



Efficient Packing of Long Flexible bis-Imidazolium Cations in the Ubiquitous Bilayers of their p-Sulfonatocalixarene Salts

Journal:	<i>CrystEngComm</i>
Manuscript ID:	CE-ART-05-2015-000994.R1
Article Type:	Paper
Date Submitted by the Author:	15-Jun-2015
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ARTICLE

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Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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Long flexible bis-imidazolium dication form discrete multi-component complexes with anionic *p*-sulfonatocalix[4]arene, cationic tetraphenylphosphonium, and hydrated lanthanide ions (La³⁺ and Gd³⁺). The terminally charged head groups of the dication reside in either one or two calixarene cavities of different bilayers depending on the length of the terminal alkyl group with the central spacer penetrating across the multi-layers and adjusted to fit in the tight bilayer.

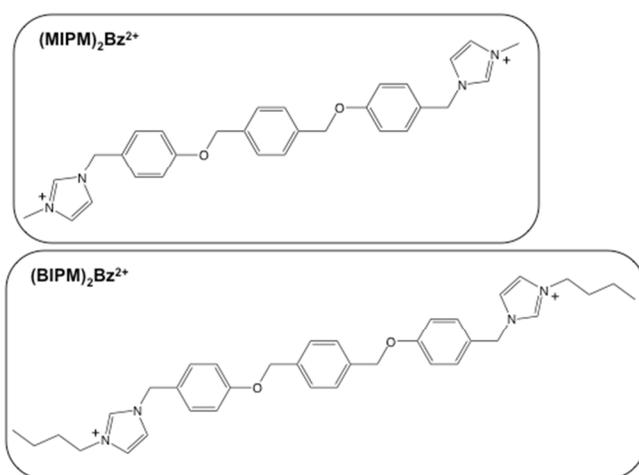
Introduction

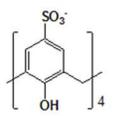
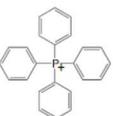
Water-soluble *p*-sulfonatocalixarenes have been extensively investigated as building blocks in crystal engineering, and supramolecular chemistry in general. *p*-Sulfonatocalix[4]arene is the smallest oligomer for these macrocycles and often assembles in the antiparallel bilayer arrangement in the solid state, concurrently creating hydrophobic and hydrophilic environments.¹⁻³ *p*-Sulfonatocalix[4]arene can also assemble into intricate structures in the solid state, including icosahedral and cuboctahedral arrangements (with the cavities directed away from their surfaces), “Russian doll” and “ferris wheel” type arrangements.⁴⁻¹² Owing to having π -electron rich cavity and extra anchoring points from the sulfonate groups, *p*-sulfonatocalix[4]arene can bind organic molecules of various sizes and shapes¹³⁻¹⁸ through multiple non-covalent interactions, which are well documented.³

Supramolecular self-assemblies using singly charged imidazoliums or doubly charged bis-imidazoliums as guest entities in crystallisation of *p*-sulfonatocalixarene related multi-component nanomaterials demonstrate a number of intriguing features.¹⁹ Crystallographic analyses based on the host-guest complexes of *p*-sulfonatocalix[4,5]arenes and bis-imidazoliums provide comprehensive insights as to how these dication affect the crystal packing as well as the nature of the interactions between the cavitated anion and the dication. For example, structural studies involving two symmetrical bis-imidazolium dication namely 1,1'-[1,4-phenylenebis(methylene)]bis(3-methylimidazolium)²⁰ and 1,1'-[1,4-phenylenebis(methylene)]bis(3-butylimidazolium)²¹ in association with *p*-sulfonatocalix[4]arene and selected phosphonium cations, along with aquated lanthanides, show that the charged terminal groups of the bis-imidazolium molecules are selectively bound in the cavities of two

calixarenes which are either (i) from adjacent bilayers facing each other and forming ‘molecular capsules’, or (ii) facing in the same direction in the same bilayer. The ability to form supermolecules with mono-imidazolium or bis-imidazolium acting as guest molecules is not limited to *p*-sulfonatocalixarenes but similar assemblies have been observed in pyrogallol[4]arenes.²²⁻²⁴

We have recently prepared two new symmetrical dication specifically, 1,1'-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylenebis(methylene))]bis(3-methylimidazolium), (MIPM)₂Bz²⁺ and 1,1'-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylenebis(methylene))]bis(3-butylimidazolium) (BIPM)₂Bz²⁺ (Scheme 1). Evolving from our interest concerning a higher degree of complexity for multi-component self-assemblies, we prepared in this work a series of new solid state complexes containing the designer dication and water-soluble *p*-sulfonatocalix[4]arene, along with an aggregate of lanthanide (lanthanum(III), La³⁺ or gadolinium(III) Gd³⁺) and phosphonium cation (tetraphenylphosphonium, Ph₄P⁺) that uniquely stabilizes the self-assembly (Table 1). Our present results demonstrate that the designer dication can effectively penetrate deep across multiple bilayers rather than spanning the bilayer-to-bilayer distance. Integrating the flexible dication in the water soluble *p*-sulfonatocalix[4]arene system in association with other cations is a significant advancement to the self-organising properties since no equivalent structurally defined example is yet known to date and to the best of our knowledge. We analyse and discuss these structures individually in order of increasing dication length, complexity within each dication and variation in the lanthanides.

Scheme 1. Schematic representation for (MIPM)₂Bz²⁺ and (BIPM)₂Bz²⁺.Table 1: Molar ratios of each component affording complexes **1**, **2** and **3**

			(MIPM) ₂ Bz ²⁺	(BIPM) ₂ Bz ²⁺	MCl ₃ ·(H ₂ O) ₆
Complex 1	2	1	1		3(a)
Complex 2	2	1	1		3(b)
Complex 3	2	1		1	3(a)

Results and discussion

Careful examination of the present solid state structures shows that the near-fourfold symmetry cone conformer of calix[4]arene in complex **1** takes on a 4- charge, whilst for complexes **2** and **3**, the overall charge on the calixarene is 5- wherein removal of a further H-atom on the lower rim is necessary for charge neutrality. We note that the *p*-sulfonatocalix[4]arenes in all complexes are self-organised into their simplest hydrogen-bonded bilayer structures. The water-soluble sulfonate moieties are aligned at the surfaces of the bilayers, essentially forming divergent hydrophilic regions containing guest molecules, aquated metal ions and clusters of disordered water molecules, with the inter-bilayer thickness being 19.3 Å, 20.0 Å and 18.9 Å for complexes **1**, **2** and **3** respectively. Calixarene sulfonate groups are known to have high affinities towards metal cations such as alkali, transition, and lanthanide metals.²⁵⁻²⁷ As a result these metal ions are readily incorporated in the solids as part of the overall cohesion in retaining bilayer arrangement with metal-sulfonate interactions (either primary or secondary sphere coordinations, or both). In this work, we selected two paramagnetic rare-earth trivalent cations, La³⁺ or Gd³⁺ that are close in the periodic table.

There are subtle differences between all of the complexes particularly with respect to the interplay of the calixarenes and the different dications. The (MIPM)₂Bz²⁺ polar imidazolium head groups are end-capped at one end, with the other head group simply reaching the sulfonate groups of the next bilayer, whereas for the (BIPM)₂Bz²⁺ dication, two calixarenes from different bilayers end-capped both the imidazolium head groups. Consequently, the flexible long dications not only can penetrate deep across different bilayers but also can breach the bilayer into segments, notably for complexes **1** and **3** as elaborated further below. The effect of incorporating long *n*-octyl, or *n*-decyl chains for the ubiquitous singly charged imidazolium molecules into multi-component bilayer arrangements has been investigated in separate studies where the end of the long alkyl chain can penetrate to the interface of the hydroxyl and phenolate groups of the calixarenes of an adjacent bilayer.²⁸⁻²⁹ Ph₄P⁺ cations in the common embrace manner, are self-associate within the calixarene lower rim hydroxyl groups likewise found in most related complexes.¹⁹ However, phosphonium cation, notably benzyltriphenylphosphonium, can self-organise and intercalate in between layers of molecular capsules that is different to the conventional packing motif.³⁰

Complex 1

Crystals of complex **1** were obtained by slow evaporation of a mixture of two molar equivalents of *p*-sulfonatocalix[4]arene, with one equimolar amount each of (MIPM)₂Bz²⁺ and Ph₄P⁺, along with a three-fold excess of aqueous GdCl₃·(H₂O)₆ in H₂O/THF solution. Complex **1** crystallises in the triclinic space group, *P* $\bar{1}$, *Z*=1, with the asymmetric unit comprised of two different *p*-sulfonatocalix[4]arenes, one and a half (MIPM)₂Bz²⁺ cations, two Ph₄P⁺ cations, one hydrated/complexed Gd³⁺ metal ion and disordered water molecules filling up the otherwise voids in the extended structure.

The calixarene arrangement in the crystal structure can be described by two different types of dimeric capsules, which build the bilayers in complex **1**, where one has a seam of trivalent hydrated Gd³⁺ around its equatorial plane while the other is devoid of metal cation (Figure 1). Both of the capsule configurations (with and without metal ions) are seemingly able to form owing to the head-to-head dimerisation of the calixarenes. Such an arrangement is well established for the *p*-sulfonatocalix[4]arene although manifestation of both configurations in the same solid state structure is rather unusual. For the capsule comprising two calixarenes that are being held together by the Gd³⁺ ion, one of the calixarenes has its sulfonate group directly bridged to a heteroleptic metal centre (Gd–O–S at 2.346(4) Å) with eight water molecules completing the coordination sphere (Gd–O_{water} at 2.369(5) to 2.519(8) Å). The Gd³⁺ metal centre further forms a secondary coordination interaction to the adjacent calixarene sulfonate groups (Gd–O···O–S at 2.733(6) to 2.853(6) Å), allowing the calixarene cavity from one bilayer to align with another calixarene cavity of an adjacent bilayer, affording a calixarene

capsule size of 16.3 Å (Figure 1). Interestingly, a water molecule is embedded in the cavity of the calixarene, associated with O-H $\cdots\pi_{\text{centroid}}$ interactions with the calculated O $\cdots\pi_{\text{centroid}}$ distances ranging from 3.56 to 4.05 Å; similar intermolecular interactions involving water and the π electrons of phenyl rings of the same calixarene have been reported.³¹

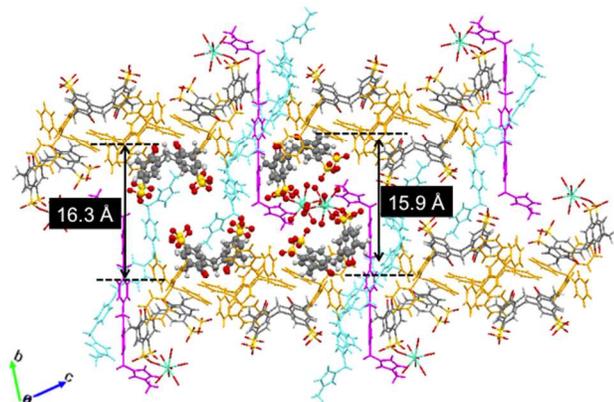


Figure 1: The bilayer arrangement for complex **1** (viewed down *a*) with ball and stick representation showing the different types of dimeric capsule arrangement (with and without metal) along with the capsule dimension for the *p*-sulfonatocalixarene. (Included (MIPM)₂Bz²⁺ cation in blue, independent (MIPM)₂Bz²⁺ cation in pink, phosphonium cation in orange).

We note that one independent calixarene devoid of coordinated metal ions is self-assembled between every second pair of coordinated calixarene molecules within the same bilayer, along with large Ph₄P⁺ cations filling the interstices inside the bilayers (Figure 1). The relative positions of the two calixarene bilayers facing each other are off-set, forming a skewed capsule with an overall size of 15.9 Å (Figure 1). Phenyl embraced Ph₄P⁺ molecules are arranged neatly within the compact calixarene bilayers with the P \cdots P distances 10.519(2) Å and 11.796(2) Å, resembling a square planar motif. The phosphonium cations and calixarene molecules participate in the C–H $\cdots\pi_{\text{centroid}}$ interactions with calculated C–H $\cdots\pi_{\text{centroid}}$ distances ranging between 2.97 to 3.72 Å (the corresponding C $\cdots\pi_{\text{centroid}}$ distances range from 3.87 to 4.67 Å). Also found throughout the structure is the intermolecular H-bonding of the phosphonium cations with the oxygen-containing fragments in the calixarene molecules where H-atoms having close contacts with O-atoms of the (i) sulfonate groups at 2.49 to 3.01 Å (the corresponding C \cdots O distances 3.38 to 3.25 Å), and (ii) hydroxyl groups 2.43 to 2.96 Å (the corresponding C \cdots O distances range from 3.37 to 2.46 Å).

The complementary interaction of the cationic five-membered imidazolium ring bearing a methyl chain with the calixarene cavity is consistent with previously reported structures related to either singly or doubly charged imidazolium based cations where the imidazolium charged head group is selectively drawn into the calixarene cavity.^{19–21} We found that the interplay of (MIPM)₂Bz²⁺ and calixarene behaves differently from other supermolecules made up of calixarene and close related dications bearing imidazolium head

groups, where only one imidazolium terminal is included in a calixarene cavity (Figure 2). One terminal methyl group in complex **1** is directed into the cone-shaped calixarene cavity, slightly pinching the guest with dihedral angles of 51.3(4)°, 55.6(5)°, 55.6(4)°, and 55.2(4)° (angles calculated between the plane of all four phenyl rings of the calixarene with respect to the basal plane defined by four methylene bridges). The incorporated imidazolium polar head group has multiple intermolecular H-bonding interactions involving: (i) the C–H $\cdots\pi_{\text{centroid}}$ interactions of the methyl group with the phenyl rings of the calixarene, with short distances at 2.68 Å and 2.70 Å (the corresponding C $\cdots\pi_{\text{centroid}}$ distances at 3.37 Å and 3.47 Å), (ii) the C–H $\cdots\pi_{\text{centroid}}$ interaction of one of the five-membered ring H-atoms to a calixarene phenyl ring, at 2.95 Å (the corresponding C $\cdots\pi_{\text{centroid}}$ distances at 3.81 Å), (iii) a five-membered ring H-atom having close C–H \cdots O contacts (sulfonate group) at 2.58 Å (the corresponding C \cdots O distance at 3.50 Å), and (iv) H-atoms of the methylene bridge having close C–H \cdots O–S contacts at 2.17 Å and 2.38 Å (the corresponding C \cdots O distances 3.16 Å and 3.17 Å). On the contrary, the other imidazolium terminal is in close proximity with the calixarene sulfonate groups of the opposite bilayer devoid of any inclusion, with C–H \cdots O–S distances at 2.50 Å and 2.78 Å (the corresponding C \cdots O contact at 3.26 Å and 3.69 Å).

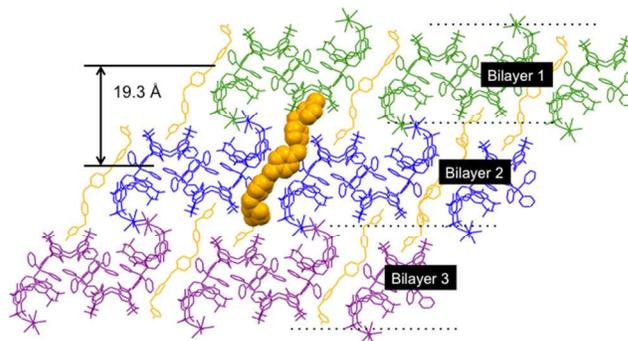


Figure 2: Partial space filling representation of (MIPM)₂Bz²⁺ dication (orange) showing one terminal of the cation being drawn into a calixarene cavity, while the other nestles close to a calixarene sulfonate group of the opposite bilayer.

The hydrophobic bis-phenoxymethyl benzene spacer of the (MIPM)₂Bz²⁺ cation adjusts itself to fit in the tight bilayer, and is associated with other cations which are not involved in host-guest interplay with the cavities of calixarenes. The spacer has various intermolecular H-bonding interactions in the extended structure such as (i) the ether oxygen atom is close to a phosphonium hydrogen atom with calculated O \cdots C–H distance at 2.68 Å (the corresponding O \cdots C distance 3.40 Å), (ii) H-atoms of the benzyl ring have short contacts with calixarene sulfonate and phenolic groups at 2.60 Å and 2.53 Å respectively (the corresponding C \cdots O distance at 3.37 Å and 3.47 Å), and (iii) H-atoms of the methylene bridge H-bond with independent calixarene sulfonate groups with C–H \cdots O–S short contacts at 2.17 to 2.87 Å (the corresponding C \cdots O at 3.16 to

3.70 Å). It is significant that the $(\text{MIPM})_2\text{Bz}^{2+}$ dication not only can penetrate across the multi-layers (Figure 2) but also divides the linear bilayers into segments of four calixarenes along with embedded phosphonium cations within the segment resulting a narrow separation between the segments of ~ 2.6 Å (Figure 3). To date these distinctive features have not been reported previously in the literature and there is no recorded guest molecule that can penetrate across multiple bilayers.

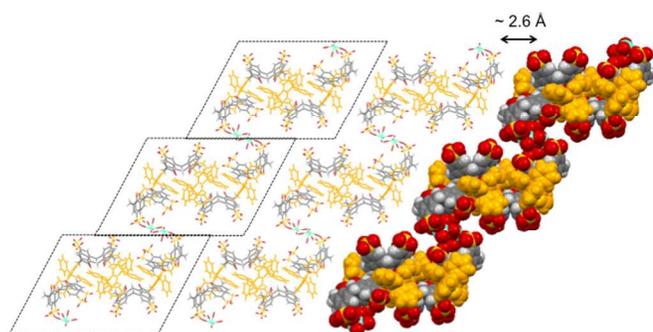


Figure 3: Bilayer arrangement for complex **1** in the absence of $(\text{MIPM})_2\text{Bz}^{2+}$ cations showing bilayer segments comprised of four calixarene anions and four phosphonium cations.

Detailed analysis of complex **1** also reveals that there is one independent centrosymmetric $(\text{MIPM})_2\text{Bz}^{2+}$ cation in a *trans*-configuration aligned vertically between two metal coordinated calixarene capsules (Figure 4), with its charged head group interacting with calixarene sulfonate groups and hydrated Gd^{3+} , C-H \cdots O distances at 2.52 to 2.69 Å (the corresponding C \cdots O 3.32 to 3.46 Å), whilst the central benzyl groups H-bond with the calixarene phenolic group and phosphonium cation, (short C-H \cdots O contact at 2.61 Å (the corresponding C \cdots O 3.55 Å) and C-H \cdots H short contact at 2.70 Å (corresponding C \cdots C 3.46 Å). The $(\text{MIPM})_2\text{Bz}^{2+}$ cation is also positioned in between two calixarene capped bis-imidazolium cations and participates in extensive H-bonding with distances ranging from 2.29 to 2.81 Å for C-H \cdots H-C interactions while the C-H \cdots π_{centroid} distance is calculated to be 3.67 Å (the corresponding C \cdots π_{centroid} at 4.59 Å).

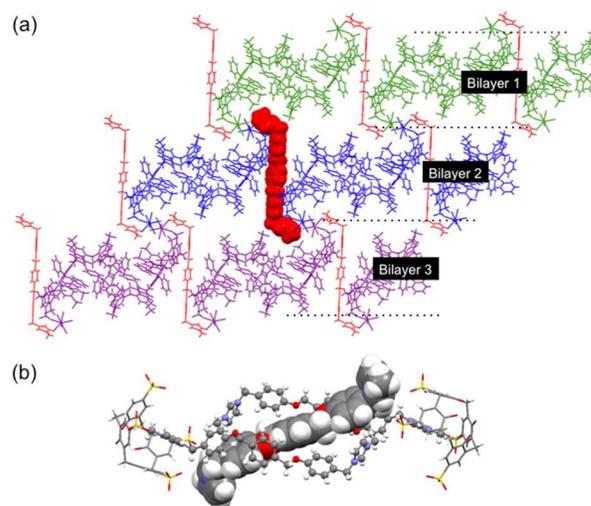


Figure 4: (a) Partial space filling representation for complex **1** showing the $(\text{MIPM})_2\text{Bz}^{2+}$ cation (red) penetrating to the opposite bilayer not participating in the host-guest interaction with the calixarene. (b) An independent $(\text{MIPM})_2\text{Bz}^{2+}$ cation (space filling) positioned in between two other $(\text{MIPM})_2\text{Bz}^{2+}$ (ball and stick).

Complex 2

Complex **2** was prepared under similar conditions as for **1** except that La^{3+} was used as the metal ion. Colourless crystals crystallised in triclinic space group, $P\bar{1}$, $Z=1$ has the asymmetric unit comprising one *p*-sulfonatocalix[4]arene, one fully occupied $(\text{MIPM})_2\text{Bz}^{2+}$ cation in a general position and its half-populated equivalent disposed at the inversion centre, one Ph_4P^+ cation, one half-populated disordered La^{3+} metal ion and disordered water molecules.

In the crystalline state of the complex **2**, the bilayers consist of calixarenes organized in an S-type motif (sulfonate groups directed away from each other) being primarily facilitated by the coordination of $\text{La}(\text{H}_2\text{O})_7$ to one sulfonate group of each calixarene molecule (Figure 5). The half-populated La^{3+} atom is seven-coordinated and disordered over a pair of symmetry related sites. In each occupied position, the coordination environment of the La atom includes a pair of O-atoms of two opposing calixarene sulfonate groups (La-O distance is 2.65(1) Å) about the crystallographic inversion center with the remaining coordination sphere completed by water molecules (La-O distances from 2.51(1) to 2.74(2) Å). The coordinated water molecules also interact intermolecularly with other oxygen containing fragments through secondary coordination sphere interactions, evidenced by the close proximity of the aquated La^{3+} cations to O-atoms of neighbouring sulfonate groups, the closest O \cdots O distances ranging from 2.664(7) to 2.756(1) Å. The solid material is also heavily hydrated with water molecules at the hydrophilic regions which are involved in extensive H-bonding with calixarene sulfonate moieties, and also between themselves, with O \cdots O distances in the range 2.665(2) to 2.944(2) Å.

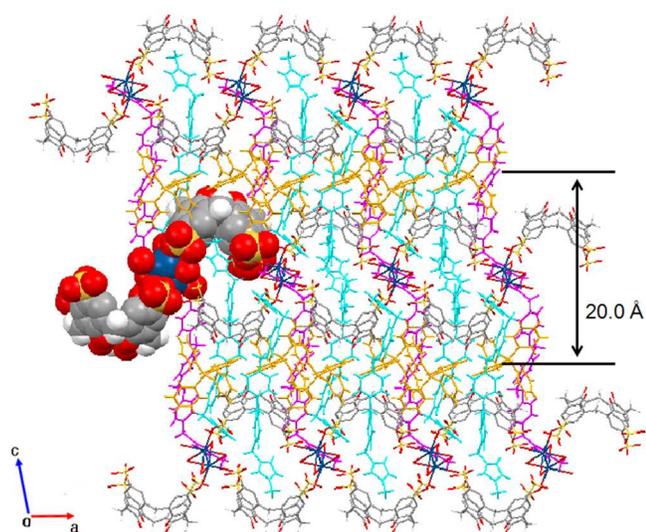


Figure 5: A projection of structure **2** viewed down *b*, showing the overall bilayer arrangement. Calixarenes organized in an S-type motif are shown as space-filling representation.

The interplay of the $(\text{MIPM})_2\text{Bz}^{2+}$ cation with the calixarene is similar to that found in complex **1** where only one polar imidazolium head group included in a calixarene cavity with the other approaches a calixarene sulfonate group of the next bilayer. It is notable that deep penetration of the dication into the opposite bilayer is achieved without significant perturbations to the overall bilayer arrangement (Figure 5). The ether-linked spacer segment interacts with the neighbouring molecules to the same extent and self-adjusts to accommodation in the tight bilayer with its central benzene ring having a $\text{C-H}\cdots\pi_{\text{centroid}}$ approach to a calixarene methylene bridge ($\text{C}\cdots\pi_{\text{centroid}}$ at 4.34 Å), Figure 6a. Subtle differences between complex **1** and complex **2** are found particularly in respect of the complementary electrostatic interactions of the cationic five-membered imidazolium ring with its nearest substituents. The methyl terminal directs into the hydrophobic cavity with the calixarene phenolic rings pinching around the imidazolium aromatic ring (cone dihedral angles are 61.5(3)°, 53.3(4)°, 50.7(4)° and 54.7(4)°) and has limited $\text{C-H}\cdots\pi_{\text{centroid}}$ interactions, with short distances of 2.65 Å and 2.86 Å (the corresponding $\text{C}\cdots\pi_{\text{centroid}}$ distances at 3.63 Å and 3.60 Å). The H-atoms of the five-membered ring H-bond to the nearest sulfonate groups with $\text{C-H}\cdots\text{O-S}$ contacts at 2.45 Å and 2.74 Å (the corresponding $\text{C}\cdots\text{O}$ distance at 3.24 Å and 3.50 Å) and the H-atom of a benzene ring in close contact with a sulfonate group $\text{C-H}\cdots\text{O-S}$ at 2.75 Å (the corresponding $\text{C}\cdots\text{O}$ distance at 3.45 Å). The terminal of the unbound five-membered ring is in close proximity to the calixarene sulfonate groups of the opposite bilayer, (Figure 6a) with the $\text{C-H}\cdots\text{O}$ distance at 2.88 Å (the corresponding $\text{C}\cdots\text{O}$ at 3.55 Å).

Like complex **1**, complex **2** possesses one independent centrosymmetric $(\text{MIPM})_2\text{Bz}^{2+}$ cation in a *trans*-configuration. It does not take part in the host-guest inclusion and has the charged head group interacting with calixarene sulfonate

groups and aquated La^{3+} , with $\text{C-H}\cdots\text{O-S}$ distances at 2.24 to 3.08 Å (the corresponding $\text{C}\cdots\text{O}$ 3.14 to 3.89 Å), and the dication methylene bridge is in close contact with the nearest calixarene sulfonate group, with the $\text{C-H}\cdots\text{O-S}$ distance being 2.56 Å (the corresponding $\text{C}\cdots\text{O}$ 3.31 Å) (Figure 6b). The hydrophobic spacer segment participates in several interactions with neighbouring molecules, where (i) the central benzyl groups H-bond with calixarene sulfonate and phenolic $\text{C-H}\cdots\text{O}$ with short contacts at 2.57 Å and 2.45 Å respectively (the corresponding $\text{C}\cdots\text{O}$ 3.49 Å and 3.36 Å), and (ii) the central benzyl groups H-bond with H-atoms and phenyl ring of the Ph_4P^+ cation, $\text{C-H}\cdots\text{H}$ and $\text{C-H}\cdots\pi_{\text{centroid}}$ short contacts at 2.70 to 2.96 Å and 3.04 Å respectively (the corresponding $\text{C}\cdots\text{C}$ distances are 3.37 to 3.46 Å, and $\text{C}\cdots\pi_{\text{centroid}}$ at 3.90 Å). The Ph_4P^+ cations located within the bilayer are organized through interdigitation of the phenyl groups from neighbouring cations, forming the common phenyl embraces through edge-to-face interactions ($\text{C}\cdots\pi_{\text{centroid}}$ distance at 3.81 Å). The Ph_4P^+ cations also feature H-bonding between H-atoms from the phosphonium cation to the O-atoms of the calixarene (sulfonate and phenolic segments), with $\text{C-H}\cdots\text{O}$ distances ranging from 2.44 to 2.94 Å.

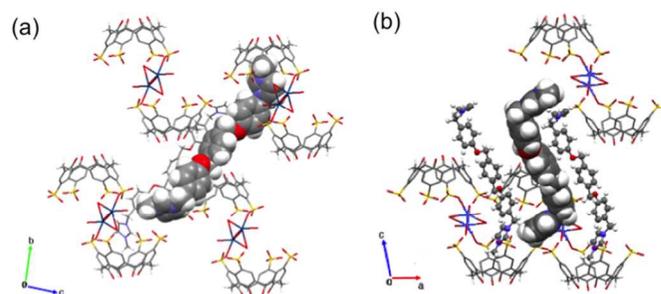


Figure 6: A section of structure **2** showing (a) the interplay of $(\text{MIPM})_2\text{Bz}^{2+}$ cation with calixarenes where one head group is included in a cavity while the other approaches a sulfonate group of the opposite bilayer (viewed down *a*-axis); (b) an independent $(\text{MIPM})_2\text{Bz}^{2+}$ cations (space filling) curled in between two capped $(\text{MIPM})_2\text{Bz}^{2+}$ components (ball and stick) (viewed down *b*).

Complex 3

Under similar preparative conditions in $\text{H}_2\text{O}/\text{THF}$ solution, *p*-sulfonatocalix[4]arene, $(\text{BIPM})_2\text{Bz}^{2+}$, Ph_4P^+ , and Gd^{3+} provided a crystalline precipitate of complex **3** that crystallises in triclinic space group, $P\bar{1}$, $Z=1$. Complex **3** has an asymmetric unit comprised of the same components as complex **1**, except that the dication has butyl terminals and there is an extra equivalent of hydrated Gd^{3+} cation. Here, as in all these complexes, symmetry expansion of the asymmetric unit for complex **3** results in the formation of an extended network made up of capsules of two calixarenes end-capping a disordered $(\text{BIPM})_2\text{Bz}^{2+}$ cation disposed over a centre of inversion (Figure 7).

The disparate bilayer construction of complex **3** as compared to complex **1** is associated with different coordination environments for the Gd^{3+} , where the metal ion is either covalently bound to a calixarene sulfonate group, or

forms a secondary coordination sphere through extensive H-bonding with neighbouring calixarenes. Dimerisation of the calixarenes can be seen as a concomitant of bridging by the hydrated Gd^{3+} cation, where a crystallographically unique Gd^{3+} centre is bound to a calixarene sulfonate group along with eight water molecules completing the coordination sphere; the O-atoms lie in close proximity to an adjacent calixarene sulfonate group ($\text{Gd}-\text{O}\cdots\text{O}-\text{S}$ distances are 2.695(5) to 2.764(9) Å). The unbound polyhydrated Gd^{3+} metal ion has close contacts with the capsule of calixarene sulfonate groups, $\text{Gd}-\text{O}\cdots\text{O}-\text{S}$ distances ranging from 2.538(7) Å to 2.808(7) Å. A compact molecular capsule interlayer relative to complex **1** is noted, which arises from the coordination of the Gd^{3+} metal centres to some of the sulfonato moieties, thus resulting in a smaller dimeric size of 15.7 Å. It is noteworthy that the calixarene capsule is more skewed than that in complex **1**, with the cavity of one calixarene overlapping over an edge of the other.

The alternating inorganic layer contains disordered water molecules and is involved in extensive H-bonding with calixarene sulfonate groups and aquated Gd^{3+} ions, $\text{O}\cdots\text{O}$ distances ranging between 2.628(2) to 3.001(8) Å. Large Ph_4P^+ cations, filling the interstices between the interfaces of calixarene hydroxyl groups in an edge-to-face multiple phenyl embrace manner, essentially form hydrophobic layers with the distance between the P-atoms at 6.503(5) Å and 9.531(4) Å along with two $\text{C}-\text{H}\cdots\pi_{\text{centroid}}$ interactions at distances of 2.99 Å and 3.14 Å (the corresponding $\text{C}\cdots\pi_{\text{centroid}}$ distances at 3.76 Å and 3.75 Å). This type of arrangement has been reported with a similar combination of calixarene and Ph_4P^+ cation.^{20,28-29} The Ph_4P^+ cations also have several $\text{C}\cdots\pi_{\text{centroid}}$ contacts ranging from 3.54 to 3.96 Å, interactions associated with the calixarene methylene bridges and the phenyl rings of phosphonium cations. The H-atoms on the Ph_4P^+ cations participate in H-bonding with the O-atoms of the calixarene molecules, for both the sulfonate and hydroxyl groups, with $\text{C}-\text{H}\cdots\text{O}$ contacts from 2.56 to 3.02 Å and 2.53 to 2.99 Å (the corresponding $\text{C}\cdots\text{O}$ distances are 3.33 to 3.77 Å and 3.40 to 3.70 Å) respectively.

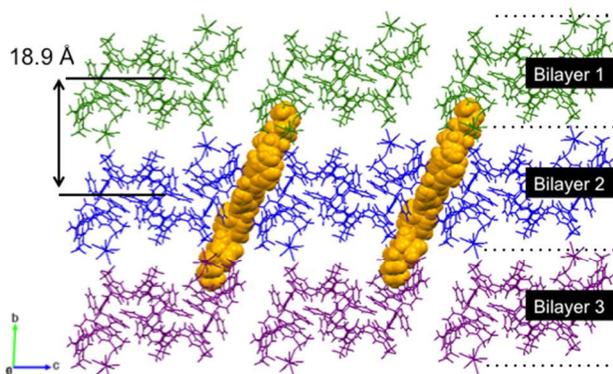


Figure 7: An extended network for complex **3** (viewed down the *a*), showing disordered $(\text{BIPM})_2\text{Bz}^{2+}$ cations (orange space-filling) having both their terminals capped by calixarenes from different bilayer. Some $(\text{BIPM})_2\text{Bz}^{2+}$ cations have been omitted for clarity.

In the case of $(\text{BIPM})_2\text{Bz}^{2+}$, the flexible longer n-butyl alkyl chain influences the calixarene cavity interplay significantly, both termini being effectively end-capped by two geometrically opposed calixarenes from different well-separated bilayers (Figure 7). The half-populated and disordered $(\text{BIPM})_2\text{Bz}^{2+}$ has the butyl chain from the charged head group being drawn deep into the calixarene cavity. The calixarene is in a slight pinched cone configuration in accommodating the butylimidazolium moiety with the calixarene dihedral angles being $63.9(3)^\circ$, $58.1(4)^\circ$, $48.0(3)^\circ$, and $55.1(3)^\circ$. Intermolecular interactions between the $(\text{BIPM})_2\text{Bz}^{2+}$ cation and calixarene involves (i) $\text{C}-\text{H}\cdots\pi_{\text{centroid}}$ interaction of butyl group with the phenyl rings of calixarene, with calculated $\text{C}-\text{H}\cdots\pi_{\text{centroid}}$ distances at 2.93 Å and 2.95 Å (the corresponding $\text{C}\cdots\pi_{\text{centroid}}$ distances at 3.52 Å and 3.88 Å), (ii) butyl chain interactions with the sulfonate group at 2.57 to 2.88 Å (the corresponding $\text{C}\cdots\pi_{\text{centroid}}$ distances of 3.38 to 3.78 Å), and (iii) an H-atom of the five-membered ring having close $\text{C}-\text{H}\cdots\text{O}-\text{S}$ contacts to a sulfonate group, with $\text{C}-\text{H}\cdots\text{O}$ distance at 2.20 Å (the corresponding $\text{C}\cdots\text{O}$ distance at 3.06 Å). The interplay of $(\text{BIPM})_2\text{Bz}^{2+}$ cation and calixarene anion is similar as it was described above in complex **1** where the dication can breach across the multiple bilayers and separates the bilayers into segments of four calixarenes and phosphonium cations. However the separation gap between the segments is slightly larger than in complex **1** with the distance being 3.2 Å (Figure 8).

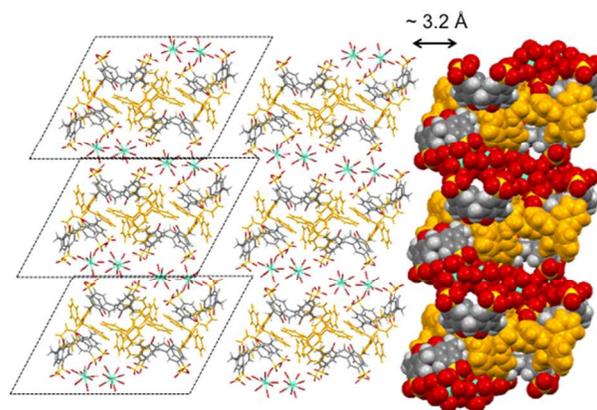


Figure 8: Truncated bilayer arrangement for complex **3** in the absence of $(\text{BIPM})_2\text{Bz}^{2+}$ cations showing bilayer segments comprised of four calixarene anions and four phosphonium cations, separated by a narrow channel.

An independent $(\text{BIPM})_2\text{Bz}^{2+}$ cation that is not accommodated in the calixarene cavity is positioned between two neighbouring $(\text{BIPM})_2\text{Bz}^{2+}$ cations, and engaged with multiple H-bonding: (i) $\text{C}-\text{H}\cdots\pi_{\text{centroid}}$ from the butyl chain to the benzene rings of adjacent $(\text{BIPM})_2\text{Bz}^{2+}$, calculated $\text{C}\cdots\pi_{\text{centroid}}$ distance being 4.98 Å, (ii) $\text{C}-\text{H}\cdots\pi_{\text{centroid}}$ from the benzene ring to a butyl chain of an adjacent $(\text{BIPM})_2\text{Bz}^{2+}$, the calculated $\text{C}\cdots\pi_{\text{centroid}}$ distance being 4.06 Å, and (iii) multiple $\text{H}\cdots\text{H}$ contacts between cations with distances ranging from 2.66 to 3.10 Å. The flexibility of the dication is apparent in that the $(\text{BIPM})_2\text{Bz}^{2+}$ is curled into a *trans*-configuration to fit into a tight bilayer (Figure 9) and thus has close interplay with

calixarene and phosphonium molecules with the entities participating in extensive H-bonding via (i) the H-atoms of (BIPM)₂Bz²⁺ cation close to a sulfonate group, (C⋯O distances being 3.11 Å to 3.67 Å), (ii) an H-atom of the methylene bridge interacts to the phenolic group, (the C⋯O distance being 4.69 Å), and (iii) the H-atoms of the (BIPM)₂Bz²⁺ cation approaching close to H-atoms of Ph₄P⁺ cation, the H⋯H distances being 2.43 to 3.22 Å.

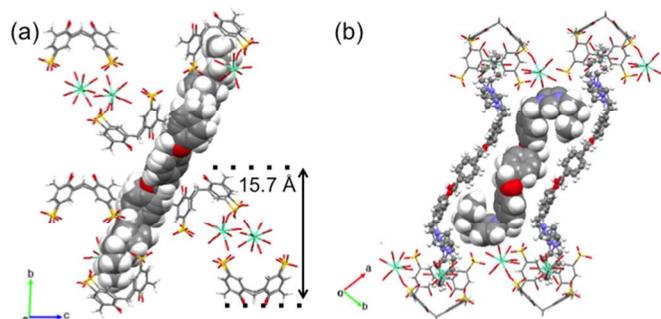


Figure 9: (a) A projection down *a*-axis of a section of structure **3** showing two calixarenes end-capping both terminals of a (BIPM)₂Bz²⁺ cation (space-filling); (b) The arrangement of a *trans* (BIPM)₂Bz²⁺ (space filled).

Conclusions

We have demonstrated the use of bis-imidazolium dications connected with bis-phenoxy methyl benzene as versatile building blocks in forming multi-component materials with water soluble *p*-sulfonatocalix[4]arene, aquated lanthanoid(III) ions, and large phosphonium cations. A feature of all complexes is that the calixarenes are self-assembled into conventional bilayers with the calixarene cavity occupied with at least one of the imidazolium terminal along with the phosphonium cations assembling in the phenyl embrace manner within the tight bilayers. The aliphatic tail-length of the imidazolium molecules is seen to affect the self-assembly properties, most notably the bilayer architecture and the cation-anion interplay involving C–H⋯π interactions and hydrogen bonding. It is important to notice that not only the dications can penetrate across the multi-layers but also divide the bilayers into segments with narrow separations between them. The effect of different aquated trivalent lanthanide ions in various metal coordination environments is substantial which resulted in different structural motifs in the supramolecular assembly of water-soluble calixarene along with the presence of other species.

Acknowledgements

The authors sincerely thank Professor Allan H. White for his professional inputs and opinions in this project. Authors thank Liew Chia Yen for her assistance for acquiring the LC-MS data. Authors gratefully acknowledge the Ministry of Higher Education Malaysia (UM High Impact Research Grant UM-MOHE UM.C/HIR/MOHE/SC/11) and the Australian Research

Council for supporting this work. Authors also acknowledge the facilities, scientific and technical assistance of the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy, Characterisation & Analysis, The University of Western Australia, a facility funded by the University, State and Commonwealth Governments.

Experimental

General procedure for synthesis of (MIPM)₂Bz²⁺ and (BIPM)₂Bz²⁺

The dications were prepared from a reaction of *α,α'*-dibromo-*p*-xylene and 4-hydroxybenzaldehyde; followed by reduction which affords 4,4'-(1,4-phenylenebis(methyleneoxy))diphenol. The crystal structure of the obtained product was elucidated by X-ray technique, results available from CCDC, reference number 1038273. The OH groups of the diphenol were replaced with Cl atoms using hydrochloric acid that furnishes 1,4-benzyloxy-bis-(4-(chloromethyl)benzene) and reaction thereafter with methyl or butylimidazole affords the dications. (Detailed synthetic procedures are recorded in the Supplementary Information).

General procedure for synthesis of complexes **1**, **2** and **3**.

Sodium *p*-sulfonatocalix[4]arene was available from earlier studies.³² Tetraphenylphosphonium bromide, lanthanum(III) chloride and gadolinium(III) chloride were purchased from Sigma Aldrich and used as received. A mixture containing one mole of 1,1'-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylene)bis(methylene)]bis(3-methylimidazolium) dichloride or 1,1'-[1,4-phenylenebis(methylene)bis(oxy)bis(4,1-phenylene)bis(methylene)bis(3-butylimidazolium) dichloride, along with two equivalents each of sodium *p*-sulfonatocalix[4]arene and tetraphenylphosphonium was dissolved in THF/water (1:1, 2 mL) and the solution left to cool and slowly evaporate, with crystals forming after several days. The homogeneity of each material was checked from single crystal X-ray diffraction of cell dimensions for a number of crystals.

Crystallography

Data were measured at T = 180(2)K for complexes **1** and **3** and T = 100(2)K for complex **2** from single crystals using an Oxford Diffraction Gemini-R Ultra diffractometer, equipped with the Ruby CCD detector, and using monochromatic CuKα radiation (λ = 1.54178 Å). Lp and absorption corrections were applied. The structures were solved by direct methods and refined by full-matrix least-squares on F² using the SHELX-97/2014³³ crystallographic package.

Crystal/refinement details for complex **1**.

2(C₂₈H₂₀O₁₆S₄⁴⁻), 2(C₂₈H₃₄GdO₂₃S₄⁺), 3(C₃₀H₃₂N₄O₂²⁺), 4(C₂₄H₂₀P⁺), 30(H₂O)
C₂₉₈H₄₀₄Gd₂N₁₂O₁₁₄P₄S₁₆, M = 6929.67, colorless needle, 0.36 × 0.19 × 0.09 mm³, triclinic, space group PT (No. 2), a = 14.4612(3), b = 22.9608(5), c = 26.3393(7) Å, α = 75.410(2), β = 77.110(2), γ = 87.870(2)°, V = 8248.7(3) Å³, Z = 1, D_c = 1.395 g/cm³, μ = 4.471 mm⁻¹. F₀₀₀ = 3632, 2θ_{max} = 134.7°, 90226 reflections collected, 29381 unique (R_{int} = 0.0566). Final GooF = 1.021, RI = 0.0852, wR2 = 0.2198, R indices based on 23388 reflections with I > 2σ(I) (refinement on F²), |Δρ_{max} = 1.2(1) e Å⁻³, 1973 parameters, 252 restraints. The CCDC reference number: 1038270.

Crystal/refinement details for complex **2**

C₂₈H₃₃LaO₂₃S₄²⁻, C₂₈H₁₉O₁₆S₄²⁻, 2(C₂₄H₂₀P⁺), 2.5(C₃₀H₃₂N₄O₂²⁺), 8(H₂O)

$C_{179}H_{188}LaN_{10}O_{52}P_2S_8$, $M = 3768.72$, colorless needle, $0.42 \times 0.06 \times 0.02 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.7609(9)$, $b = 18.6592(15)$, $c = 20.5626(13) \text{ \AA}$, $\alpha = 94.542(6)$, $\beta = 100.478(6)$, $\gamma = 106.892(7)^\circ$, $V = 4561.2(6) \text{ \AA}^3$, $Z = 1$, $D_c = 1.372 \text{ g/cm}^3$, $\mu = 3.542 \text{ mm}^{-1}$. $F_{000} = 1963$, $2\theta_{\text{max}} = 134.7^\circ$, 44919 reflections collected, 16158 unique ($R_{\text{int}} = 0.1462$). Final $GooF = 1.058$, $RI = 0.1607$, $wR2 = 0.3545$, R indices based on 6453 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\text{max}} = 1.0(1) \text{ e \AA}^{-3}$, 1104 parameters, 286 restraints. Lp and absorption corrections applied. The CCDC reference number: 1038271.

Crystal/refinement details for complex 3.

$C_{28}H_{35}GdO_{24}S_4^{2-}$, $C_{28}H_{19}O_{16}S_4^{5-}$, $GdH_{16}O_8^{3+}$, $C_{36}H_{44}N_4O_2^{2+}$, $2(C_{24}H_{20}P^+)$, $13(H_2O)$

$C_{140}H_{180}Gd_2N_4O_{63}P_2S_8$, $M = 3559.80$, $0.48 \times 0.10 \times 0.09 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 14.0820(2)$, $b = 19.2969(4)$, $c = 30.2780(8) \text{ \AA}$, $\alpha = 86.912(2)$, $\beta = 79.794(2)$, $\gamma = 78.073(2)^\circ$, $V = 7921.4(3) \text{ \AA}^3$, $Z = 2$, $D_c = 1.492 \text{ g/cm}^3$, $\mu = 7.324 \text{ mm}^{-1}$. $F_{000} = 3676$, $2\theta_{\text{max}} = 134.7^\circ$, 85797 reflections collected, 28178 unique ($R_{\text{int}} = 0.0599$). Final $GooF = 1.002$, $RI = 0.1450$, $wR2 = 0.3709$, R indices based on 22675 reflections with $I > 2\sigma(I)$ (refinement on F^2), $|\Delta\rho|_{\text{max}} = 4.0(1) \text{ e \AA}^{-3}$, 1917 parameters, 255 restraints. The CCDC reference number: 1038272.

Notes and references

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† 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: [Synthetic procedure and characterisation data]. See DOI: 10.1039/b000000x/

1. A. W. Coleman, S. G. Bott, S. D. Morley, C. M. Means, K. D. Robinson, H. Zhang and J. L. Atwood, *Angew. Chem., Int. Ed. Engl.* 1988, **27**, 1361.
2. S. J. Dalgarno, J. L. Atwood and C. L. Raston, *Cryst. Growth Des.* 2006, **6**, 174–180.
3. J. L. Atwood, L. J. Barbour, M. J. Hardie and C. L. Raston, *Coord. Chem. Rev.* 2001, **222**, 3–32.
4. G. W. Orr, L. J. Barbour and J. L. Atwood, *Science*, 1999, **285**, 1049–1052.
5. J. L. Atwood, L. J. Barbour, S. J. Dalgarno, M. J. Hardie, C. L. Raston and H. R. Webb, *J. Am. Chem. Soc.* 2004, **126**, 13170–13171.
6. S. J. Dalgarno, J. L. Atwood and C. L. Raston, *Cryst. Growth Des.* 2007, **7**, 1762–1770.
7. A. Drljaca, M. J. Hardie, C. L. Raston and L. Spiccia, *Chem. Eur. J.*, 1999, **5**, 2295–2299.
8. A. Drljaca, M. J. Hardie and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1999, 3639–3645.
9. A. Drljaca, M. J. Hardie, T. J. Ness and C. L. Raston, *Eur. J. Inorg. Chem.*, 2000, **10**, 2221–2229.
10. M. J. Hardie, C. L. Raston, H. R. Webb and J. A. Johnson, *Chem. Commun.*, 2000, 849–850.
11. A. Drljaca, M. J. Hardie, C. L. Raston, H. R. Webb and J. A. Johnson, *Chem. Commun.*, 1999, 1135–1136.
12. J. L. Atwood, L. J. Barbour, S. J. Dalgarno, C. L. Raston and H. R. Webb, *J. Chem. Soc., Dalton Trans.*, 2002, 4351–4356.
13. P. J. Nichols, M. Makha and C. L. Raston, *Cryst. Growth Des.*, 2006, **6**, 1161–1167.
14. S. J. Dalgarno, M. J. Hardie and C. L. Raston, *Cryst. Growth Des.*, 15,

2004, **4**, 227–234.

15. D. Guo, X. Su and Y. Liu, *Cryst. Growth Des.*, 2008, **8**, 3514–3517.
16. Y. Liu, Q. Li, D. Guo and K. Chen, *CrystEngComm*, 2008, **10**, 675–680.
17. M. Makha, C. L. Raston, A. N. Sobolev and A. H. White, *Chem. Commun.*, 2004, 1066–1067.
18. M. Makha, Y. Alias, C. L. Raston and A. N. Sobolev, *New J. Chem.*, 2008, **32**, 83–88.
19. I. Ling, Y. Alias and C. L. Raston, *New J. Chem.*, 2010, **34**, 1802–1811.
20. I. Ling, Y. Alias, A. N. Sobolev and C. L. Raston, *Cryst. Growth Des.*, 2009, **9**, 4497–4503.
21. I. Ling, Y. Alias, A. N. Sobolev, L. T. Byrne and C. L. Raston, *CrystEngComm*, 2011, **13**, 787–793.
22. D. A. Fowler, S. J. Teat, G. A. Baker and J. L. Atwood, *Chem. Commun.*, 2012, **48**, 5262–5264.
23. D. A. Fowler, C. R. Pfeiffer, S. J. Teat, C. M. Beavers, G. A. Baker and J. L. Atwood, *CrystEngComm*, 2014, **16**, 6010–6022.
24. D. A. Fowler, J. L. Atwood and G. A. Baker, *Chem. Commun.*, 2013, **49**, 1802–1804.
25. J. L. Atwood, G. W. Orr, F. Hamada, R. L. Vincent, S. G. Bott and K. D. Robinson, *J. Inclusion Phenom. Mol. Recognit. Chem.* 1992, **14**, 37–46.
26. J. L. Atwood, L. J. Barbour, S. Dalgarno, C. L., Raston and H. R. Webb, *J. Chem. Soc., Dalton Trans.*, 2002, 4351–4356.
27. I. Ling, Y. Alias, A. N. Sobolev and C. L. Raston, *CrystEngComm*, 2010, **12**, 573–578.
28. I. Ling, Y. Alias, A. N. Sobolev and C. L. Raston, *CrystEngComm*, 2013, **15**, 2888–2896.
29. I. Ling, Y. Alias, A. N. Sobolev and C. L. Raston, *CrystEngComm* 2010, **12**, 1869–1875.
30. I. Ling, A. N. Sobolev and C. L. Raston, *CrystEngComm*, 2015, **17**, 1526–1530.
31. J. L. Atwood, F. Hamada, K. D. Robinson, G. W. Orr and R. L. Vincent, *Nature* 1991, **349**, 683–684.
32. M. Makha and C. L. Raston, *Tet. Lett.* 2001, **42**, 6215–6217.
33. G. M. Sheldrick, *Acta Crystallogr.* 2015, **C71**, 3–8. (<http://shelx.uni-ac.gwdg.de/SHELX/index.php>)

Efficient Packing of Long Flexible bis-Imidazolium Cations in the Ubiquitous Bilayers of their p-Sulfonatocalixarene Salts

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The terminally charged head groups of the bis-imidazolium dication reside in one calixarene cavity while the other only reaching the sulfonate groups of the next bilayer with the central spacer penetrating across the multi-layers and adjusted to fit in the tight bilayer.

