CHAPTER 8

Host-guest Chemistry: p-sulfonatocalix[4]arene –pyrrolidinium complexation in building multi-component layered arrays

p-Sulfonatocalix[4]arene and mono-phosphonium ions, in the presence of N-butyl-N-methylpyrrolidinium ions and aquated lanthanide ions, assemble into bilayers comprised of calixarenes with the phosphonium cations embedded between them; pyrrolidinium ions reside in the calixarene cavities which are normal to the bilayer plane. Replacing the phosphonium cations with bis-phosphonium ions results in the same interplay of the calixarene and pyrrolidinium cations, but with the formation of a different layered structure, which is now devoid of the lanthanide ions, unlike the other bilayers, with all the sulfonate groups of the calixarenes residing in a plane where adjacent calixarenes are in alternating directions. A 1:1 supermolecule of the calixarene and pyrrolidinium ion is evident in aqueous solution using ^{1}H NMR spectroscopy.

8.1 Introduction

Low melting pyrrolidinium compounds have been prepared by association of organic cations with very weakly basic anions such as $N(CF_3SO_2)_2^-$, BF_4^-, $CF_3SO_3^-$, PF_6^-, and CH_3COO^- and as such anions cannot participate in strong ionic interactions with the cations [205, 206]. This is reflected for example, in the $N(CF_3SO_2)_2^-$ anion depressing melting points by approximately 100 °C compared with analogous halide compounds of the same organic cation [205-208].

Molten organic salts based on pyrrolidinium cations have been of interest for their use in a variety of electrochemical applications including electrochemical capacitors, high energy density batteries, solar cells and electrochromic windows. This relates to their high conductivity and wide electrochemical window and high thermal stability [205, 207, 209-211]. Alkylpyrrolidinium based ionic liquids have higher intrinsic ionic conductivity and wider nature electrochemical windows compared to imidazolium based ionic liquida for the same counterion, and therefore alkylpyrrolidinium based ionic liquids feature extensively as electrochromic windows and in dye-sensitized solar cells [212-213]. Amide salts in the pyrrolidinium family can exhibit ion conduction in the solid state due to the presence of plastic crystal phases [164]. By doping the salt with lithium salts of the same anion the conductivity increases up to 2 orders of magnitude and this generated the start of fast-ion conducting materials [214, 215].

Pyrrolidinium based ionic liquids have high solubility of lanthanide salts and forming interesting discrete complexes with various lanthanide(III) metal ions, including trivalent ions of ytterbium, lanthanum, erbium, praseodymium, neodymium and terbium[216].

8.2 Structural features involving N-butyl-N-methylpyrrolidinium

Herein the self assembly of N-butyl-N-methylpyrrolidinium, **17**, in investigated which like imidazolium cations, it is a common component of ionic liquids is investigated. The self-assembly is with *p*-sulfonatocalix[4]arene, **1**, various phosphonium cations, and lanthanide(III) metal ions, Figure 8.1. In all derived complexes, the pyrrolidinium cation has the five-membered heterocyclic residing in the calixarene cavity rather than a phenyl ring of a phosphonium cation.

Colourless crystals of complexes of **XIX**, **XX** and **XXI** (Figure 8.1) were obtained by slow evaporation of a water/tetrahydrofuran (THF) solution containing an equimolar mixture of **1** and **17** with different phosphonium cations, in the presence of a three-fold excess of aqueous gadolinium(III) chloride. All complexes crystallise in the triclinic space group *P*-1, with each comprised of calixarene anions, pyrrolidinium cations and phosphonium cations, as well as lanthanide(III) ions (complex **XXI** excepted) in the ratio 1:1:1:3(0), and included water molecules. In all cases, the pyrrolidinium cations reside in the calixarene cavities with the N-butyl chain directed away from the cavity of the calixarene. The N-butyl chain is bent in complex **XX** which presumably relates to the difference in the mode of coordination of the gadolinium(III) cations, which is manifested in different thicknesses between the calixarene bilayers.

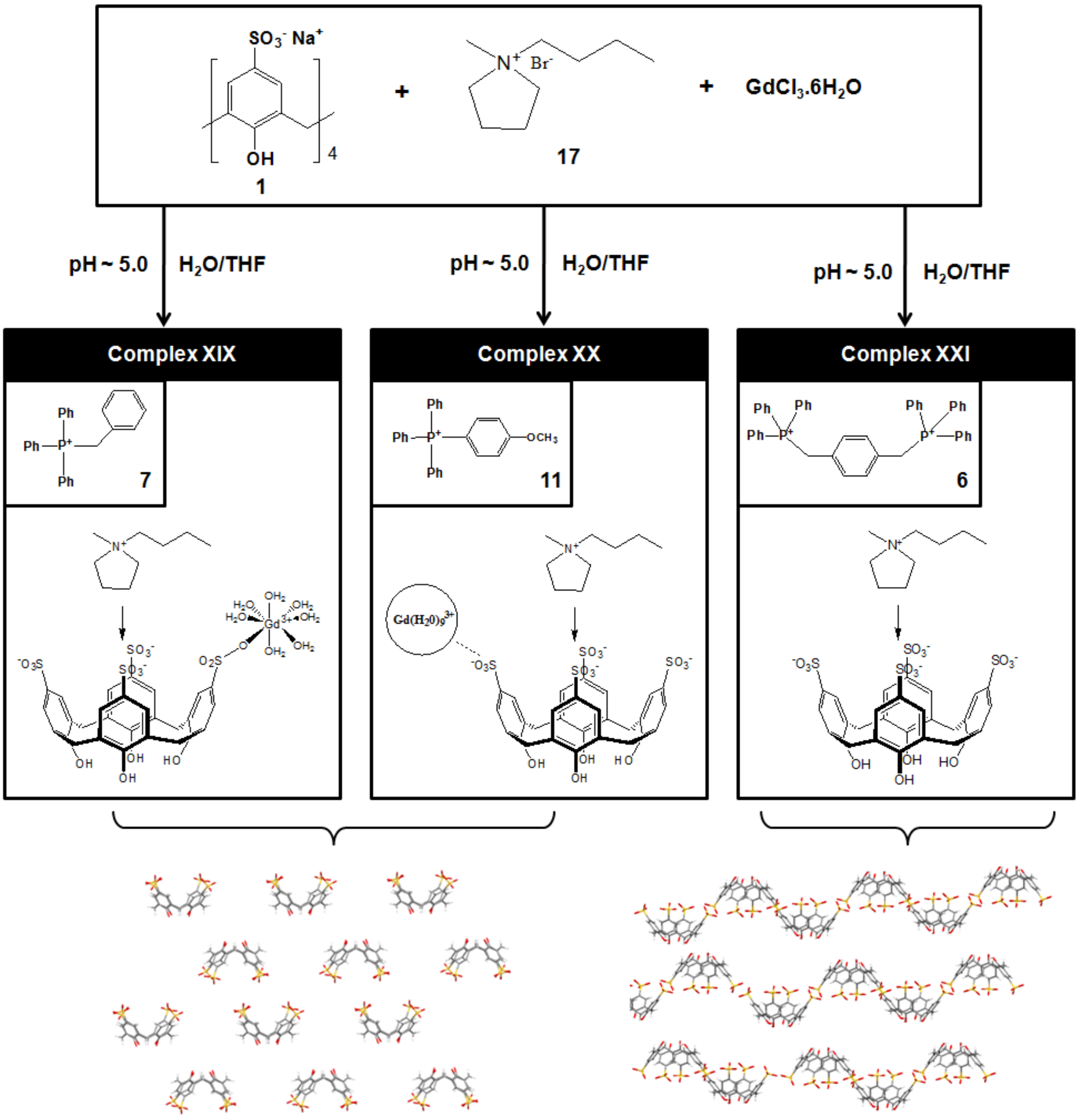

Figure 8.1. Synthesis of complexes **XIX** – **XXI**, showing the arrangement of calixarenes in the solid state structures.

8.2.1 Solid state structures of Complex XIX

Complex **XIX** has one each of the calix[4]arene, pyrrolidinium, benzyltriphenyl phosphonium ions, and a coordinated lanthanide ion in the asymmetric unit, along with, included water molecules. The conformationally restricted cone-shaped calix[4]arenes, take on a 5- charge (removal of one H-atom on the lower rim) in the structures they are arranged back-to-back in bilayer arrangements. Each heteroleptic gadolinium(III) metal centre is attached to a sulfonate group (Gd–O at 2.437(1) Å) and is coordinated by seven water molecules (Gd–O at 2.355(1) to 2.447(1) Å). The water molecules in general are involved in an extensive hydrogen bonding with O···O distances in the range 2.706(2) to 2.958(2) Å. Some of the coordinated water molecules are in close proximity with the calixarene sulfonate groups, with short O···O contacts at 2.682(2) to 2.873(2) Å**,** consistent with H-bonding interactions.

The calixarenes are arranged in bilayers 14.2 Å thick, in the antiparallel arrangement with phosphonium ions embedded between them, which are in their common phenyl embrace mode of interplay in a grid–like layer. The phosphonium ions have π···π interactions with the distance between calixarene phenyl rings at 3.46 Å. Another close contact is the C···π interaction between a calixarene methylene bridge and the phenyl ring of phosphonium cation with a C-H···π distance at 2.66 Å (corresponding C···π distance at 3.62 Å). The phosphonium ions are also involved in weak H-bonding with the oxygen containing fragments in the calixarene molecules, namely the sulfonate groups and hydroxyl groups, the H···O contacts ranging from 2.50 to 2.79 Å, and 2.46 to 2.84 Å, respectively. The distance between the central plane of one bilayer to the same of another bilayer is 18.9 Å, Figure 8.2.

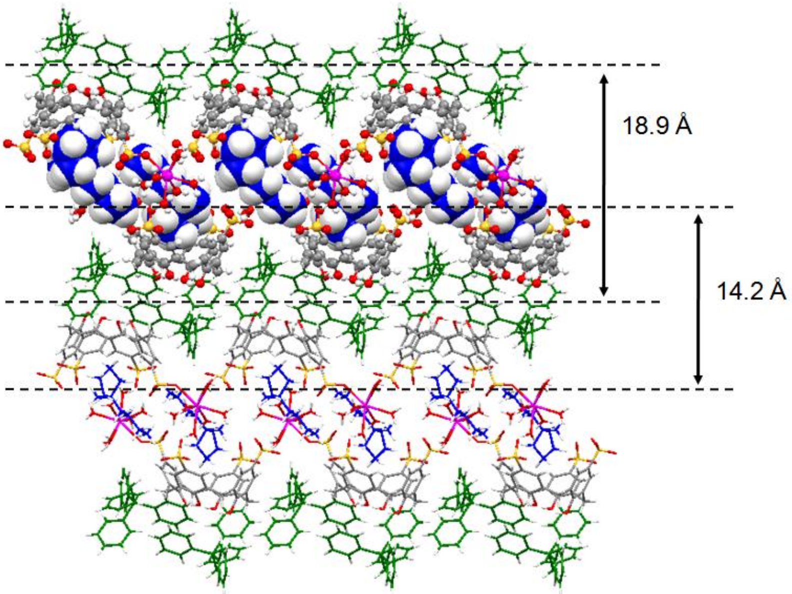

Figure 8.2. Complex **XIX** projected down the *b*-axis with some space filling of pyrrolidinium cation (blue), showing layers of phosphonium cations (green).

In complex **XIX**, the pyrrolidinium cation is selectively drawn into the calixarene in a splayed fashion, rather than a phenyl moiety of a phosphonium cations, with angles between the plane of all four phenyl rings of the calixarene with respect to the four methylene bridges at 56.63(4)°, 39.61(4)°, 68.08(4)°, and 48.70(4)°, and the pyrrolidinium alkyl chain is directed away from the cavity, positioned close to the aquated gadolinium(III) cation. The complementarity of interaction of the pyrrolidinium cation with the calixarene cavity relates to the size of the components and both C–H···π interactions and weak H-bonding at 2.69 Å (nearest C···π distance of 3.61 Å) and 2.50 Å to 2.75 Å (corresponding C···O distance of 3.31 to 3.53 Å) respectively. The H-atoms of the butyl chain of pyrrolidinium cations have close contacts with the H-atoms of water molecules of gadolinium(III) cation, with H···H distances ranging from 2.76 to 2.99 Å (corresponding C···O distance from 3.44 to 3.88 Å). The pyrrolidinium cations are nestled close to each other, with the closest H···H contacts at 2.47 to 2.51 Å (nearest C···C distances of 3.89 to 3.94 Å), Figure 8.3.

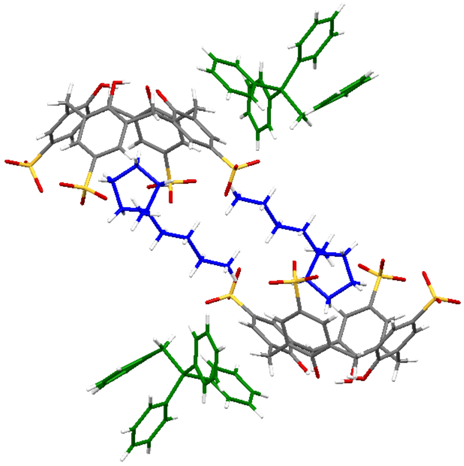

Figure 8.3. Stick representation of the supermolecules and pyrrolidinium cations in complex **XIX**.

8.2.2 Solid state structures of Complex XX

The combination of components **1**, **2**, and (3-methoxyphenyl)triphenylphosphonium cation in the presence of gadolinium(III) cations results in colourless crystalline prisms of complex **XX**. The asymmetric unit is comprised of one *p*-sulfonatocalix[4]arene, a half-populated pyrrolidinium cation which is disordered between two positions in the cavity of the calixarene molecule, two phosphonium cations surrounding the calixarene, and a gadolinium(III) centre with half occupancy (disordered relatively to an inversion centre), forming a secondary coordination sphere through hydrogen bonding with the calixarenes. The homoleptic metal ions are coordinated by nine water molecules, and have close contacts with the sulfonate groups of the calixarene through hydrogen bonding, with Gd–O···O distances ranging from 2.646(1) Å to 2.858(9) Å. There are also disordered water molecules in the extended structure, which are involved in H-bonding with O···O distances ranging from 2.551(8) to 2.960(5) Å.

The mode of interaction of the metal centres to the calixarenes is different to complex **XIX**, with the gadolinium now being exclusively bound to water molecules, and this is relayed to a significantly larger distance between the bilayers at 18.9 Å. Seemingly this is offset by the bilayer now being slightly more compact (and skewed) relative to complex **XIX,** at 11.9 Å, Figure 8.4. It is noteworthy that the electrostatic attraction of the negatively charged lower rim of the calixarenes with the phosphonium cations in complex **XIX** (but neutral lower rim for complex **XX**) expands the bilayer arrangement, as noted in Chapter 4. In complex **XX**, the phosphonium cations are arranged in the multiple phenyl embrace manner with multiple interactions with the calixarene; (i) C–H···π interactions involving the methylene bridges of calixarene and the phenyl groups of phosphonium cation, the H-atoms to centroid distance being 2.65 and 2.98 Å (corresponding C···π distance at 3.35 and 3.76 Å), (ii) H-bonds between the H-atoms from the phenyl rings of phosphonium and calixarene sulfonate groups, with distances ranging from 2.63 to 2.83 Å (corresponding C···O distances at 3.32 and 3.33 Å), and (iii) H-bond between the H-atom from the methoxy group of phosphonium and calixarene methylene bridge at 2.71 Å (corresponding C···C distance at 3.77 Å).

As in complex **XIX**, the pyrrolidinium cation resides in the calixarene through the five membered ring, with the alkyl group directed away from the cavity. Close C···π distances for the C-atoms of the pyrrolidinium ring to the calixarene phenyl rings are 3.51 and 3.60 Å. Other close contacts involve H-bonds from (i) H-atoms of the N-methyl to the sulfonate group with the C···O distances at 3.46 and 3.62 Å, (ii) H-atoms of the N-butyl to the sulfonate group with the C···O distances at 2.68 and 3.84 Å, and (iii) H-atom from the pyrrolidinium ring to the sulfonate group with C···O distances at 3.44 Å. The calixarenes in complex **XX** also have a splayed configuration associated with binding of the guest molecule, the angles between the plane of the aromatic rings and the basal plane of the four methylene bridges being 60.9(3)°, 49.4(3)°, 44.4(3)°, and 61.3(3)°. The N-butyl chain of the pyrrolidinium cation is kinked, which is presumably in consequence of its pre-organisation to fit in the tightly packed bilayer, and has the distance between each end in the same bilayer, is 4.44 Å, corresponding to C···C, Figure 8.5.

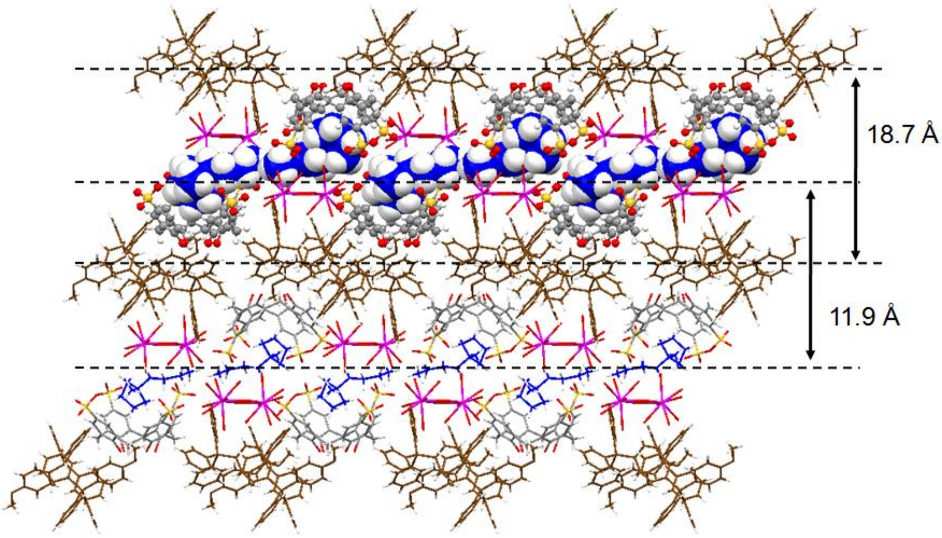

Figure 8.4. Packing in complex **XX** with some space filling of pyrrolidinium cations (blue), showing layers of phosphonium cations (brown).

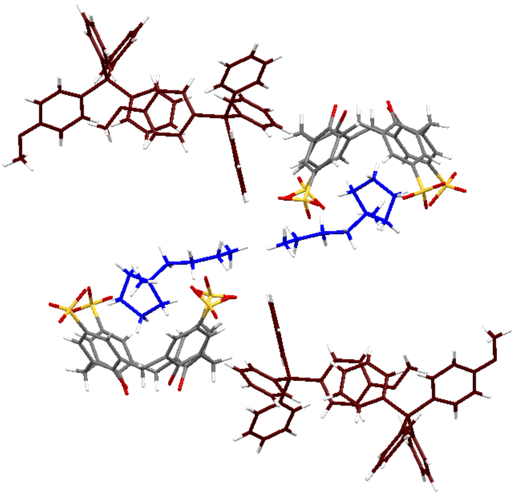

Figure 8.5. Close arrangement of the pyrrolidinium cations in the same bilayer in complex **XX**.

8.2.3 Solid state structures of Complex XXI

Complex **XXI** has one *p*-sulfonatocalix[4]arene, one pyrrolidinium cation residing in the calixarene cavity, two *bis*-phosphonium cations in the *cis*-configuration, and disordered water molecules in the asymmetric unit. No lanthanide metal ions are present even though it was present during the synthesis. Attempts to prepare complex **XXI** in the absence of lanthanide ions afforded colorless crystals, but they were poorly diffracting and a structure determination was not possible. Nevertheless, powder diffraction data was consistent with the bulk of the material being a different complex, and thus it can be concluded that the presence of the lanthanide ions in forming complex **XXI** is important in controlling the organisation of the other species, yet it is not taken up in the final complex.

The calixarenes in complex **XXI** necessarily take on a 5- charge, as in complex **XIX**, in contrast to the 4- charge in complex **XX**, with one proton removed from the lower rim of the calixarene. The disordered water molecules are positioned close to the plane of sulfonate groups, as expected having short O···O contacts between themselves and with the sulfonate groups (consistent with hydrogen bonding), the close O···O distances being in the range 2.124(4) to 3.092(5) Å.

The interplay of the cationic five membered pyrrolidinium ring with the calixarene cavity is similar to that in complexes **XIX** and **XX**, having multiple interactions with the calixarene as follows: (i) H-atoms of the five member ring of pyrrolidinium cation are involved in C–H···π contacts with the phenyl rings of calixarene, at distances of 2.70 Å to 2.80 Å (corresponding C···π distances at 3.58 to 3.71 Å), and (ii) H-bonds between H-atoms from the five membered ring and N-butyl chain of pyrrolidinium cation and calixarene sulfonate groups, with distances at 2.51_4 Å and 2.51_3 Å respectively (corresponding C···O distance at 3.42 and 3.39 Å). The angles between the four phenyl rings with respect to the basal plane of the calixarene are $53.6(2)^o$, $67.2(2)^o$, $48.4(2)^o$, and $54.5(2)^o$, with the macrocycle in a slightly pinched cone conformation.

However, beyond the arrangement of the pyrrolidinium cations with the calixarenes, which is similar to the arrangement of the two components in **XIX** and **XX**, the overall structure is distinctly different, representing a new type of layered arrangement of calixarenes, which is devoid of gadolinium(III) cations, Figure 8.6. In complex **XXI** the calixarenes are arranged with the cavities aligned in opposite directions, as for the above conventional up-down bilayers, but with the calixarenes arranged such that the upper rim sulfonate groups are in close proximity to adjacent calixarenes, effectively creating a plane of such polar groups. The rest of the structure is therefore dominated by hydrophobic-hydrophobic connections, as well as the overall electrostatic cohesion of the material.

The high content of phosphonium cations relative to calixarene, in consequence of the lack of lanthanide ions, results in the phosphonium cations dominating the interplay of the three components. The methylene bridges of the *bis*-phosphonium cations have close contacts with the sulfonate groups of calixarenes, with C–H···O distances in the range 2.30 to 2.67 Å (close C···O distance at 3.26–3.60 Å). The *bis*-phosphonium cations are orthogonally π-stacked at 3.56 Å between the centroids of the central phenyl rings of two *bis*-phosphonium cations, Figure 8.7. The N-butyl chain nestles close to the *bis*-phosphonium cation, with H···H contacts ranging from 2.40 to 2.53 Å (nearest C···C distances of 3.60 to 3.71 Å). The *bis*-phosphonium cations are close the O-atoms of the hydroxyl groups of the calixarenes, with CH···O at 2.49 to 2.56 Å (corresponding C···O distance at 3.27 to 3.41 Å).

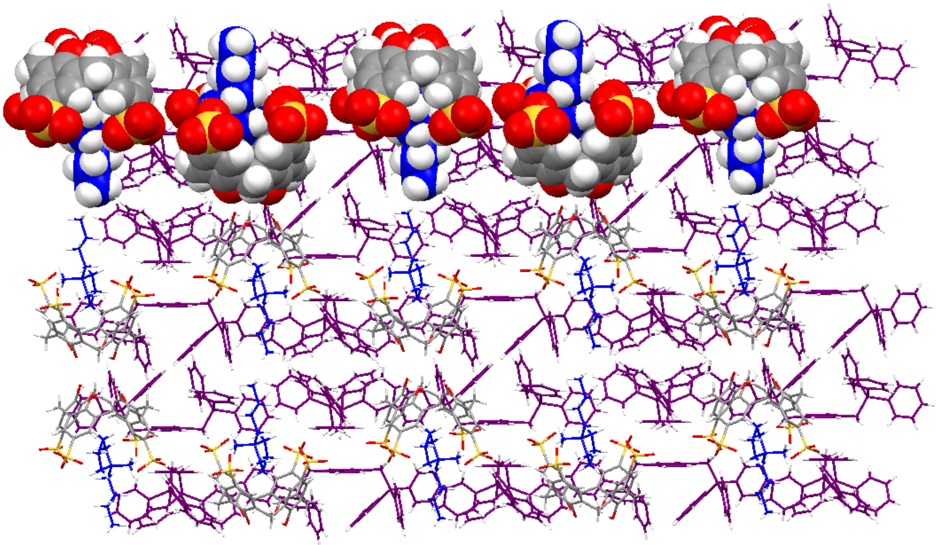

Figure 8.6. Some space filling of complex **XXI** showing some of the 1:1 supermolecules in space filling mode.

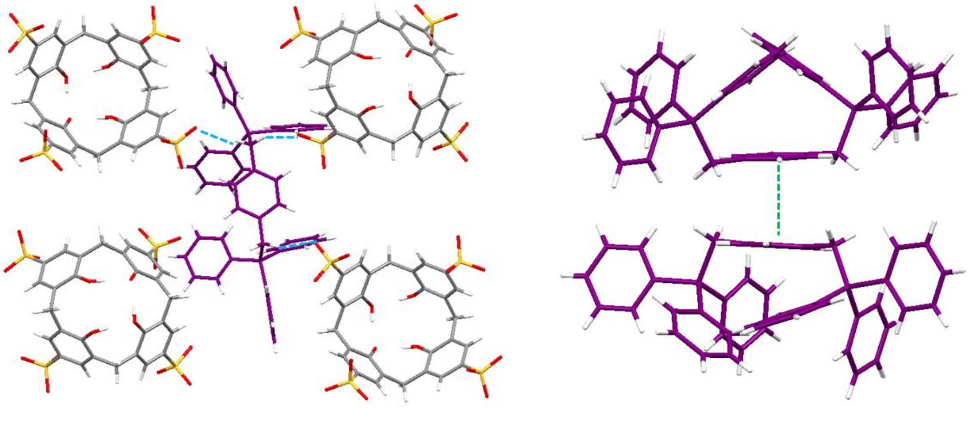
(a) (b)

Figure 8.7. Intermolecular interactions between (a) *bis*-phosphonium cations and calixarenes in complex **XXI** (C–H···O shown as blue dashed lines) and (b) *bis*-phosphonium cations held by π···π stacking (green dashed line).

8.3 Solution studies

Given the preferential binding of the pyrrolidinium cation in the calixarene cavity for all structures, the interplay of pyrrolidinium cations and *p*-sulfonatocalix[4]arene anions was studied in solution using a ^{1}H NMR titration experiments, Figure 8.8, which were carried out at 25^{o}C in D_2O (calibrated to solvent protons at 4.63 parts per million (ppm)) with the *p*-sulfonatocalix[4]arene concentration kept constant at 34 mM. The chemical shifts of the pyrrolidinium five-membered ring protons (**4** & **5**), Figure 8.8, were monitored and plotted, Table 8.1, giving an association constant of 35.2±0.5 M^{-1}. On gradual addition of the pyrrolidinium cations to the solution containing calixarene, all protons of the cation shift upfield with the largest shift for the N-methyl and for the ring protons, Figure 8.9. This is consistent with the pyrrolidium five membered ring residing in the cavity of the macrocycle, as found in the structures of **XIX** – **XXI** in the solid state, experiencing the shielding effect of the aromatic rings of the calixarene. The diminishing upfield shifts for the methylene groups and terminal methyl groups, are then expected as the distance from the shielding effect of the calixarene increases. In addition, this is concentration dependant with the upfield shifts overall diminishing as the concentration of the pyrrolidinium cations increases. Thus, the data show a rapid exchange between the host-guest ions on the NMR time scale. Also noteworthy is that the conformation mobility of the calixarene on the NMR time scale decreases with increasing concentration of the cation, with the appearance of a well resolved AB spin system for the methylene protons (*). The formation of molecular capsule in solution, comprised of two calixarenes shrouding one or indeed two pyrrolidinium cations can be ruled out. This is on the basis that the changes in chemical shifts for the alkyl chain for an excess of the calixarene are relatively small. Competition experiments on the binding of pyrrolidinium cations versus phosphonium cations, through the phenyl rings or other moieties attached to phosphorous, require the use of solvent mixtures because of solubility issues, and need to be investigated as a separate study.

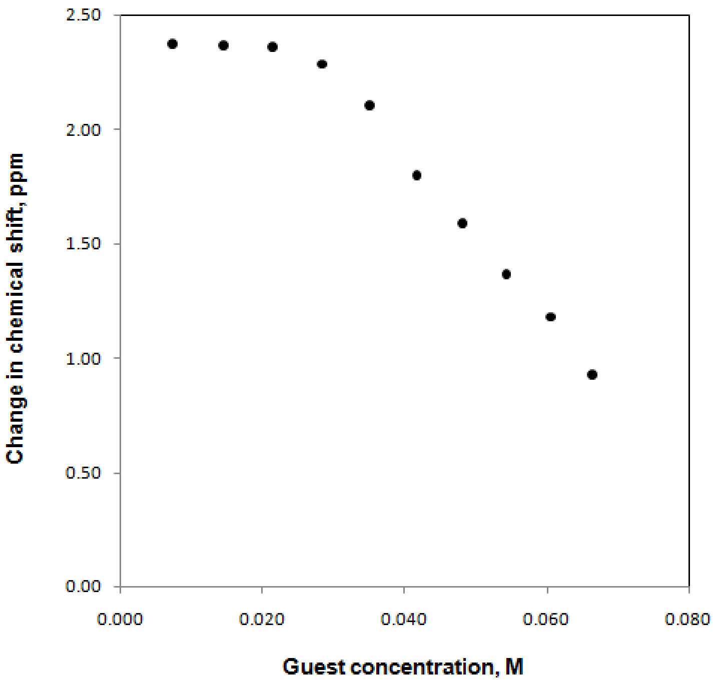

Figure 8.8. ^{1}H NMR titration curve for the complexation of *p*-sulfonatocalix[4]arene and N-butyl-N-methylpyrrolidinium.

Table 8.1. ^{1}H NMR titration results for complexation of *p*-sulfonatocalix[4]arene and N-butyl-N-methylpyrrolidinium in D_2O.

Sample	V_{Host}/ µL	V_{Guest}/ µL	Guest/ mM	$\delta H_{4,5}$ [ppm]	$\Delta\delta$ [ppm]
1	800	0	0.0000	2.066	0.000
2	800	10	7.3788	-0.309	2.375
3	800	20	14.5776	-0.296	2.362
4	800	30	21.5023	-0.300	2.366
5	800	40	28.4604	-0.220	2.286
6	800	50	35.1571	-0.039	2.105
7	800	60	41.6981	0.269	1.797
8	800	70	48.0887	0.531	1.535
9	800	80	54.3334	0.703	1.363
10	800	90	60.4385	0.890	1.176
11	800	100	66.4091	1.043	1.023

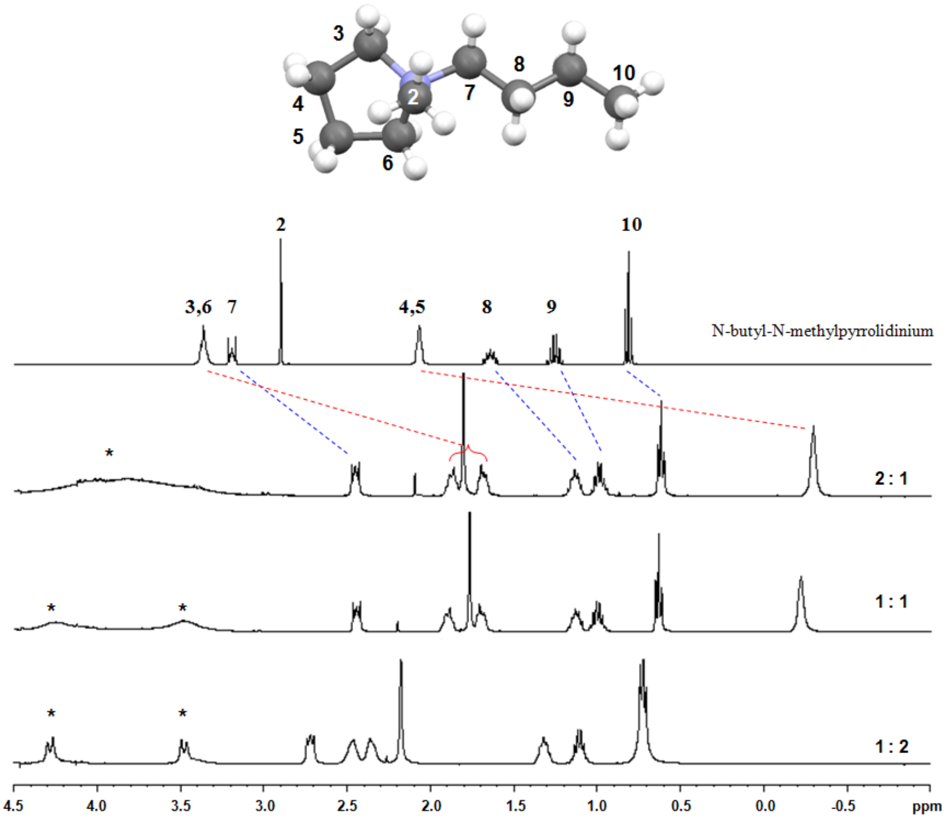

Figure 8.9. ^{1}H NMR spectra for N-butyl-N-methylpyrrolidinium (top), and *p*-sulfonatocalix[4]arene and pyrrolidinium at different mole ratios (calixarene : pyrrolidinium), measured in D_2O.

8.4 Conclusions

The N-butyl-N-methylpyrrolidinium cations, which is a common component in some ionic liquids, and in the presence of various phosphonium cations, and gadolinium ions, form complexes with the bowl shaped anionic *p*-sulfonated calix[4]arene, where the five membered cationic head group preferentially binds in the calixarene cavity rather than its butyl chain or a phenyl ring of a phosphonium cation. This is both in the solid state and in solution. The host-guest interplay of the pyrrolidinium cations with the calixarenes is similar to the findings for imidazolium cations as discussed in Chapters 3 to 7, which also reside in calixarene cavities.

The new findings, coupled with other recent studies on imidazolium cations, gives further credence to a level of predictability of the structures, notably the persistence of binding of pyrrolidinium and imidazolium cations in calixarene cavities, with the formation of bilayers based on calixarenes and phosphonium cations, depending on the size of the cations in general, and the length of any alkyl chains. There are, however, limitations, with a long alkyl chain on the imidazolium cation (greater than hexyl) and the use of large *bis*-phosphonium cations, leading to other structures dominated by the alkyl chain and/or phosphonium cations. In the present study, the large *bis*-phosphonium cation is effective in generating a different type of packing arrangement in the supramolecular building blocks relative to those in the conventional bilayer arrangement. Indeed, the large phosphonium cation can win out over the incorporation of lanthanide ions in the complex, in so doing affording a different packing motif of calixarenes, complex **XXI**. For an *n*-octyl alkyl chain on imidazolium cations, the chain penetrates an adjacent bilayer.

8.5 Experimental Section

A. General remarks on crystal growth

p-Sulfonatocalix[4]arene sodium salt, **1**, was synthesised as described in Section 3.4. N-butyl-N-methylpyrrolidinium bromide was synthesized according to literature procedures [217]. $[Ph_4P]Br$, $[Ph_3PPhOMe]I$ and $[Ph_3PCH_2PhCH_2PPh_3]Cl_2$ were purchased from Sigma Aldrich. A hot solution of $GdCl_3 \cdot 6H_2O$ in water (0.5 mL) was added to a hot solution of phosphonium salt with *p*-sulfonatocalix[4]arene in a mixture of THF and water (1:1). The prepared solutions were left to cool and slowly evaporate, with the crystals forming after several days.

B. Synthesis of N-butyl-N-methylpyrrolidinium bromide

n-Bromobutane was slowly added to freshly distilled methylpyrrolidine in a two-necked round-bottom flask fitted with a reflux condenser maintained at 40^oC. This mixture was then stirred with a magnetic stirrer for one day to give a yellow solid.

C. NMR Studies

^1H NMR spectra were collected on a Varian 400 MHz spectrometer using D_2O at 25^oC. Titrations were carried out by adding aliquots of a solution of the pyrrolidinium ion (66 mM) to a solution of a *p*-sulfonatocalix[4]arene (34 mM, 800 μL) in a NMR tube fitted with a rubber septum.

D. Crystallography details

X-ray Crystallography

All data were measured as described in Section 3.4.

Crystal/refinement details for complex XIX:

$C_{28}H_{33}GdO_{23}S_4^{2-}$, $C_{25}H_{22}P^+$, $C_9H_{20}N^+$, 3(H_2O), $C_{62}H_{81}GdNO_{26}PS_4$, M = 1572.74, colorless needle, 0.34 × 0.16 × 0.09 mm^3, a = 12.5895(3), b = 14.5373(3), c = 19.6811(3) Å, α = 78.959(2), β = 75.828(2), γ = 73.233(2)°, V = 3315.41(12) $Å^3$, D_c = 1.575 g/cm^3, λ = 0.71073 Å, μ = 1.235 mm^{-1}, F_{000} = 1622, 2θ_{max} = 75.3º, 125644 reflections collected, 33737 unique (R_{int} = 0.0451). Final *GooF* = 0.999, $|\Delta\rho_{max}|$ = 2.1(1) e $Å^{-3}$, *R1* = 0.0336, *wR2* = 0.0765, *R* indices based on 25650 reflections with I >2σ(I), 856 parameters, 0 restraints. CCDC number: 748997.

Crystal/refinement details for complex XX:

2($C_{28}H_{20}O_{16}S_4^{4-}$), 4($C_{25}H_{22}OP^+$), $Gd^{3+}(OH_2)_9$, $C_9H_{20}N^+$, 17(H_2O), $C_{165}H_{200}GdNO_{62}P_4S_8$, M = 3726.87, colorless prism, 0.45 × 0.37 × 0.10 mm^3, a = 16.9108(8), b = 18.3084(9), c = 19.8976(10) Å, α = 106.555(4), β = 100.355(4), γ = 115.038(5)°, V = 5020.1(4) $Å^3$, D_c = 1.233 g/cm^3, λ = 1.54178 Å, μ = 3.870 mm^{-1}. F_{000} = 1945, θ_{max} = 135.2º, 74903 reflections collected, 17872 unique (R_{int} = 0.0739). Final *GooF* = 1.038, $|\Delta\rho_{max}|$ = 1.2(1) e $Å^{-3}$, *R1* = 0.1405, *wR2* = 0.3466, *R* indices based on 9568 reflections with I >2σ(I), 1054 parameters, 190 restraints. CCDC number: 748998.

Crystal/refinement details for complex XXI:

$C_{28}H_{19}O_{16}S_4^{5-}$, $2(C_{44}H_{38}P_2^{2+})$, $C_9H_{20}N^+$, $12(H_2O)$, $C_{125}H_{139}NO_{28}P_4S_4$, M = 2355.49, colorless prism, 0.18 × 0.10 × 0.05 mm^3, a = 15.7145(6), b = 20.0041(6), c = 20.9917(8) Å, α = 80.315(3), β = 72.723(3), γ = 69.539(3)°, V = 5888.2(4) Å^3, D_c = 1.329 g/cm^3, λ = 1.54178 Å, μ = 1.882 mm^{-1}, F_{000} = 2488, $2\theta_{max}$ = 134.8º, 56333 reflections collected, 20556 unique (R_{int} = 0.0817). Final $GooF$ = 1.001, $|\Delta\rho_{max}|$ = 1.3(1) e Å^{-3}, $R1$ = 0.0875, $wR2$ = 0.2266, R indices based on 12292 reflections with I >2σ(I), 1455 parameters, 0 restraints. CCDC number: 748999.