Controlling the organization of phosphonium cations relative to p-sulfonatocalix[4]arene anions

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Controlling the organization of phosphonium cations relative to \( p \)-sulfonatocalix[4]arene anions

Irene Ling, \( ^{a,b} \) Alexandre N. Sobolev\( ^c \) and Colin L. Raston\( ^b \)

Solution mediated organization of \( p \)-sulfonatocalix[4]arene, benzyltriphenylphosphonium cations, and bis(triethylammoniomethyl)-benzene dications in the solid state, results in the ammonium dications preferentially binding in the cavity of two opposing calixarenes which take on a 3- charge, with the phosphonium cations arranged in separate 2D sheet relative to the calixarene bilayer.

Ionic organic solids based on \( p \)-sulfonated calix[4]arene (\( = p \)-sulfonatocalix[4]arene) and phosphonium cations have been previously investigated using a systematic approach, varying a number of parameters including the ratio of the ions, pH and the ionic strength of the solutions.\(^1\) \( p \)-Sulfonated calix[4]arene is usually arranged in the solid state in an up-down anti-parallel bilayer manner, Figure 1, stabilised through H-bonding in part by the sulfonate groups and in part by the lower rim hydroxyl groups, where the calixarenes are arranged back-to-back.\(^2\) In most of the studies, the phosphonium cations self-associate at the interface of the hydroxyl and phenolate groups of the calixarenes, thereby expanding the bilayer, which is facilitated in part by electrostatic attraction between the large ionic components.\(^3,4\) Such arrangement of phosphonium cations and calixarenes increases the hydrophobic nature of the two divergent surfaces of the bilayer relative to the conventional bilayer formed in the absence of phosphonium cations. However, there is the possibility of a phenyl ring of the cation residing into the cavity of the calixarene.\(^5\) This disrupts the bilayer arrangement of the calixarenes, affording pseudo polymorphic tetraphenylphosphonium complexes of \( p \)-sulfonated calix[4]arene assembled in columnar arrays.\(^5\)

The hydrophobic cavity of the \( p \)-sulfonated calix[4]arene can bind water molecules,\(^6\) however upon exposure of suitably sized neutral or charged organic molecule, preferential binding towards the organic molecules occurs.\(^7\) We have established the ability of water-soluble \( p \)-sulfonated calix[4]arene and several organic mono- and bis-cations to form multi-component materials.\(^8\) Solid-state structures of these complexes reveal that the calixarenes are assembled in the ubiquitous bilayer arrangement with phosphonium cations embedded in them. For the case of bis-cations, the termini are end-capped by two adjacent calixarenes forming a molecular capsule in the solid state while retaining the same bilayer configuration in the presence of phosphonium cations.\(^8\) The nature of the interplay of the bis-cations and the calixarene molecules in solution has been investigated using \(^1\)H NMR spectroscopy, with evidence for the presence of supermolecules made up of bis-cations and calixarenes.
Recently we reported the inclusion of one 1,4-bis(triethylammoniomethyl)benzene, BTEA, in the cavity of two p-sulfonated calix[4]arenes which assemble in an array of skewed molecular capsules, along with phosphonium molecules being embedded within the bilayer. The preferential binding of bis-triethylammonium cations in the cavity of p-sulfonated calixarene, as part of molecular capsules, has been established in aqueous medium. We now explore the interplay of the same host and guest molecules, for a different phosphonium cation, and report new types of material resulting from an unusual interplay of the benzyltriphenylphosphonium cation, BzPh,P, with a molecular capsule comprising two p-sulfonated calix[4]arene and bis-triethylammonium cations. These are not organised in the common composite bilayer with calixarene anions and phosphonium cations, of the type discussed above.

Slow evaporation of a water/tetrahydrofuran solution containing sodium p-sulfonated calix[4]arene, 1,4-bis(triethylammoniomethyl)benzene bromide and benzyltriphenylphosphonium bromide resulted in the formation of material crystallizing in the monoclinic space group P2_1/c, with the asymmetric unit comprised of one calix[4]arene anion, one half-populated bis-triethylammonium cation, two BzPh,P cations, and water molecules which fill up the otherwise voids in the structure. Molecular capsules comprising a BTEA molecule and two face-to-face calixarenes is commonly observed. In the present study, the solid-state structure has BTEA cations in the cis-configuration, disordered across an inversion center. These are end-capped by two calixarenes and aligned to form a ‘molecular capsule’ approximately 19 Å in length, Figure 2a. This is comparable to an earlier structure containing the same bis-cation, although there are a number of differences in the structures. This includes the alignment of the included BTEA cation where the plane of the central aromatic ring of the cation is tilted 73.9° relative to the normal axis of the calixarene basal plane, whereas in the previous structure the central aromatic ring is aligned close to the principal axes of the calixarenes. The termini of the BTEA cation reside in the hydrophobic calixarene cavities with the calixarene phenolic rings pinched around the triethylammonium moieties. The dihedral angles between each of the four phenolic rings and the basal plane containing the four calixarene methylene bridges are 60.4(1)°, 49.9(1)°, 48.7(1)° and 41.9(1)°. While the two calixarenes are too far apart for hydrogen bonding interactions, the term ‘molecular capsule’ is used as a descriptor of the supermolecule in the solid state, noting the persistence of such species in solution.

The interplay of BTEA and calixarene involves extensive H-bonding, notably for the triethylammonium moieties, Figure 1b. One of the three ethyl groups has the methyl terminus directed into the calixarene cavity, with C–H···π(centroid) interactions to three phenyl rings of the calixarenes at 2.66, 2.81 and 3.03 Å (corresponding C···π(centroid) distances are 3.48, 3.71 and 3.65 Å). Other weak interactions associated with the remaining ethyl groups include the H-bonding to the calixarene upper rim sulfonate moieties where C–H···O–S distances are 2.363(13), 2.582(5), 2.714(20), 2.710(6), 2.836(22), 2.899(7) and 2.999(5) Å (corresponding C···O distances are 2.585(21), 3.358(22), 3.415(26), 3.620(13), 3.406(24), 3.642(23) and 3.498(13) Å). The methylene bridges are also in close proximity with the calixarene sulfonate groups, with the C–H···O–S distances at 2.360(6) to 2.622(7) Å (equivalent C···O distances are 3.333(12) to 3.553(14) Å), as weak ‘H-bonding’ interactions.

The construction of the composite material is distinctive in the way that the overall structure is built up, having multiple repeating layers of well-separated hydrophilic layers comprising molecular capsules of calixarenes and BTEA, and hydrophobic layers consisting densely packed organic phosphonium cations, the thickness of each layer being 11 Å and 7 Å respectively (Figure 3). The molecular capsules are organized in the conventional bilayer arrangement with respect to the calixarenes, with water molecules bridging the sulfonate groups between adjacent calixarenes, effectively completing a molecular capsule’ arrangement. Molecular capsules are connected through H-bonding interactions between one another involving methylene bridges and phenyl rings (C–H···π(centroid) distances at 2.99 and 3.07 Å, corresponding C···π(centroid) distances at 3.47 and 3.50 Å). An O-atom of a sulfonate group is close to the basal hydroxyl group with a O···O distance of 3.24 Å.

Interestingly, the BzPh,P cations are self-associated in between layers of molecular capsules rather than being embedded within calixarene bilayers, of the type established in other structures. In general, when phosphonium cations are
self-assembled through various embraces\textsuperscript{10} within the calixarene bilayer, the hydrophobic bilayer is thicker (approx. 12-14 Å thick). In the present structure, the 8.9 Å thick bilayer is more compact, being devoid of included phosphonium cations close to the lower rims of the calixarenes. $p$-Sulfonatocalix[4]arene complexes often have electrostatic interactions and H-bonding through aquated metal ions at the hydrophilic head groups which stabilize the alternately arranged organic and inorganic regions.\textsuperscript{11} It is noteworthy that the composite material herein is devoid of metal ions, with now the bilayers being held tightly by the phosphonium molecules which are in close proximity to the sulfonate groups, and are involved in H-bonding (C−H⋯O−S distances are 2.390(6), 2.528(6), 2.609(7) and 3.005(7) Å). Also noteworthy, is that the calixarene exists in the 3- species, rather than the 4- species, and also 5- species arises from deprotonation of all the sulfonic acid groups and one of the phenolic groups.

$\text{BzPh}_3\text{P}^+$ cations are organized with interdigitation of the phenyl groups from neighbouring cations, forming a mixed mode of phenyl embraces. The phosphonium cation bearing a benzyl arm associate with (i) pairs of phosphonium molecules connected through phenyl rings edge-to-face interactions (C⋯π\textsubscript{centroid} distance at 3.95 Å) with the benzyl arm facing each other, with P⋯P separation at 7.807(1) Å, and (ii) one edge-to-face and offset face-to-face interaction between one another forming continuous networks, with P⋯P at 8.354(2) Å and C⋯π\textsubscript{centroid} and C⋯C distances at 3.81 Å and 3.49 Å respectively (Figure 4). The embraced $\text{BzPh}_3\text{P}^+$ molecules are propagated by translation operations resulting in an infinite network, forming densely packed hydrophobic layers running parallel to the $b$-axis.

Figure 4. $\text{BzPh}_3\text{P}^+$ cations engaged in different phenyl embrace arrangements; benzyl arms are colored in yellow and brown.

Figure 5 displays side-on projections of the Hirshfeld surfaces mapped with $d_{norm}$ for the layer of phosphonium cations separating molecular capsules of $p$-sulfonated calix[4]arenes. (c) Red spots indicate the close contacts of sulfate O-atoms to H-atoms of $\text{BzPh}_3\text{P}^+$. (d) Curvedness of the $\text{BzPh}_3\text{P}^+$ packing near the calixarene and (e) the corresponding fingerprint plot.

A separate Hirshfeld surface analysis was undertaken for an independent complex with the analogous $\text{BzPh}_3\text{P}^+$ ions self-assembled within the bilayer of $p$-sulfonated calix[4]arenes, as a representative for ascertaining the efficiency of packing for this more common arrangement of $\text{BzPh}_3\text{P}^+$ cations relative to the $p$-sulfonated calixarenes.\textsuperscript{8(a,12} Phosphonium cations are arranged in their common phenyl embrace mode and are organized into a grid-like layer, with the lower rim of the calixarene residing in a pocket within the layer. The calixarenes and phosphoniums cations are intimately involved in the
supernolecular structure and the surface reflects a greater area associated with close H⋯O contacts at the top and bottom of the rims of each calixarene, relative to the present structure. The BzPh$_2$P$^+$ ions in the above grid-like layer have weak H-bonding with the oxygen containing fragments (sulfonate groups and hydroxyl groups) in the calixarene ions, contributing 11.7% to the overall surface.\textsuperscript{12} Here there are less C-H⋯C contacts between BzPh$_2$P$^+$ ions and calixarene anions, but more C-H⋯C interactions engaged between themselves, unlike in the present structure, contributing 21.8% to the overall surface (Figure 6), compared to 22.6% for the present structure (Figures 5). The grid like structure is smoother relative to the present structure, compared to 22.6% for the present structure (Figures 5). The grid like structure is smoother relative to the present structure, contributing 60.6% to the overall surface.\textsuperscript{3} The grid like structure is smoother relative to the present structure, contributing 60.6% to the overall surface.

**Conclusions**

We have established a new composite material comprised of two p-sulfonated calix[4]arene end-capping a bis-triethylammonium cation, as ‘molecular capsules’. These are intercalated between layers of embraced phosphonium cations, rather than having the calixarenes forming a bilayer arrangement with the phosphonium cations arranged in between the bilayers. Interestingly the calixarenes must be taken on 3+ charge, instead of the 4+ and 5+ species as established in most of the solid-state structures, further highlighting the flexibility of the molecule in varying its overall charge. Importantly, we establish that the use of metal ions to build up complex arrays between the two large ions can be avoided, and this provides insight in gaining access to other materials based on the ternary system, p-sulfonated calixarene, phosphonium cations and ammonium cations, and then to be able to gain access to materials of even higher complexity.

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**Notes and references**

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\( ^d \) Electronic Supplementary Information (ESI) available: [Synthesis of 2(C$_6$H$_5$O$_2$)$_4$, 4(C$_6$H$_5$P$^+$), C$_6$H$_3$N$_2^{2-}$, 22(H$_2$O), crystallographic data in CIF format, and details of crystallographic analysis. CCD deposition number: 1023016]. See DOI: 10.1039/b000000c/

\( ^\dagger \) Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.


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Irene Ling,*\(^{a,b} \) Alexandre N. Sobolev\(^{c} \) and Colin L. Raston\(^{b} \)

A composite material containing supermolecules of 1,4-bis(triethylammoniomethyl)benzene and \( p \)-sulfonated calix[4]arene involves preferential binding of the ammonium moieties in the cavities of two geometrically opposed calixarenes with mono-phosphonium cations arranged \textit{endo}- with respect to the calixarene bilayers, as a multi-layered structure.