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Complete List of Authors:	Ling, Irene; University of Malaya, Chemistry Department Sobolev, Alexandre; University of Western Australia, School of Biomedical, Biomolecular and Chemical Sciences Raston, Colin; Flinders University, School of Chemical and Physical Sciences

ARTICLE

Gadolinium(III) mediated multi-component confinement of imidazolium cations in *p*-sulfonated calix[4]arene

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Irene Ling,^{a,c} Alexandre N. Sobolev^b and Colin L. Raston^cReceived 00th January 2012,
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Molecular capsule based on two *p*-sulfonated calix[4]arenes along with Gd(III) coordination spheres arranged around the equator of the capsule effectively confined a 1-butyl-3-methylimidazolium cation affording a relatively small capsule size. For a bis-imidazolium cation, only one of the imidazole rings is included in the calixarene cavity with the other ring extending towards a sulfonate group of an adjacent calixarene. Thus the included molecule breaches the equatorial seam of the larger capsule, but here there is no incorporation of Gd(III). In both complexes the capsules themselves are arranged such that the calixarenes are in bilayer arrangements, with (3-methoxyphenyl)triphenylphosphonium cations at the interface of the hydroxyl groups of the calixarene. The interplay of the components was also investigated using Hirshfeld surface analysis.

Introduction

Interest in the investigation and development of molecular capsules either in the solid state or in solution is revealing important properties contributing not only towards biology applications but also in materials sciences.¹ Versatile molecule capsules built from at least two organic moieties having well defined confined space with specific volume were initially targeted for drug delivery, gas storage and separation science.² More recent interest includes the use of molecular capsules to control chemical reactivity and selectivity in organic synthesis,³ control the growth of nanoparticles,⁴ and perturb the photo-physics and redox characteristics of included molecules.⁵ This highlights the diversity of potential application of molecular capsules.

Molecular capsules are readily accessible for two water-soluble *p*-sulfonated calix[n]arenes, at least for the smaller analogues calix[4]arene and calix[5]arene in the common cone conformation, in the presence of various aquated lanthanide(III) ions.⁶ Driven by multiple non-covalent interactions, notably hydrogen bonding along with primary and secondary metal coordination in constructing such calixarene based capsules, encapsulation of guest molecules depends on their size and geometrical constraints. There is also dependence on the functional group complementarity within the confined space of the two geometrically opposed calixarenes.⁷ Moreover, the conformational, rotational and translational degrees of freedom of the encapsulated guest molecules within the restricted space of the capsules are also important.⁷ A diverse range of guest molecules and ions have been incorporated within molecular capsules in the solid

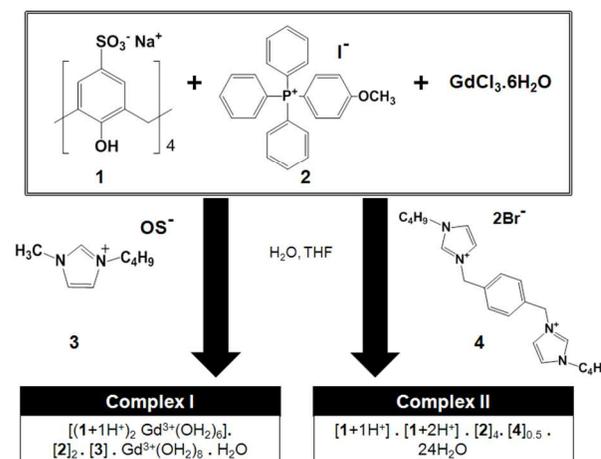
state, based on the two *p*-sulfonated calix[4]arene or *p*-sulfonated calix[5]arene, including amino acids and related molecules,⁸ crown ethers and related macrocycles,⁹ viologens,¹⁰ imidazoliums,¹¹ and organic cations¹² such as mono- and bis-phosphonium cations.

We have been particularly interested in the multi-component self-assembly related to the complexation of different imidazolium cations, which reside in the cavity of *p*-sulfonated calixarenes, along with large phosphonium cations, in building up hierarchical structures. A level of predictability on how such cations nestle within the bilayers has been established. In addition, a substantial level of control of the formation of molecular capsules involving *p*-sulfonated calix[4]arene and lanthanide(III) ions has been mapped out, for encapsulating a number of structural diverse mono and bis-imidazolium cations bearing variable *n*-alkyl termini.^{11,12} Interestingly, molecular capsules comprised of two *p*-sulfonated calix[4]arenes have remarkable versatility in encapsulating long *n*-octyl dimethylimidazolium, with the capsules having gadolinium(III) ions at the equator of the capsule.¹³ These capsules are snugly embedded in the usual bilayer arrangement for the same calixarene, with (3-methoxyphenyl)triphenylphosphonium cations occupying space between adjacent bilayers. Following these findings, we have synthesized inclusion complexes containing *p*-sulfonated calix[4]arene and (3-methoxyphenyl)triphenylphosphonium, incorporating a relatively small imidazolium cation, namely 1-butyl-3-methylimidazolium, and a large bis-imidazolium cation, namely 1,10-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl), formed in the presence of aquated gadolinium(III) ions.

Overall, this contribution concerns extending the lanthanide(III) assisted self-assembly work on the inclusion of imidazolium cations into the calixarenes, and ascertaining the influence of mono and bis-imidazolium molecules on forming supramolecular assemblies of *p*-sulfonated calix[4]arene, and any capsule formation. The flexibility of the lanthanide ion coordination is likely to be an important aspect in the growth of the crystals, in being able to adopt a coordination sphere to pack efficiently in the continuous structure. Two structures comprised of bilayer arrangements of *p*-sulfonated calix[4]arene, in the presence and absence of lanthanide(III) cations are reported, which highlight the prevalence of ‘molecular capsules’ in the solid state for one of the complexes, along with a study on the self-assembly of the (3-methoxyphenyl)triphenylphosphonium cation as its iodide salt in the solid state for comparative purposes.

Results and discussion

The reaction of a 1:1:1 ratio of *p*-sulfonated calix[4]arene, **1**, with (3-methoxyphenyl)triphenylphosphonium, **2**, and 1-butyl-3-methylimidazolium, **3**, cations, in aqueous/THF solution (pH < 3) in the presence of three mole equivalents of gadolinium(III) chloride afforded complex **I**. Crystals of complex **II** formed in an aqueous/THF solution containing equimolar ratios of *p*-sulfonated calix[4]arene, (3-methoxyphenyl)triphenylphosphonium, **2**, 1,10-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl), **4**, and three mole equivalents of gadolinium(III) chloride, Scheme 1. Crystals of (3-methoxyphenyl)triphenylphosphonium iodide (**II**) were also grown, in aqueous/THF solution. All compounds were characterized using single crystal X-ray diffraction data. The extended structures of complexes **I** and **II** are considered as being built of ‘molecular capsules’ with bilayer arrangements of the calixarenes. The ‘molecular capsule’ of different sizes are made up of two cone conformer calixarenes. A relatively small ‘molecular capsule’ is formed in complex **I** where the lanthanide(III) ions bind directly to the calixarene sulfonate groups or are involved exclusively in secondary coordination interactions. Complex **II**, has larger capsules but here no Gd(III) ions are incorporated. We have undertaken Hirshfeld surface analysis¹⁴ for both structures in mapping out the interactions and understanding on how the components come together through complementary interactions.



Scheme 1. Details for the synthesis of complexes **I** and **II**.

Complex I

Complex **I** crystallises in the orthorhombic space group *Pnmm*, (*Z*=2) with the asymmetric unit comprising half of a *p*-sulfonated calix[4]arene molecule coordinated by one of two aquated Gd(III) ions (located at different 222 sites), one *n*-butyl methylimidazolium cation (0.25 occupancy) disordered over 222 site symmetry, one (3-methoxyphenyl)triphenylphosphonium cation located about a 2-fold axis, and a quarter of water molecule located at a 222 position. A salient feature of complex **I** is the presence of discrete dimeric capsules held together by Gd(III) coordination and hydrogen bonding. Pairs of calixarenes with close to fourfold *C*_{4v} symmetry (dihedral angles at 60.57(5)° and 60.10(9)°) are arranged as molecular capsules, with concomitant ionisation of hydrogen ions, as judged on the basis of charge neutrality. This is despite the solution being at a pH of 3 prior to crystallisation of the complex. In complex **I**, one of the calixarenes of each capsule must take on a 5- charge, the other 4- charge, albeit in a disordered fashion given the crystallographically imposed symmetry of the calixarene.

Analysis of the crystal packing reveals a bilayer structure, comprising a linear polymeric arrangement of Gd(III) coordination environments around the equatorial seam of the capsules. Two types of Gd³⁺ centres are present, with the overall structure having a mixture of Gd–O–S linkages and GdOH₂–OS hydrogen bonding interactions. Eight-coordinated Gd1 is located at 222 site symmetry and is directly coordinated to a disordered 1,3-arranged sulfonate groups of the calixarene (Gd1–OS at 2.346(9) Å and 2.381(9) Å), with the other coordination sphere occupied by water molecules with uniform Gd–O distance (Gd1–Ow at 2.363(9) Å). Homoleptic Gd2 is bound by eight water molecules (Gd2–Ow at 2.360(7) to 2.367(9) Å). This aquated metal ion interacts extensively with the calixarene through hydrogen bonding, at the seam of the molecular capsules, based on the close proximity of the O-atom of the sulfonate group relative to the ligated water molecules, closest O···O distances 2.491(6) to 3.001(7) Å. Overall, the capsules are sealed through interplay of the sulfonate groups, closest O···O distances range from 3.183 to 3.481 Å.

Within the structure the calixarenes act as ditopic receptors, with each ‘capsule’ shrouding one disordered n-butyl methylimidazolium cation, Figure 1. Such inclusion complex formation is consistent with our earlier studies where at least one mono-imidazolium molecule can be confined within the space of two calixarenes.¹¹ The confined n-butyl methylimidazolium molecule has its charged head group directed into the calixarene cavity, with the calixarene pinching around the molecule, with multiple interactions with the internal walls of the capsules involving hydrogen bonding and C–H $\cdots\pi$ interactions. The imidazolium head group is involved in C $\cdots\pi$ interactions from the methyl group to the phenyl ring of the calixarene, with C $\cdots\pi$ distances at 3.545 Å and 3.567 Å. The butyl chain nestles in the calixarene cavity, with C–H \cdots O close contacts ranging from 2.090 to 2.336 Å (corresponding C \cdots O distances at 2.990 to 3.153 Å). In addition, there are C–H $\cdots\pi$ interactions to the phenyl ring of calixarene, distances ranging from 2.614 to 2.920 Å (corresponding C $\cdots\pi$ distances are 3.464 to 3.756 Å). All the aforementioned interactions are revealed in the calixarene Hirshfeld surface generated from *CrystalExplorer*¹⁴ with bright red spots highlighting contacts

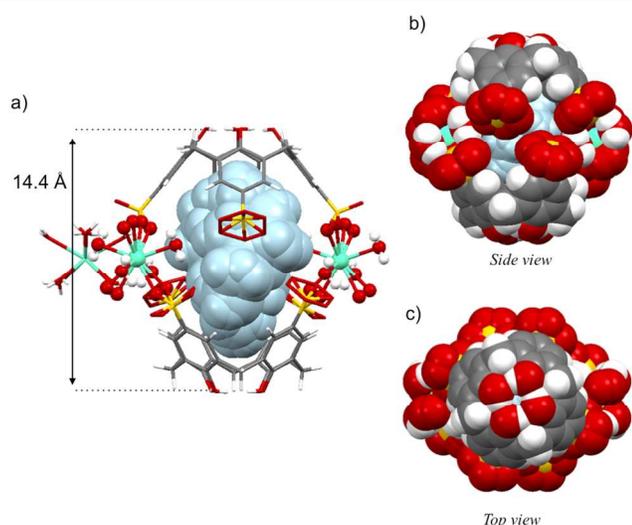


Figure 1. (a) Molecular capsule arrangement in complex I and corresponding space filling representations, with (b) and (c) showing side view top views respectively.

shorter than the sum of their van der Waals radii, Figure 2(a). From the corresponding fingerprint plots, hydrogen bonding is the dominant contributor to the overall intermolecular interactions, making up 53% of the Hirshfeld surface (O \cdots H interactions = 36.6%, H \cdots H interactions = 16.4%). The remaining intermolecular interactions include C–H $\cdots\pi$ interactions contributing 21% with short O \cdots O contacts contributing 25.6% to the Hirshfeld surface, Figure 2(b). Hirshfeld surface analysis for n-butyl methylimidazolium cation was problematic because of its disorder.

The molecular capsule in complex I, involving lanthanide(III) coordination is approximately 14.4 Å (Figure 1) in length along the principal axis, and the confined volume is calculated to be 116 Å³, Figure 3(a). We compare this configuration with our analogous inclusion complex based on a larger guest molecule, namely n-octyl dimethylimidazolium with the same calixarene,¹³ along with

analogous phosphonium molecule. Here the capsule size is much larger with a length of ca. 16.2 Å and an internal volume ca. 210 Å³, which is possible with now exclusively secondary coordination by the Gd(III) ions at the equator of the molecular capsule, Figure 3(b). The present results further highlight the importance and correlation of the nature of lanthanide coordination interactions (primary and secondary) in forming different sized capsules, which presumably self-adjust to confine guests of various sizes and shapes.

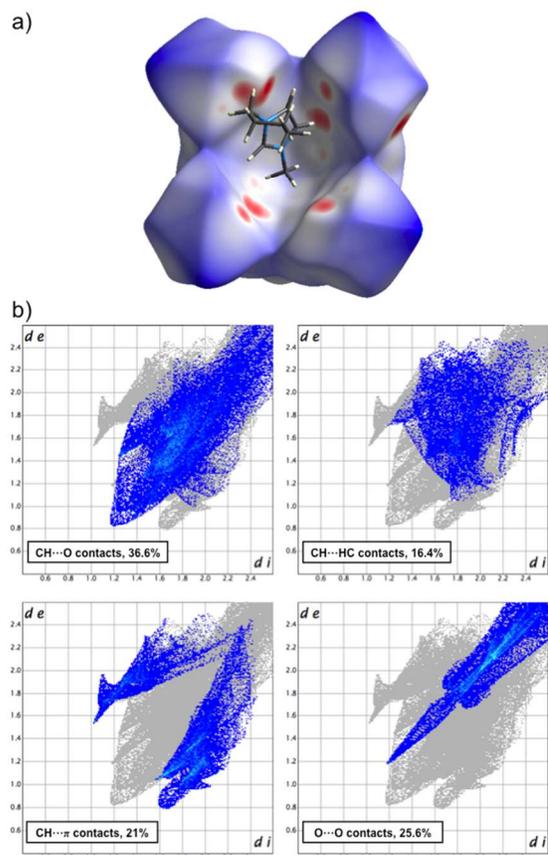


Figure 2. (a) Hirshfeld surface for the calixarene in complex I, and (b) corresponding fingerprint plots showing all close contacts of 1-butyl-3-methylimidazolium and calixarene.

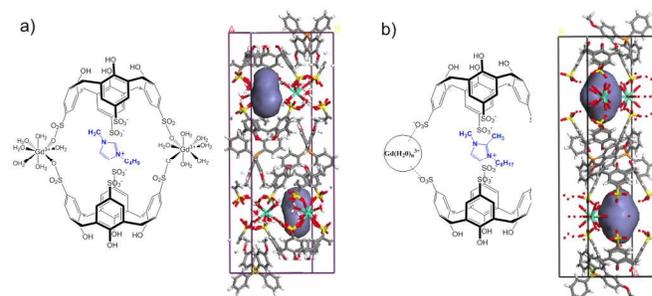


Figure 3. Comparative volumes for (a) molecular capsule confining 1-butyl-3-methylimidazolium, 116 Å³, and (b) molecular capsule confining 1-butyl-2,3-dimethylimidazolium, 210 Å³.

The area between the interface of calixarene hydroxyl groups (O \cdots O distance at 4.33 Å) is occupied by phosphonium cations, with

an overall bilayer thickness of 13.9 Å (Figure 4). However, the phosphonium molecules interact differently relative to previous structures for the same phosphonium molecule, although no significant change in the thickness of the bilayer is evident, and where the phosphonium molecules now do not form the common phenyl embrace arrangement. Rather the phosphonium molecules form linear polymeric associations ($P\cdots P$ distance at 12.371 Å) with the molecules located on mirror planes, and the methoxy termini face each other between adjacent cations. The methoxy terminus has close $O\cdots H$ contacts with the neighbouring molecules, $CH_3-O\cdots H-C$ distances 2.708 to 2.773 Å. The calixarene interacts with the phosphonium molecules in several ways: (i) $C\cdots\pi$ close contacts at 3.421 Å involving calixarene methylene bridges to the centroid of the phosphoniums, (ii) $C\cdots\pi$ contacts at 3.593 Å involving calixarene aromatic ring to a benzene ring of the phosphonium molecule. The H-atoms on the phosphonium cations are also involved in hydrogen bonding with O-atoms of the calixarene molecules, for both the sulfonate and hydroxyl groups, with short contacts from 2.537 to 2.985 Å and 2.951 to 2.988 Å (corresponding $C\cdots O$ distances are 3.227 to 3.415 Å and 3.305 to 3.557 Å) respectively. Hirshfeld surface analysis for the phosphonium cations and a summary of all close contacts involving phosphonium cations and calixarenes, shown as percentage constituents, are depicted in Figure 5.

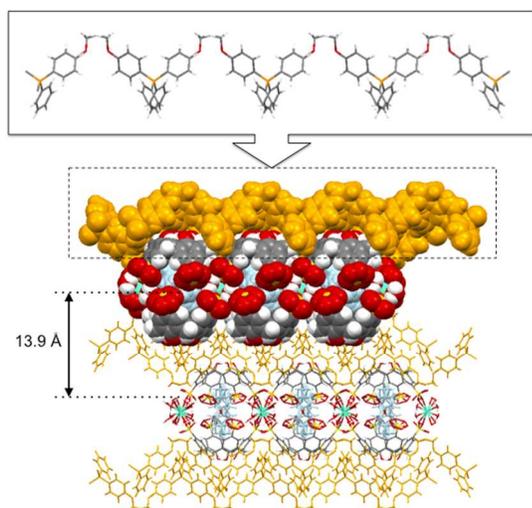


Figure 4. Bilayer arrangement in complex I. Inset showing the polymeric chains of phosphonium cations.

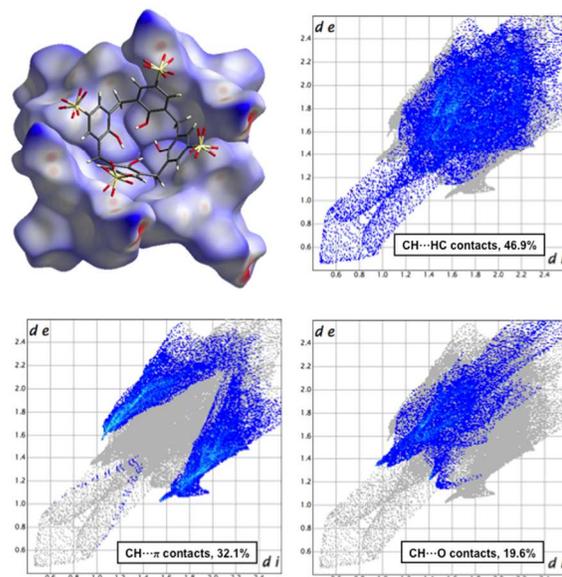


Figure 5. Hirshfeld surface for phosphonium cations along with the corresponding fingerprint plots showing all close contacts, for complex I.

Complex II

Complex II crystallised as colourless plates in the triclinic space group $P\bar{1}$, ($Z=1$), with the asymmetric unit comprised of one *p*-sulfonated calix[4]arene, one partially occupied bis-butyl-methylimidazolium cation, two (3-methoxyphenyl)triphenylphosphonium molecules and included water molecules. In the extended structure, the calixarenes are retained in the typical bilayer arrangement of the molecules, having the distinct alternating hydrophilic and hydrophobic layers. The inclusion complex here behaves differently from other supermolecules made up of calixarene and analogous dication bearing similar imidazolium head groups, where the end-capping of the bis-imidazolium by two calixarenes is not observed. In the present structure, only one independent imidazolium terminus is included in a calixarene cavity, the other is directed towards a calixarene sulfonate group in the adjacent bilayer, and indeed it breaches the bilayer, Figure 6. The two opposing calixarene sulfonate head groups do not face each other but are offset (tilt angle 7° relative to the principal axis of the calixarene). Also noteworthy is that for charge balance, one calixarene must take on a 3- charge and the other a 2- charge, i.e. the calixarenes possess some protonated sulfonate groups, which is a feature of a number of other complexes of the calix[4]arene.¹⁵ Complex II is devoid of lanthanide cations, having a significantly different distance between the bilayers.

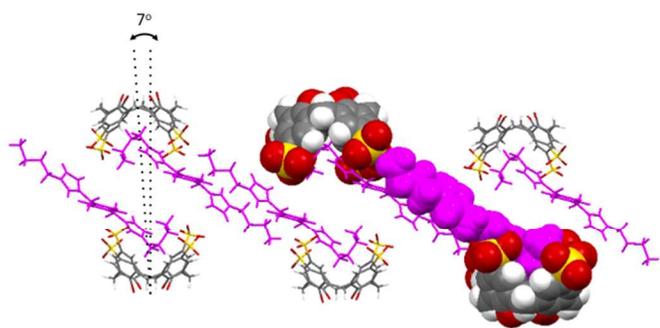


Figure 6. Partial space filling representation for complex **II** showing one independent imidazolium termini included in a calixarene cavity, with the other imidazolium terminus extending toward a calixarene sulfonate group in the adjacent bilayer.

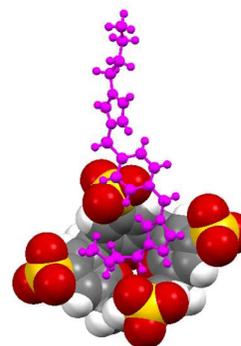


Figure 7. Partial space filling projection of the unique calixarene in **II** showing the inclusion of the bis-butyl-methylimidazolium molecule in the calixarene cavity (ball and stick).

In complex **II**, the disordered bis-butyl-methylimidazolium cation (0.25 occupancy) has one of its terminus directed into the calixarene cavity (Figure 7). The confined n-butyl chain is folded in fitting snugly in the cavity, having multiple non-covalent interactions with the internal wall of the calixarene notably C–H $\cdots\pi$ interactions for the butyl group to the phenolic ring of calixarene, C–H $\cdots\pi$ distances being 2.429 Å, 2.435 Å and 2.905 Å, and hydrogen bonding from H-atoms on the imidazole ring and benzene ring to neighbouring sulfonate groups with close distances ranging from 2.489 to 3.022 Å (corresponding C \cdots O distances from 3.305 to 3.803 Å). H-atoms of the butyl terminus are also close to the calixarene sulfonate groups with distances at 2.725 Å, 2.803 Å and 2.998 Å (corresponding C \cdots O distance 3.660 Å, 3.703 Å and 3.489 Å). As evident from the space-filling representation in Figure 7, the calixarene aromatic rings are more splayed relative to complex **I**, pinching around the bis-imidazolium cation within the cavity; the dihedral angles of the four calixarene phenolic rings are 41.99(8) $^\circ$, 62.17(8) $^\circ$, 42.29(3) $^\circ$, and 67.83(8) $^\circ$. The independent non included five-membered ring terminus has its butyl chain extended to the calixarene sulfonate groups of the opposite bilayer, with slightly longer C–H \cdots O distances at 3.036 Å and 3.123 Å (corresponding C \cdots O contact at 3.720 Å and 3.643 Å). The calixarene–bis-imidazolium interplay was similarly mapped out using Hirshfeld surface analysis and the red spots on the Hirshfeld surfaces identify the closest contacts between each component, Figure (8a & 8c). Here the Hirshfeld surface analysis is based on the electron distribution taking the average electron densities weighted by their partial occupancies of a disordered bis-butyl-methylimidazolium cation. In consequence, the fingerprint plot generated for the bis-imidazolium cation is smeared and elongated. From the fingerprint plots (Figure 8b & 8d) hydrogen bonding based on C–H \cdots O is dominant in the overall intermolecular interactions associated with both calixarene and bis-imidazolium, contributing 38.5% and 71.1% respectively for the fully occupied pairs. Other key interactions involved in the calixarene–bisimidazolium interplay comprise C–H $\cdots\pi$ and C–H \cdots H–C interactions with the contributing percentages summarized in Figure 8(e).

In spite of the presence of Gd(III) ions in the syntheses of complex **II**, it is not included in the final product, but its presence is essential in templating the formation of the product.¹⁶ The absence of lanthanide ions in the crystal structure has been noted for the inclusion complexes based on the same bis-butyl-methylimidazolium and presumably the role of the labile ions in building up the crystal is important in drawing the calixarenes together through electrostatic interactions for which the cation is end-capped by two opposing calixarenes. In the present structure, the arrangement of geometrically opposed calixarenes involves hydrogen bonding of the bis-imidazolium cation at the calixarene upper rims, C–H \cdots O distance at 2.50 Å, with the distance between the two opposing calixarenes at approximately 18.4 Å, along the principal axis of the calixarenes, Figure 9, and the average calixarene upper rim to upper rim distance is 9.4 Å. Crystals of complex **II** are more hydrated than complex **I**, with the water molecules interacting extensively with the sulfonate groups through hydrogen bonding (O \cdots O distances in the range of 2.534 to 2.937 Å).

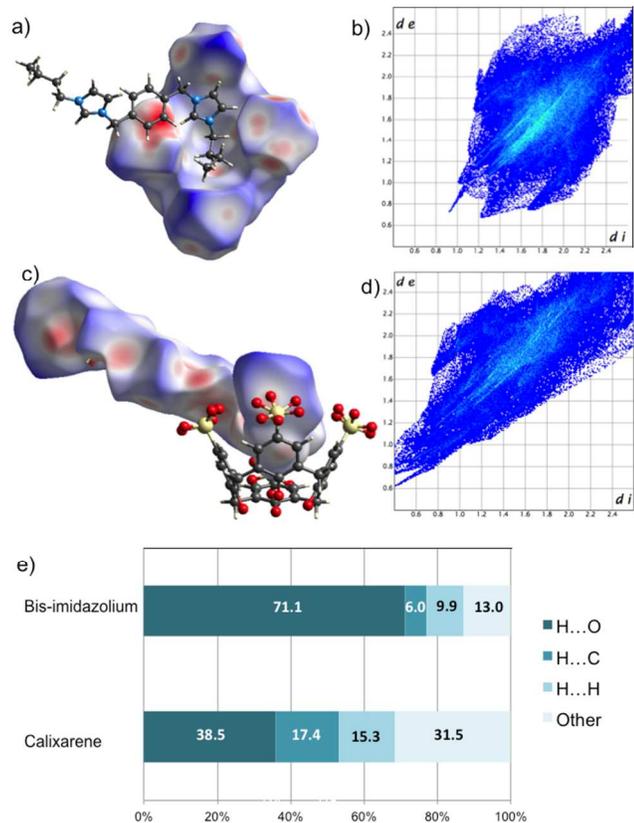


Figure 8. Hirshfeld surfaces for calixarene (a) and bis-butyl-methylimidazolium (b) with the corresponding fingerprint plots (b & d) for complex II. (e) Relative contributions to the Hirshfeld surface for the major intermolecular contacts associated with the calixarene and bis-butyl-methylimidazolium cation.

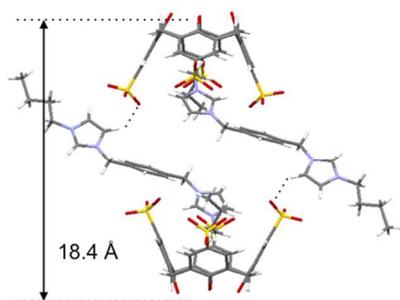


Figure 9. Hydrogen bonding (black dashed lines) interactions for the bis-butyl-methylimidazolium cations in complex II.

The bilayer in II is similarly built up of alternating phosphonium cation filled regions between the interfaces of the hydroxyl groups of the calixarenes, with an overall bilayer thickness of 13.7 Å, Figure 10. The puckered layers (average thickness 12.6 Å) in between the calixarene bilayers are occupied by zigzag chains of phosphonium cations with an inter-chain P...P distance of 8.82 Å and are connected through their common multiple phenyl embrace, edge-to-face distance at 3.86 Å. Individual zigzag chains are constructed of phosphonium pairs associated with edge-to-face embrace, 3.83 Å and

the P...P distance is 10.00 Å. Each discrete pair is identified by a P...P separation of 8.15 Å and the edge-to-face distances range from 4.05 to 4.20 Å. Every zigzag chain is further connected to each other (P...P separation at 9.05 Å) through an offset face-to-face phenyl embrace related to a phenyl moiety for a neighbouring methoxyphenyl moiety, by 4.27 Å. Interestingly two methoxyphenyl termini face each other interact through hydrogen atoms (H...H at 2.82 Å) whilst another two methoxyphenyl termini are directed away from each other, arranged interchangeably with two connected zigzag chains self-assembled in the extended structure, Figure 11. The interplay of the phosphonium molecules and calixarene is mapped out using Hirshfeld surface analysis with all close contacts summarized Figure 12.

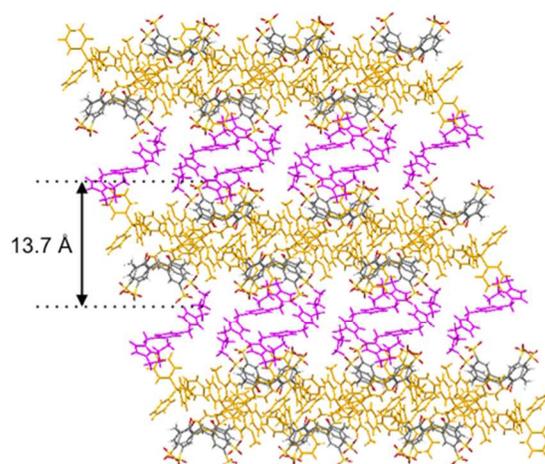


Figure 10. Projection of complex II showing the bilayer arrangement.

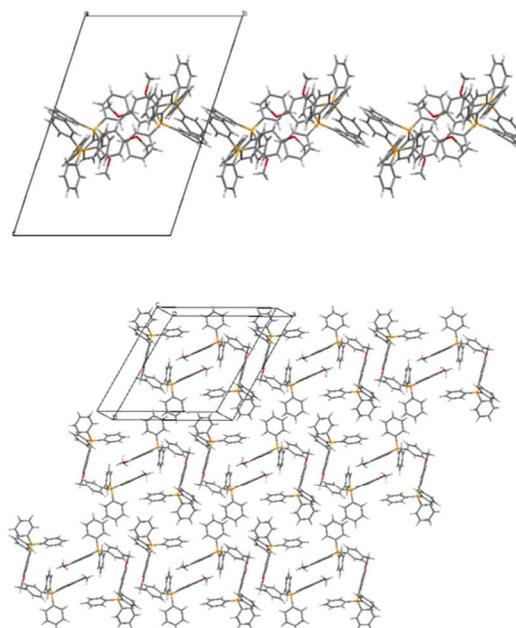


Figure 11. Self-assembly of the phosphonium cations within the calixarene bilayer in II, along a-axis (top) and c-axis (bottom).

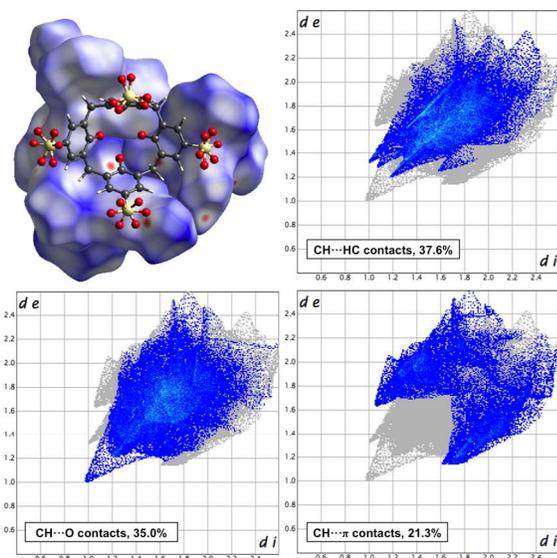


Figure 12. Hirshfeld surface for phosphonium cations along with the corresponding fingerprint plots showing all close contacts for complex II.

We now compare the packing motif of the structure of the simple (3-methoxyphenyl)triphenylphosphonium iodide salt, **III**, that crystallizes in the triclinic space group $P\bar{1}$. Here the molecules are compactly arranged in planar layers (thickness ca. 9.5 Å), Figure 13, similarly in infinite zigzag chains as in complex **II** but with much shorter P...P distances at 6.08 and 6.39 Å. Within each chain, the molecules are self-assembled orthogonal to each other and therefore form four edge-to-face phenyl embraces between pairs of these orthogonal phenyl and methoxyphenyl groups, with C-H... π distances ranging from 3.99 to 4.07 Å. Interestingly, the methoxyphenyl moieties are symmetrically orientated away from each other interchangeably located at the exterior of the plane of the zigzag chains. Thus, the methoxy groups are involved in hydrogen bonding with adjacent chains with C-H...O distances ranging at 2.55 to 2.90 Å, which connect the chains together. Fingerprint plots generated for the phosphonium cation revealed that intermolecular interactions related to C-H... π and C-H...O contribute 28.5 % and 5.0 % to the overall Hirshfeld surface, Figure 13.

Our understanding of the crystal packing in complex **II** relates to the self-assembly of phosphonium molecules within the calixarene bilayer, being made up of embracing phosphonium cations in balancing the hydrophobicity of the bilayers which self-adjusts to fit in the limited space within the bilayer. The arrangement of phosphonium cations transform from the tightly arranged planar arrangement to puckered and distantly arranged molecules when incorporated into the calixarene system. We note that the phosphonium cations interact extensively with sulfonated calixarenes having C-H... π close contacts at 2.811 Å (corresponding C... π distance at 3.46 Å) involving the interaction between the calixarene methylene bridge and the phenyl ring of phosphonium cation. The H-atoms on the phosphonium cations are also involved in weak hydrogen bonding with O-atoms of the calixarene molecules, for both the sulfonate and hydroxyl groups, with short contacts from 2.63 to 2.99 Å and 2.63 to 2.82 Å (corresponding C...O distances are 3.13 to

3.53 Å and 3.18 to 3.28 Å) respectively. The methoxy group of phosphonium cations also interact with the sulfonated calixarenes through hydrogen bonding at 2.81 Å (corresponding C...O distance of at 3.49 Å).

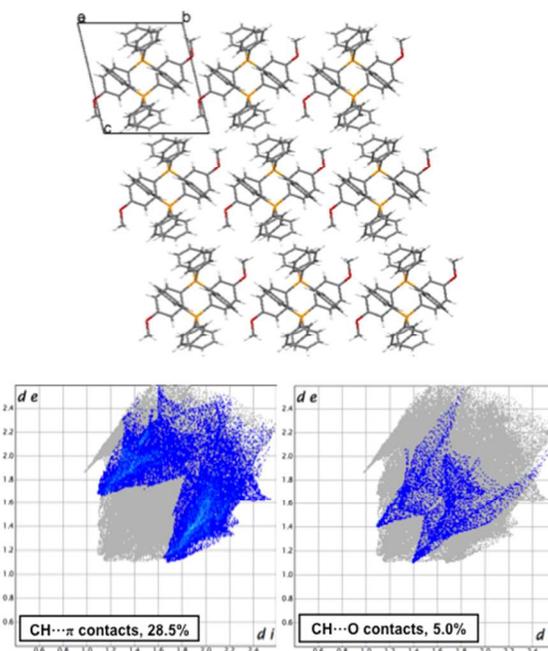


Figure 13. Self-assembly of the (3-methoxyphenyl)triphenylphosphonium cations (iodide anions omitted for clarity) along a-axis (top), and fingerprint plots showing contributions of C-H... π and C-H...O contacts to the overall Hirshfeld surface.

Conclusion

In the present work we have established the ability to confine smaller mono-imidazolium cations in the cavity of two geometrically opposed *p*-sulfonated calix[4]arenes, in the presence of a lanthanide(III) ion. Thus, it is possible to build essentially ‘molecular capsules’ with Gd(III) ions forming a seam around the equator of the capsules, with the metal ions involved in both primary and secondary coordination interactions to the sulfonate groups. From our collective literature observations and experimental findings, we note that larger bis-imidazolium cations can be encapsulated between two geometrically opposed calixarenes affording ‘molecular capsules’, with and without including metal ions in the structure. However, departure from the full encapsulation of the large bis-imidazolium cation was found for complex **II** where one of the imidazolium head groups can extend towards an adjacent calixarene without being included in a cavity. This further adds to a detailed understanding on the limitation to the size of the species that can be encapsulated. In addition, this provides an insight into how the encapsulation process may take place, which would be useful in designing molecular capsules in the solid state where they are incorporated into multi-component systems.

These structurally authenticated complexes based on *p*-sulfonated calix[4]arene along with mono- and bis-imidazolium based cations

demonstrate the preferential binding of more polar calixarene towards these components, rather than towards selected phosphonium cations that are less polar and bulkier. Phosphonium cations in particular can take on well ordered intermolecular embraced arrangements, adjusting to their confinement within the bilayers of the calixarenes. The present study clearly highlights the potential influence of charge on the encapsulation process where the imidazolium cation with its delocalized positive charge wins out on binding an aromatic ring in the cavity of the negatively charge calixarene. However, for an aromatic ring of a phosphonium cation, it has the positive charge primarily on the phosphorus atom. Nevertheless, the difference in the size of a five membered ring (imidazolium) versus a six membered ring (phenyl) residing in the cavity of the calixarene may also be important.

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Experimental

Synthetic procedures

Synthesis of **I** and **II**: *p*-Sulfonated calix[4]arene and 1,10-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl) bromide were synthesized according to literature procedures.¹⁷ 1-Butyl-3-methylimidazolium octyl sulfate, [(3-methoxyphenyl)triphenylphosphonium] iodide and gadolinium(III) chloride hexahydrate salts were purchased from Sigma Aldrich and used as received. For complex **I**, a hot solution of GdCl₃·6H₂O in water/THF (0.030 M) was added to a hot solution (2 mL) of an equimolar (0.010 M) each of *p*-sulfonated calix[4]arene, 1-butyl-3-methylimidazolium and [(3-methoxyphenyl)triphenylphosphonium]. For complex **II**, a hot solution of *p*-sulfonatocalix[4]arene in water/THF (0.010 M) was added to a hot solution (2 mL) of an equimolar (0.010 M) of 1,10-[1,4-phenylenebis(methylene)]bis(3-butyl-1H-imidazolium-1-yl) and [(3-methoxyphenyl)triphenylphosphonium]. Crystals of **III**, (3-methoxyphenyl)triphenylphosphonium iodide were grown in a hot solution of water/THF. All solutions were left to cool and slowly evaporate, with crystals forming after several days. The homogeneity of the materials was checked from the determination of cell dimensions of several crystals for each sample.

Crystallography

Crystal structure data were measured at T = 100(2) K for complexes **I**, **II** and compound **III** from single crystals using an Oxford Diffraction Gemini-R Ultra CCD diffractometer using monochromatic CuK α radiation ($\lambda = 1.54178 \text{ \AA}$). Data were corrected for Lorentz and polarization effects and analytical absorption correction. The structures were solved by direct methods and refined

by full-matrix least-squares on F^2 using the SHELX-2014 crystallographic package.¹⁸ Non-hydrogen atoms of non-disordered fragments were refined anisotropically using all reflections. The positions of hydrogen atoms were calculated and their atomic parameters were constrained to the bonded atoms during the refinement. Residual electron density that could not be modelled as such was effectively removed by use of the program SQUEEZE¹⁹.

Hirshfeld surfaces and the corresponding fingerprint plots were generated using CrystalExplorer¹⁴ and internal volumes within the 'molecular capsule' were calculated using Materials Studio 5.5.²⁰

Crystal data for complex I: C₅₆H₄₇GdO₃₆S₈⁶⁻, 2(C₂₅H₂₂OP⁺), C₈H₁₅N₂⁺, Gd(OH₂)₈³⁺, H₂O
C₁₁₄H₁₂₄Gd₂N₂O₄₇P₂S₈, $M = 2907.06$, colorless prism, $0.22 \cdot 0.19 \cdot 0.17 \text{ mm}^3$, orthorhombic, space group *Pnmm* (No. 48), $a = 12.3714(3)$, $b = 13.3655(2)$, $c = 37.5272(6) \text{ \AA}$, $V = 6205.1(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.556 \text{ g/cm}^3$, $\rho = 9.105 \text{ mm}^{-1}$. $F_{000} = 2968$, $2\theta_{\max} = 134.4^\circ$, 80713 reflections collected, 5560 unique ($R_{\text{int}} = 0.0583$). Final $\text{Goof} = 1.042$, $RI = 0.1027$, $wR2 = 0.2818$, R indices based on 3999 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\max} = 1.0(1) \text{ e \AA}^{-3}$, 423 parameters, 192 restraints. CCDC reference: 1426675

Crystal data for complex II: C₂₈H₂₁O₁₆S₄⁻³, C₂₈H₂₂O₁₆S₄⁻², 4(C₂₅H₂₂OP⁺), 0.5(C₂₂H₃₂N₄²⁺), 24(H₂O)
C₁₆₇H₁₉₅N₂O₆₀P₄S₈, $M = 3570.60$, colorless needle, $0.45 \cdot 0.22 \cdot 0.13 \text{ mm}^3$, triclinic, space group *P* $\bar{1}$ (No. 2), $a = 17.4699(8)$, $b = 18.0265(7)$, $c = 23.3461(9) \text{ \AA}$, $\alpha = 102.788(3)$, $\beta = 96.123(3)$, $\gamma = 118.576(4)^\circ$, $V = 6099.4(4) \text{ \AA}^3$, $Z = 1$, $D_c = 0.972 \text{ g/cm}^3$, $\mu = 1.459 \text{ mm}^{-1}$. $F_{000} = 1879$ (1921 in consideration of disordered solvent density removed by program SQUEEZE¹⁹), $2\theta_{\max} = 124.5^\circ$, 36795 reflections collected, 18492 unique ($R_{\text{int}} = 0.0349$). Final $\text{Goof} = 1.019$, $RI = 0.1719$, $wR2 = 0.4089$, R indices based on 7102 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\max} = 1.0(1) \text{ e \AA}^{-3}$, 1112 parameters, 326 restraints.

Crystal data for compound III: C₂₅H₂₂OP⁺, I⁻
C₂₅H₂₂IOP, $M = 496.30$, pink prism, $0.12 \cdot 0.07 \cdot 0.04 \text{ mm}^3$, triclinic, space group *P* $\bar{1}$ (No. 2), $a = 10.4708(6)$, $b = 10.5478(6)$, $c = 11.0342(6) \text{ \AA}$, $\alpha = 72.783(5)$, $\beta = 75.786(5)$, $\gamma = 70.243(5)^\circ$, $V = 1081.09(11) \text{ \AA}^3$, $Z = 2$, $D_c = 1.525 \text{ g/cm}^3$, $\rho = 12.422 \text{ mm}^{-1}$. $F_{000} = 496$, $2\theta_{\max} = 134.3^\circ$, 8211 reflections collected, 3805 unique ($R_{\text{int}} = 0.0336$). Final $\text{Goof} = 1.000$, $RI = 0.0407$, $wR2 = 0.0978$, R indices based on 3428 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\max} = 1.3(1) \text{ e \AA}^{-3}$, 254 parameters, 0 restraints. CCDC reference: 1426677

Notes and references

^a Centre for NanoScale Science and Technology, School of Chemical and Physical Sciences, Flinders University, Bedford Park, S.A. 5042, Australia. E-mail: ireneling@siswa.um.edu.my; colin.raston@flinders.edu.au

^b School of Chemistry and Biochemistry, M310, The University of Western Australia, 35 Stirling Highway, Perth, W.A. 6009, Australia. E-mail: alexandre.sobolev@uwa.edu.au

† 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.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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Gadolinium(III) mediated multi-component confinement of imidazolium cations in *p*-sulfonated calix[4]arene

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

Multi-component materials have supermolecules made up of mono- or bis-imidazolium cations shrouded by two *p*-sulfonated calix[4]arene essentially form molecular capsules as part of the extended structure, with their formation mediated by Gd(III), which is only incorporated in complex I.

