Controlling the interplay of large organic ions: *para*-sulfonato-calix[4]arene and phosphonium cations†

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Materials based on polyanionic *para*-sulfonato-calix[4]arene and tetraphenylphosphonium (Ph_4P^+) or benzyltriphenylphosphonium ($BzPh_3P^+$) cations are built up *via* partial inclusion and extensive phenyl embracing in association with trivalent cations (Yb^{3+}, Gd^{3+} and Er^{3+}). The crystalline materials have layered structures and feature negatively-charged channels propagating through the solids.

Introduction

Amphiphilic *para*-sulfonato-calix[4]arene is a renowned supramolecular tecton, serving as a platform in the construction of inorganic/organic clay mimics.[1,2] Layered materials that mimic the structure and properties of naturally occurring clays are of interest in supramolecular chemistry[2] and crystal engineering.[3] Major research efforts have been directed towards developing solids that intercalate or adsorb ions and small molecules, especially hydrogen, for storage,[4] separation[5] and catalysis.[6] Atwood *et al.* pioneered the use of *para*-sulfonato-calix[4]arene in building up such structures, initially as a bilayer arrangement with the calixarenes in an up/down fashion.[7] Subsequent investigations on the solid-state supramolecular complexes of the same calixarene[8] revealed a prevalence of this structural motif, and perturbations thereof.[7]

The clay or bilayer arrangement is comprised of hydrophobic layers of adjacent calixarenes engaged in π-stacking interactions, and a hydrophilic domain between these layers containing included water molecules, metal ions and various organic molecules such as crown ethers, amino acids, peptides, and nucleic acids and bases.[9,10] Ionic organic solids based on sulfonated calixarenes and phosphonium cations is an area that we have been investigating, and a plethora of supramolecular structures have been established. Both ions are well known for self association *via* either π···π or C–H···π interactions, including, for the latter, phenyl embraces. We envisaged that these ions could engage in such interactions, and variations thereof, in association with their electrostatic attraction, as a route to building up new materials. There is the possibility of phenyl ring inclusion in the calixarene cavity and disruption of the usual modes of association for the separate ions. In developing this concept, we have embarked on a systematic study of the ability of the Ph_4P^+/*para*-sulfonato-calix[4]arene system to generate extensive self-assembled arrays, taking into account the ratio of the ions, pH and the ionic strength of the solutions using a combinatorial approach. We have reported the pseudo polymorphic tetraphenylphosphonium complexes of *para*-sulfonato-calix[4]arene,[11] which have a phenyl group of the cation snugly fitting into the cavity of the calixarene. This is consistent with electrostatic considerations for the components in the structures, and is associated with a disruption of the bilayer arrangement for the calixarene.[11] Other departures from such a bilayer arrangement for the same calixarene include the formation of an expanded or supersized bilayer.[12] Formation of the above tetraphenylphosphonium complexes is templated by trivalent lanthanide ions, which are not necessarily incorporated into the structures at the expense of the less dense and hydrophilic/organic phosphonium cations.[11]

Herein we report profound structural variations based on the same supramolecular tectons, notably tetraphenylphosphonium cations and *para*-sulfonato-calix[4]arene anions, and closely related, structurally authenticated arrays based on tetraphenylphosphonium (Ph_4P^+) or benzyltriphenylphosphonium ($BzPh_3P^+$) cations with *para*-sulfonato-calix[4]arene (Fig. 1). These complexes were obtained by varying the molar ratio of the ions, in addition to both the type of organic (Ph_4P^+ or $BzPh_3P^+$) and metal (Yb^{3+} or Gd^{3+}) cation.

The rigid cone conformation of *para*-sulfonato-calix[4]arene provides a level of control for molecular capsule formation based on two calixarenes, and is a subunit of spheroidal arrays and of ”Russian doll” inclusion complexes.[13] In pursuing a study on organic ionic solids based on *para*-sulfonato-calix[4]-arene and phosphonium cations, the ultimate goal is to predict the structure of the complexes. Molecular capsules of *para*-sulfonato-calix[4]arene in the presence of phosphonium cations have proved elusive, in contrast with other *para*-sulfonato-calix[*n*]arenes (*n* = 6, 8), which have a higher conformation flexibility, molecular capsules of which have been recently authenticated.[14,15] Indeed, *para*-sulfonato-calix[6]arene forms a bis-molecular capsule shrouding a pair of phosphonium cations, and the two sulfonated calixarenes associate through hydrogen bonding to a pair of aquated lanthanide metal ions.[14] In the case of *para*-sulfonato-

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† Dedicated to Professor George Gokel on the occasion of his 60th birthday.

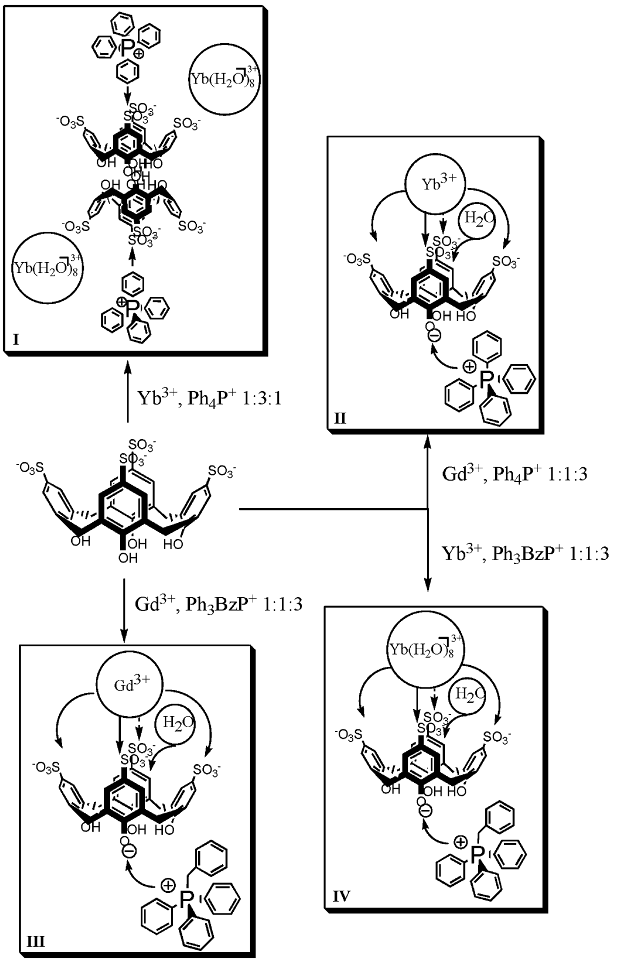

Fig. 1 Interplay of phosphonium cations (Ph_4P^+ or Ph_3Bz^+) with *para*-sulfonato-calix[4]arene involving lanthanide metal cations in different molar ratios.

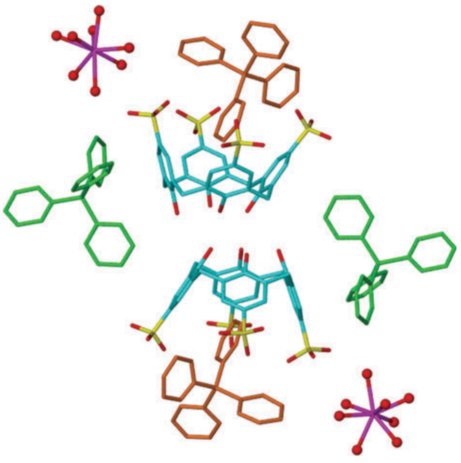

Fig. 2 The asymmetric unit in complex **I** showing the back-to-back arrangement of *para*-sulfonato-calix[4]arene, with included and intercalated phosphonium cations, and ytterbium cations shown in different colours (water solvent molecules are omitted for clarity).

calix[8]arene, 'molecular capsules' are formed based on two calixarenes and four encapsulated phosphonium ions, with the linking of the calixarenes through coordination of Ln^{3+} ions.[15] More recently, we have established the effect of varying the molar ratio of the anions and cations on the building of expanded bilayer mimics.[12] We are investigating the influence of different molar ratios of the ions, in addition to introducing other types of phosphonium cation. Mapping out the structural diversity of these ionic organic solids is of interest in the building of materials, with potential applications in gas separation/storage, catalysis and more.[16]

Results and discussion

Crystal structure of complex I

Slow evaporation of an equimolar mixture of sodium *para*-sulfonato-calix[4]arene and ytterbium(III) chloride, and a three-fold excess of tetraphenylphosphonium bromide afforded a crystalline complex, **I**,‡ which was characterised by single crystal diffraction studies. The reproducibility of the formation of the complex was checked by repeated cell dimension determinations on different samples that appeared to be of uniform morphology. Complex **I** crystallises in the space group *Pc*, $Z = 4$ and has an overall composition [{sulfonato-calix[4]arene^{5-}}{$(C_6H_5)_4P^+$)}$_2${$Yb(H_2O)_8{}^{3+}$}$(H_2O)_{20}$]. (Fig. 2) The asymmetric unit consists of two closely related components, each comprised of one calixarene, two phosphonium cations and a lanthanide ion, the components being strongly related by a pseudo centre of symmetry. The two components feature hydrogen bonding through the calixarene hydroxyl groups in a back-to-back arrangement, with short O···O contacts of 2.94(2) Å. There are also twenty water molecules of crystallization. The breaking of the centre of inversion is associated with the ytterbium cations, whereby one metal centre is ordered and coordinated to eight water molecules while the other is distributed between two positions in a ratio of 2 : 1. The aquated ytterbium cations reside in close proximity to the sulfonato group of the calixarene, with a short Yb–O···O contact of 2.56(7) Å that is indicative of hydrogen bonding.

Both calixarenes adopt the expected cone conformation, with the cavity of each occupied by a phenyl ring of a phenylphosphonium cation. This is associated with a CH···π interaction to the aromatic moieties of the calixarene, with two C–H protons directed towards the centroids of opposite calixarene phenyl rings. Each calixarene has inclusion with one phosphonium cation through a phenyl ring, with C–H···centroid distances of 2.74 and 2.74, and 2.72 and 3.00 Å. The overall structure is intricate and does not feature the usual bilayer arrangement of the calixarene with well recognised hydrophobic and hydrophilic domains. Instead, the 'layer' in this structure is composed of divergent back-to-back calixarenes that are at right-angles to each other and linked by the phosphonium cations (Fig. 3(a)). These

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‡ **Crystal/refinement details for compound I:** $C_{76}H_{115}O_{44}P_2S_4Yb$, M = 2095.90, $F(000)$ = 4348, monoclinic, *Pc*, Z = 4, T = 153 K, a = 14.566(2), b = 25.954(3), c = 25.644(3) Å, β = 99.295(2)°, V = 9567(2) Å^3; D_c = 1.45 g cm^{-3}; sin θ/λ_{max} = 0.5955; N_{unique} = 16 458 (merged from 59 415, R_{int} = 0.0429, R_{sig} = 0.0496), N_o ($I > 2\sigma(I)$) = 12 244; R = 0.1476, $wR2$ = 0.3611 (A, B = 0.15, 300.0), GOF = 1.11, $|\Delta\rho_{max}|$ = 3.5(3) e Å^{-3}. CCDC 625507. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h

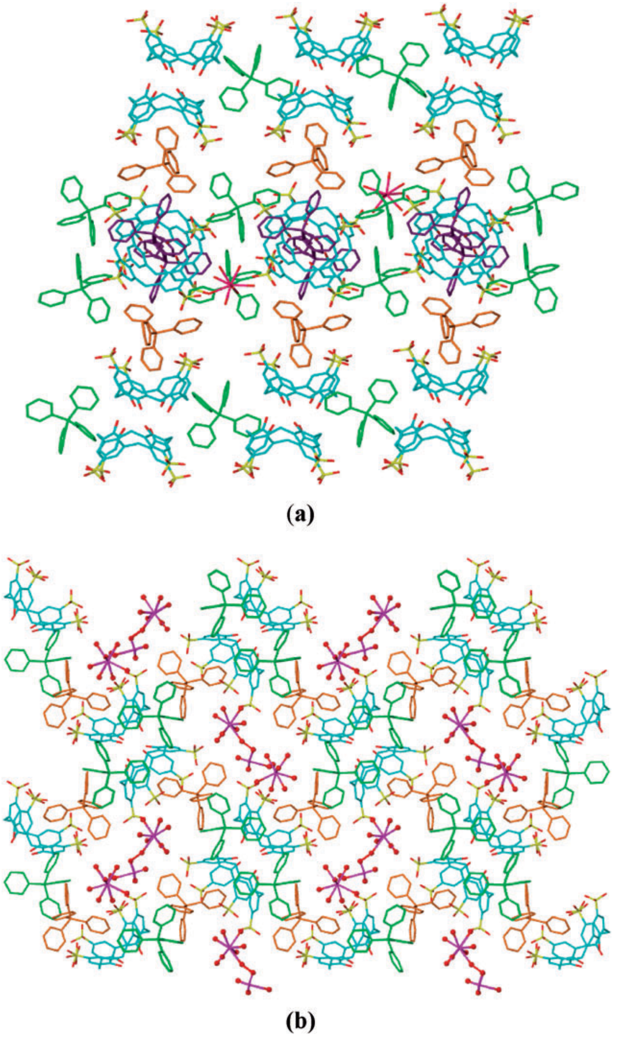

Fig. 3 Packing diagram in complex **I** showing (a) the intricate association of sulfonato-calix[4]arene and tetraphenylphosphonium cations, with back-to-back pairs of calixarenes at right angles to each other, and (b) connection of these layers *via* a similar mode of interaction, showing hydrophilic channels occupied by ytterbium cations and water molecules (water solvent molecules are omitted for clarity).

heteroleptic layers are connected in a similar fashion, generating channels filled with ytterbium cations and water molecules (Fig. 3(b)). It is noteworthy to mention that the interplay of the same components in a 1 : 1 : 3 ratio is similar but not isostructural to a previously reported bilayer arrangement.[12]

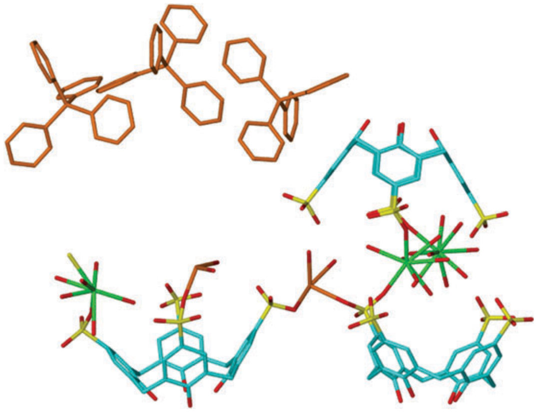

Fig. 4 The asymmetric unit in complex **II** showing the capsular arrangement and coordination of sulfonato-calix[4]arenes *via* gadolinium and sodium complexation, and a phenyl embrace between phosphonium cations (water solvent molecules are omitted for clarity).

Crystal structure of complex II

Slow evaporation of equimolar mixtures of tetraphenylphosphonium chloride and sodium *para*-sulfonato-calix[4]arene, and a three-fold excess of gadolinium(III) chloride afforded a crystalline complex, **II**.§ The complex crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$ and the asymmetric unit consists of three *para*-sulfonato-calix[4]arene and three tetraphenylphosphonium molecules, along with sodium and gadolinium cations and water molecules, with an overall composition of [{*para*-sulfonato-calix[4]arene^{4-}}$_3$ {($C_{24}H_{20}P$)}$_3${{Cl}{Na_2}{$Gd_{2.67}$}(H_2O)$_{30}$] (Fig. 4).

All three gadolinium centres are coordinated to a sulfonate group and have coordination numbers of 8 or 9. Two of the gadolinium centres are coordinated to sulfonate groups through one oxygen centre, with one having a Cl atom in its coordination sphere (Gd–O 2.36(2) and 2.39(1) Å, and Gd–Cl 2.65(1) Å). The third gadolinium bridges two calixarenes arranged face-to-face (Gd–O distances 2.30(2) Å). One sodium cation is bound to three sulfonate groups and the second to two sulfonate groups of the nearest-neighbouring calixarenes (Na–O distances 2.12(3)–2.65(4) Å). Within the bilayers, individual layers of calixarenes form a 2D coordination polymer, similar to what has been reported for the structure of 1 : 1 : 1 ratio.[12] Moreover, the structure features the intercalation of tetraphenylphosphonium cations between the layers of calixarenes at the interface of their hydroxyl and phenolate groups

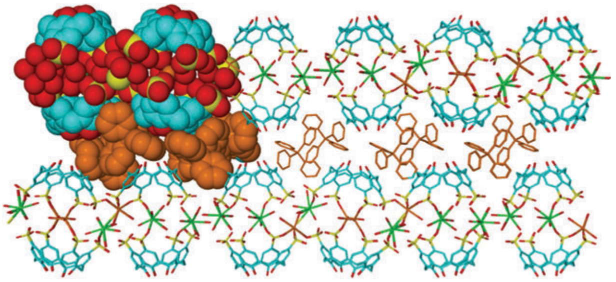

Fig. 5 Extended structure along the b-axis of **II** showing the restriction of the coordination polymer within each layer of calixarenes and the interaction of phosphonium cations between these layers.

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§ **Crystal/refinement details for compound II:** $C_{156}H_{180}ClGd_{2.67}Na_2O_{78}P_3S_{12}$, $M = 4281.52$, $F(000) = 8747$, monoclinic, $P2_1/c$, $Z = 4$, $T = 153$ K, $a = 32.032(5)$, $b = 11.430(2)$, $c = 50.944(7)$ Å, $\beta = 91.744(2)°$, $V = 18\,643(5)$ Å^3; $D_c = 1.52$ g cm^{-3}; $\sin\theta/\lambda_{\max} = 0.5946$; $N_{\text{unique}} = 31\,808$ (merged from 112 794, $R_{\text{int}} = 0.1582$, $R_{\text{sig}} = 0.2100$), N_o ($I > 2\sigma(I)$) = 13 113; $R = 0.1206$, $wR2 = 0.2898$ (A, B = 0.15, 250.0), GOF = 1.063; $|\Delta\rho_{\max}| = 3.2(2)$ e Å^{-3}. CCDC 625508. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h

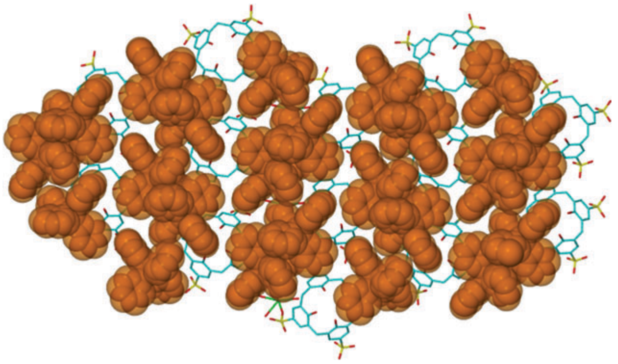


Fig. 6 Packing diagram in complex **II** showing a top view projection into the surface of the bilayer, highlighting the hydrophobic expansion of the layer *via* phosphonium cation associations in linear arrays (water solvent molecules are omitted for clarity).

(Fig. 5). Thus, the electrostatic attraction of the negatively-charged lower rim of the calixarenes with the organic cations expands the bilayer arrangement.[12] The phosphonium cations, through their usual associations, form linear arrays, filling the dimples of the calixarene bilayer. Hence, these hydrophobic cations impart hydrophobic properties to the surface of the bilayer, beyond the hydrophobic property of the calixarene cavities (Fig. 6).

Crystal structure of complex III

Slow evaporation of an aqueous solution of equimolar mixtures of benzyltriphenylphosphonium chloride and sodium *para*-sulfonato-calix[4]arene, and a three-fold excess of gadolinium(III) chloride afforded a crystalline complex, **III**,¶ which has a complicated molecular bilayer arrangement in the triclinic space group *P*-1, *Z* = 1. The calixarene molecules are linked by gadolinium cations through the sulfonate groups, forming polymeric chains, with one of chains residing on a center of symmetry. The asymmetric unit comprises several components, which can be expressed as $2[(C_{28}H_{20}O_{16}S_4)(C_{25}H_{22}P)]\cdot Gd(H_2O)_7 \cdot Gd[(H_2O)_6(CH_3OH)_{1.5}] \cdot Gd_{0.67}[(H_2O)_{4.5}Cl_{0.5}(CH_3OH)]\cdot 14(H_2O)$, where some of components are disordered and/or partially occupied (Fig. 7). During structure refinement, some fragments of the molecules were constrained to their idealized geometries and non-hydrogen ordered atoms were refined anisotropically. The positions of hydrogen atoms were generated geometrically and refined in constraint with their bonded atoms.

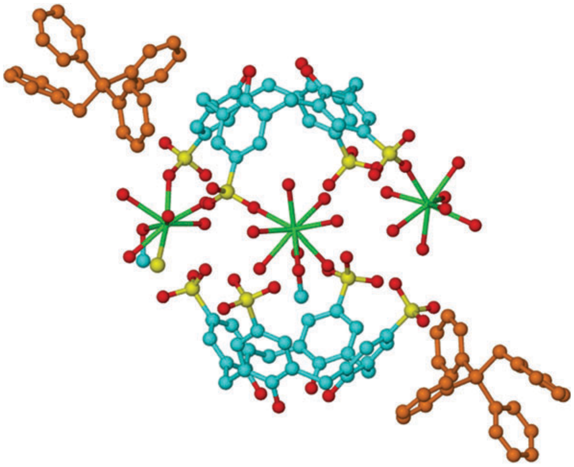


Fig. 7 The asymmetric unit in complex **III** showing the capsular arrangement and coordination of sulfonato-calix[4]arenes through gadolinium metal cations, and benzyltriphenylphosphonium forming part of the hydrophobic domain (water solvent molecules are omitted for clarity).

In the structure, there are two different calixarenes, one devoid of gadolinium cations and the other having three sulfonate groups coordinated to solvated gadolinium cations. Two of the gadolinium cations have full occupancy and each is coordinated to one oxygen of a sulfonate group, with coordination numbers of 8 or 9. The partially occupied gadolinium (0.666 occupancy) also has half a Cl atom in its coordination environment. The gadolinium centres are also bound to the water molecules, with one of them having a methanol molecule in its coordination sphere (Gd–O(CH$_3$) 2.36(1)–2.45(1) Å; Gd–O(SO$_2$) 2.344(3), 2.365(4) and 2.425(4) Å; Gd–O(H$_2$O) 2.26(1)–2.58(1) Å; and Gd–Cl 2.869(5) Å). The methanol molecules are residual solvent originating from the calixarene work-up. The uncoordinated calixarene caps a gadolinium centre, bearing a methanol molecule as part of its coordination sphere, forming an inclusion within the cavity, with a CH···π short contact to the calixarene aromatic ring of 3.00 Å (Fig. 7). Thus, the calixarenes are arranged in a head-to-head fashion, forming a linear pseudo 1D coordination polymeric array of skewed capsules (Fig. 8). These linear arrays are aligned next to each other and are held together by hydrogen bonding, involving water molecules acting as 'glue', to the second coordination sphere of gadolinium metal cations radiating from the median of these arrays. The resulting pseudo 2D calixarene coordination bilayer is separated by phosphonium

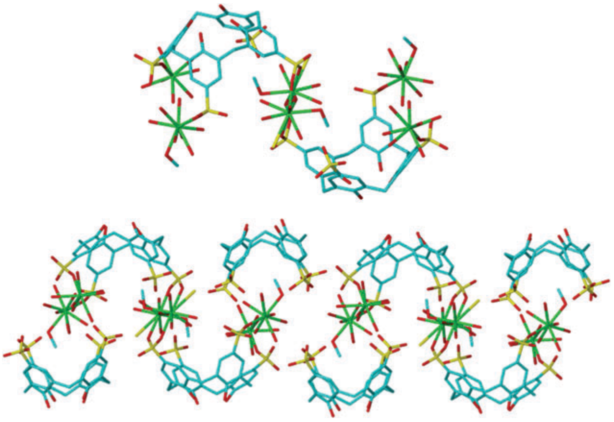


Fig. 8 View along the a-axis of complex **III** showing the gadolinium-bridged biscalixarene unit (top) and the building up of the linear arrays, aided by methanol inclusion (bottom).

¶ **Crystal/refinement details for the compound III:** $C_{217}H_{314}ClGd_{5.33}O_{132}P_4S_{16}$, M = 6545.11, $F(000)$ = 3346, triclinic, *P*-1, Z = 1, T = 153 K, a = 14.624(1), b = 19.987(2), c = 25.192(2) Å, α = 67.801(1), β = 74.982(1), γ = 89.740(1)°, V = 6548.7(9) Å^3; D_c = 1.60 g cm^{-3}; sin θ/λ_{max} = 0.6664; N_{unique} = 31 133 (merged from 60 999, R_{int} = 0.0192, R_{sig} = 0.0328), N_o ($I > 2\sigma(I)$) = 24 915; R = 0.0699, w$R2$ = 0.1794 (A, B = 0.091, 50.714), GOF = 1.05; $|\Delta\rho_{max}|$ = 4.5(2) e Å^{-3}. CCDC 625509. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h

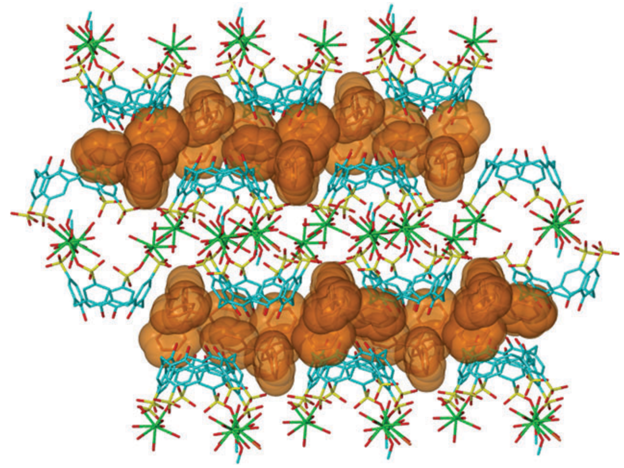


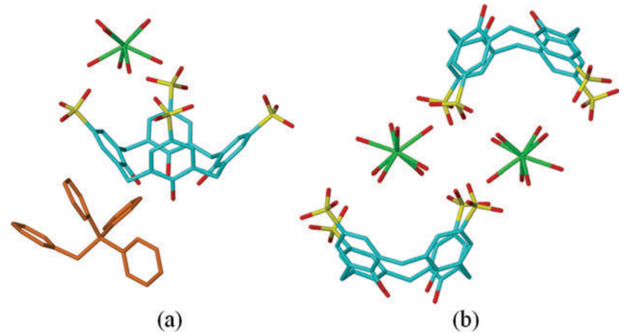
Fig. 9 Packing diagram of the bilayer in complex **III** showing the overall interplay between the calixarene layer and the $BzPh_3^+$ phosphonium cation intercalation (water molecules omitted for clarity).

cations, which fill the interstices between calixarene layers at the interface of their hydroxyl and phenolate groups (Fig. 9). An isostructural compound is obtained by the interplay of the same components, but with erbium as the lanthanide. The erbium derivative is isostructural to compound **III** with unit cell parameters: a = 14.545(1), b = 19.911(1), c = 25.089(2) Å, α = 67.937(1), β = 74.890(1), γ = 89.740(1)°, V = 6465(1) Å^3.

Crystal structure of complex IV

Slow evaporation of an equimolar mixture of tetraphenylphosphonium chloride and sodium *para*-sulfonato-calix[4]arene, and a three-fold excess of ytterbium(III) chloride afforded a crystalline complex, **IV**,[‖] which crystallizes in triclinic space group, P-1, Z = 2. The asymmetric unit consists of one *para*-sulfonato-calix[4]arene, one benzyltriphenylphosphonium cation, an aquated ytterbium cation and a number of water molecules, and has the overall composition of $[\{para\text{-sulfonatocalix[4]arene}^{4-}\}\{(C_{25}H_{22}P^+)\}\{Yb^{3+}(H_2O)_8\}(H_2O)_{9.5}]$ (Fig. 10).

On first inspection, the structure, remarkably, resembles that of complex **III**, albeit the metal lanthanide this time is ytterbium, which is not coordinated to the sulfonate groups of the calixarenes. The head-to-head arrangement of the calixarenes is aided by the aquated sphere of $[Yb(H_2O)_8]^{3+}$, with both hydrogen bonds arising from two aquated oxygen donors, and showing contacts to a sulfonate oxygen atom (O···O 2.72(1) and 2.729(7) Å) (Fig. 10). The calixarenes in the opposite direction in the bilayer are separated by phosphonium cations, thereby expanding their hydrophobic domain (Fig. 11). This extension of the bilayer is profoundly dissimilar to that seen in structure **II**, where the somewhat loosely bound calixarenes (uncoordinated) have less control on the organisation of the hydrophobic phosphonium cations. Unlike the restrictive behaviour of the coordination polymer in complex



(a) (b)

Fig. 10 The asymmetric unit in complex **IV** showing (a) one sulfonatocalix[4]arene, one benzyltriphenylphosphonium cation and an aquated ytterbium cation, and (b) the skewed ionic capsule as the basic unit for forming the calixarene bilayer (water solvent molecules are omitted for clarity).

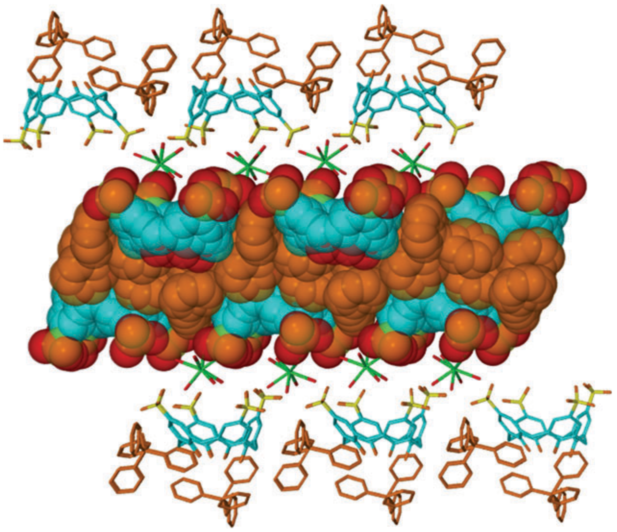


Fig. 11 A view along the a-axis in complex **IV** depicting the overall packing of the layered structure, and where the $BzPh_3^+$ cations separate the calixarene layers (water molecules omitted for clarity).

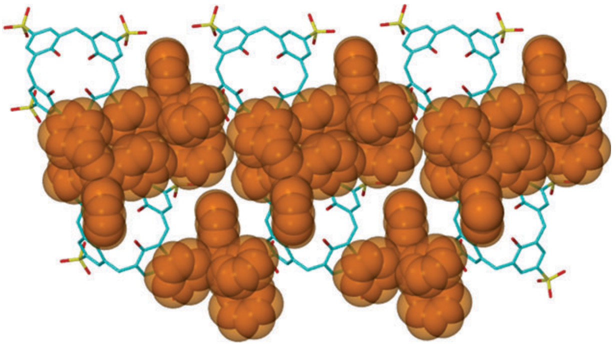


Fig. 12 Packing diagram in complex **IV** showing a top view projection of the surface of the bilayer, highlighting the hydrophobicity expansion of the layer *via* phosphonium cation association in a corrugated layer (water solvent molecules are omitted for clarity).

[‖] **Crystal/refinement details for the compound IV:** $C_{53}H_{59.5}O_{33.5}PS_4Yb$, M = 1564.76, F(000) = 1589, triclinic, P-1, Z = 2, T = 100(2) K, a = 12.6687(8), b = 14.9526(9), c = 18.497(2) Å, α = 96.405(7), β = 100.594(8), γ = 107.678(6)°, V = 3228.7(4) Å^3; D_c = 1.610 mg m^{-3}; sin θ/λ_{max} = 0.6484; N_{unique} = 12 488 (merged from 35 165, R_{int} = 0.0378, R_{sig} = 0.0772), N_o ($I > 2\sigma(I)$) = 8262; R = 0.0556, w$R2$ = 0.1384 (A, B = 0.09, 0.65), GOF = 1.007; $|\Delta\rho_{max}|$ = 1.7(1) e Å^{-3}. CCDC 625510. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h

II, forcing the hydrophobic cations to organise into linear arrays, the hydrophobic surface in complex **IV** forms a corrugated layer, giving a slightly larger bilayer expansion. This corrugation and larger expansion may also be due to the nature of the phosphonium cation bearing a benzyl group, and breaking away from the tetrahedral symmetry mode of association (Fig. 12).

Conclusions

We have established the structures of four complexes based on calix[4]arene sulfonate and phosphonium cations, their formation catalysed by or incorporating lanthanide cations at a resolution suitable for a detailed understanding of the interplay of the various components. The synthesis of the complexes involved a systematic study associated with varying the molar ratio of the components, and the nature of the phosphonium and lanthanide metal cations. It demonstrated the utility of this combinatorial approach in forming novel supramolecular ionic solids and established some design rules. The investigation showed that there is little structural impact on substituting Ph_4P^+ with $BzPh_3P^+$. Work is continuing with other phosphonium derivatives, noting also that increasing the organic cation ratio leads to novel arrays. Controlling the interplay and structural outcome of the supramolecular interactions of *para*-sulfonato-calix[4]arene with phosphonium cations is a challenge, and recent results have yielded materials of novel porosity and clay like mimics. Overall, the work highlights a remarkable structural versatility, and the exciting potential of building materials with applications in catalysis and supramolecular devices. Hydrophobic phosphonium cations serve to extend the hydrophobic surface and increase the thickness of bilayers, effectively augmenting the hydrophobicity of these cations. In addition, varying the phosphonium cation leads to a change in the organization of the hydrophobic surface of the bilayers themselves, altering the hydrophobic surface created by the calixarene.

Experimental

General procedure:

Calix[4]arene sulfonic acid,[17] $[Ph_4P]Cl$ and $[Ph_3BzP]Cl$[18] were synthesised according to literature procedures. A hot solution of $LnCl_3 \cdot 6H_2O$ in water (0.5 ml) was added to a hot solution of either $[Ph_4P]Cl$ or $[Ph_3BzP]Cl$ with sulfonato-calix[4]arene pentasodium salt in water (2 ml) at different molar ratios. The prepared solutions were left to cool and slow-evaporate, and crystals of **I–IV** formed after several days.

X-Ray crystallography

The X-ray diffraction intensities were measured from single crystals at about 153 or 100 K on a Bruker ASX CCD diffractometer or an Oxford Diffraction X-caliburs-S using monochromatized Mo-K_α (λ = 0.71073 Å) radiation. Data were corrected for Lorentz and polarization effects, and absorption corrections were applied using multiple symmetry equivalent reflections. The structures were solved by direct methods and refined on F^2 using the Bruker SHELXTL crystallographic package.[19,20]

Acknowledgements

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