'Molecular capsules' based on *p*-sulfonatocalix[6]arene shrouding two tetraphenylphosphonium cations

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***p*-Sulfonatocalix[6]arene in the double cone conformation forms a molecular capsule-like arrangement confining two tetraphenylphosphonium cations, as part of an extended structure involving layers of additional tetraphenylphosphonium cations, aquated lanthanide ions and a large array of water molecules.**

Crystal engineering is a major area of research which defines and exploits modes of weak interactions between the components of molecular crystals.[1] Sulfonatocalixarenes are a widely investigated class of water soluble tectons prominent in supramolecular chemistry and separation science.[2] In general, their ready accessibility and rich structural chemistry, *e.g.*, the formation of molecular capsules, coordination polymers and spheroidal or tubular arrays, is well documented, particularly for *p*-sulfonatocalix[4]arenes.[3] Tetraphenylphosphonium cations, Ph_4P^+, can self-associate in the solid through interdigitation of the phenyl groups from adjacent cations forming $\{Ph_4P^+\}_2$ pairs as the sextuple or lower order 'phenyl embraces'.[4] This self-association capability enhances their utility in crystallising a diverse range of anions. Polyanionic *p*-sulfonatocalix[*n*]arenes can also interact by way of π-stacking forming bilayer structures or perturbations thereof.[5]

p-Sulfonatocalix[4]arenes typically adopt a cone conformation and form bilayer arrangements in the solid state.[6] We have recently reported complexes with the tetraphenylphosphonium cation in two closely related isomorphous structures.[7] *p*-Sulfonatocalix[6]arenes, by contrast, have a greater degree of conformational flexibility and generally adopt either an 'up–down' double partial cone conformation or an 'up–up' double cone conformation, both conformational arrangements being structurally authenticated.[8] Molecular capsules based on *p*-sulfonatocalix[6]arene with a bigger cavity than its calix[4]analogue are less well-documented. A prerequisite here is an 'up–up' conformation, and achieving control *vis-à-vis* the formation of other conformations is difficult. In previous studies we showed that molecular capsules derived from upper-rim to upper-rim interplay between a pair of *p*-sulfonatocalix[6]arenes can be achieved with an appropriate choice of the encapsulated species, notably 18-crown-6 in the presence of the smaller lanthanide ions.[9] However, the calixarene may adopt an 'up–up' double cone conformation, or (centrosymmetric) 'up–down' double partial cone conformation, depending on the ratio of the guest used and the nature of the lanthanide metal.[9]

Herein we report a 'molecular capsule' like array, formed in the presence of tetraphenylphosphonium cations, where the guest is a pair of such cations in contact with each other at the van der Waals' limit, and the two sulfonated calixarenes associate through hydrogen-bonding to a pair of aquated lanthanide metal ions. In the extended structure, these capsules, which are slightly skewed, are arranged into layers, interleaved by layers of tetraphenylphosphonium cations, Fig. 1, so that the structure is devoid of the bilayer type arrangement prevalent for sulfonated calixarenes. The encapsulated $\{Ph_4P^+\}_2$ pair has the usual mode of self-association interaction, with, as well some of the phenyl groups residing in the pseudo-cavities of the 'up–up' double cone conformation of the two calixarenes.

Interplay of the encapsulated pair of tetraphenylphosphonium cations involves two *meta*-CH···π contacts with the CH···centroid distances at 2.7 Å, the phosphorus centres being separated by 8.043(4) Å. The interaction of the cations with the calixarenes involves a further four such contacts to the aromatic rings of the calixarene, Fig. 2. Two sets of aryl *para* hydrogens from each of the included Ph_4P^+ cations are directed towards the aromatic rings of the calixarenes with CH···π centroid distances at 2.5 Å. Moreover, mutual CH···π interactions are found between pairs of planar aryl groups at the centre of each capsule from each of the included cations. Their *meta* hydrogens are directed to the centroid of each other at 2.7 Å.

Phenyl embrace pairing is also evident in the tetraphenylphosphonium layers sandwiching the calixarene, albeit with less pronounced CH···π contacts involving *meta* hydrogens with CH···π centroid distances at 2.8 and 2.9 Å, Fig. 2. The remaining aryl group from each of the included Ph_4P^+ cations protrudes out of the capsule into the hydrophilic domain. The 'pinched' 'up–up' cone conformation of the calixarene optimises CH···π interactions between the six aryl hydrogens by forming a pair of pseudo

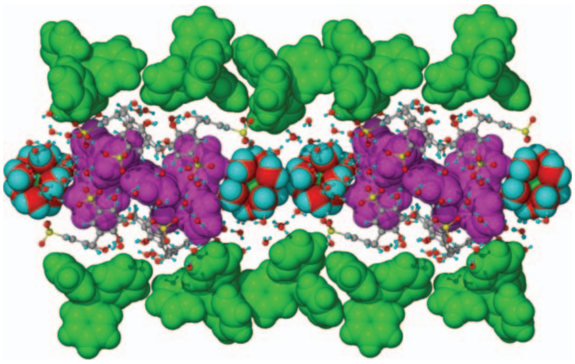

Fig. 1 Partial packing diagram showing the array of skewed 'molecular capsules' separated by $[Yb(H_2O)_8]^{3+}$cations and sandwiched by layers of tetraphenylphosphonium cations.

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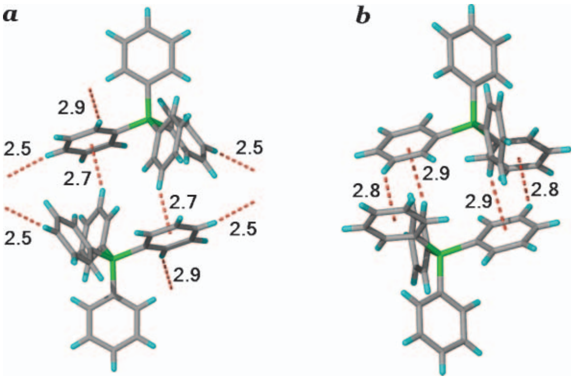

Fig. 2 Centrosymmetric tetraphenylphosphonium pairing (a) within the capsule and (b) within the layers (Å).

'calix[3]arene' cavities, which have a complementarity of fit with the aryl groups of the tetraphenylphosphonium cation pair. In the extended structure the 'capsules' are well separated from each other, in contrast to the usual bilayer arrangement where the calixarenes are π-stacked. The 'capsules' are connected through hydrogen bonding to two aquated ytterbium cations, $[Yb(H_2O)_8]^{3+}$, and a large number of water molecules. The aquated ytterbium cations are offset and in a non-linear arrangement with respect to the continuous chain of calixarene capsules (Yb···Yb separation of 7.237(2) Å). Within the calixarene layer, the continuous array of calixarene capsules/metal cations presumably optimises the overall hydrophobic/hydrophilic interactions, Fig. 3. The slightly skewed capsules are separated by aquated lanthanide cations, and a large number of water molecules, Fig. 1.

The asymmetric unit is comprised of a calixarene, one aquated lanthanide and four Ph_4P^+ cations, requiring the calixarene to be a hepta-anion where one hydroxyl, either O–H(3) or O–H(4), is deprotonated to satisfy the overall charge neutrality, O(3)···O(4) being 2.47(1) Å. The hydrogen atoms were located and refined as riding, with O–H distances of 0.85 Å for both hydroxyls and water molecules with O···O distances ranging between 2.47(1)–2.79(1) Å and 2.67(1)–2.87(1) Å respectively. On the basis of the observed O···O contacts, extensive hydrogen bonding is presumed between the large number of water molecules clustered around the sulfonate groups and the second coordination sphere of the $[Yb(H_2O)_8]^{3+}$ cations. Each centrosymmetric 'molecular capsule' has two ytterbium cations appended to one sulfonate group from each of the two different calixarenes through hydrogen bonds; each of these coordinated cations also hydrogen bonds to one sulfonate group of the attached calixarene with closest YbO···OS distances of 2.778(9) and 2.769(12) Å. The layers sandwiching the calixarene are formed by pairs of $\{Ph_4P^+\}_2$ which are held together by CH···π interactions.

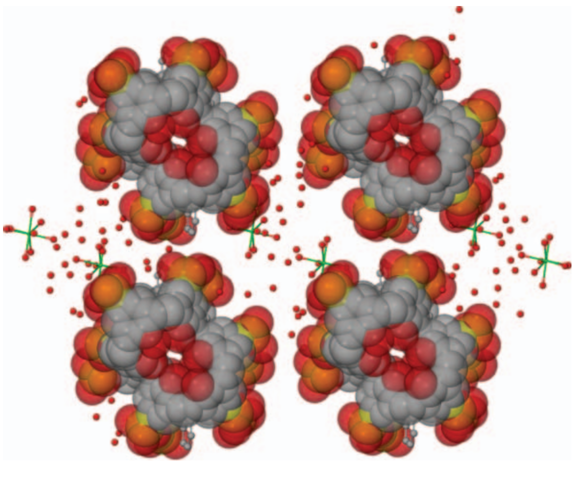

Fig. 3 Partial packing diagram showing the top view of a calixarene layer (space filling for calixarenes only).

Overall the synthesis of compound **1** is remarkable, having the confluence of multiple prerequisites—size matching and the extensive number of hydrogen bonds and CH···π interactions. The possibility of forming capsules in solution was investigated with and without the presence of aquated ytterbium ions. ^{31}P NMR in D_2O simply showed the presence of several different magnetic environments. ^{1}H NMR was uninformative, the AB spin system of the methylene protons of the calixarene being absent. The NMR experiments were hampered by the rapid crystallization of the complex resulting in line broadening. Dynamic light scattering measurements on solutions prior to crystallisation at various component ratios showed them to be polydisperse, with aggregates of average diameter of 100 nm. Attempts to leach out the metal ions with mineral acids were unsuccessful, resulting in dissolution of the solid, in contrast to related structures which allow leaching of the metal ions while maintaining structural integrity.[10]

The potential for water soluble *p*-sulfonatocalix[6]arenes to form novel structural arrays has been displayed, here *via* the formation of an unprecedented 'molecular capsule' like array in the solid state, in contrast to the usual bilayer arrangement. This structure offers numerous possibilities, *e.g.* as molecular filters, amongst others. The present work is being pursued with different phosphonium cations with a view to accessing larger arrays such as spheres and nano-rods.†

p-Sulfonatocalix[6]arene was synthesised according to the literature[11] whilst tetraphenylphosphonium chloride was purchased from Aldrich.

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Notes and references

† Synthesis of compound **1**, modelled as $2(C_{42}H_{29}O_{24}S_6)\cdot 8(C_{24}H_{20}P)\cdot 2(H_{16}O_8Yb)\cdot 71H_2O$: to a warm aqueous solution of calix[6]arene hexasulfonic acid (20 mg, 15.5 mmol) and tetraphenylphosphonium chloride (40 mg), an excess of ytterbium(III) chloride was added. The warm mixture was allowed to slowly evaporate overnight, affording large colourless crystals which were suitable for X-ray diffraction studies. *Crystal data:* $C_{276}H_{392}O_{135}P_8S_{12}Yb_2$, $M = 6848.5$, triclinic space group $P\bar{1}$, $a = 19.680(5)$, $b = 20.579(5)$, $c = 21.631(5)$ Å, $\alpha = 71.369(5)$, $\beta = 84.534(5)$, $\gamma = 89.451(5)^\circ$, $V = 8262(3)$ Å^3, D_c $(Z = 1) = 1.377$ g cm^{-3}; $\mu_{Mo} = 0.77$ mm^{-1}, $T = 153$ K, Mo–Kα radiation ($\lambda = 0.71073$ Å), $\theta_{max} = 28^\circ$, $N_t = 35404$, $R_1 = 0.12$, $wR_2 = 0.30$, GOF = 1.03 for 17216 reflections with $I > 2\sigma(I)$. CCDC 251661; see also http://www.rsc.org/suppdata/cc/b4/b416590j/ for crystallographic data in .cif format. ^{31}P NMR (Ph_4P, D_2O, s) $\delta = 23.33$ ppm; ^{31}P NMR (Ph_4P/SO_3H-calix[6], D_2O, s) $\delta = 22.73$ ppm; ^{31}P NMR (Ph_4P/SO_3Hcalix[6]/$YbCl_3$, D_2O, m) $\delta = 31–32$ ppm .

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