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

Yatimah Alias, University of Malaya
Controlling the interplay of large organic ions: para-sulfonato-calix[4]arene and phosphonium cations†

Mohamed Makha,*a Yatimah Alias,b Colin L. Raston*a and Alexandre N. Soboleva

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Materials based on polyanionic para-sulfonato-calix[4]arene and tetraphenylphosphonium (Ph₄P⁺) or benzyltriphenylphosphonium (BzPh₃P⁺) cations are built up via partial inclusion and extensive phenyl embracing in association with trivalent cations (Yb³⁺, Gd³⁺ and Er³⁺). 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 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 separation5 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 revealed a prevalence of this structural motif, and perturbations thereof.8–10

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 Ph₄P⁺/para-sulfonato-

Department of Chemistry, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia
† Dedicated to Professor George Gokel on the occasion of his 60th birthday.

Department of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, W.A. 6009, Australia. E-mail: mmakha@chem.uwa.edu.au. E-mail: chraston@chem.uwa.edu.au. Fax: +61 86488 1005; Tel: +61 86488 1572

School of Biomedical, Biomolecular and Chemical Sciences, University of Western Australia, 35 Stirling Highway, Crawley, W.A. 6009, Australia. E-mail: mmakha@chem.uwa.edu.au. E-mail: chraston@chem.uwa.edu.au. Fax: +61 86488 1005; Tel: +61 86488 1572
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.\textsuperscript{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.\textsuperscript{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.\textsuperscript{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,\textsuperscript{1} 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 \{\text{[sulfonato-calix[4]arene$^{5-}$]}(\text{C$_6$H$_5$)$_4$P}$^{+}\}$_2$\text{[Yb(H$_2$O)$_{8}$$^{3+}$]}(\text{H$_2$O})$_{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–C 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 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

Fig. 1 Interplay of phosphonium cations (Ph$_3$P$^+$ or Ph$_3$Bz$^+$) 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).

Crystal/refinement details for compound I: C$_{76}$H$_{115}$O$_{44}$P$_2$S$_4$Yb, $M = 2095.90$, $F(000) = 4348$, monoclinic, $Pc$, $Z = 4$, $T = 153$ K, $a = 14.566(2)$, $b = 25.954(3)$, $c = 25.644(3)$ Å, $\beta = 99.295(2)$, $V = 9567(2)$ Å$^3$, $D_x = 1.45$ g cm$^{-3}$, $\sin \theta/\lambda_{\text{max}} = 0.5955$, $N_{\text{unique}} = 16458$ (merged from 59415, $R_{\text{int}} = 0.0429$, $R_{\text{wp}} = 0.0496$, $N_{\text{sym}}(\sigma > 2\sigma(I)) = 12244$, $R = 0.1476$, $wR_2 = 0.3611$ ($A$, $B = 0.15$, 300.0), $GOF = 1.11$, $\Delta p_{\text{max}} = 3.5(3)$ e Å$^{-3}$. CCDC 625507. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h

\[1\] Crystal/refinement details for compound I: C$_{76}$H$_{115}$O$_{44}$P$_2$S$_4$Yb, $M = 2095.90$, $F(000) = 4348$, monoclinic, $Pc$, $Z = 4$, $T = 153$ K, $a = 14.566(2)$, $b = 25.954(3)$, $c = 25.644(3)$ Å, $\beta = 99.295(2)$, $V = 9567(2)$ Å$^3$, $D_x = 1.45$ g cm$^{-3}$, $\sin \theta/\lambda_{\text{max}} = 0.5955$, $N_{\text{unique}} = 16458$ (merged from 59415, $R_{\text{int}} = 0.0429$, $R_{\text{wp}} = 0.0496$, $N_{\text{sym}}(\sigma > 2\sigma(I)) = 12244$, $R = 0.1476$, $wR_2 = 0.3611$ ($A$, $B = 0.15$, 300.0), $GOF = 1.11$, $\Delta p_{\text{max}} = 3.5(3)$ e Å$^{-3}$. CCDC 625507. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h
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

**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 $[\text{para-sulfonato-calix[4]arene}^{4-}]_3 [\text{C}_{24}\text{H}_{20}\text{P}]_3\{\text{Cl}\}_{\text{Na}_2}\{\text{Gd}_{2.67}\}(\text{H}_2\text{O})_{30}$ (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.

### Crystal/refinement details for compound II:

- **Formula**: $C_{156}H_{180}ClGd_{2.67}Na_{2}O_{78}P_{3}S_{12}$
- **M** = 4281.52, $F(000)$ = 8747, monoclinic, $P2_1/c$, $Z = 4$, $a = 153.83(2)$ Å, $b = 11.430(2)$ Å, $c = 50.944(7)$ Å, $\beta = 91.744(2)^\circ$, $V = 18643(5)$ Å$^3$, $D_x = 1.52$ g cm$^{-3}$, $\sin \theta/\lambda_{\text{max}} = 0.5946$, $N_{\text{unique}} = 31808$ (merged from 112794), $R_{\text{int}} = 0.1582$, $R_{\text{sig}} = 0.2100$, $N_{\text{e}}(I > 2\sigma(I)) = 131133$, $R = 0.1206$, $wR^2 = 0.2898$ ($A$, $B = 0.15$, 250.0), GOF = 1.063; $\Delta F_{\text{max}} = 3.2(2)$ e Å$^{-3}$.
- **CCDC**: 625508.

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615639h.
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 poly-
meric chains, with one of chains residing on a center of sym-
metry. The asymmetric unit comprises several components,
which can be expressed as 2[H25(OH)2(SO3)2][C25H22P]·Gd(H2O)2·Gd([H2O]2(CH3OH)1.5][H2O].4Cl0.5(CH3OH)1.5·H2O, 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.

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(CH3) 2.36(1)–2.45(1) Å; Gd–O(SO3) 2.344(3), 2.365(4) and 2.425(4) Å; Gd–O(H2O) 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. 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. 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).

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).
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, $a = 67.937(1)$, $b = 74.890(1)$, $g = 89.740(1)^\circ$, $V = 6465(1)$ 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, $P\overline{1}$, $Z = 2$. 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-sulfonatocalix[4]arene}$^4$/C$_{0}$]/{(C$_{25}$H$_{22}$P$^+$)}/{Yb$^{3+}$/(H$_2$O)$_{8}$} (H$_2$O)$_{9.5}$ (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$_2$O)$_{8}$]$^{3+}$, with both hydrogen bonds arising from two aquated oxygen donors, and showing contacts to a sulfonate oxygen atom (O$^1$/C$^1$/C$^1$/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

Crystal/refinement details for the compound IV: C$_{53}$H$_{59.5}$O$_{33.5}$PS$_4$Yb, $M = 1564.76$, $F(000) = 1589$, triclinic, $P\overline{1}$, $Z = 2$, $T = 100(2)$ K, $a = 12.6687(8)$, $b = 14.9526(9)$, $c = 18.497(2)$ Å, $\alpha = 96.405(7)$, $\beta = 100.594(8)$, $\gamma = 107.678(6)^\circ$, $V = 3228.7(4)$ Å$^3$; $D_c = 1.610$ mg m$^{-3}$; $\sin \theta/\lambda_{\text{max}} = 0.6484$; $N_{\text{unique}} = 12$ 488 (merged from 35 165, $R_{\text{int}} = 0.0378$, $R_{\text{sig}} = 0.0772$), $N_{\text{ref}} (I > 2\sigma(I)) = 8262$; $R = 0.0556$, $wR^2 = 0.1384$ ($A$, $B = 0.09$, 0.65), GOF = 1.007; $|\Delta p_{\text{max}}| = 1.7(1)$ 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$_2$P$^+$ with BzPh$_2$P$^+$. 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 novel porosity and clay like mimics. Overall, the work has yielded materials of applications in catalysis.

Experimental

General procedure:

Calix[4]arene sulfonic acid,$^{17}$ [Ph$_4$P]Cl and [Ph$_3$BzP]Cl$^{18}$ were synthesised according to literature procedures. A hot solution of LnCl$_3$·6H$_2$O in water (0.5 ml) was added to a hot solution of either [Ph$_4$P]Cl or [Ph$_3$BzP]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 AXS CCD diffractometer or an Oxford Diffraction X/calibur-S using monochromatized Mo-K$_\alpha$ ($\lambda = 0.71073$ 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.$^{19,20}$

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