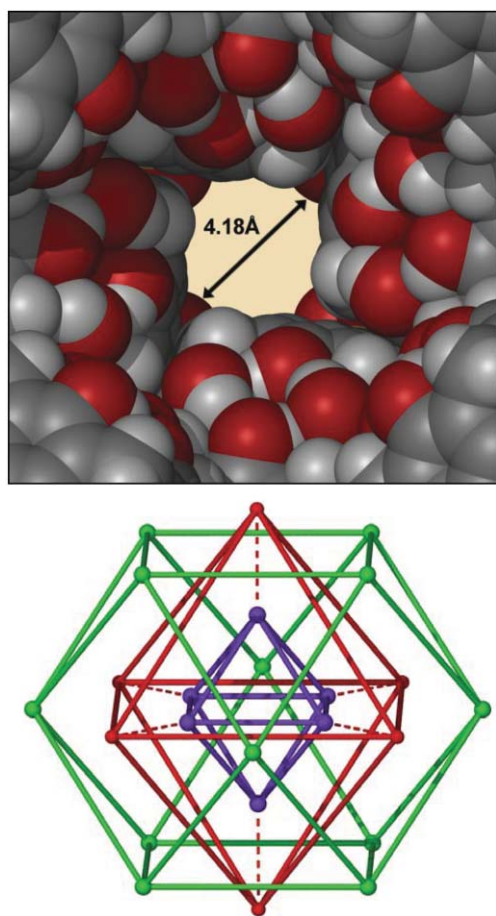
six pores in the 'spheroid shell', Fig. 6. While the formation of icosahedral arrangements is general for the lanthanide metals, the formation of the cuboctahedral spheroids is limited to Nd, Pr, and Sm. This is related to lanthanide metal size and binding within 18-crown-6, as La and Ce have been shown to form different supramolecular architectures under similar conditions (Fig. 3). The extended cuboctahedral structure also shows that adjacent cuboctahedra are linked through the 'Russian dolls' in a cubic close packed arrangement.

Icosahedra and cuboctahedra are dual solids that can be considered as interchangeable *via* a sextuple diamond–square process.[19] In the present examples the internal volume of the dual solids differ by approximately 30% in favour of the cuboctahedron. Thus, changing the nature of the species in the hydrophobic cavity of the calixarene (pyridine-*N*-oxide to 18-crown-6) results in expansion of the spheroid, whilst at the same time opening up channels in the spheroid 'shell' as discussed above. This control of pore size and interchangeable spheroid shell structure is reminiscent of the behaviour of the cowpea chloritic mottle virus under specific pH control, a system that can be used to trap molecular material for study within the virion shell.[20] The larger cuboctahedral array appears to allow 'communication' from the *endo*-hydrophilic





**Fig. 6** Projections showing (a) a pore from the cuboctahedral spheroid shell and (b) the various geometrical properties of one spherical assembly; within each spheroid, the twelve calixarenes reside over cuboctahedral vertices (green) whilst the core lanthanide ions (purple) are oriented on the same vertices as the six spheroid pores (occupied by disordered water molecules as shown in red).[8b]
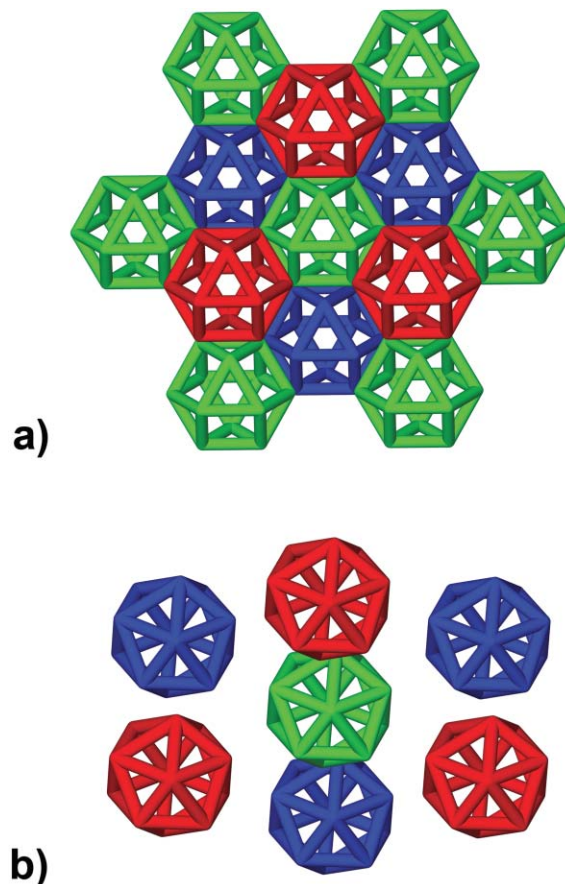


**Fig. 7** Packing diagram for (a) cuboctahedral and (b) icosahedral spheroids based on *p*-sulfonatocalix[4]arene. In (a), the Archimedean solids are arranged in a cubic close packed fashion. In (b), the Platonic solids are packed in a trigonal antiprismatic fashion. In both diagrams, the solids have been reduced in size to aid clarity.

cavity of the dual solid through hydrophobic channels/pores to *exo*-hydrophilic regions *via* the presence of water molecules within these voids (Fig. 6), although studies have not yet dealt with water movement through these channels. An additional feature of the vertex sharing cuboctahedra is that a central cuboctahedron and its twelve neighbours are arranged in a cubic close packed manner (Fig. 3, 5 and 7). Notably, icosahedra cannot pack in such a way and this is evidenced by the fact that a central spheroid and its six neighbours are arranged in a trigonal antiprismatic fashion, linked together by the aforementioned C-shaped dimers (Fig. 5 and 7).

Yet another remarkable feature (also associated with circumventing the bilayer) is the ability to control the self-organisation of $SO_3[4]$ by varying the stoichiometries of lanthanide metal and PNO in the crystallisation solution.[8a] By changing the $Na_5SO_3[4]$ : PNO : $La(NO_3)_3$ ratio from 2 : 2 : 1 to 2 : 8 : 1, the components assemble as nanotubules rather than icosahedral arrays (Fig. 8).[8a] In this arrangement, the tubules have a diameter similar to that of the icosahedral array, and 'sodium bound' pyridine *N*-oxide molecules act as 'spacers' to facilitate different packing to that found in the icosahedron **F** (Fig. 8). The tubule core is composed of
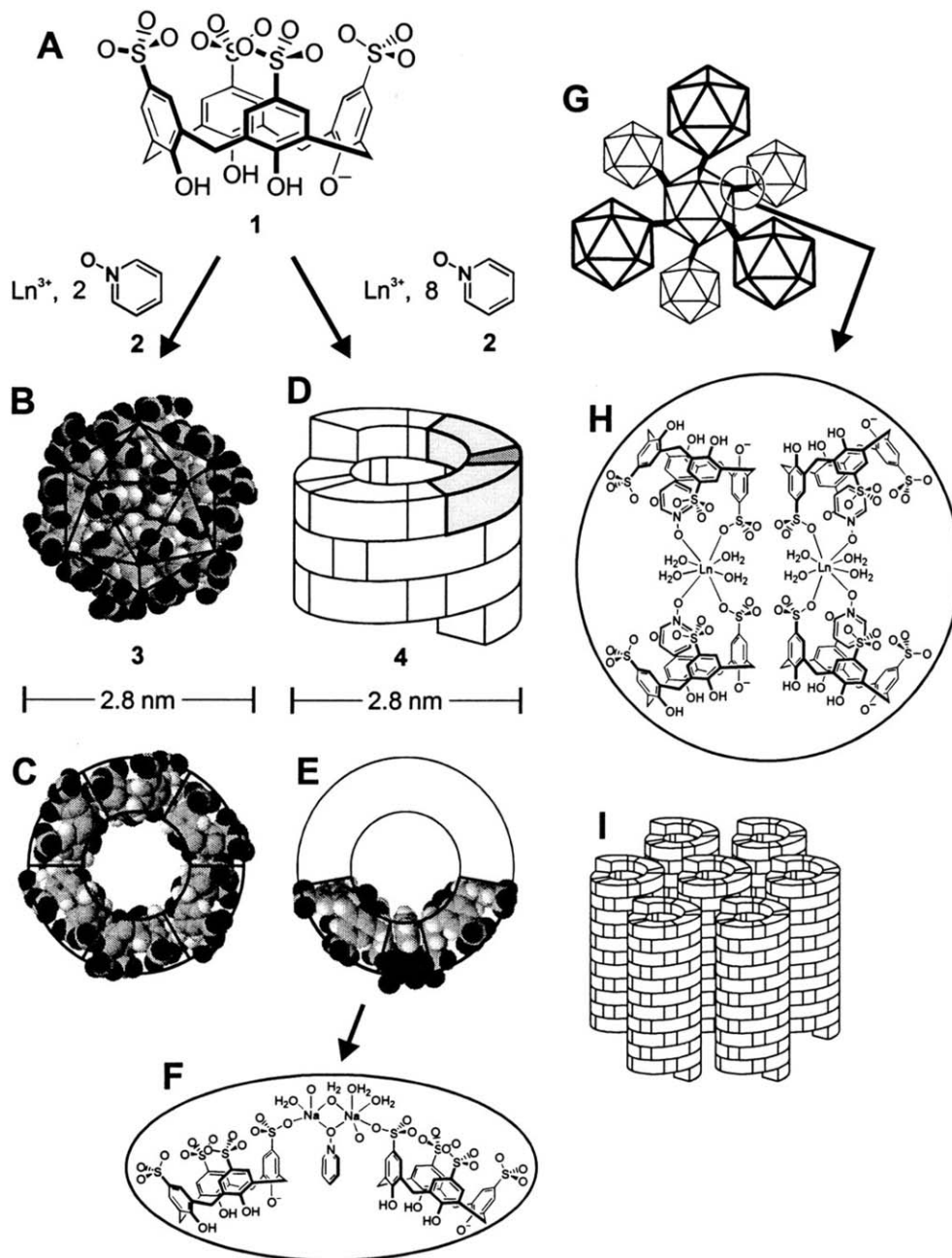


**Fig. 8** Diagram showing: **A–E**, the crystallisation conditions required for the formation of either icosahedral or nanotubule arrays based on $SO_3[4]$; **E, F**, the interstitial 'spacer' role of PNO in the nanotubule framework; **G, H**, the packing and coordination links between neighbouring icosahedra; **I**, the hexagonal packing found between neighbouring nanotubules.[8a]

hydrated sodium and lanthanum cations whilst adjacent tubules are linked by *exo* sodium and lanthanum cations that are coordinated to upper rim SO$_3$[4] sulfonate groups. Further to this, recent results show that praseodymium ions induce the formation of tubule helical arrays based on host–guest supermolecules comprised of sulfonated calix[4]arene and a Co(III) sepulchrate complex.[21]

## Advances in 'molecular capsules' based on pairs of *p*-sulfonatocalix[5, 6, 8]arenes

In contrast to SO$_3$[4], the solid-state supramolecular chemistry of the corresponding calix[5, 6 or 8]arenes is less well developed. For *p*-sulfonatocalix[5]arene, this may be related to the intensive and low yielding synthesis of *p*-$^t$Bu-calix[5] arene, although this has recently been improved.[22] Whilst the synthesis of *p*-sulfonatocalix[6 and 8]arene are straightforward, the molecules possess a greater degree of conformational flexibility, and this may render single-crystal growth of the supramolecular arrays inherently more difficult.

Of the eleven SO$_3$[5] based supramolecular structures on the CSD, in addition to two recently reported structures, three are based on molecular capsule motifs, *i.e.* 'upper rim' to 'upper rim' interplay of two calixarenes thereby confining space.[10,23] In two of these three structures, lanthanide(III) ions are coordinated to calixarene sulfonate groups from both SO$_3$[5] molecules within the capsules, with additional pyridine *N*-oxide ligands residing in the calixarene cavities.

The third example of molecular capsule formation is based on hydrogen bonding interactions as part of the confinement of dimeric sulfuric acid.[23c] In all of these examples, including those not highlighted here, SO$_3$[5] adopts a splayed bowl conformation in the solid state.[23] In more recent studies, complexation of diprotonated DABCO with SO$_3$[5] markedly distorted the conformation of the calixarene, resulting in the formation of a bis-molecular capsule motif **A** (Fig. 9).[9a] The small dications act simultaneously as guests on the interior of the double capsule, and also as additional counterions on the exterior of the assembly (not shown in Fig. 9).

For *p*-sulfonatocalix[6]arene, two general conformations are observed for the host; 'up–down double partial cone' and 'up–up double cone'.[9b,c,10,24] In the former of the two, the calixarene is typically found to reside around a crystallographic inversion centre in the solid state, and to generate the 'up–down double partial cone' conformation in the extended structure.[24,25] Three of the eleven SO$_3$[6] structures on the CSD, in addition to two more recently published examples, show the calixarene in the 'up–up double cone' conformation.[9b,c,10] Of all of these 'up–up' examples, two arrangements form as bis-molecular capsules where two SO$_3$[6] molecules shroud either two 18-crown-6 molecules (**B**) or two tetraphenylphosphonium cations (**C**) (Fig. 9) whilst complexing lanthanide metal cations.[9b,c] While the formation of supramolecular complexes with SO$_3$[6] remains more difficult than for SO$_3$[4] or SO$_3$[5], the first supramolecular structure incorporating *p*-sulfonatocalix[8]arene has recently been reported.[26] In addition, we have recently established that SO$_3$[8] forms a complicated structure with Yb$^{3+}$ and tetraphenylphosphonium ions.[9d] Two calixarenes, in the pleated
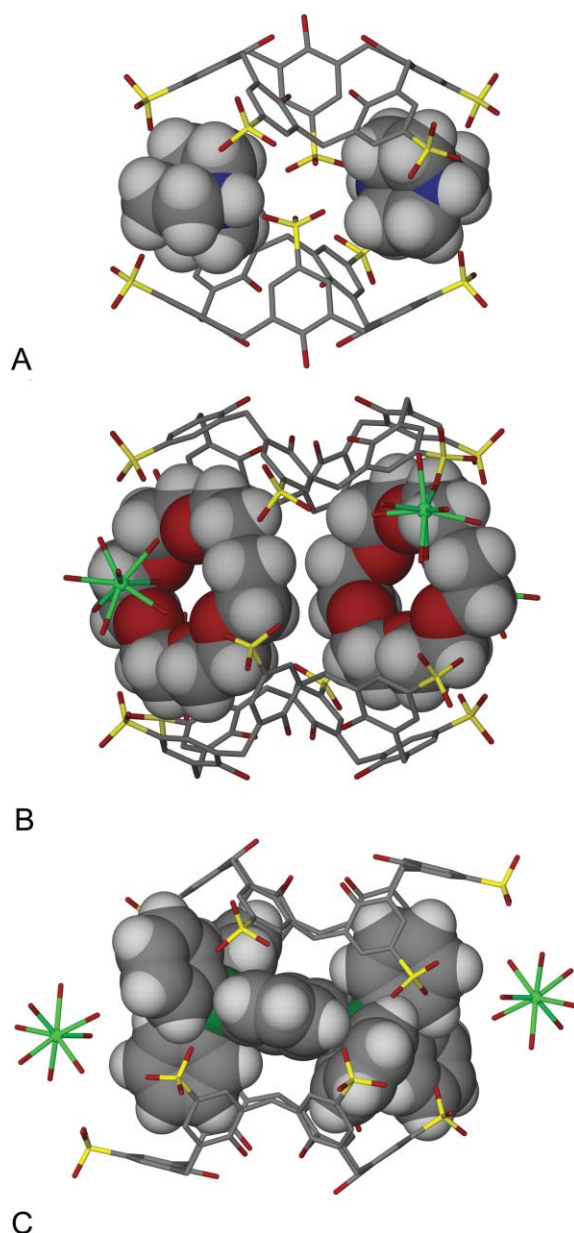


A

B

C

**Fig. 9** Examples of bis-molecular capsule arrangements formed with SO$_3$[5] (**A**) and SO$_3$[6] (**B** and **C**). In **A**, two SO$_3$[5] molecules shroud two diprotonated DABCO molecules and two waters of crystallisation involved in hydrogen bonding with 'lower-rim' OH groups.[8a] In **B**, two 18-crown-6 molecules are shrouded by two SO$_3$[6] molecules that are in the previously unobserved up–up double cone conformation.[8b] In **C**, two tetraphenylphosphonium cations are also shrouded by two SO$_3$[6] molecules within the double capsule arrangement.[8c]

loop conformation, effectively shroud three phosphonium ions, with disordered lanthanide ions binding to sulfonate groups as is often observed for many of the lanthanide complexes with smaller sulfonated calixarenes. Once a better level of control over the interplay of larger *p*-sulfonatocalix-[*n*]arenes in association with metal ions and organic moieties is established, the formation of larger spherical multi-component superstructures, tubular arrays, and arrays of higher complexity may be possible.

## Conclusions

The formation of large spherical dodecahedral *p*-sulfonatocalix[4]arenes structures is dependent on the guest molecule and respective capsule formation, as well as the nature of the lanthanide metal cations and their relative stoichiometries.[8] The synthesis of other large spherical or highly symmetric structures based on SO$_3$[4] is a significant challenge. Expansion of SO$_3$[4] bilayer arrays using the tetraphenylphosphonium ion lends insight into this problem and demonstrates the ability to finely tune the hydrophobic characteristics of these supramolecular architectures by employing non-covalent interactions.[27] This approach may help in 'breaking the bilayer' to form other alternative architectures.

A level of control has been achieved with respect to molecular capsule formation between SO$_3$[4], crown ethers and various lanthanide metal cations. These arrangements may prove useful in spheroid formation through variance in pH or other reaction conditions using combinatorial supramolecular chemistry in future studies.

For *p*-sulfonatocalix[5]arene, molecular capsule formation is less straightforward, although not unprecedented.[23a] The formation of a bis-molecular capsule with distorted SO$_3$[5] demonstrates the versatility of the host. In this conformation, SO$_3$[5] could act as a two-vertex species in spheroid or superstructure formation.[9a] Similarly, *p*-sulfonatocalix[6]arene can assemble into bis-molecular capsules or other structural motifs (with other molecular components) that have two-vertex character when the host molecules are in the 'up–up double cone' conformation.[9b,c] Although control over the conformational flexibility of SO$_3$[6] remains somewhat problematic in forming the complexes, the *p*-sulfonatocalix[5, 6]arenes and the corresponding octamer show potential for the assembly of more complex superstructures in the solid state.

## Acknowledgements

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