CHAPTER 3

Host-guest Chemistry: Lanthanide assisted self assembly of imidazolium cations in organic bilayers

Multi-component solutions containing 1-n-ethyl-3-methylimidazolium or 1-n-butyl-3-methylimidazolium cations, p-sulfonatocalix[4]arene and large mono- or bis-phosphonium cations, as well as lanthanide metal ions, afford self assembled material incorporating all four components. The calixarenes and phosphonium cations are organised into usual bilayers, with the imidazolium cations and gadolinium(III) species incorporated between the bilayers. The imidazolium cations are confined within essentially 'molecular capsules' based on two calixarenes from adjacent bilayers, with these cations taking on different orientations, depending on the nature of the phosphonium cation, and whether the metal also binds to sulfonate moieties.

3.1 Introduction

Calix[4]arene functionalized at the upper rim with sulfonate groups, *p*-sulfonatocalix[4]arene, **1**, acting as versatile water soluble amphiphilic macrocyclic receptor molecule, usually assembles into bilayer structures with an 'up–down' antiparallel arrangements of the cones in the crystalline material [118]. The bilayers are able to confine a diverse range of guest molecules and ions including amino acids and related molecules [99], crown ethers and related macrocycles [114], viologens [116], quinolines [176], aquated metal ions, and organic cations including *mono*- and *bis*-phosphonium cations [124, 125, 177]. The nature of the included species which can involve coordination, electrostatic, and hydrogen bonding interactions in turn control the distance between the bilayers. The formation of 'molecular capsules'[178] is often encountered, with more complex structures possible, based on large spheroidal arrays[120], nanotubules [73], 'Russian doll' and 'ferris wheel'[73]. In general 'molecular capsules' are of interest because of their potential applications in separation technology and sensors [179-181]. The confined guess molecules have inherently weak interactions involving hydrogen bonding, π-stacking, which presumably contribute to the formation and stabilization of the capsules within the extended structures [114].

The focus of this chapter is on the construction and structural diversity of water-soluble **1** complexes, particularly in relation to the host-guest interactions between the calixarene and different imidazolium cations which features in ionic liquid components. In the present systems in the solid state there is also a tendency for the calixarene to be arranged into 'molecular capsules', with the two calixarenes being part of different bilayers. The study also describes the strategy of using large organic phosphonium cations in constructing other complex structures as alternative building blocks for the construction of multi-component layers in solid state. This study was deemed as an important strategy in defining the limits in utilising the ubiquitous imidazolium cations in constructing multi-component bilayers. It is noteworthy that such imidazolium cations feature extensively in ionic liquids, with their physical and chemical properties varying according to the length of the alky chain, and the nature of the anions [153].

Structurally authenticated complexes based on **1** and a diverse range of imidazolium based cations, demonstrates the preferential binding of calixarene towards these components rather than selected phosphonium cations (*mono*- or *bis*-). The inclusion complexes are drawn into the calixarene cavity and assembled through weak supramolecular interactions, notably $\pi\cdots\pi$ and C-H$\cdots\pi$ interactions, and hydrogen bonding. In the multi component solid state structures involving **1** and other organic cations (imidazolium and phosphonium), the conformationally restricted cone-shaped **1** is consistently self arranged into an ‘up–down’ antiparallel bilayer arrangements, with the lower rim hydroxyl groups arranged in a back-to-back manner at the van der Waals limit or possibly with the phenolic groups involved in close H-bonding. Phosphonium cations and **1**, along with the larger ring size sulfonated calix[6 and 8]arenes, have recently been established in their own right to form discrete crystalline complexes, at least in the presence of aquated lanthanide ions [129, 136]. Also noteworthy is that a phenyl ring of the phosphonium cation can bound within the cavity of a calixarene [125].

3.2 Structural features involving 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium

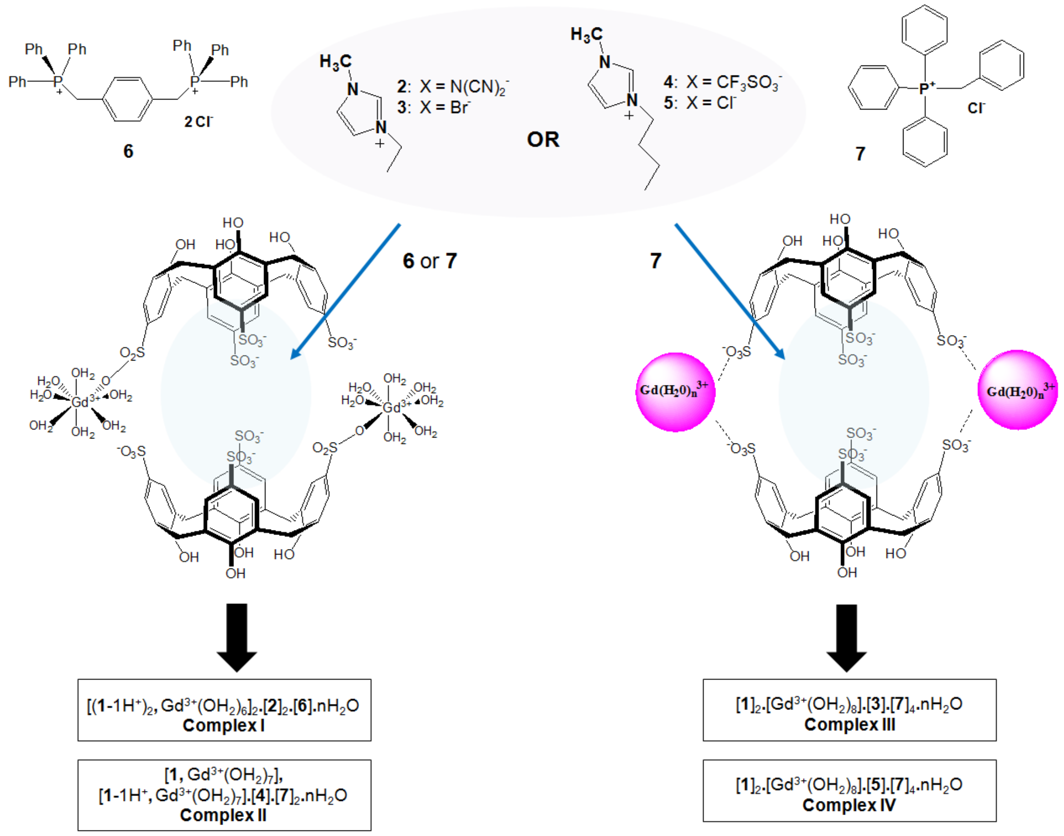

Figure 3.1. Synthesis of the four complexes based on four different component; **1** as a cavitand, **2** or **3** as imidazolium cations, **4** or **5** as phosphonium cations, and aquated gadolinium(III), showing the formation of 'molecular capsule'.

The reaction of a 1:1:1 ratio of **1** to 1-ethyl-3-methylimidazolium, (**2** or **3**) or 1-butyl-3-methylimidazolium (**4** or **5**) cations, and 1,4-*bis*(triphenylphosphoniomethyl) benzene, **6** or benzyltriphenyl phosphonium, **7** cations, in aqueous solution (pH 3.5-4.9) in the presence of excess gadolinium(III) chloride afforded four discrete complexes as colourless crystals, Figure 3.1. Complexes **I**–**IV** were characterised using single crystal x-ray diffraction data, with all four structures revealing the effective templating effects of lanthanide metal ion connecting the calixarenes from two adjacent bilayer forming 'molecular capsule', with the imidazolium cations reside in the cavities. These ‘capsules’ are slightly skewed in the bilayer arrangement, separated by a hydrophobic layer of phosphonium cations through common multiple phenyl embraces. The different alkyl chain lengths of the imidazolium cation are accommodated in different ways. For the shorter chain length, the imidazolium cation has a methyl or ethyl group directed into a calixarene cavity. In the case of butyl-imidazolium, the flexible longer *n*-butyl alkyl chain interplays with the calixarene cavity in different ways. It is also noteworthy that the mode of interaction of the lanthanide ions with the calixarenes is reflected in different interlayer thicknesses (distance measured between centres of neighbouring bilayers), with a more compact arrangement of ‘molecular capsules’ when the metal ion is directly bound to the calixarene sulfonate groups.

3.2.1 Solid state structures of Complex I

Ions of **1**, **2**, **4** and gadolinium(III) come together in a crystalline solid with the asymmetric unit containing one calixarene (taking on a 5- charge, with one proton removed from the lower rim) with a covalently bound aquated gadolinium(III) ion, one ethyl-imidazolium cation, one *bis*-phosphonium cation, and included water molecules which form an extended H–bond network with O···O distances at 2.518(2) to 3.092(4) Å. A key feature of the structure is the centrosymmetric dimers of calixarenes are bridged by aquated gadolinium(III) cations, where the gadolinium centres are bound to two adjacent sulfonate groups of calixarenes along with six water molecules. The bond distances of the O-atoms of sulfonate group to gadolinium are 2.330(1) and 2.381(2) Å. A compact ‘molecular capsules’ arrangement in the extended array is noted, which presumably arises from the coordination of the metal centres to some of the sulfonato moieties and this is manifested in the closer packing between the bilayers, with the interlayer distance at 18.19 Å Figure 3.2.

The imidazolium ethyl group of the imidazolium cation is directed into the cavity of the calixarene and is involved in two C–H···π close distances to two phenolic rings of the calixarene, with C–H···ring centroid distances at 2.66 and 2.94 Å. Two H-atoms of the five-membered ring are involved in C–H···O interactions with sulfonate groups with C···O distance at 3.36 and 3.59 Å, Figure 3.3. The five-membered ring of the imidazolium cation is positioned parallel to one of the phenolic rings of the calixarene, and the distance between the centroids of the two encapsulated imidazolium cations is 4.65 Å, as measured between centroids of the five-membered ring. One of the phenolic rings of calixarene is splayed apart greater than the other phenolic rings with the angle between the basal plane and the phenyl ring at 38.9(1)°. Other angles are 53.7(1)°, 75.9(1)°, and 54.2(1)°, with two of the phenyl rings pinched around the imidazolium cation.

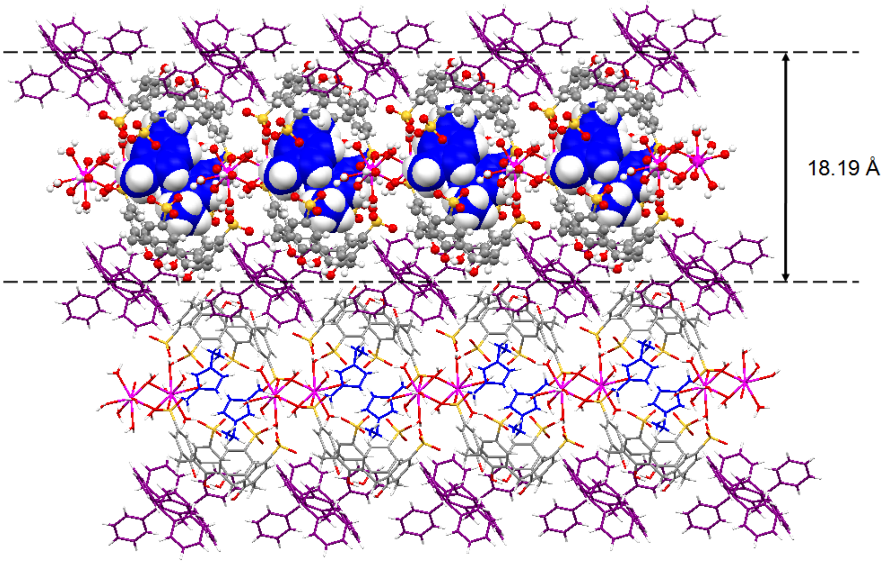

Figure 3.2. Partial space filling of complex **I** showing imidazolium guest molecules (blue) confined in the ‘molecular capsules’, separated by layers of phosphonium cations (purple), projected along *b*-axis.

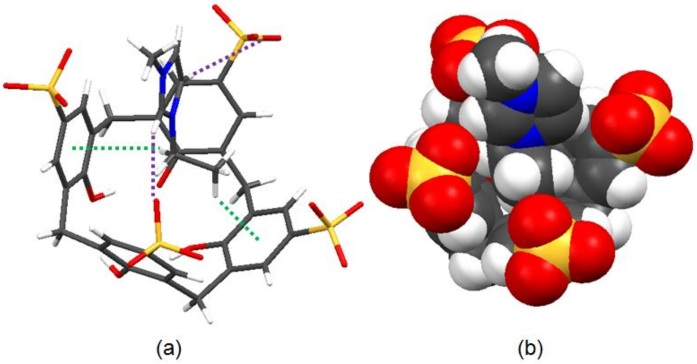

Figure 3.3. Complex **I**: (a) Stick representation showing close contacts between imidazolium and calixarene (H-bonds and C–H···π are shown as purple and green dashed lines respectively), and (b) space filling showing the inclusion of imidazolium cation in the calixarene cavity (different orientation to (a)).

The *trans*-arranged *bis*-phosphonium cations have multiple C–H···π interactions between themselves with C–H···phenyl centroid distances at 3.0 to 3.7 Å. These cations are embedded in between calixarenes, having C–H···π interactions from an H-atom of the central ring of the *bis*-phosphonium cation to the centroid of a calixarene phenolic ring at 3.55 Å. Close C–H···O distances for an H-atom of phenyl rings of the cations to the hydroxyl groups at the lower rim of calixarene are evident, with distances ranging from 2.36 to 2.97 Å. There is a grid-like formation of *bis*-phosphonium cations which is revealed in projection along the *c*-axis, being effectively embedded in between the 'capsules', tucked in close to the lower rim of calixarenes within the bilayers.

3.2.2 Solid state structures of Complex II

Crystals are comprised of **1**, **3**, **5** and gadolinium(III), as for complex **II**, with the asymmetric unit containing two *p*-sulfonatocalix[4]arenes with covalently attached gadolinium(III) bearing seven coordinated water molecules, one butyl-imidazolium cation, distributed between cavities of two calixarenes, two benzyltriphenyl phosphonium cations, and solvent molecules. All water molecules are half-populated, and there are also included methanol molecules (residual solvent from recrystallization of *p*-sulfonatocalix[4]arene) which are involved in the H-bonding network, with O···O distances down to 2.50(2) Å.

The 'molecular capsule' is generated by an inversion centre, but electrical neutrality requires one of them taking on a 4- charge, the other 5- charge within each 'capsule' (necessitating one proton being removed from the lower rim of calixarene). Two crystallographically unique gadolinium metal centers are bound to O-atoms of sulfonate groups with Gd–O at 2.371(4) and 2.429(9) Å and the direct coordination of the gadolinium cations with the calixarenes, forms a compact arrangement with interlayer thickness at 18.07 Å, Figure 3.4, which has approximately the same interlayer thickness in complex **I**.

The butyl-imidazolium cation residing in the 'capsule' is disordered with half population across the inversion centre having the methyl group directed into the calixarene cavity with a C···π close distance for the C-methyl group to centroid of a phenolic ring at 3.61 Å. Other close contacts involve an H-atom of the five-membered ring to the sulfonate group with the C···O distances at 3.01 to 3.20 Å. At the other end of the imidazolium cation, the butyl group is close to the calixarene phenolic rings with C···π close distance at 3.59 to 3.65 Å, and an H-atom of the butyl group is close to the sulfonate group at 2.69 Å (C···O distance at 3.65 Å). The calixarenes in complex **II** also have a pinched cone configuration associated with binding of the guest molecule, with the angles between the plane of the aromatic rings and the basal plane of the four hydroxyl groups at the lower rim being 70.2(2)°, 51.2(2)°, 64.6(2)°, and 46.3(2)°, Figure 3.5.

Pairs of phosphonium cations embrace in an offset face-to-face manner with C···π (centroid) between the phenyl rings at 3.93 Å. Close contacts between calixarene and phosphonium cations are π···π interactions between the phenyl rings of calixarene and phosphonium with the centroid to centroid distance at 3.50 Å, and C–H···π interactions involving the methylene bridge of calixarene and the phenyl group of phosphonium, the H-atom to centroid distance being 2.98 Å. Phosphonium cations link each other with common embraces as part of a grid network, with the calixarenes in the openings.

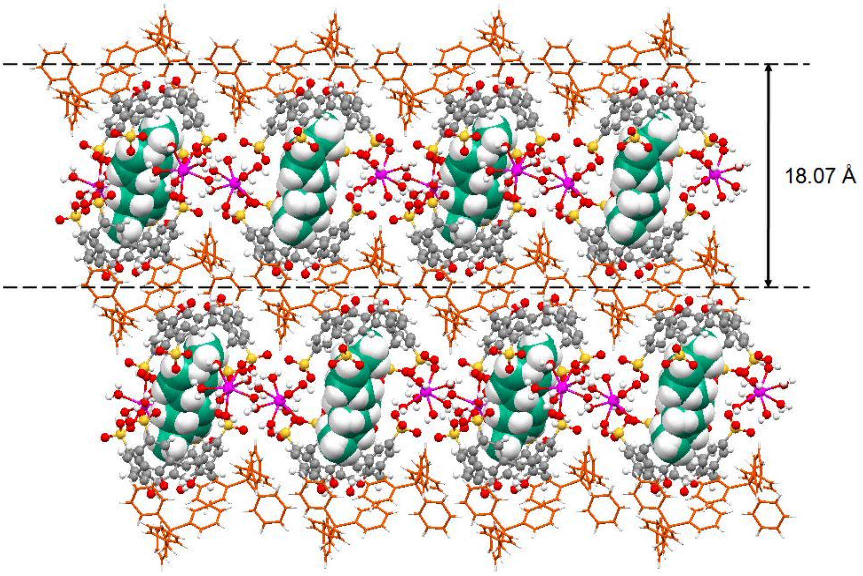

Figure 3.4. Some space filling of complex **II** showing imidazolium guest molecules (green) confined in the 'molecular capsules', separated by layers of phosphonium cations (orange), projected along the *a*-axis.

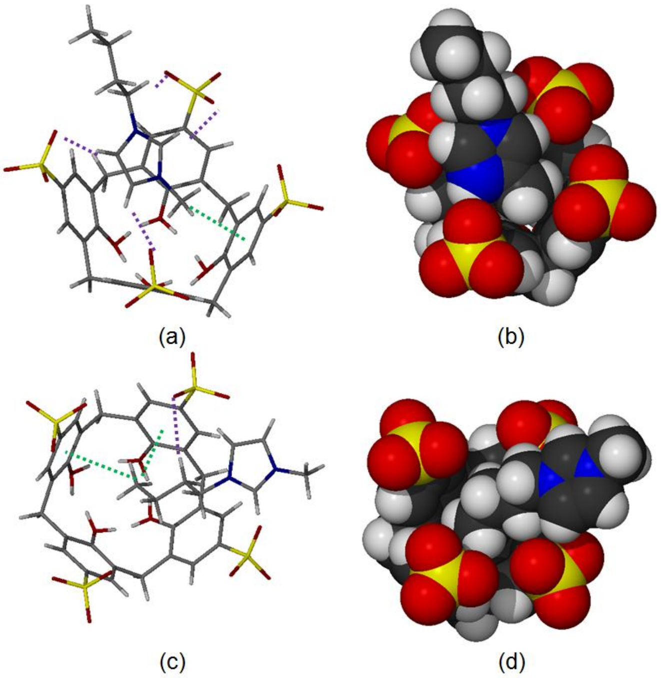

Figure 3.5. (a) and (c) Stick representation showing close contacts between imidazolium and calixarene in complex **II** (H-bonds and C···π are shown as purple and green dashed lines respectively) with (b) and (d) as equivalent space-filling representations.

3.2.3 Solid state structures of Complex III

The combination of components **1**, **2**, **5** and gadolinium(III) afforded colorless prisms of complex **III**. The asymmetric unit consists of one *p*-sulfonatocalix[4]arene, with one half-populated ethyl-imidazolium cation residing in the cavity of the calixarene molecule, two phosphonium cations surrounding the calixarene and a gadolinium(III) cation with half occupancy (disordered relative to an inversion centre), forming a secondary coordination sphere through hydrogen bonding with the calixarenes, effectively creating ‘molecular capsules’ in the extended structure, Figure 3.6, rather than binding directly to calixarenes as opposed to complex **I**. Each adjacent ‘capsule’ is skewed presumably in maximising electrostatic interaction between the sulfonate groups and the polyaquated lanthanide cations. This homoleptic metal ion is coordinated by eight water molecules, and has close contacts with the sulfonate groups with the upper rim of the calixarene through extensive hydrogen bonding, the GdO···OS distances ranging from 2.76(2) Å to 2.77(2) Å. The ‘molecular capsules’ interlayer is now slightly greater relative to complex **I**, with the interlayer thickness at 21.13 Å, Figure 3.6.

The ‘molecular capsules’ contain one ethyl-imidazolium cation distributed between two positions, with the imidazolium cation having the methyl group directed into the cavity of calixarene, the methyl C-atom having a short distance to the centroid of a phenyl ring at 3.47 Å. The imidazolium ring has a C–H···π interaction to the phenolic ring of calixarene, with C–H···ring centroid distance at 2.74 Å, and two H-atoms on the five-membered ring are involved in C–H···O interactions with the sulfonate group, the C···O distances being 3.44 and 3.47 Å, Figure 3.7. The calixarenes are slightly distorted from a symmetrical cone shape with two opposite 1,3-disposed aromatic rings pushed away, with the angles between the plane of the aromatic rings and the basal plane of the four hydroxyl groups at the lower rim of calixarene at 49.1(3)°, 65.9(3)°, 40.3(3)° and

62.7(3)°. One of the rings is splayed apart slightly greater and it is parallel with the five-membered ring of the imidazolium cation, the centroid to centroid distance being 3.97 Å. Disordered water molecules (albeit with no H-atoms located) are present within 'molecular capsule' along with the imidazolium cation, having strong O···O (H-bonds) interactions, the distances ranging from 2.44(2) to 3.28(5) Å.

The phosphonium cations interact in the common multiple phenyl embrace forming layers, embedded in between the back-to-back arrangement of calixarenes, Figure 3.6. The phosphonium cations have C–H···π close contacts from the phenyl ring of phosphonium to the centroid of a calixarene phenolic ring, with the C···π distance at 3.63 Å.

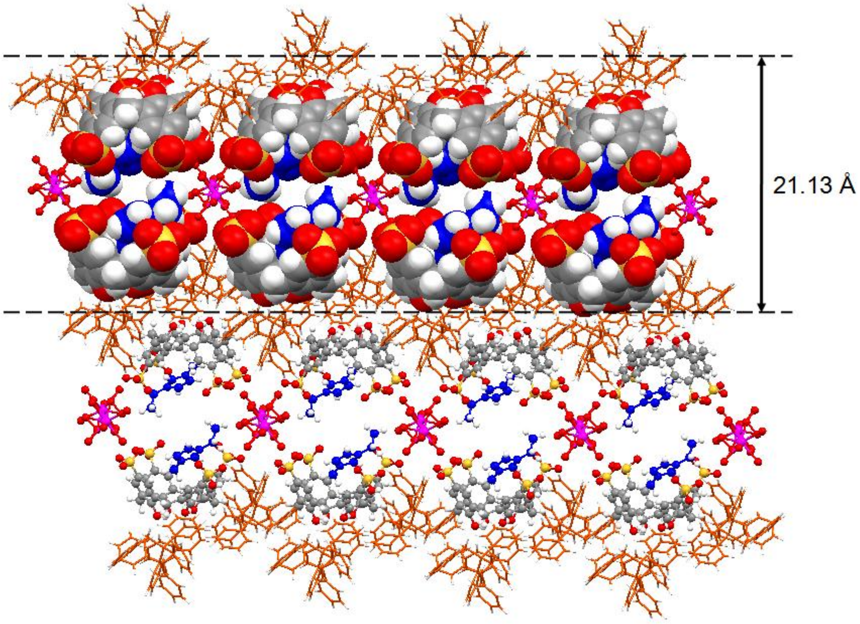

Figure 3.6. Projection along *b*-axis with some space filling of imidazolium guest molecules (blue) confined in the 'molecular capsules', and layers of phosphonium cations (orange) in the extended bilayer of complex **III**.

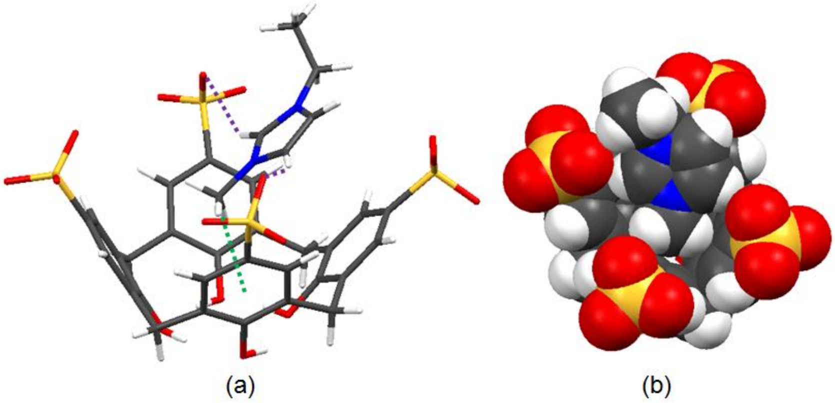

Figure 3.7. (a) Stick representation showing close contacts between imidazolium and calixarene in complex **III** (H-bonds and C–H···π are shown as purple and green dashed lines respectively), (b) space filling showing the inclusion of imidazolium cation in the calixarene cavity (different orientation to (a)).

3.2.4 Solid state structures of Complex IV

Crystals are comprised of **1**, **3**, **5** and gadolinium(III), with the unit cell containing one *p*-sulfonatocalix[4]arene, one disordered butyl-imidazolium cation distributed between two positions, two benzyltriphenyl phosphonium cations and a half populated gadolinium cation coordinated by eight water molecules, and a large quantity of disordered included water molecules (with no H-atoms located) filling the voids. The homoleptic metal centre is in close contact with the calixarene through extensive hydrogen bonding, as judged by the close proximity of the O-atom of the sulfonate group to the aquated gadolinium cations, O···O being 2.65(2) to 2.98(2) Å. The distance from the centre of the bilayer to the next bilayer is 20.92 Å, which is close to the size of the interlayer distance in complex **III**.

The calixarenes are arranged in slightly skewed ‘capsules’ forming bilayers in the extended structure, Figure 3.8, with each ‘capsule’ shrouding one imidazolium cation. In the present structure the half populated imidazolium cation (also disordered between two positions) is folded into a ‘V’-shape, having multiple interactions with the walls of the ‘capsules’; (i) C–H···π from the butyl group to the phenolic ring of calixarene, C–H···ring centroid distances being 2.76 Å and 2.77 Å, (ii) an H-atom on the five-membered ring close to a sulfonate group, C···O distances being 3.28 Å to 3.54 Å, (iii) an H-atom of the methyl group close to the sulfonate group, C···O distance being 3.31 Å, and (iv) an H-atom of the butyl group close to the sulfonate group, C···O distance being 3.16 Å. As seen from the space-filling representation in Figure 3.9, the butyl-imidazolium cation is positioned deep within the calixarene cavity, with the calixarene pinching around the guest. The angles of all four phenolic rings with the basal plane of the four hydroxyl groups at the lower rim of calixarene are 40.0(3)°, 59.8(3), 49.6(3)°, and 66.6(3)°, for the pinching and splaying phenyl ring pairs (respectively) within each calixarene.

Phosphonium cations essentially form layers within the bilayers with edge-to-face embrace, and are involved in two C–H···π (centroid) contacts, at distances of 3.0 Å and 3.2 Å. They are embedded in between calixarenes having multiple close contacts involving C–H···π (centroid) interactions between an H-atom at the phenyl ring of phosphonium with the centroid of the phenolic calixarene ring, at distances ranging from 2.71 to 2.98 Å.

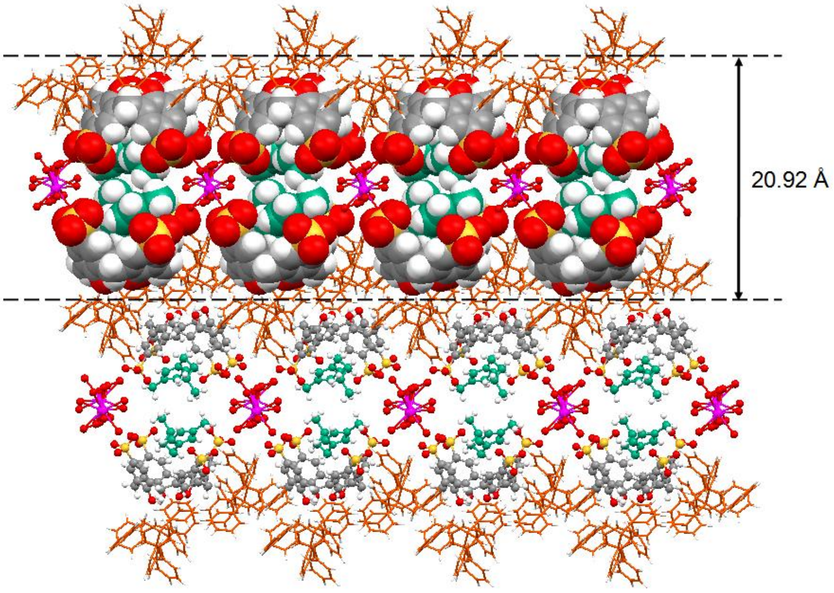

Figure 3.8. Partial space filling of complex **IV** showing imidazolium guest molecules (green) confined in the 'molecular capsules', separated by layers of phosphonium cations (orange) projected along *b*-axis.

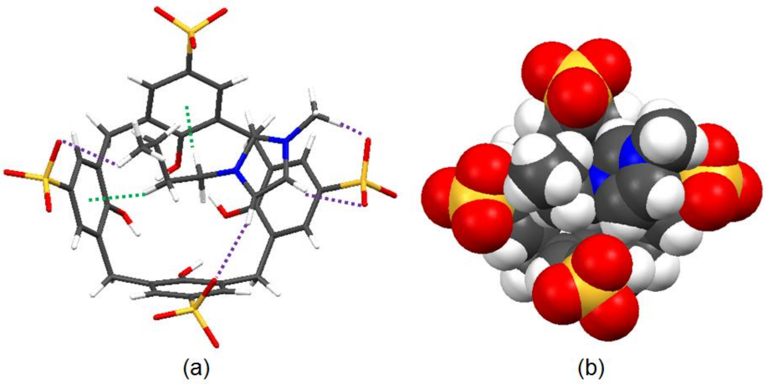

Figure 3.9. Complex **IV**: (a) Stick representation showing close contacts between imidazolium and calixarene ions (H-bonds and C–H···π are shown as purple and green dashed lines respectively), and (b) space-filling showing inclusion of imidazolium cation in the calixarene cavity.

3.3 Conclusions

Structural features arising from the assembly of multi-component materials containing water soluble sulfonated calix[4]arene, aquated gadolinium(III) ions, and a range of phosphonium cations have been established, with a common ‘molecular capsule’ or skewed ‘molecular capsule’ motif based on two calixarenes surrounding one or two imidazolium cations, depending on the choice of unsymmetrical 1-ethyl- or 1-*n*-butylimidazolium cations, as shown in cartoon form in Figure 3.10. The shorter alkyl chain can afford ‘capsules’ containing one cation, with the ring methyl directed into a calixarene cavity, the ‘capsule’ also containing solvent molecules, complex **III**, Figure 3.10(a). Alternatively two such cations can be in a ‘capsule’, complex **I**, but now with the ethyl groups directed into the calixarene cavities, Figure 3.10(b). Thus the ‘capsules’ are flexible in confining the number and the orientation of the imidazolium cations, which is likely to depend in a subtle way on the choice of phosphonium cation, and how the metal centres interact with the calixarene *i.e.* covalent bond versus H-bonding formation, for complexes **I** and **III** respectively.

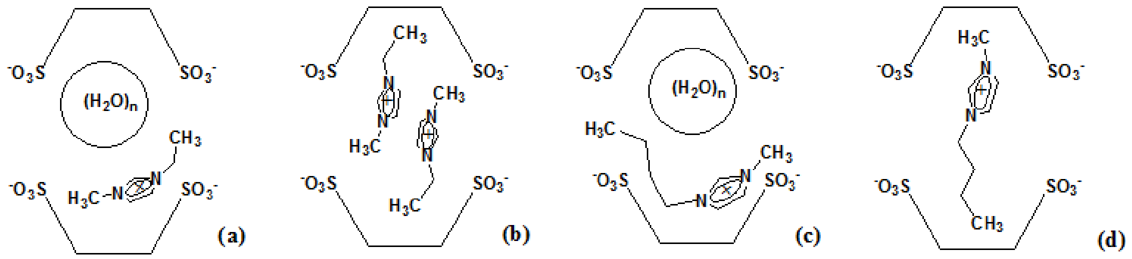

Figure 3.10. Cartoon of the different arrangement of imidazolium cations within ‘molecular capsules’, (a) – (d).

The longer *n*-butyl alkyl chain gives scope for the two ends of the imidazolium cation to reside in different calixarenes, as found in complex **II**, Figure 3.10(d). The same cation can also be common to two calixarenes in a distinctly different way, complex **IV**, with the alkyl chain being V-shaped and snugly fitting into one cavity, the other cavity presumably occupied by disordered solvent molecules, Figure 3.10(c). Thus for the longer chain alkyl group, the number of cations in the ‘capsules’ in set at one, but the orientation and conformation of the alkyl chain can be varied, in a way depending on the choice of phosphonium cation, and also on how the metal centres interact with the calixarenes (covalent bond versus H-bonding formation), for complexes **II** and **IV** respectively.

The thickness of the bilayer can be controlled by the choice of the imidazolium cation (alkyl chain length) and the coordination of lanthanide metal ions. Another design feature of the complexes is the packing of the phosphonium cations into layers or grid arrays around the aromatic rings of the calixarene within all the bilayers. Overall the four components come together with selective interplay of the sulfonated calix[4]arene with either a *mono*-phosphonium or *bis*-phosphonium cation in forming bilayers, even though the complexes can be of different composition. It is also noteworthy that the calixarene has some flexibility in its conformation, with subtle changes in forming pinched cones, for example, and it is also versatile in taking on a 4- or 5- charge for each ‘molecular capsule’, or indeed both of these within the same structure.

3.4 Experimental Section

A. General remarks on crystal growth

1-Ethyl-3-methylimidazolium trifluoromethanesulfonate and bromide, (**2** and **3**) and 1-butyl-3-methylimidazolium dicyanamide and chloride (**4** and **5**) salts were synthesized according to published methods by Bonhote *et al.* [182], and Cammarata *et al.* [183]. *Bis*-phosphonium and phosphonium chloride salts, **6** and **7** were purchased from Sigma Aldrich. A hot solution of three fold $GdCl_3 \cdot 6H_2O$ in water (19.0 mg, 0.5 ml) was added to a hot solution of equimolar of imidazolium salt (4.9–5.6 mg) and phosphonium salt (9.3–16.1 mg) with *p*-sulfonatocalix[4]arene, **1**, (25.2 mg) in a mixture of THF and water (1:1, 2 mL). The prepared solutions were left to cool and slow-evaporate, affording colourless crystals of complexes which were suitable for X-ray diffraction studies after several days.

B. Synthesis of *p*-sulfonatocalix[4]arene

To an ice cooled solution of calix[4]arene in anhydrous dichloromethane was added dropwise 20 equivalents of chlorosulfonic acid ($ClSO_3H$). Stirring was continued at 0°C for 2 hours after which the ice bath was removed and stirring was continued at room temperature overnight. The reaction mixture was poured onto ice water and dichloromethane was removed under reduced pressure and later the aqueous phase was boiled for 2 to 3 hours. The water was then evaporated under reduced pressure and the residue was recrystallised from methanol/acetone to afford the sulfonic acid of calix[4]arene as hydroscopic solids. The sodium salt sulfonates of calix[4]arenes were prepared by titration of sulfonic acid calix[4]arene with 1 M sodium hydroxide to neutral pH and recrystallized with ethanol/acetone. Sample was characterised by ^{1}H NMR (300MHz, D_2O) δ: 7.2 [s, 8H], 3.8 [s, 8H].

C. Synthesis of 1-ethyl-3-methylimidazolium bromide

Under vigorous stirring, 1-bromoethane (0.69 mol) was added dropwise to a solution of 1-methylimidazole (0.63 mol) in 1,1,1-trichloroethane in a round-bottom flask stirred and heated under reflux under a nitrogen atmosphere for 2 hours. The molten salt was decanted from the hot solution in a separatory funnel and washed twice with 100 mL of trichloroethane, and further dried in *vacuo* at 70°C, giving 1-ethyl-3-methylimidazolium bromide in approximately 85% yield. Sample was characterised by ^{1}H NMR (300MHz, D_2O) δ: 8.6 (s, 1H), 7.4 (d, 1H), 7.3 (d, 1H), 4.2 (t, 2H), 3.8 (s, 3H), 1.4 (t, 3H).

D. Synthesis of 1-butyl-3-methylimidazolium chloride

1-Chlorobutane (1.38 mol) was added to a vigorously stirred solution of 1-methylimidazole (1.25 mol) in toluene at 0^oC and was kept at -20^oC for 12 hours. The solutions were heated to reflux at 110^oC for 24 hours. The toluene was decanted from the remaining semi-solids and recrystallized from acetonitrile and further recrystallized from ethyl acetate to yield white crystalline solids to give 1-butyl-3-methylimidazolium chloride in approximately 90% yield and characterised by ^{1}H NMR (300MHz, D_2O) δ: 8.6 (s, 1H), 7.4 (d, 1H), 7.3 (d, 1H), 4.1 (t, 2H), 3.8 (s, 3H), 1.7 (m, 2H), 1.2 (m, 2H), 0.8 (t, 3H).

E. Synthesis of 1-ethyl-3-methylimidazolium trifluoromethansulfonate and 1-butyl-3-methylimidazolium dicyanamide

The respective metal salts, $NaCF_3SO_3$ and $Ag[N(CN)_2]$ (0.32 mol), were added to a solution of 1-ethyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium chloride (0.29 mol) respectively in dichloromethane and stirred for 24 hours. The suspension was filtered to remove the precipitated chloride salt and the organic phase was washed repeatedly with small volumes of water until no precipitation of AgCl occurred in the aqueous phase on addition of a concentrated $AgNO_3$ solution. The organic phase was then washed twice more with water to ensure complete removal of the chloride salt. The solvent was removed in *vacuo* and the resulting ionic liquid stirred with activated charcoal for 12 hours to give a colourless ionic liquid and was dried in vacuo. Yields obtained are in the range of 70 to 80%. The ionic liquids were characterised by ^{1}H NMR (300MHz, chloroform-*d*): 1-ethyl-3-methylimidazolium trifluoromethansulfonate δ: 9.1 (s, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 4.4 (t, 2H), 4.0 (s, 3H), 1.5 (t, 3H), 1-butyl-3-methylimidazolium dicyanamide δ: 9.0 (s, 1H), 7.8 (d, 1H), 7.7 (d, 1H), 4.4 (t, 2H), 4.0 (s, 3H), 1.9 (m, 2H), 1.3 (m, 2H), 0.8 (t, 3H).

F. Crystallography details

X-ray Crystallography

All data were measured from single crystals using Oxford Diffraction Xcalibur or Gemini CCD diffractometers at T = 100(2)K with monochromatic MoKα (λ = 0.71073 Å) or CuKα (λ = 1.54178 Å) radiation. Data corrected for Lorentz and polarization effects, absorption correction applied using multiple symmetry equivalent reflections. The structures were solved by direct method and refined on full matrix least-squares procedures using the SHELX-97 crystallographic package[184] and X-seed interface [185]. A full matrix least-squares refinement procedure was used, minimizing $w(F_o^2-F_c^2)$, with $w = [\sigma^2(F_o^2)+(AP)^2+BP]^{-1}$, where $P = (F_o^2+2F_c^2)/3$. Agreement factors ($R1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ and $GooF = \{\Sigma[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$ are cited where n is the number of reflections and p is the total number of parameters refined. Non-hydrogen non-disordered atoms were refined anisotropically. The positions of hydrogen atoms were partly localized from difference Fourier synthesis, partly calculated and their atomic parameters were constrained to the bonded atoms during the refinement with C_{Ph}–H =0.95 Å, C_{Me}–H =0.98 Å, and 0.99 Å in CH_2.

Crystal/refinement details for Complex I:

$C_{56}H_{62}Gd_2O_{44}S_8^{4-}$, $C_{44}H_{38}P_2^{2+}$, $2(C_6H_{11}N_2^+)$, $15(H_2O)$; $C_{112}H_{152}Gd_2N_4O_{59}P_2S_8$, M = 3131.30, colorless prism, 0.40 x 0.28 x 0.19 mm^3, triclinic, space group P-1 (No. 2), a = 12.7621(4), b = 15.4557(5), c = 19.2632(6) Å, α = 106.004(3), β = 93.474(3), γ = 112.632(3)°, V = 3311.07(18) Å^3, Z = 1, D_c = 1.570 g/cm^3, μ = 1.240 mm^{-1}, F_{000} = 1610, $2\theta_{max}$ = 76.4º, 128317 reflections collected, 33803 unique (R_{int} = 0.0492). Final $GooF$ = 1.001, $|\Delta\rho_{max}|$ = 6.9(2) e Å^{-3}, $R1$ = 0.0501, $wR2$ = 0.1436, R indices based on 25260 reflections with I >2σ(I), 847 parameters, 0 restraints. CCDC number: 728616.

Crystal/refinement details for Complex II:

$C_{28}H_{34}GdO_{23}S_4^-$, $C_{28}H_{33}GdO_{23}S_4^{2-}$, $C_8H_{15}N_2^+$, $2(C_{25}H_{22}P^+)$, $8.5(H_2O)$,$0.5(CH_4O)$; $C_{114.50}H_{145}Gd_2N_2O_{55}P_2S_8$, M = 3062.25, colorless prism, 0.35 x 0.30 x 0.13 mm^3, triclinic, space group P-1 (No. 2), a = 12.8192(1), b = 18.6718(3), c = 28.8700(4) Å, α = 100.278(1), β = 99.635(1), γ = 98.348(1)°, V = 6593.41(15) Å^3, Z = 2, D_c = 1.542 g/cm^3, μ = 1.241 mm^{-1}, F_{000} = 3144, $2\theta_{max}$ = 61.6º, 155673 reflections collected, 37896 unique (R_{int} = 0.0512). Final $GooF$ = 1.005, $|\Delta\rho_{max}|$ = 5.7(2) e Å^{-3}, $R1$ = 0.0869, $wR2$ =

0.2271, *R* indices based on 27377 reflections with I >2σ(I), 1591 parameters, 126 restraints. CCDC number: 728617.

Crystal/refinement details for Complex III:

2($C_{28}H_{20}O_{16}S_4^{4-}$), 4($C_{25}H_{22}P^+$), $Gd^{3+}(H_2O)_8$, $C_6H_{11}N_2^+$, 43(H_2O); $C_{162}H_{241}GdN_2O_{83}P_4S_8$, M = 4082.18, colorless needle, 0.45 x 0.38 x 0.14 mm^3, triclinic, space group *P*-1 (No. 2), a = 14.7508(8), b = 17.847(1), c = 22.1096(9) Å, α = 100.112(5), β = 102.224(4), γ = 97.190(5)°, V = 5519.9(5) Å^3, Z = 1, D_c = 1.228 g/cm^3, μ = 0.488 mm^{-1}, F_{000} = 2143, $2\theta_{max}$ = 57.7º, 92749 reflections collected, 25866 unique (R_{int} = 0.1070). Final *GooF* = 1.003, $|\Delta\rho_{max}|$ = 1.3(1) e Å^{-3}, *R1* = 0.1569, *wR2* = 0.3047, *R* indices based on 12311 reflections with I >2σ(I), 1130 parameters, 135 restraints. CCDC number: 728618.

Crystal/refinement details for Complex IV:

2($C_{28}H_{20}O_{16}S_4^{4-}$), 4($C_{25}H_{22}P^+$), $C_8H_{15}N_2^+$, $Gd^{3+}(H_2O)_8$, 36(H_2O); $C_{164}H_{231}GdN_2O_{76}P_4S_8$, M = 3984.12, colorless needle, 0.45 x 0.38 x 0.14 mm^3, triclinic, space group *P*-1 (No. 2), a = 14.7749(2), b = 17.8871(4), c = 21.7909(5) Å, α = 100.797(2), β = 100.493(2), γ = 97.627(2)°, V = 5478.7(2) Å^3, Z = 1, D_c = 1.208 g/cm^3, μ = 3.625 mm^{-1}, F_{000} = 2089, $2\theta_{max}$ = 103.7º, 59744 reflections collected, 11972 unique (R_{int} = 0.0553). Final *GooF* = 1.009, $|\Delta\rho_{max}|$ = 0.96(9) e Å^{-3}, *R1* = 0.1142, *wR2* = 0.2475, *R* indices based on 8049 reflections with I >2σ(I), 1140 parameters, 157 restraints. CCDC number: 728619.