Constructing 2D porous material based on the assembly of large organic ions: *p*-sulfonatocalix[8]arene and tetraphenylphosphonium ions

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In the presence of tetraphenylphosphonium and aquated ytterbium(III) ions, conformationally flexible *p*-sulfonato-calix[8]arene forms an extended structure with two dimensional porosity involving the assembly of phosphonium cations and 'molecular capsules' comprised of two calixarenes shrouding three phosphonium cations.

Crystal engineering is a major area of research which defines and exploits modes of weak interactions between the components of molecular crystals.[1] Sulfonated calixarene are a widely investigated class of water soluble cavitands which feature in crystal engineering, and beyond into supramolecular chemistry and separation science.[2] 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*-sulfonato-calix[4]arenes.[3]

While *p*-sulfonato-calix[4]arene has been extensively studied, and to a lesser extent sulfonato-calix[5 and 6]arenes, there are limited structural studies on *p*-sulfonato-calix[8]arene.[4] This presumably relates to the self assembly chemistry of the calix[8]arene being more challenging because of its larger size and inherent difficulties in obtaining single crystals and authentication using X-ray diffraction data coupled with its unrestricted conformational flexibility. There is only one structural study on the self assembly of the *p*-sulfonato-calix[8]arene, as a lanthanide biphenyl *N*-oxide complex.[4]

Recently we reported the interplay of sulfonated calix[4,6]arenes with tetraphenylphosphonium cations, Ph_4P^+, in assembling unique structural motifs.[5–7] In extending this investigation, we reasoned that the large annular cavity of *p*-sulfonato-calix[8]arene with flexible conformation could preorganise in binding tetraphenylphosphonium cation, as an entry to building up new materials. Moreover, the highly charged calixarene anion is likely to induce a specific self aggregation or association of the mono-charged phosphonium cations. Tetraphenylphosphonium cations are well known to self-associate in the solid through interdigitation of the phenyl groups from adjacent cations *via* the sextuple or lower order 'phenyl embraces'.[8] This self-association prowess enhances the utility of the cations in crystallising a diverse range of anions, although such self-association mode of interaction can be perturbed depending on the nature of the anions involved.[5–7]

In taking this chemistry forward we have prepared and structurally authenticated a molecular assembly involving *p*-sulfonato-calix[8]arene with Ph_4P^+ and trivalent ytterbium cations, [*p*-sulfonato-calix[8]arene]$_2$[Ph_4P]$_9$$Yb_{0.75}$Cl·72($H_2O$), **1**. Crystals of the complex were grown from an aqueous solution containing *p*-sulfonato-calix[8]arene as the sulfonic acid, ytterbium(III) chloride and an excess of tetraphenylphosphonium chloride, Fig. 1.† They crystallise in a triclinic system (space group *P*-1) with the asymmetric unit comprised of two calixarenes, nine tetraphenylphosphonium cations, a chloride anion and disordered ytterbium cations with fractional occupancies, Fig. 2. Charge neutrality for the system implies that some of the sulfonate moieties are protonated. The low proportion of the lanthanide cations in this structure is noteworthy. We have reported various degrees of incorporation of lanthanide cations in structures based on the assembly of sulfonated calixarenes and Ph_4P^+. Lanthanide ions are either fully incorporated into the structure[6] or act as a template in forming the complex but yet not involved in the structure.[5] In the present structure, the partial uptake of the lanthanide metal cations is not understood, although it may be related to the ionic strength and pH of the solution.

The basic structural motif consists of two calixarenes confining three Ph_4P^+ cations in a skewed 'molecular capsule' arrangement which are interspersed between an envelope of tetraphenylphosphonium cations. The capsular arrangement involves the linking of the dimers of calixarenes bridged by disordered ytterbium ions as part of an extended bilayer arrangement, Fig. 1 and 3. The bilayers are linked through hydrophobic interactions involving the phosphonium cations. The three phosphonium cations are within

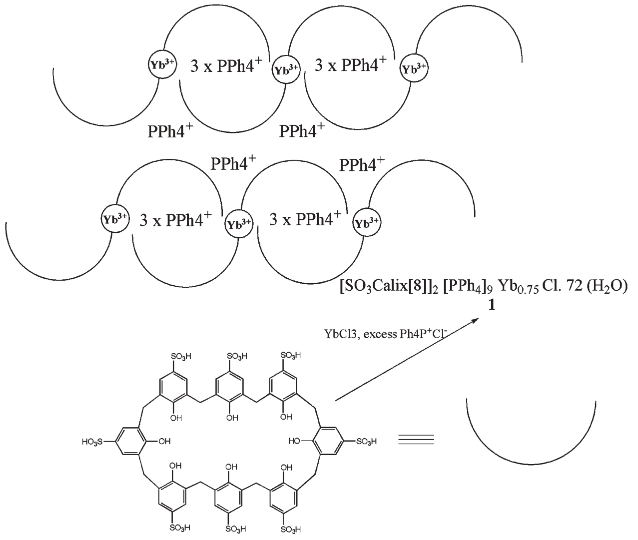

Fig. 1 Synthesis of complex **1**, and a cartoon of the basis bilayer arrangement.

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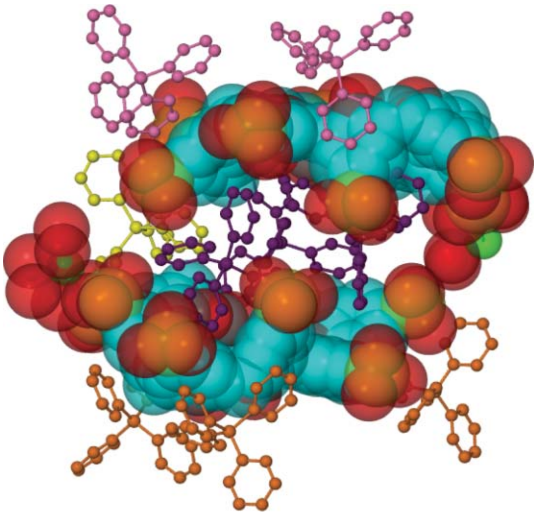

Fig. 2 The asymmetric unit of **1** showing the basic 'molecular capsule', based on two calixarenes (space filling) and three encapsulated Ph_4P^+ ions (magenta), and other species.

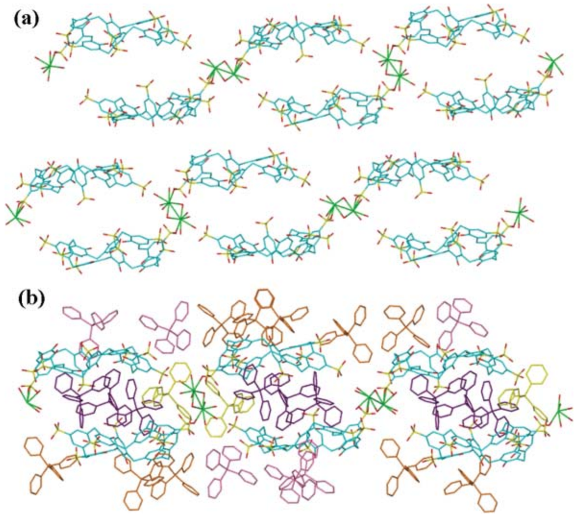

Fig. 3 (a) Projection of the calixarenes dimers for the 'molecular capsules', and associated metal interactions with the sulfonato groups in a bilayer arrangement (tetraphenylphosphonium cations and water molecules are omitted for clarity). (b) Full projection of the bilayer including the tetraphenylphosphonium interactions.

the 'molecular capsule', and one of them interacts at the van der Waals limit with a phenyl group of another phosphonium cation. Thus, a phenyl group protrudes into the capsule cavity, essentially acting as a hydrophobic connection from inside the capsule to the *exo*-capsule phosphonium cations.

The sulfonated calix[8]arene adopts an unusual conformation, presumably in optimising the hydrogen bonding associated with the hydroxyl groups, and the hydrophobic (and electrostatic) interactions with the tetraphenylphosphonium cations. Within the capsular arrangement, two of the included tetraphenylphosphonium cations have CH···π interactions with a pseudo 'calix[3]arene' cavity of the calixarenes. Two sets of aryl *para* hydrogens from each of two included Ph_4P^+ cations are directed towards the aromatic rings of the calixarenes with CH···π centroid distances at 2.601 Å. In addition to mutual CH···π interactions between pairs of planar aryl groups from each of these included cations, they have their *meta* hydrogens directed towards the centroid of an aryl group, at 2.521 Å. The third included Ph_4P^+ interacts with a calixarene cleft created by two aryl groups with an *ortho* hydrogen of the phenyl group directed towards the aromatic ring of the calixarene with CH···π centroid distances at 2.597 Å.

The structure is complicated, consisting of pseudo molecular capsules of sulfonato-calixarene forming an overall layered structure where the calixarenes are in a bilayer arrangement, Fig. 3(a). 'Molecular capsules' in these layers have hydrophobic connections along the *a* and *c* axes, as shown in cartoon form in Fig. 4, and for the *bc* plane in Fig. 5. There are large channels, *ca.* 1.5 nm, in diameter filled with water molecules, Fig. 5, which are lined by sulfonate groups as polar moieties on the surface of the 'molecular capsules'. Slightly bigger channels, *ca.* 2 nm filled with water and aquated ytterbium cations, run orthogonal to the latter at the exposed region of the sulfonate groups leading to a criss-cross of these water channels, as a 2D porous solid, Fig. 4.

The potential for water soluble *p*-sulfonato-calix[8]arene to form novel structural arrays with higher complexity has been established with the formation of a 2D large porous material. In addition, the ability of using large and highly charged anions to induce specific self aggregation or association of species of the same charge has been established. The structure gives insight into numerous possibilities, *e.g.* as nano-pore reactors or molecular filters, amongst others. The present work is being pursued with different phosphonium and metal cations with a view to accessing larger

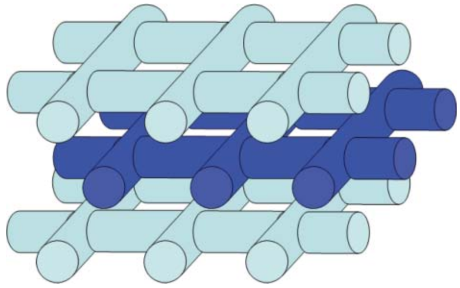

Fig. 4 Cartoon for the 2D porous structure of complex **1** where the rods designate the channels and the other open space the hydrophobic regions.

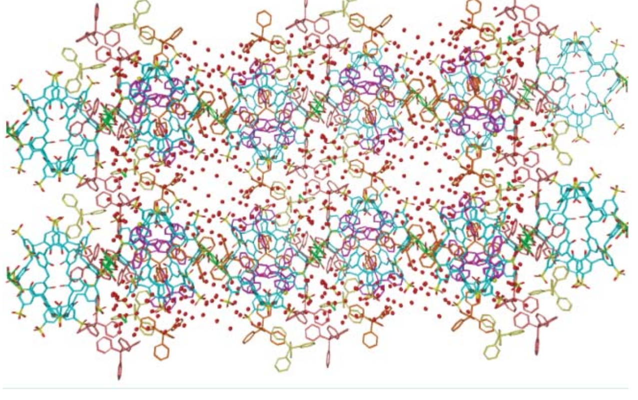

Fig. 5 Partial packing diagram down the *a* axis showing the top view of the 'molecular capsules', and hydrophyllic channels.

arrays such as spheres and nano-rods. The channels offer the possibility to substitute water molecules with larger guest molecules or as a membrane for separating molecular components.[‡]

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Notes and references

[†] Synthesis of compound **1**, modelled as $2[C_{56}H_{40}O_{32}S_8]\cdot 9[C_{24}H_{20}P]\cdot 0.75Yb\cdot Cl\cdot 72(H_2O)$: To a warm aqueous solution of calix[8]-arene octasulfonic acid (20 mg, 13.5 μmol) and tetra-phenylphosphonium chloride (40 mg, 107 μmol), an excess of ytterbium(III) chloride hexahydrate (40 mg, 103 μmol) was added. The warm mixture was allowed to slowly evaporate over several weeks, affording colourless crystals which were suitable for X-ray diffraction studies (30 mg, 4 μmol). Cell dimensions were checked on several crystals to show the sample was of uniform composition. *Crystal data:* $C_{328}\ H_{404}\ O_{136}\ P_9\ S_{16}\ Cl\ Yb_{0.75}$, M = 7479.43, triclinic space group P-1, a = 25.355(8), b = 26.787(9), c = 36.371(12) Å, $\alpha = 83.334(5)$, $\beta = 81.724(5)$, $\gamma = 62.437(4)°$, V = 21636(12) $Å^3$, D_c (Z = 2) = 1.14_8 g cm^{-3}; μ_{Mo} = 0.36 mm^{-1}, T = 150 K, Mo-Kα radiation (λ = 0.71073 Å), θ_{max} = 25°, N_t = 72522, R_1 = 0.16, $wR2$ = 0.34, GOF = 0.97 for 29399 reflexions with $I > 2\sigma(I)$. CCDC 286779. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b514833b

[‡] Calix[8]arene octasulfonic acid was synthesised according to a modified literature preparation[9] whilst tetraphenylphosphonium chloride and ytterbium chloride were purchased from Aldrich.

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