CHAPTER 5

Host-guest Chemistry: Preferential interplay of imidazolium in directing multi-component layers

Addition of imidazolium cations to a mixture of large bis-phosphonium cations and sodium p-sulfonatocalix[4]arene in the presence of lanthanide ions results in selective binding of the imidazolium cations into the cavities of the calixarenes, affording multi-layered solid material with an inherently flexible interplay of the components, being able to accommodate different imidazolium cations. Incorporating ethyl, n-butyl or n-hexyl cations into the multi-layers results in significant perturbation of the structure, the most striking effect being the tilting of the plane of the bowl shaped calixarenes relative to the plane of a multi-layer, with tilt angles of 7.2, 28.9 and 65.5^{o} respectively. The lanthanide ions facilitate complexation but are not incorporated in the structures, and in all cases the calixarene takes on a 5- charge, with one of the lower rim phenolic groups deprotonated. ROESY NMR experiments and other ^{1}H NMR studies establish the formation of 1:1 supermolecules of imidazolium cation and calixarene regardless of the ratio of the two components, and that the supermolecules undergo rapid exchange on the NMR time scale.

5.1 Introduction

Thicker bilayers based on the assembly of *p*-sulfonatocalix[4]arene are accessible in the presence of large organic cations which are embedded within the bilayers. These were first developed for the tetraphenyl phosphonium cation, Ph_4P^+ [125] with the cations also incorporated between the bilayers in the place of the small organic molecules, with a phenyl ring of the cation bound within the cavity of a calixarene, and the distances between the bilayers is larger. The phosphonium cations are versatile in being *endo*- or *exo*- with respect to the bilayers, and for either they can engage in phenyl embraces with themselves [194].

This was subsequently extended to a larger *bis*-phosphonium cation, with can also be embedded in the extended structure, *endo*- or *exo*- and *endo*- with respect to the bilayers[177]. In association with certain lanthanide ions, the large organic cation forms remarkably porous materials scaffolding between calixarene bilayers, as well as assembled into a more compact complex. Porosity in organic solids is deemed an important strategy for guest exchange, a field which has been critically discussed in a review by Barbour [197].

The focus of this chapter is the self-assembly of ethyl, *n*-butyl or *n*-hexyl imidazolium cations with large *bis*-phosphonium cations and sodium *p*-sulfonatocalix[4]arene in the presence of lanthanide ions. There is selective binding of the imidazolium cations into the cavities of the calixarenes, affording multi-layered solid material with an inherently flexible interplay of the components, being able to accommodate different imidazolium cations. Remarkably in this study, (i) the imidazolium cations are selectively taken up into the cavities of *p*-sulfonatocalix[4]arene, as part of multi-layered structures made up of the calixarene and *bis*-phosphonium cations, (ii) there is a dramatic and systematic perturbation of the interplay of the components within the layers which is quantified by a tilting of the plane of the calixarene from the plane of the multi-layer, as the chain is extended from ethyl to *n*-butyl and *n*-hexyl, (iii) the presence of a lanthanide ion is necessary to form the complexes, but they are not incorporated into the structures, and (iv) the calixarene takes on an overall 5- charge in all structures, with one of the lower rim phenolic groups deprotonated. Also reported are detailed ^{1}H NMR experiments including the use of the ROESY sequence to show the presence of 1:1 supermolecules of imidazolium and calixarene ions, of the type found on the solid state, also persist in solution.

5.2 Structural features involving interlocking 1,4-*bis*(triphenylphosphoniomethyl)benzene

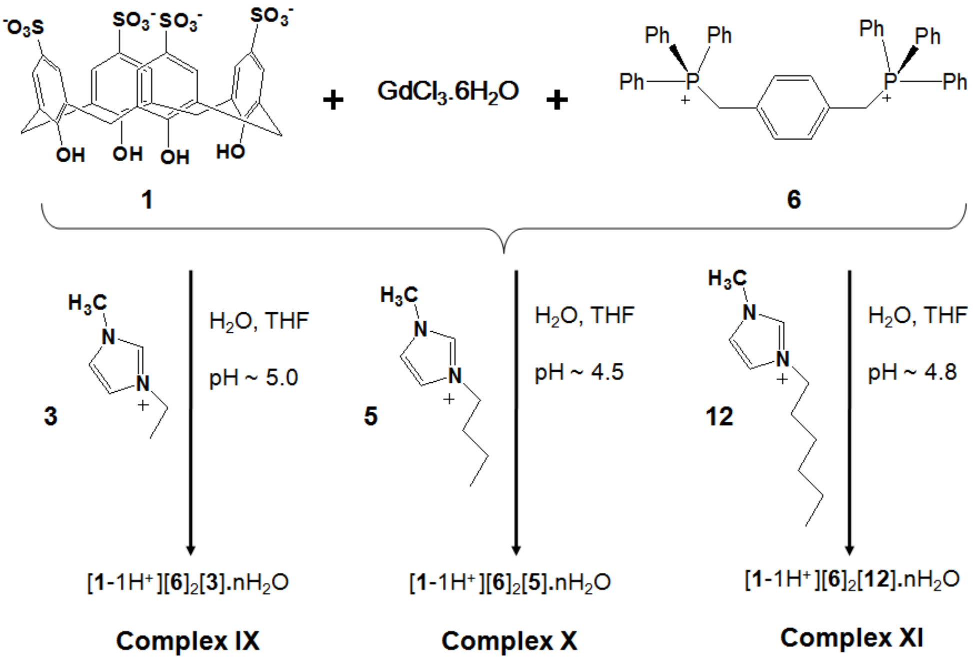

Figure 5.1. Synthesis of complexes **IX** – **XI**.

Multi-component complexes **IX**–**XI** were prepared by slow evaporation of an equimolar aqueous solutions of *p*-sulfonatocalix[4]arene (**1**), *bis*-phosphonium cations (**6**), and different imidazolium-based cations (**3**, **5, 12**), in the presence of excess gadolinium(III) chloride, Figure 5.1. Despite the need for gadolinium(III) metal ions in solution to effect crystal growth, they are not present in the isolated complexes. The solid state structures show multiple stacking of layers, with the calixarenes positioned in the up-down manner intertwined with a network of *bis*-phosphonium cations, and these layers of calixarenes and *bis*-phosphonium cations are separated by a layer of *bis*-phosphonium cations. The imidazolium moieties are selectively bound within the cavitands, rather than a phenyl group of the *bis*-phosphonium cations [177], and have contacts with *bis*-phosphonium cations. The formation of calixarene and imidazolium complexes in solution was examined using ^{1}H NMR spectroscopy where the chemical shift differences were observed.

5.2.1 Solid state structures of Complex IX

Colourless crystals of complex **IX** crystallises in the monoclinic space group *P*2, Z=4, with the asymmetric unit containing two calixarenes (with 5- charge), four *bis*-phosphonium cations, two ethyl-imidazolium cations, and disordered included water molecules. The *bis*-phosphonium cations are all in the *cis*-configuration with both triphenyl phosphine groups on the same side of the plane of the central aromatic ring. Multiple repeating layers are built up by calixarenes in the antiparallel up-down manner along with a network of *bis*-phosphonium cations, with a minor tilt of the plane of the calixarenes by 7.2^o with respect to the normal axis of the multi-layer. (The plane of the calixarene is defined by its four methylene carbon atoms). These composite layers of calixarene and *bis*-phosphonium cations are separated by a layer of hydrophobic *bis*-phosphonium cations, even though the surface of the composite layers is essentially hydrophilic. The structure relates to a complex based on the same phosphonium cations and calixarenes, and not the imidazolium cation [177, 196], where a phenyl group resides in the cavity of the calixarenes. In the present structure the imidazolium cations are exclusively positioned in the cavities.

The overall packing of the composite layers and the interposed layers of phosphonium cations are shown in Figure 5.2, which are denoted as layers of **B** and **A** respectively. The distance between the upper rims of calixarene in the composite bilayer for which they are arranged back-to-back is 14.8 Å, and the distance between the center of two repeating layers is 26.8 Å. The closest approach between the back of the calixarenes have O···O distances at 6.53 to 7.87 Å.

The calixarene cavity contains an ethyl-imidazolium cation and is in a slightly pinched cone configuration with angles for all the four phenolic rings with respect to the basal plane of the four methylene C-atoms of calixarene at 53.6(2)°, 43.5(2)°, 68.4(2)° and 38.3(2)°. The imidazolium cation has close C–H···π contacts with the phenolic ring of calixarene, involving the two adjacent C-H groups from the five member ring and the ethyl group, with C–H···ring centroid distances at 2.51 to 2.69 Å (corresponding C···π distances 3.36 to 3.50 Å), and 2.71 Å (corresponding C···π distance 3.67 Å) respectively. The unique H-atom of the five member ring, and H-atoms of the methyl and ethyl groups have close C–H···O contacts with sulfonate groups, with C···O distances at 3.26 Å, and 3.38 Å respectively, Figure 5.3.

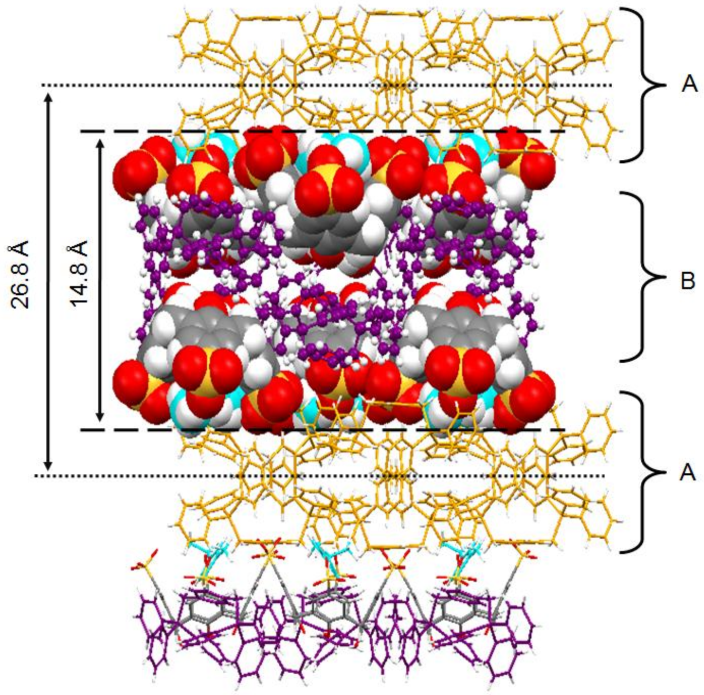

Figure 5.2. Extended multi-component layers of complex **IX** (with selected space filling of the calixarene) and confined imidazolium cations, separated by two layers of *bis*-phosphonium cations (orange and purple). Included water molecules are omitted for clarity.

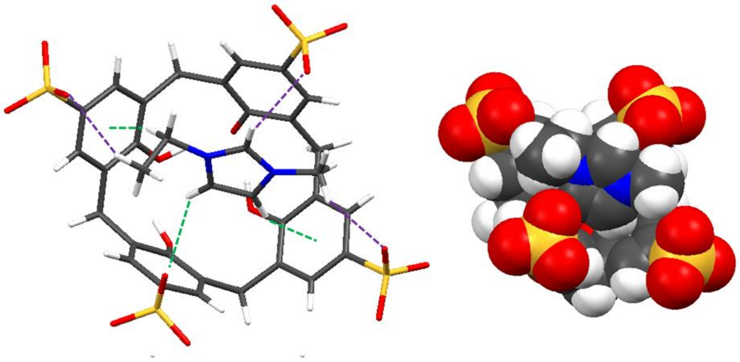

Figure 5.3. Projection of the calixarene and imidazolium cation supermolecule in complex **IX** showing the nearest contacts, and also space filling (H-bonds and C–H···π are shown as purple and green dashed lines respectively).

The *bis*-phosphonium molecules embedded within the extended structures have different interplay and can be divided into two separate layers; (i) in between the calixarene sulfonate head groups (layer **A**), and (ii) in between the back-to-back lower rim of calixarenes (layer **B**). The *bis*-phosphonium cations for layer **A** are packed differently relative to the structure devoid of the imidazolium cations [177]. In layer **A**, the *cis*-*bis*-phosphonium cations have close contacts to two calixarenes involving the H-atoms of two *bis*-phosphonium methylene bridges, and the sulfonates group with C–H···O distances at 2.29 to 2.48 Å (corresponding C···O distances range 3.23 to 3.27 Å), with their triphenylphosphine groups directed away from the sulfonate groups. The *bis*-phosphonium cation also have close proximity to the imidazolium moeties which reside in the calixarene, with C–H···H–C distances from the *bis*-phosphonium central phenyl ring to the imidazolium methyl group at 2.27 to 2.90 Å (corresponding C···C distances 3.55 Å). In the extended structure the *bis*-phosphonium cations in layer **A** have π···π centroids stacking with the ring centroid-to-centroid distance at 3.89 Å, Figure 5.4. The calixarene head groups from adjacent **B** layer are directed towards each other with the phosphonium cations orthogonally stacked between the calixarenes in the up and down arrangement.

In the other hydrophobic area, in which the *bis*-phosphonium molecules are embedded between the calixarene back-to-back layers (layers **B**), the interplay of the *bis*-phosphonium cations with the calixarenes includes C–H···π interactions, with the C–H to centroid distances at 2.65 to 3.23 Å (corresponding C···π distances 3.59 to 4.09 Å). These interactions involve the H-atoms of the calixarene methylene bridge and aromatic rings of the pendant arms of the *bis*-phosphonium cations which shroud the calixarenes in the same plane, Figure 5.5.

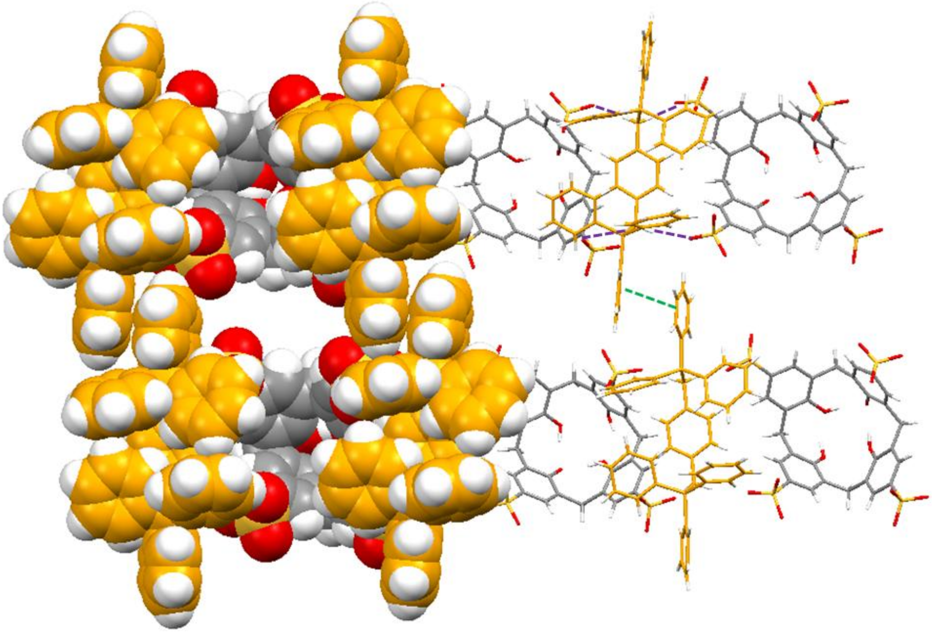

Figure 5.4. Cross section of layer **A** in complex **IX** showing the adjacent upper layer of calixarenes for layer **B**, with some space filling for *bis*-phosphonium cations and calixarenes (H-bonds and π···π contacts shown as purple and green dashed lines).

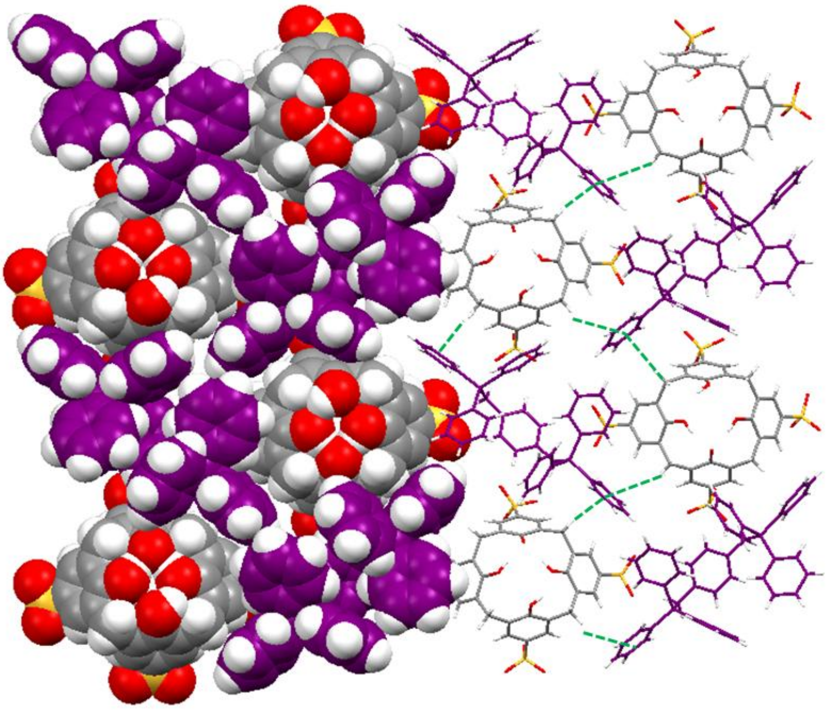

Figure 5.5. Projection of layer **B** in complex **IX** with the upper layer of calixarenes removed, and some space filling of the calixarenes and *bis*-phosphonium cations (C–H···π contacts shown as green dashed lines).

5.2.2 Solid state structures of Complex X

Combination of components **1**, **2** and **4** afforded colorless crystal which crystallise in monoclinic space group $P2_1/c$, Z=4. The asymmetric unit consists of one sulfonated calixarene with a 5- charge, one *n*-butyl-imidazolium cation (disordered between two positions) residing in the cavity, two *bis*-phosphonium cations in *cis*- configuration, and disordered included water molecules in close proximity to calixarene sulfonate groups. The multiple layers are different relative to those in complex **IX**, now with the sulfonate head groups tilted towards the lower O-rim of the calixarene molecules with O···O distance at 6.47 to 6.56 Å. The overall layered structure can be considered as an array of skewed molecular capsules, embedded within *bis*-phosphonium cations, with the plane of the calixarenes (and capsules) having a larger tilt angle of 28.9^{o} relative to the normal axis of the multi-layer arrangement, Figure 5.6. The distance between the upper rims of the calixarenes is 17.99 Å, while the distance between the lower rims of two calixarenes is 20.22 Å.

In complex **X**, a longer analogue of the imidazolium cation resides in the calixarene cavity in a V-shape with the termini protruded close to the upper rim of the cavitand. The calixarene is in a slightly pinch cone configuration in accommodating the *n*-butyl-imidazolium moiety, with two phenyl rings splayed and the other two pinched at 41.8(3)°, 50.2(3)°, 52.4(3)° and 68.4(3)°, with respect to the basal plane of the calixarene methylene bridges. The *n*-butyl-imidazolium cation which resides in the cavity of the calixarene has close C–H···π contact involving phenolic rings and protons from the butyl group with H···ring centroid distance at 2.67, 2.79 and 2.89 Å (corresponding C···π distances 3.49, 3.71 and 3.69 Å). Other close distances involve C–H···O contacts with the sulfonate group, from H-atoms of the five member ring, methyl group and butyl group with close C···O contacts at 3.30, 3.44 and 3.49 Å respectively, Figure 5.7.

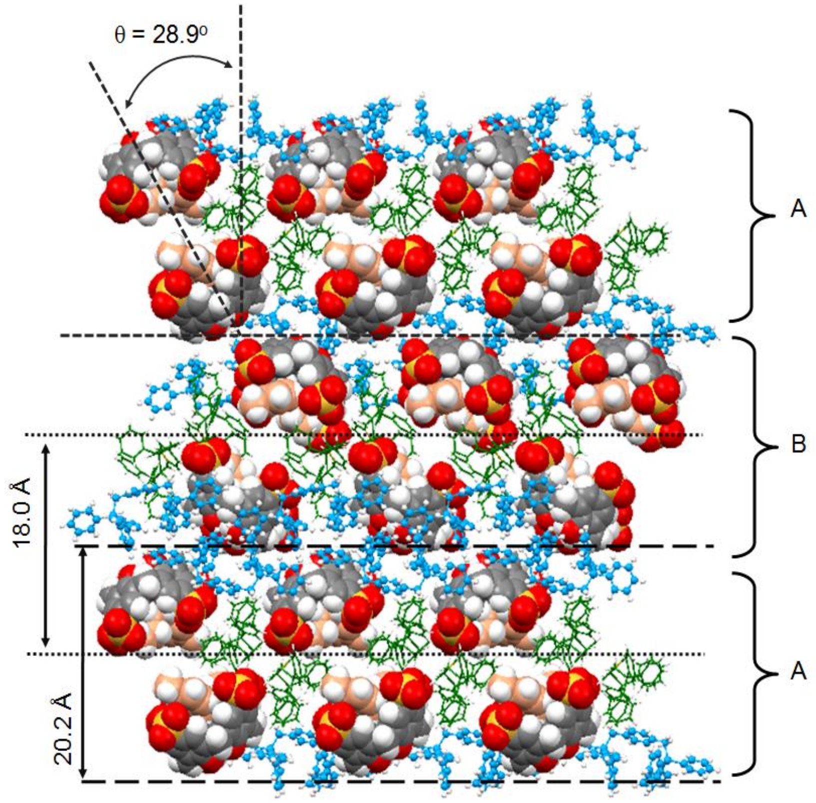

Figure 5.6. Extended multi-layers of complex **X** with some space filling of calixarene and confined imidazolium cations, embedded within *bis*-phosphonium cations (blue and green). Included water molecules are omitted for clarity.

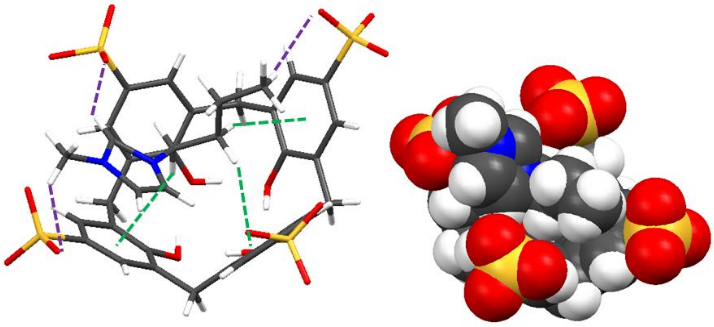

Figure 5.7. Stick representation in complex **X** showing close contacts between imidazolium and calixarene (H-bonds and C–H···π shown as purple and green dashed lines respectively) (left), with equivalent space-filling representation at a different orientation (right).

The *bis*-phosphonium cations have different connections compared to the components in complex **IX**. Two *bis*-phosphonium cations have close interactions with one calixarene and the *n*-butyl-imidazolium guest molecule, in opposite directions relative to each other. One *bis*-phosphonium cation has the central phenyl ring directed away from the sulfonate groups, with close contacts to the methyl-group, with C–H···π contact at 2.41 Å (corresponding C···π distance 3.22 Å), and with the triphenylphosphine moiety close to a sulfonate group, C···O distance 3.39 Å. Another *bis*-phosphonium cation has the central phenyl ring close to a calixarene sulfonate group with multiple short contacts: (i) C–H···H–C from the *bis*-phosphonium central phenyl ring to the imidazolium methyl group, at 2.28 and 2.40 Å (corresponding C···C distances at 3.00 and 3.10 Å), and (ii) H-atoms from two *bis*-phosphonium methylene bridge the sulfonates groups with C–H···O contacts at 2.49 and 2.57 Å (corresponding C···O distance at 3.34 to 3.54 Å). The equatorial part of the molecular capsules are also associated with centroid-to-centroid π···π stacking of the *bis*-phosphonium cations, from one capsule to another, Figure 5.8, at 3.66 Å.

Layer **A** and **B** are separated by *bis*-phosphonium cations with different packing motifs. The cations embedded organic in the bilayer have short for C–H···π contacts between phenyl rings, with a C···π distance at 3.66 Å. The pendant arm of the *bis*-phosphonium cation is directed towards the hydroxyl groups at the lower rim of a calixarene, with C–H···O contacts at 2.54 Å (C···O distance at 3.33 Å), Figure 5.9.

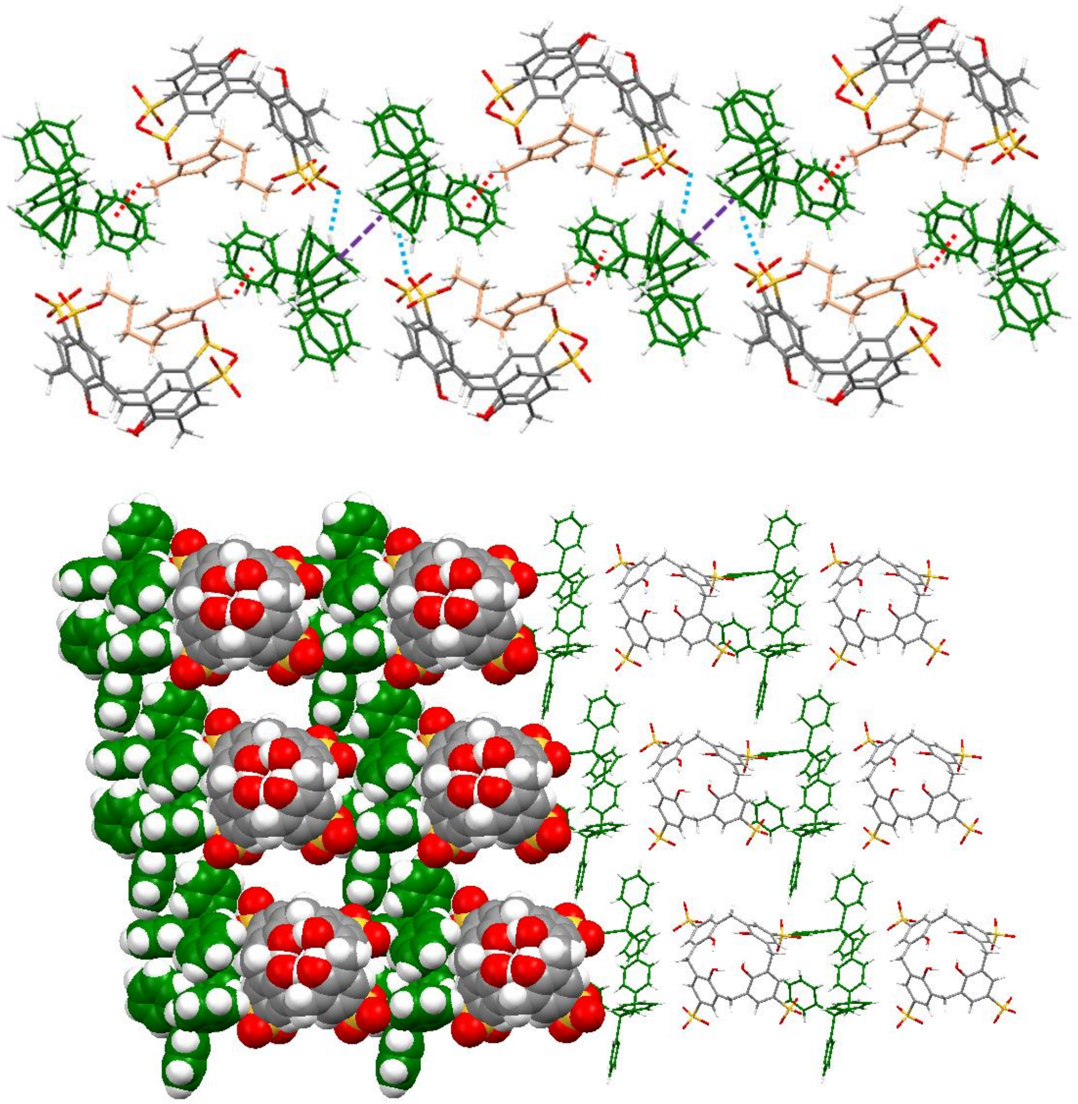

Figure 5.8. (Top) H-bonds, C–H···π and π···π close contacts between imidazolium, bis-phosphonium and calixarene in complex **X** (shown as blue, red and purple dashed lines respectively) and some space filling of *bis*-phosphonium and calixarene molecules (bottom).

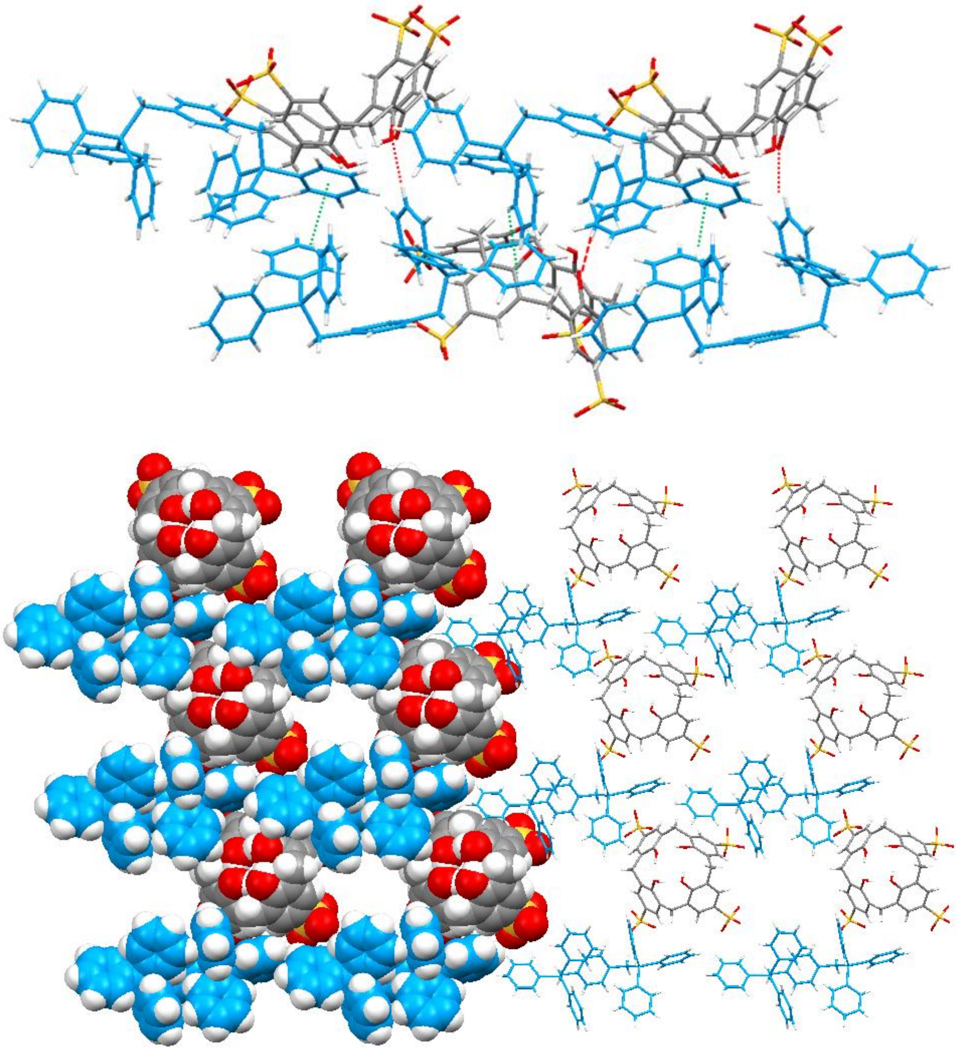

Figure 5.9. Close contacts involving H-bonds and C–H···π between *bis*-phosphonium and calixarene in complex **X** (shown as red and green dashed lines respectively) (Top) and some space filling of *bis*-phosphonium and calixarene molecules (bottom).

5.2.3 Solid state structures of Complex XI

Colourless crystals of complex **XI** crystallise in the monoclinic space group *P*2/*c*, Z=4, with one sulfonated calixarene with a 5- charge, one *n*-hexyl-imidazolium cation residing in the calixarene cavity, two *bis*-phosphonium cations in the *cis*-configuration, and disordered crystalline water molecules in the asymmetric unit. The overall structure is based on multiple layers, Figure 5.10, having alternately positioned calixarenes in a back-to-back arrangement (closest O···O contacts 7.06 to 7.81 Å), with *bis*-

phosphonium cations embedded in between (layer **A**), and adjacent calixarenes in contact with the *bis*-phosphonium cations (layer **B**). The sulfonate head groups of the calixarenes are arranged linearly and the tilt angle of the calixarene molecules with respect to the normal axis of the interlayer is even higher relative to that in **IX** and **X**, at 65.5°.

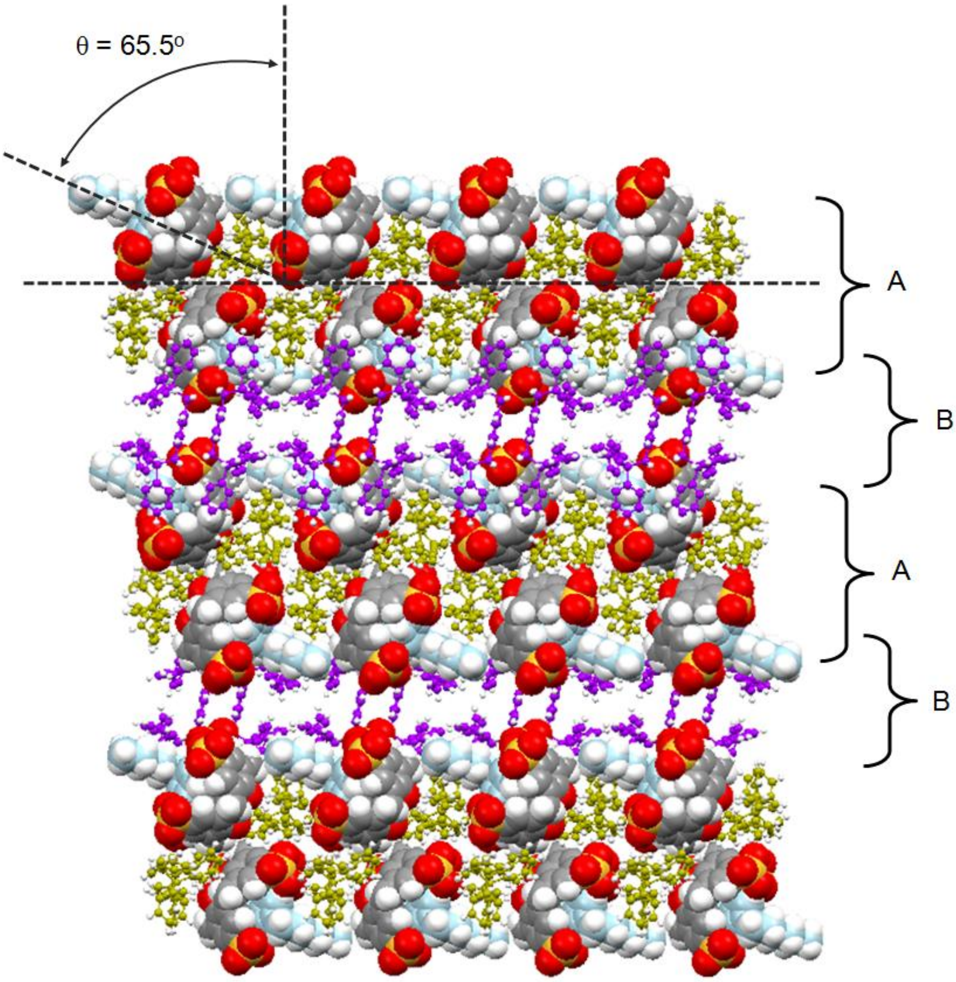

Figure 5.10. Multi-layers of complex **XI** showing some space filling of calixarene and confined imidazolium, separated by layers of *bis*-phosphonium molecules (purple and green).

The *n*-hexyl-imidazolium cation resides in the calixarene cavity with the long alkyl chain protruding and directed towards the lower rim of another adjacent calixarene, with the end of the alkyl chain having close contacts to the calixarene methylene bridge with

C···C at 3.66 Å, Figure 5.11. The calixarenes in **XI** are splayed in one direction and pinched in the other to accommodate the guest molecule with the angles between the plane of the aromatic rings and the basal plane of the four methylene C-atoms at 41.0(1)°, 50.2(1)°, 56.1(1)°, and 66.9(1)°. The *n*-hexyl-imidazolium cation which has the imidazolium ring in the cavity of the calixarene is in close proximity to the phenolic ring of calixarene, with C–H···π ring centroid contacts distances for the methyl group at 2.59 Å (corresponding C···π distance 3.23 Å). Other short contacts involve the C–H···O for a sulfonate group and two H-atoms of the five member ring, with C···O distances at 3.12 Å and 3.27 Å respectively, Figure 5.11.

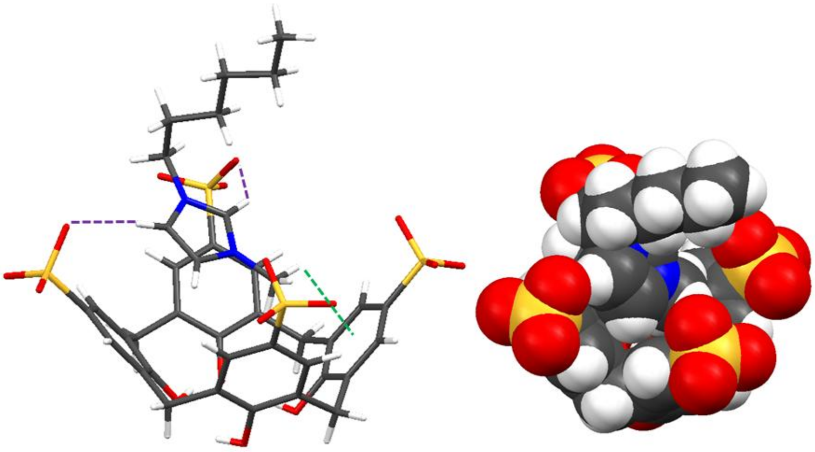

Figure 5.11. Stick representation showing close contacts between imidazolium and calixarene in complex **XI** (H-bonds and C–H···π shown as purple and green dashed lines respectively) (left), with equivalent space-filling (right).

The interplay of the *cis*-*bis*-phosphonium cations with the calixarenes can be distinguished between the two different layers. In layer **A**, the calixarene is shrouded by *bis*-phosphonium cations and two calixarenes, having C–H···O close contacts with the *bis*-phosphonium methylene bridges to the sulfonate groups at distances of 2.36 and 2.40 Å (corresponding C···O distance 3.32 and 3.36 Å). The triphenylphosphine groups are directed away from the cavity, with a phenyl ring π stacked, ring centroid-to-centroid distance being 3.32 Å. The *bis*-phosphonium cations are close to the calixarenes anions through C–H···π contacts at 2.80 Å, for the H-atom of calixarene methylene bridge to the *bis*-phosphonium phenyl ring (corresponding C···π distance 3.55 Å), with the calixarenes packed in up-down manner side by side, Figure 5.12. In layer **B**, the *bis*-phosphonium cations are directed away from the cavity, having C–H···O contacts involving the methylene bridge of the *bis*-phosphonium and a sulfonate groups, at 2.15 to 2.88 Å (corresponding C···O distance 3.14 to 3.82 Å), and are π stacked with centroid-to-centroid distance at 3.58 Å, Figure 5.13.

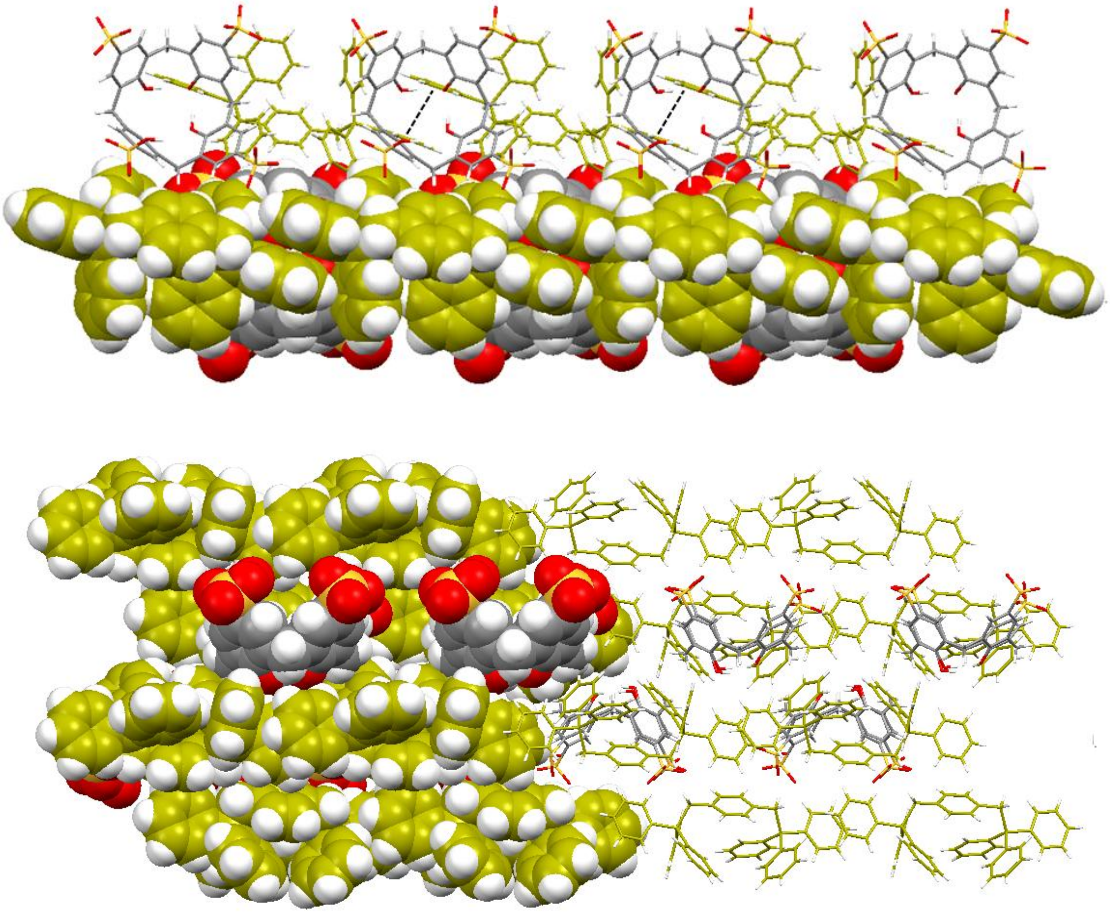

Figure 5.12. Some space filling of complex **XI** in layer **A** showing *bis*-phosphonium molecules and calixarene, viewed along *a*-axis (top) and *b*-axis (bottom).

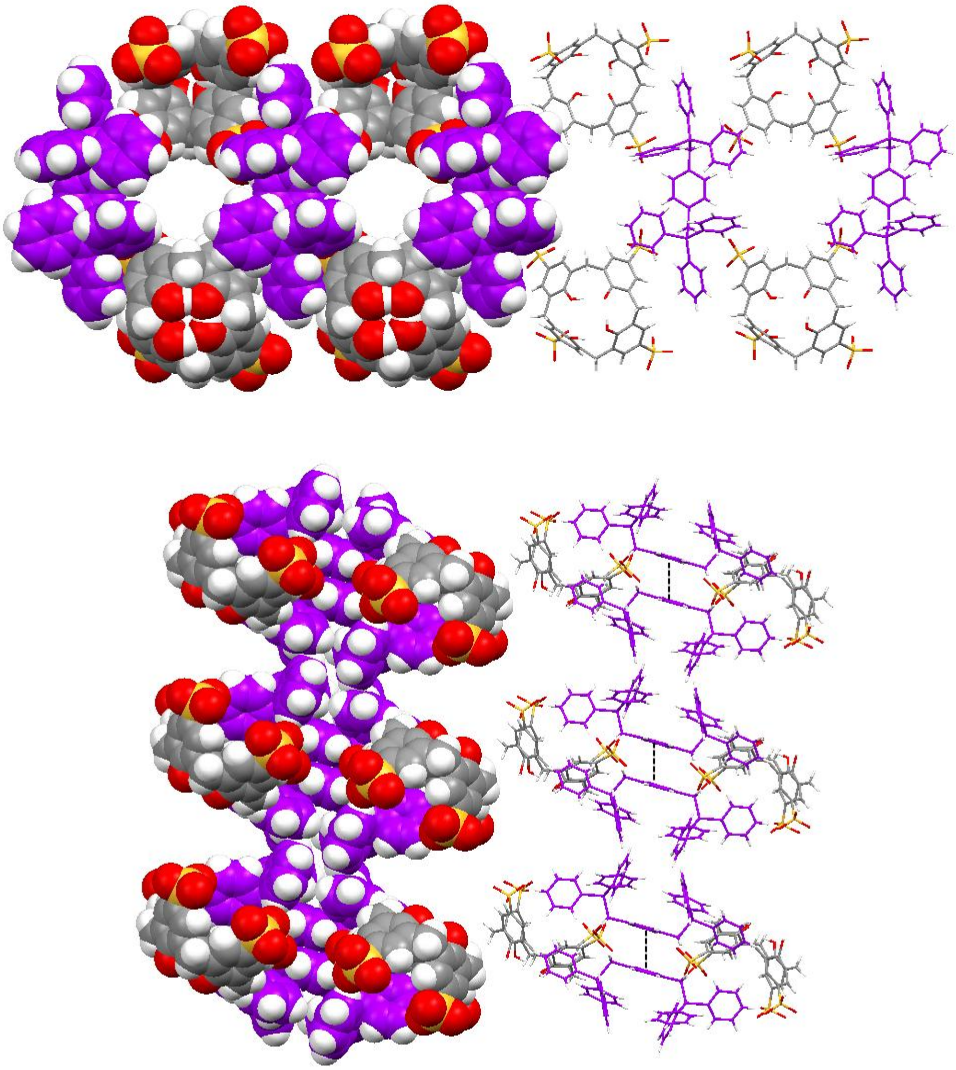

Figure 5.13. Cross section in layer **B**, complex **XI**, showing some space filling arrangement of calixarene and phosphonium molecules (purple), viewed along *a*-axis (top) and *b*-axis (bottom).

5.3 Solution studies

The interaction of the ethyl, *n*-butyl and *n*-hexyl imidazolium cations and *p*-sulfonatocalix[4]arene in aqueous solution at 1:1 molar ratio was studied using ^{1}H NMR spectroscopy, Figure 5.14, Figure 5.15 and Figure 5.16, with the induced shift, $\Delta\delta$, defined as the difference in chemical shifts in the presence and absence of the imidazolium cations ($\Delta\delta_{free} - \Delta\delta_{complex}$) with positive and negative values representing upfield and downfield shifts respectively).

All protons of the imidazolium cation experience upfield shifts, which are more pronounced for the N-methyl (H-4), the ring protons, (H-2 and H-3) and the unique proton (H-1). This is consistent with shielding effect of the calixarene aromatic rings for the imidazolium five-membered ring residing in the cavity. A characteristic upfield shift for the aliphatic protons of the ethyl and *n*-butyl imidazolium cation was also evident, especially for the methylene protons closest to the N-atom, and this agrees with the shielding from the calixarene, while only small changes are evident for the other *n*-hexyl protons. The results support the preferential binding of the imidazolium head group in the cavity of the calixarene in solution, which is consistent with the findings in the solid state as found in the structures of **IX** – **XI**, albeit for more complex mixtures. It is noteworthy H-1 on the aromatic ring can undergo chemical exchange as an acid proton, which results in peak intensity diminishing over time.

1:1 Supermolecules of the calixarene and imidazolium cations are present on the NMR time scale, and this does not change if additional calixarene is present noting that for a 2:1 ratio, the formation of ‘molecular capsule’ is possible. However, this is not the case, on the grounds that the terminal protons on the hexyl group show no additional shift and the AB spin system for the calixarene methylene protons is well defined.

NMR titration experiments were undertaken at 25^{o}C in D_2O (calibrated to solvent protons at 4.63 ppm) with the *p*-sulfonatocalix[4]arene concentration kept constant at 42 mM. The proton chemical shifts for H-1 to H-5 (methylene protons closest to the N-atom) and the terminal methyl group on the aliphatic chain (H-6, H-8 or H-10) were monitored and plotted, Figure 5.14, Figure 5.15 and Figure 5.16. On gradual addition of the imidazolium cations to the solution containing calixarene, significant large chemical shifts for the ring protons H-1 and H-2 were observed, which is concentration dependent with the upfield shifts overall diminishing as the concentration of the imidazolium cations increases. Thus there is rapid exchange between the host-guest molecules on the NMR time scale. Diminishing upfield shift for the terminal methyl group was apparent, depending on the distance of the carbon centres from the calixarene cavity, with the terminal methyl proton of *n*-hexyl-imidazolium having the least chemical shift in contrast to ethyl-imidazolium and *n*-butyl-imidazolium.

Table 5.1 shows a summary of the NOEs between the imidazolium cations and calixarene for which were determined using 1D-ROESY experiments involving sequential selective excitation of individual resonances in the ^{1}H NMR spectrum. Overall, 1D-ROESY experiments were significantly more efficient than the 2D-ROESY experiments. The NOEs between aromatic protons of calixarene (Ar-H) and all protons of the imidazolium were studied to further understand the host-guest interactions in solution. Selective excitation of Ar-H gave strong NOEs for the imidazolium protons (H-1 to H-5) for all complexes. Strong NOE between Ar-H and the calixarene methylene CH_2 groups are expected for the rapid exchange of the *exo*- and *endo*-protons on the NMR time scale where this type of exchange is well-established for calixarenes[200]. Weak NOEs between Ar-H and protons at terminal methyl group of the imidazolium were observed, and this is consistent when the selective irradiation is positioned at the terminal protons of the aliphatic chain. Irradiating the resonance line of all other protons of the imidazolium cation (H-1 to H-10) leads to the expected complimentarity NOEs at the Ar-H of calixarene, Table 5.1. Thus the ROESY experiments are also consistent with the presence of 1:1 supermolecule present in solution.

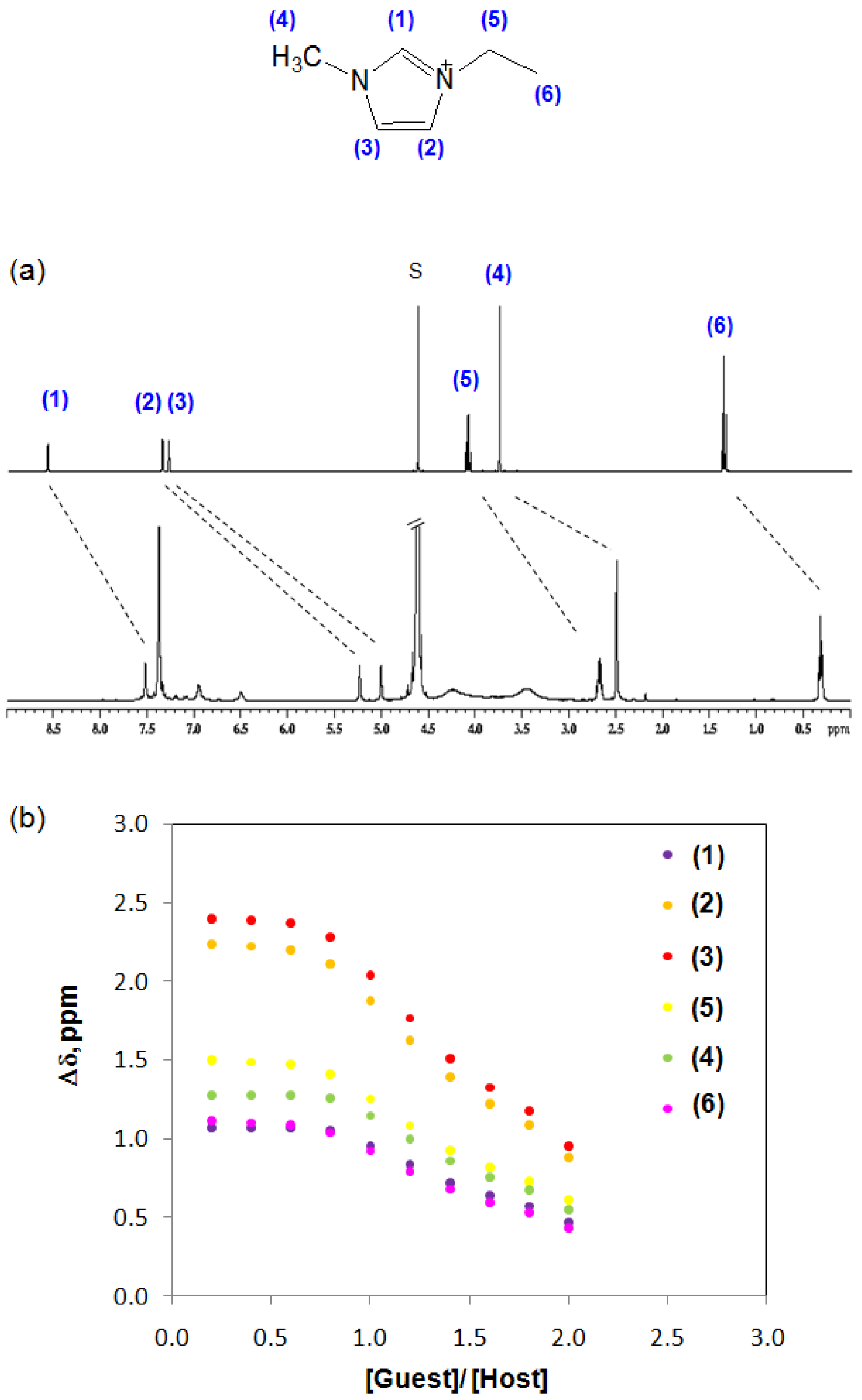

Figure 5.14. ^{1}H NMR spectra for a 1:1 mixture of (a) (i) ethyl-imidazolium, (ii) ethyl-imidazolium in *p*-sulfonatocalix[4]arene measured in D_2O (**S**) and ^{1}H NMR titration experiments for ethyl-imidazolium (b) with *p*-sulfonatocalix[4]arene as the host molecule.

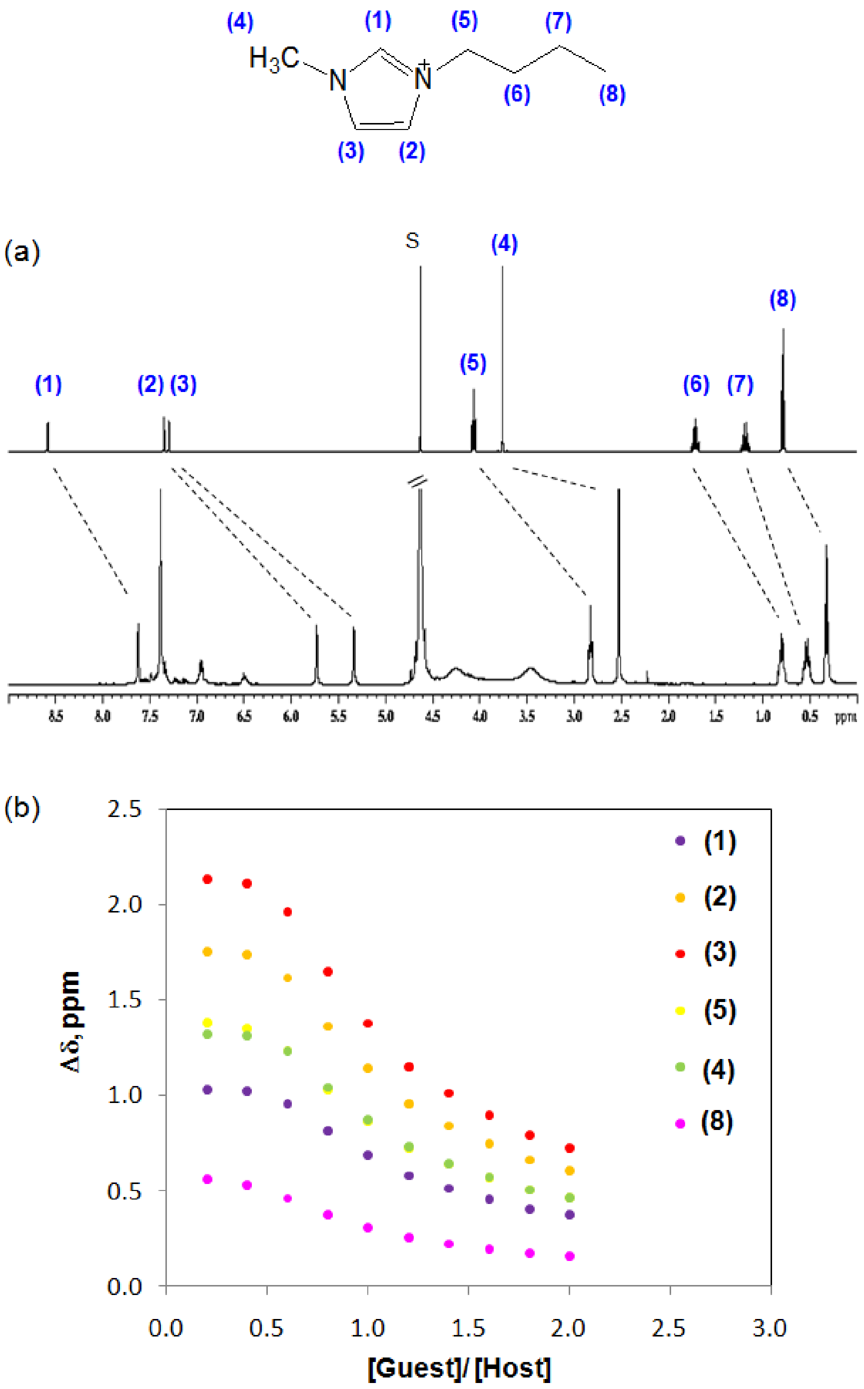

Figure 5.15. ^{1}H NMR spectra for a 1:1 mixture of (a) (i) *n*-butyl-imidazolium, (ii) *n*-butyl-imidazolium in *p*-sulfonatocalix[4]arene measured in D$_2$O (**S**) and ^{1}H NMR titration experiments for *n*-butyl-imidazolium (b) with *p*-sulfonatocalix[4]arene as the host molecule.

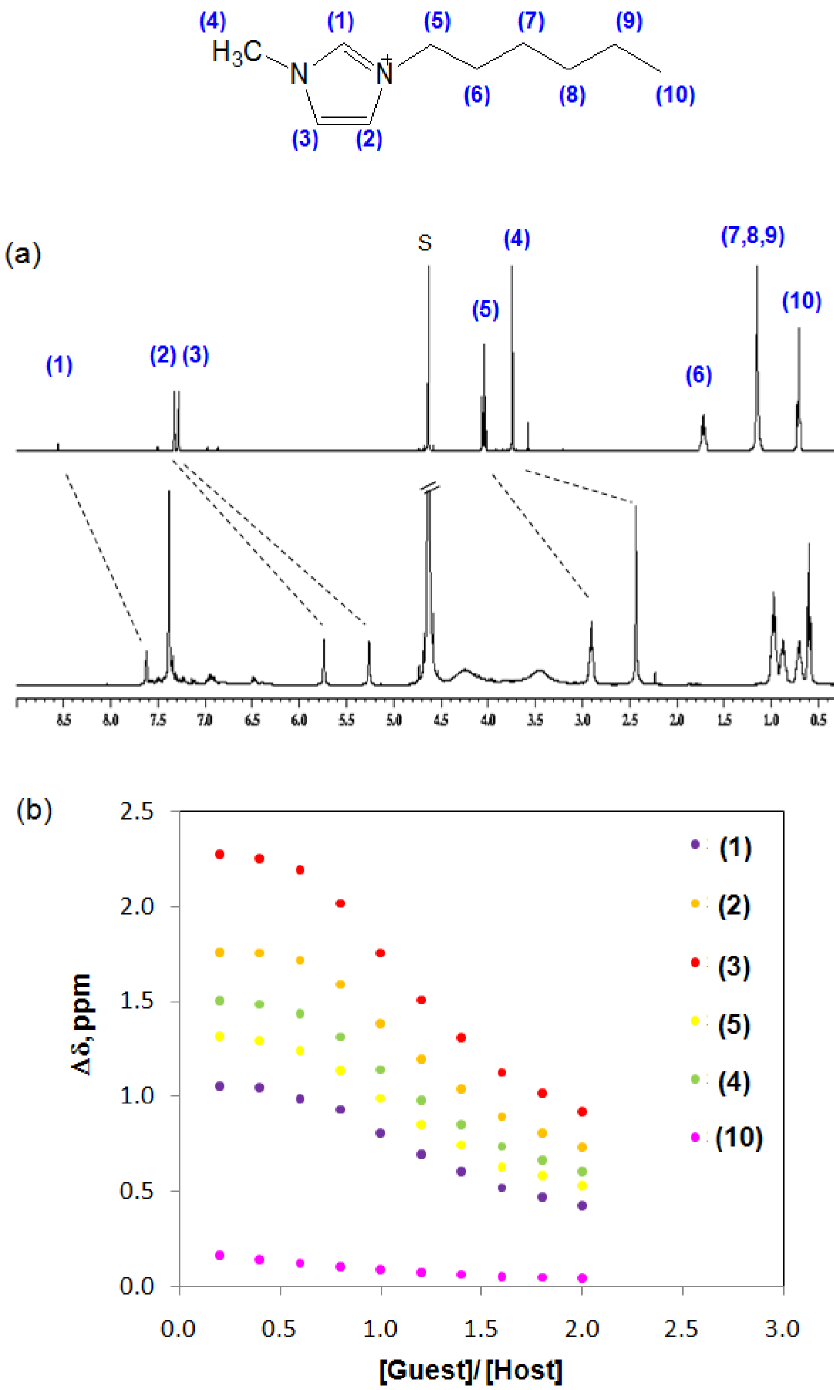

Figure 5.16. ^{1}H NMR spectra for a 1:1 mixture of (a) (i) *n*-hexyl-imidazolium, (ii) *n*-hexyl-imidazolium in *p*-sulfonatocalix[4]arene measured in D_2O (**S**) and ^{1}H NMR titration experiments for *n*-hexyl-imidazolium (b) with *p*-sulfonatocalix[4]arene as the host molecule.

Table 5.1: NOEs (ROESY) between guest molecules **3-5** and *p*-sulfonatocalix[4]arene in D_2O solution [strong (++), medium (+) or absence (-)].

	Selective resonance irradiation at:								
	Calixarene proton	Imidazolium protons							
	Ar-H	H-1	H-2	H-3	H-4	H-5	H-6	H-8	H-10
Complex **I**									
Ar-H		−	++	++	++	++	+		
H-1	−		−	−	++	++	−		
H-2	++	−		−	+	++	−		
H-3	++	−	−		++	+	−		
H-4	++	++	-	+		−	−		
H-5	++	++	+	−	−		++		
H-6	++	−	−	−	−	++			
Complex **II**									
Ar-H		+	++	++	++	++		+	
H-1	++		−	−	++	++		−	
H-2	++	−		−	−	++		−	
H-3	++	−	−		++	−		−	
H-4	++	++	−	++		−		−	
H-5	++	++	++	−	−			++	
H-6	−	−	−	−	−	++		−	
H-7	−	−	−	−	−	+		−	
H-8	−	−	−	−	−	+			
Complex **III**									
Ar-H		−	++	++	++	++			+
H-1	−		−	−	++	++			−
H-2	++	−		−	+	++			−
H-3	++	−	−		++	−			−
H-4	++	++	-	++		−			−
H-5	++	++	++	−	−				++
H-6	−	−	−	−	−	++			−
H-7	−	−	−	−	−	+			−
H-8	−	−	−	−	−	+			−
H-9	−	−	−	−	−	+			−
H-10	−	−	−	−	−	+			

5.4 Conclusions

Multi component combinatorial studies using different analogues of imidazolium cations yielded three complexes with a common structural feature that the cations reside in the calixarene cavity regardless of the length of the alkyl chain. One remarkable effect is the tilting of the plane of the bowl shaped calixarene relative to the plane of a multi-layer, with the ethyl, *n*-butyl and *n*-hexyl containing cations induced tilt angles at 7.2, 28.9 and 65.5^{o} respectively. The presence of lanthanide ions is essential in forming the complexes, but yet they are not included in the final products, and this is likely to be an important consideration in building up other complex systems based on the assembly of the calixarene, and indeed the larger ring size analogues. Also noteworthy in the present study is that under the experimental conditions, the calixarene exists in the 5-

species, rather than the 4- species based exclusively on the deprotonation of all the sulfonic acid groups. This also is an important consideration in further studies. Finally, the preferential binding of the imidazolium head group in the calixarene cavity over a phenyl ring of a positively charged phosphonium cation persists both in solution and the solid state. It is tempting to conclude that the primary process in forming the complexes is the initial formation of a 1:1 supermolecule based on the calixarene and imidazolium cation. This is based on the NMR studies, including ROESY experiments, which unambiguously show that the 1:1 supermolecules are present in solution. The preferential binding of imidazolium cation over phosphonium cation presumably relates to the positive charge on the five-membered ring, as well as the complementarity of the size of the two interacting components.

5.5 Experimental Section

A. General remarks on crystal growth

p-Sulfonatocalix[4]arene sodium salt, **1**, 1-ethyl-3-methylimidazolium, **3** and 1-butyl-3-methylimidazolium, **5** were synthesised as described in Section 3.4. 1-hexyl-3-methylimidazolium, **12** halide salt was synthesized according to literature procedures [141]. 1,4-*Bis*(triphenylphosphoniomethyl)benzene chloride salt, **6** was purchased from Sigma Aldrich and used as received. A hot solution of three fold $GdCl_3 \cdot 6H_2O$ in water (0.5 mL) was added to a hot solution of equimolar of imidazolium salt and *bis*-phosphonium salt with *p*-sulfonatocalix[4]arene in a mixture of THF and water (1:1, 2 mL, pH 1.2-4.0). The prepared solutions were left to cool and slowly evaporated over several days, affording colourless crystals of complexes which were suitable for X-ray diffraction studies.

B. NMR studies

^{1}H NMR spectra were collected on a Varian 400 MHz spectrometer using D_2O at 25^{o}C. Titrations were carried out by adding aliquots of a solution of the imidazolium ion (72 mM) to a solution of a *p*-sulfonatocalix[4]arene (42 mM, 800 μL) in a NMR tube fitted with a rubber septum. ROESY experiments were carried out on Bruker AV-600 using Gaussian pulses for selective excitation and a mixing time of 225 ms.

C. Synthesis of 1-hexyl-3-methylimidazolium chloride

Excess of 1-chlorohexane were added to 1-methylimidazole in a round-bottomed flask fitted with a reflux condenser and the mixture was heated for 24 to 72 h at 70°C with vigorous stirring. The top phase containing unreacted starting material was decanted and the bottom phase was washed twice with ethyl acetate to remove any unreacted material. The product was dried under vacuum at 80^{o}C and characterised by ^{1}H NMR (300MHz, D_2O) δ: 8.6 [s, 1H], 7.3 [s, 1H], 7.2 [s, 1H], 4.0 [t, 2H], 3.7 [s, 3H], 1.7 [m, 2H], 1.1 [m, 6H], 0.7 [t, 3H].

D. Crystallography details

X-ray Crystallography

All data were measured as described in Section 3.4.

Crystal/refinement details for Complex IX:

$C_{28}H_{19}O_{16}S_4^{5-}$, $2(C_{44}H_{38}P_2^{2+})$, $C_6H_{11}N_2^{+}$, $12(H_2O)$, $C_{122}H_{130}N_2O_{28}P_4S_4$, $M = 2324.40$, colorless prism, 0.29 x 0.21 x 0.12 mm^3, monoclinic, space group *P*2 (No. 3), $a = 23.1719(2)$, $b = 19.4641(2)$, $c = 26.8325(2)$ Å, $\beta = 107.764(1)°$, $V = 11524.99(18)$ Å^3, $Z = 4$, $D_c = 1.340$ g/cm^3, $\mu = 1.920$ mm^{-1}, $F_{000} = 4896$, $2\theta_{max} = 134.3°$, 97639 reflections collected, 35174 unique (R_{int} = 0.0419). Final *GooF* = 0.999, $|\Delta\rho_{max}|$ = 2.9(1) e Å^{-3}, *R1* = 0.0941, *wR2* = 0.2347, *R* indices based on 30710 reflections with I >2σ(I), 2866 parameters, 7 restraints. CCDC number: 734880.

Crystal/refinement details for Complex X:

$C_{28}H_{19}O_{16}S_4^{5-}$, 2($C_{44}H_{38}P_2^{2+}$), $C_8H_{15}N_2^+$, 9.5(H_2O), $C_{124}H_{129}N_2O_{25.5}P_4S_4$, *M* = 2307.41, colorless needle, 0.48 x 0.02 x 0.01 mm^3, monoclinic, space group $P2_1/c$ (No. 14), *a* = 14.8450(5), *b* = 44.227(1), *c* = 17.8220(9) Å, β= 100.088(4)°, *V* = 11520.1(7) Å^3, *Z* = 4, D_c = 1.330 g/cm^3, μ = 1.900 mm^{-1}, F_{000} = 4860, $2\theta_{max}$ = 136.1°, 62509 reflections collected, 19846 unique (R_{int} = 0.3252). Final *GooF* = 0.997, $|\Delta\rho_{max}|$ = 0.68(8) e Å^{-3}, *R1* = 0.0954, *wR2* = 0.0907, *R* indices based on 5272 reflections with I >2σ(I), 1413 parameters, 66 restraints. CCDC number: 734881.

Crystal/refinement details for Complex XI:

$C_{28}H_{19}O_{16}S_4^{5-}$, 2($C_{44}H_{38}P_2^{2+}$), $C_{10}H_{19}N_2^+$, 14(H_2O), $C_{126}H_{142}N_2O_{30}P_4S_4$, *M* = 2416.54, colorless prism, 0.34 x 0.26 x 0.16 mm^3, monoclinic, space group $P2/c$ (No. 13), *a* = 14.8519(2), *b* = 15.1600(2), *c* = 53.4813(15) Å, β = 94.181(2)°, *V* = 12009.5(4) Å^3, *Z* = 4, D_c = 1.337 g/cm^3, μ = 1.875 mm^{-1}, F_{000} = 5104, $2\theta_{max}$ = 136.0°, 89025 reflections collected, 21604 unique (R_{int} = 0.0545). Final *GooF* = 1.073, $|\Delta\rho_{max}|$ = 1.5(1) e Å^{-3}, *R1* = 0.0801, *wR2* = 0.2161, *R* indices based on 19346 reflections with I >2σ(I), 1508 parameters, 0 restraints. CCDC number: 734882.