CHAPTER 1

General Introduction

1.1 Background

Supramolecular chemistry is an area of chemistry beyond the molecules which focuses on the self-assembly systems involving discrete molecular subunits or components. Self-assembly processes are engaged in the molecular recognition events between supramolecular tectons with some complementarity of interactions which are inherently weak. Such processes provide access to complicated and diversified architectures with a level of prediction of the structures, depending of the design strategies incorporated into the tectons.

Calixarenes are a class of macrocycle that can be functionalised at the lower rim through the phenolic -OH groups which the synthetic procedures are well documented in supramolecular chemistry, as well as through the upper rim at the *p*-position relative to these groups. Calixarenes functionalized only at the upper rim with sulfonate groups, *p*-sulfonatocalix[n]arenes, are essentially versatile water soluble amphiphilic cavitands which have been extensively investigated as supramolecular tectons in crystal engineering, and supramolecular chemistry in general. These cavitands are of interest for their water solubility, with potential in mimicking biological processes, and gaining access to new materials in a benign reaction medium.

p-Sulfonatocalix[4]arene, the smallest oligomer for the water-soluble macrocycles is typically in the rigid cone conformation, however the cavitand can also be designated as partial cone, 1,2-alternate and 1,3-alternate as a result of spatial orientations from the rotations of the methylene groups between phenols. The cone conformer can bind a wide range of guest molecules in the cavity, where the sulfonate groups at the calixarene upper rim in general provide anchoring points for the complexation of organic and inorganic moieties. The cone conformer cavitand often assembles in the up-down anti-parallel bilayer arrangement in the infinite networks, simultaneously creating hydrophobic and hydrophilic environments. Lanthanide metal ions play an important role in the supermolecule formation, stability and overall cohesion of the structures through charge balance, hydrogen bonding, bridging, and templating effects, either in primary or secondary coordination sphere interactions.

1.2 Objectives of research

The key objectives of the research are to design and synthesize molecular solid-state structures with desired properties, based on an understanding and exploitation of intermolecular interactions in the field of crystal engineering. The preparation and the characterization of multi-component solid state structures being built by water-soluble cavitand, *p*-sulfonatocalix[4]arene, and various cations such as imidazolium, pyrrolidinium and phosphonium, in the presence of lanthanide metal ion, gadolinium(III) are being conducted in this research. Primarily, the host-guest interaction concerning a series of *N*-heterocyclic molecules bearing different alkyl chains is carefully analysed and assessed both in solid and solution state *via* crystallography (single crystal structure elucidation) and solution analysis (^{1}H NMR and ROESY experiments) respectively. Higher complexities of supramolecular structures are also studied with the incorporation of *mono*- and *bis*-phosphonium cations which affords different structural motifs depending on the nature of the cations. Contribution of the intermolecular complementarity interactions involving hydrogen bonding, C-H···π interaction and π-π interaction to constructing the supramolecular architecture is investigated wherein a detailed visualisation and quantitative distribution of such interactions has been performed using the Hirshfeld surface analysis to further understand the host-guest system within its environment.

Complexation studies of *p*-sulfonatocalix[4]arene engaging in larger molecules such as fullerenes and carbon nanotubes is performed in this research, with the aim to prepare stable suspension of water-soluble nano-composite materials in aqueous solution. The composite nanomaterials are characterised qualitatively and quantitatively using various characterisation techniques.

1.3 Thesis Outline

This thesis reports on the extensive study of supramolecular chemistry and crystal engineering for twenty one (21) structures with high complexities based on water-soluble cavitand, *p*-sulfonatocalix[4]arene with a series of *N*-heterocyclic molecules featured in ionic liquids and phosphonium cations in the presence of gadolinium(III) metal ions which designate a supramolecular framework. The bowl shaped *p*-sulfonatocalix[4]arene host molecule demonstrates the versatility in build multi-component self assembled materials with the basis of incorporating small organic cations including imidazolium or pyrrolidinium cations within the cavity of the calixarene through their polar head groups. The host-guest inclusion is persistent in liquid state as established in the solution studies. Metathetical exchange involving phosphonium halide salts with anions based on imidazolium salts yields eleven (11) crystalline materials which are discussed in the thesis.

Chapter 3 reports on the self-assembly of multi-component complexes engaging smaller analogues of imidazolium based cations *i.e.* 1-*n*-ethyl-3-methylimidazolium and 1-*n*-butyl-3-methylimidazolium cations. The imidazolium cations are confined within essentially ‘molecular capsules’ based on two calixarenes from adjacent bilayers with the capsule formation effectively assisted by lanthanide metal ion. Chapter 4 describes the influence of imidazolium molecule bearing *n*-octyl chain in the design strategy for penetrating organic bilayers. The nature of the supermolecules in aqueous state is investigated using ^{1}H NMR. Another design strategy is the assembly of interlocking (embracing) large phosphonium cations around the outer exo-surface of the cavity of the calixarene which is described in Chapter 5. The selectivity of interplay of the different terminal alkyl chains from imidazolium and *bis*-phosphonium cations with the *endo*- and *exo*- surfaces of the calixarene occurs in the presence of aquated gadolinium(III) ions, but these ions are not necessarily incorporated into the extended structures. The most striking effect of these crystalline complexes is the tilting of the plane of the bowl shaped calixarenes relative to the plane of a multi-layer. 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.

Chapter 6 focuses the self-assembly of *bis*-imidazolium cations with *n*-methyl or *n*-butyl terminal alkyl groups being end-capped by two geometrically opposed calixarenes either adjacent to each other, where they face the same direction in the same bilayer of calixarenes, or where they face opposite directions. The host-guest interplay of calixarene-hydroxyethyl-methylimidazolium cation is described in Chapter 7 and the findings are comparable to the findings in Chapters 3 and 5 for imidazolium cation bearing *n*-ethyl terminal, which also reside in calixarene cavities in the solid state and in solution. Importantly, the hydroxy group from the imidazolium cation effectively restricts the conformation of calixarene as compared to the previous findings in Chapters 4, 5, and 6. Chapter 8 reports the self-assembly of *p*-sulfonatocalix[4]arene–*N*-butyl-*N*-methylpyrrolidinium complexes in building multi-component layered arrays. It is noteworthy that by replacing the *mono*-phosphonium cations with *bis*-phosphonium ions results in similar interplay of the calixarene and pyrrolidinium cations, but with the formation of a different layered structure, which is devoid of the lanthanide ions, unlike the other bilayers. In Chapter 9, a detailed Hirshfeld surface analysis was carried out on the crystalline phosphonium salts including the polymorphs, which are essentially formed by metathetical exchange involving phosphonium halides (Cl^- or Br^-), with ionic liquid anions based on imidazolium salts, in the presence of the sodium salt of *p*-sulfonatocalix[4]arene. This is presumably facilitated by the binding of the imidazolium cation in the cavity of the calixarene. The interaction between the cations and anions is dominated by CH···X non-classical hydrogen-bonding.

Chapters 11 and 12 focus on the utilization of *p*-sulfonatocalix[4]arene in solubilising carbon rich nanomaterials *i.e.* single-walled carbon nanotubes and fullerenes in aqueous solution. Composites of calixarene-carbon nanotube and calixarene-fullerene were prepared by a solventless grinding method, followed by the addition of water then sonication. The composite materials are decorated with nanoparticles of *p*-sulfonatocalix[4]arene which render the nanotubes soluble in water. Samples were characterized by various qualitative and quantitative characterization methods. Finally, Chapter 13 summarizes the substantial results from the overall research findings.