Abstract

Fundamental investigations of host-guest interactions on the supramolecular self-assembly involving water-soluble *p*-sulfonatocalix[4]arene, with a series of imidazolium-based cations and pyrrolidinium cation with variable alkyl chain lengths, which featured extensively in ionic liquids have been established. Combinatorial studies incorporating multiple components concerning *p*-sulfonatocalix[4]arene, imidazolium cations or pyrrolidinium cation, phosphonium cations and lanthanide ions have been developed, which yielded diverse solid state motifs with a common structural characteristic that the imidazolium or pyrrolidinium cation resides in the cavity of the calixarene. Shorter terminal alkyl chain of *mono*-imidazolium molecules, *i.e.* *n*-ethyl and *n*-butyl imidazoliums are confined in the 'molecular capsule', being encapsulated by two calixarenes and coordinated by lanthanide metal ions, whilst terminal alkyl chain longer than *n*-butyl will have the alkyl chain directed away from the calixarene cavity. Longer terminal alkyl chain from the imidazolium cation also results in penetration into the adjacent calixarene bilayer. Calixarenes end-capping *bis*-imidazolium cation effectively creates 'molecular capsule' or skewed 'molecular capsule'. The *mono*- or *bis*-phosphonium cations as part of the self-assembled material are not being taken up in the cavity nevertheless are self-assembled in between the calixarene bilayers, creating thicker hydrophobic bilayers and in some cases forms scaffold network which shroud the calixarenes. The nature of the interplay of the multi-component systems is well understood using Hirshfeld surface analysis and solution studies, with the results further highlighting the power of the technique in mapping out the interactions in a complex system, and how the components come together with complementarity interactions. The research was deemed as an important strategy in defining the limits in utilising the ubiquitous imidazolium cations or pyrrolidinium cation in constructing multi-component bilayers.

Complexation of *p*-sulfonatocalix[4]arene with carbon rich nanomaterials *i.e.* single wall carbon nanotubes (SWNTs) and fullerenes (C_{60} and C_{70}) shows these nanomaterials can be solubilised and stabilised in water by solventless mechanical grinding the component with *p*-sulfonatocalix[4]arene, followed by sonication in water This approach has possibilities in using other amphiphiles in solubilising carbon nanomaterials in general, where other techniques for dispersing such material are limited. The composite material has nano-particles of the calixarene randomly arranged on the surface of the carbon nanotube or fullerenes which render the hydrophobic material soluble in aqueous solution. However solubilisation is not possible when the two components are sonicated only in water without prior grinding.

Table of Contents

Abstract i

Table of Contents iii

List of Figures viii

List of Tables xvii

Abbreviations xviii

Acknowledgements xix

Details of Publications and Abstracts xx

Statement of Candidate Contribution xxiii

Chapter 1 - General Introduction 1

- 1.1 Background 2
- 1.2 Objective of Research 3
- 1.3 Thesis Outline 4

Chapter 2 - Host-guest Chemistry: an Introduction 5

- 2.1 Supramolecular chemistry 7
  - 2.1.1 Intermolecular interactions 10
- 2.2 Calixarene chemistry 13
  - 2.2.1 Overview of calixarene chemistry 13
  - 2.2.2 Synthesis 15
  - 2.2.3 Mechanism of calixarene formation 18
  - 2.2.4 Conformations of calixarenes 20
  - 2.2.5 Water soluble calixarenes 24
  - 2.2.6 Sulfonated calix[n]arenes 26
  - 2.2.7 General structural motifs of sulfonated calix[4]arene 27
    - 2.2.7.1 Bilayers 27
    - 2.2.7.2 Molecular capsules 33
    - 2.2.7.3 Russian doll and ferris wheel 36
    - 2.2.7.4 Spheroids and tubules 38
    - 2.2.7.5 Interlocking of large organic cation 40
  - 2.2.8 General structural motifs of sulfonated calix[6]arene 42

2.2.9 General structural motifs of sulfonated calix[8]arene 44

2.3 Ionic liquids 47

2.3.1 Synthesis 51

Chapter 3 - Host-guest Chemistry: Lanthanide assisted self assembly of imidazolium cations in organic bilayers 53

3.1 Introduction 54

3.2 Structural features involving 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolium……………………… ………………………………… 56

3.2.1 Solid state structures of Complex **I** 57

3.2.2 Solid state structures of Complex **II** 59

3.2.3 Solid state structures of Complex **III** 62

3.2.4 Solid state structures of Complex **IV** 64

3.3 Conclusions 66

3.4 Experimental Section 68

Chapter 4 - Host-guest Chemistry: Influence of *n*-octyl chain in the design strategy for penetrating organic bilayers 73

4.1 Introduction 74

4.2 Structural features involving 1-octyl-3-methylimidazolium and 1-octyl-3-dimethylimidazolium 75

4.2.1 Solid state structures based on 1-octyl-3-methylimidazolium complexes75

4.2.2 Hirshfeld surface analysis for structures based on 1-octyl-3-methyl-imidazolium complexes 82

4.2.3 Solid state structures based on 1-octyl-3-dimethylimidazolium complexes 85

4.2.4 Hirshfeld surface analysis for structures based on 1-octyl-3-dimethylimidazolium complexes 90

4.3 Solution studies involving 1-octyl-3-dimethylimidazolium complexes……92

4.4 Conclusions 94

4.5 Experimental Section 96

Chapter 5 - Host-guest Chemistry: Preferential interplay of imidazolium in directing multi-component layers 100

5.1 Introduction 101

5.2 Structural features involving interlocking 1,4-*bis*(triphenylphosphoniomethyl)benzene……………………………………………………….........102

5.2.1 Solid state structures of Complex **IX**..103

5.2.2 Solid state structures of Complex **X** 108

5.2.3 Solid state structures of Complex **XI**..112

5.3 Solution studies..116

5.4 Conclusions..122

5.5 ExperimentalSection…...………...……………………..………………..…… 123

Chapter 6 - Host-guest Chemistry: Supramolecular assemblies containing end capping *bis*-imidazolium cations...126

6.1 Introduction..127

6.2 Structural features involving 1,1’-[1,4-phenylene*bis*(methylene)]*bis*(3-methyl-1H-imidazolium-1-yl) and 1,1’-[1,4-phenylene*bis*(methylene)]*bis*(3-butyl-1H-imidazolium-1-yl) ………………………………………………………………..127

6.2.1 Solid state structures of Complexes **XII** and **XIII**...............................129

6.2.2 Solid state structures of Complexes **XIV** and **XV**...............................136

6.2.3 Solid state structures of Complexes **XVI** and **XVII**............................143

6.2.4 Hirshfeld surface analysis for complex **XVI** and **XVII**........................148

6.3 Solution studies..150

6.4 Conclusion 156

6.5 Experimental Section...157

Chapter 7 - Host-guest Chemistry: Influence of hydroxyethyl imidazolium group on host-guest interplay in building multi-component bilayers 162

7.1 Introduction..163

7.2 Structural features involving 3-(2-hydroxyethyl)-1-methylimidazolium.......164

7.3 Solution studies..169

7.4 Conclusions..170

7.5 Experimental Section...171

Chapter 8 - Host-guest Chemistry: *p*-sulfonatocalix[4]arene –pyrrolidinium complexation in building multi-component layered arrays 172

8.1 Introduction..173

8.2 Structural features involving N-butyl-N-methylpyrrolidinium 174

8.2.1 Solid state structures of Complex **XIX** 176

8.2.2 Solid state structures of Complex **XX** 178

8.2.3 Solid state structures of Complex **XXI** 180

8.3 Solution studies 183

8.4 Conclusions 186

8.5 Experimental Section 187

Chapter 9 - Host-guest Chemistry: Hirshfeld surface analysis of phosphonium salts .. 190

9.1 Introduction 191

9.2 Solid state structures of phosphonium salts 194

9.3 Hirshfeld surface analysis of phosphonium salts 204

9.4 Conclusions 209

9.5 Experimental Section 210

Chapter 10 - Nano-Chemistry: an Introduction 211

10.1 Introduction to Carbon nanotube 212

10.2 Carbon nanotube functionalization 213

10.3 Carbon nanotubes and calixarenes 216

10.4 Introduction to fullerenes 217

10.5 Water soluble fullerenes 219

10.6 Fullerenes and calixarenes 220

10.6.1 Fullerenes and calix[8]arenes 221

10.6.2 Fullerenes and calix[6]arenes 221

10.6.3 Fullerenes and calix[5]arenes 223

10.6.4 Fullerenes and calix[4]arenes 224

Chapter 11 - Nano-Chemistry: Water solublisation of single-walled carbon nanotubes using *p*-sulfonatocalix[4]arene 226

11.1 Introduction 227

11.2 Materials and methods 228

11.2.1 Synthesis of water soluble SWNTs 228

11.2.2 Characterization of the water-soluble SWNTs 230

11.3 Results and discussion 230

11.3.1 Raman spectroscopy 230
11.3.2 FTIR spectroscopy 232
11.3.3 Fluorescence spectroscopy...234
11.3.4 Transmission electron microscopy (TEM) 235
11.3.5 Thermogravimetric analysis (TGA)...236
11.4 Conclusions 237
Chapter 12 - Nano-Chemistry: Stabilised nano-arrays of fullerene C_{60} and C_{70} in water using *p*-sulfonatocalix[4]arene 238
12.1 Introduction 239
12.2 Materials and methods 239
12.2.1 Synthesis of Brønsted acidic ionic liquids. 240
12.2.2 Synthesis of water soluble *p*-sulfonatocalix[4]arene/fullerenes C_{60} and C_{70}……………………………………………………………………..……..241
12.2.3 Synthesis of *p*-sulfonatocalix[4]arene/ionic liquid/fullerenes C_{60} and C_{70}…………………………………………………………………………242
12.2.4 Synthesis of ionic liquid/fullerenes C_{60} and C_{70}. 242
12.3 Results and discussion 244
12.3.1 Electronic absorption spectroscopy. 244
12.3.2 Solution studies 247
12.3.3 Particle size measurement 249
12.4 Conclusions 253
Chapter 13 - Executive Summary and Conclusion 254
Appendices 262
References 270

List of Figures

Figure 2.1. Supramolecular system from molecular building blocks: (a) host-guest complexation and (b) self assembly [5].. 9

Figure 2.2. (a) Offset face-to-face and (b) edge-to-face arrangements.................... 11

Figure 2.3. (a) Calix crater, (b) calix[n]arene and (c) representation of calix[4]arene in cone conformation showing upper and lower rim.. 14

Figure 2.4. Influence of base concentration on the yield of *p*-tert-butylcalix[4]arene [51]…………………………………………………………………………………..17

Figure 2.5. Overview of the molecular mitosis mechanism test. (Black and white circles represents deuterated and protonated residues respectively) [56].. 20

Figure 2.6. Four possible conformations of calix[4]arene [36]. 21

Figure 2.7. Lower rim intramolecular hydrogen bonded interactions in calix[4]arene, which stabilise the cone conformation.. 22

Figure 2.8. (i) Calix[5]arene, (ii) calix[6]arene and (iii) calix[7]arene.................... 23

Figure 2.9. Examples of anionic, cationic and neutral calixarenes......................... 25

Figure 2.10. Cartoon representation of typical bilayer arrangement for *p*-sulfonatocalix[4]arene... 27

Figure 2.11. a) Bilayer structure of *p*-sulfonatocalix[4]arene · 5 Na^+. $12H_2O$ in the crystal and b) layer structure of hydrated sodium vermiculite [85]........................... 28

Figure 2.12. Projection of the calixarene showing the water molecule in the cavity of a sulfonated calixarene [87].. 28

Figure 2.13. (a) 2D hydrogen bonded polymers and (b) 2D coordination polymers [87]…………………………………………………………………………………..30

Figure 2.14. (a) Molecular packing showing: (a) typical bilayer, (b) zig-zag bilayer and (c) stepped bilayer structural motif of p-sulfonatocalix[4]arene [103]................ 32

Figure 2.15. (a) Molecular capsule and (b) slipped face to face interaction [98]. 34

Figure 2.16. Molecular capsule encapsulating (a) (2.2.2)-cryptand, (b) crown ether and (c) cyclam [110,112, 114]... 35

Figure 2.17. Molecular capsule encapsulating (a) phenanthroline and (b) benzyl viologen [115, 116]. 36

Figure 2.18. (a) "Russian doll" and (b) " Ferris wheel" [105, 107].............................. 37

Figure 2.19. (a) The icosahedron (Platonic) and the cuboctahedron (Archimedean) [117]…………………………………………………………………………………...39

Figure 2.20. Interaction of tetraphosphonium and ytterbium cations with *p*-sulfonatocalix[4]arene at different molar ratios [126]... 41

Figure 2.21. Bis-molecular capsule arrangement formed by *p*-sulfonatocalix[6]arene shrouding (a) two 18-crown-6 molecules and (b) two tetraphenylphosphonium cations [117]………………………............................ 43

Figure 2.22. (a) 4,4'-dipyridine-N,N'- dioxide molecules in the grooves of the calixarene and complexation with aquated europium(III) ions and (b) 'molecular capsule' based on two calixarenes and three encapsulated tetraphenylphosphonium ions [135, 136].. 45

Figure 2.23. Supramolecular array showing the occupation of the channels by aquated ytterbium (III) ions [137].. 46

Figure 2.24. Imidazolium (**i**), pyridinium (**ii**), pyrrolidinium (**iii**), ammonium (**iv**), phosphonium (**v**), SCN^- (**vi**), $N(CN)_2^-$(**vii**), $C(CN)_3^-$ (**viii**), PF_6^-(**ix**), BF_4^- (**x**), $CF_3SO_3^-$(**xi**), $N(CF_3SO_2)_2^-$(**xii**).. 48

Figure 2.25. Crystal packings of dialkylimidazolium cation, illustrating the supramolecular arrangement of molecules as (a) chains, (b) layers and (c) 3-D framework [173]. 50

Figure 2.26. Preparation and work-up procedures for ionic liquid synthesis [175]. . 52

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' 56

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.. 58

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)). 59

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. 61

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. 61

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**. 63

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)). 64

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. 65

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. 66

Figure 3.10. Cartoon of the different arrangement of imidazolium cations within ‘molecular capsules’, (a) – (d). 67

Figure 4.1. Synthesis of complexes **V** and **VI**. 75

Figure 4.2. Projection down the *b*-axis with some space filling of imidazolium guest molecules (blue) confined in calixarenes, and layers of phosphonium cations (purple) in the extended bilayer of complex **V**. Crystalline water molecules were omitted for clarity. 77

Figure 4.3. Projection down the *b*-axis of calixarene - imidazolium supermolecules in complex **V** with some space filling of imidazolium guest molecules (blue) and layers of phosphonium cations (purple). Crystalline water molecules were omitted for clarity. 78

Figure 4.4. Stick representation of embedded phosphonium ions projected down *c*-axis in (a) complex **V** and (b) complex **VI**. 78

Figure 4.5. Multiple phenyl embraces of phosphonium paired molecules in complex **V** (left) and complex **VI** (right). 79

Figure 4.6. Close contacts for the calixarene - imidazolium supermolecules in complex **V** (a) and complex **VI** (b) with equivalent space-filling representation (right). 80

Figure 4.7. Hirshfeld surfaces for imidazolium cations (a) complex **V**, and (b) complex **VI** showing all close contacts of imidazolium cation and nearest components, with two views related by a 180^o rotation about the vertical axis. 83

Figure 4.8. Fingerprint plots for complex **V** (left) and **VI** (right) showing regions of close intermolecular contacts. 84

Figure 4.9. Relative contributions to the Hirshfeld surface for the major intermolecular contacts associated with the imidazolium cations in complexes **V** and **VI**. 84

Figure 4.10. Synthesis of complexes **VII** and **VIII** 85

Figure 4.11. Projection of complex **VII** down *a*-axis showing the arrangement of *n*-octyl dimethylimidazolium cations (green) encapsulated in the ‘capsules’ of calixarenes. 87

Figure 4.12. Arrangement of *n*-octyl dimethylimidazolium cation in the ‘molecular capsule’ in complex **VII**, showing nearest contacts (left) and the corresponding space filling (right). The disordered parts of the imidazolium cation are omitted for clarity. 88

Figure 4.13. Stick representation of embedded phosphonium molecules projected along the *b*-axis in complex **VII**. 88

Figure 4.14. Projection of the extended structure in complex **VIII** down the *a*-axis, with some space filling of the imidazolium cations (green). 90

Figure 4.15. Hirshfeld surfaces for (a) calixarene and (c) dimethylimidazolium molecules for complex **VIII**, showing all close contacts of dimethylimidazolium cation and calixarene, with their respective fingerprint plots (b & d). 92

Figure 4.16. ^{1}H NMR spectrum for (a) *n*-octyl dimethylimidazolium and (b) *n*-octyl dimethylimidazolium in *p*-sulfonatocalix[4]arene (1:1), measured in DMSO (S1) and D_2O (S2)……... 94

Figure 5.1. Synthesis of complexes **IX** – **XI**. 102

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. 105

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). 105

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)... 107

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). 107

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. 109

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). 109

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). 111

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). 112

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). 113

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). 114

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).. 115

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).. 116

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……………………………………………………………..................119

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_2O (S) and ^{1}H NMR titration experiments for *n*-butyl-imidazolium (b) with *p*-sulfonatocalix[4]arene as the host molecule. 120

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. 121

Figure 6.1. Summary of the components affording crystalline complexes **XII** – **XVII** which have been structurally authenticated. 128

Figure 6.2. Arrangements of sulfonated calixarenes and *bis*-imidazolium cations (blue) bridged by gadolinium metal ion for (a) complex **XII** and (b) complex **XIII**.130

Figure 6.3. (a)(i) and (b)(i): Arrangement of *bis*-imidazolium cations residing in the cavities of calixarenes in complex **XII**, showing nearest contacts. (a)(ii) and (b)(ii): Space filling showing only the lower portion of a *bis*-imidazolium cation. 132

Figure 6.4. (i) Close contacts of the *bis*-imidazolium cation residing in the cavity of the calixarene in complex **XIII**, and (ii) space filling showing only the lower portion of the *bis*-imidazolium cation. 133

Figure 6.5. Packing diagram (viewed along *a*-axis) in complex **XII** showing the arrangement of *bis*-imidazolium cations (blue) and phosphonium cations (purple) (water molecules are omitted for clarity). 133

Figure 6.6. Packing diagram (viewed along *c*-axis) in complex **XIII** showing the arrangement of *bis*-imidazolium cations (blue) and phosphonium cations (purple) (water molecules are omitted for clarity). 134

Figure 6.7. Partial space filling of complex **XII** showing the arrangement of phosphonium cations (purple) within a single bilayer. 135

Figure 6.8. Packing diagram of complex **XIII** showing the space filling for phosphonium cations within a single bilayer. 135

Figure 6.9. Arrangements of sulfonated calixarene and N-butyl *bis*-imidazolium cation (blue) in complex **XIV**, (a), and complex **XV**, (b). 137

Figure 6.10. Packing diagram (viewed along *a*-axis) in complex **XIV** showing the arrangement of *bis*-imidazolium cations (blue) shrouded by phosphonium cations (purple) (water molecules are omitted for clarity). 137

Figure 6.11. (a)(i) and (b)(i): *Bis*-imidazolium cations of different configuration residing in the cavity of the calixarene in complex **XIV** showing close contacts. (a)(ii) and (b)(ii): Corresponding space filling images, but not for all of the cations. 139

Figure 6.12. Space filling diagram of complex **XIV** showing phosphonium cations in a single bilayer. 139

Figure 6.13. (a) Closest contacts of *bis*-imidazolium cation and calixarene in complex **XV**, and (b) space filling of the *bis*-imidazolium residing in the cavities of the calixarenes. 141

Figure 6.14. Partial space-filling diagram for complex **XV** along the *b*-axis showing the calixarenes in the crevice of the grid built-up from the phosphonium cations. 141

Figure 6.15. Partial space-filling diagram (viewed along *a*-axis) for complex **XV** showing bilayer arrangement with an N-methyl *bis*-imidazolium cation incorporated into two adjacent calixarenes (blue) and aligned in between calixarene (orange). (Water molecules and second parts of disorder are omitted for clarity). 142

Figure 6.16. (a) Extended structure of complex **XVI** with some space filling of calixarene and confined *bis*-imidazolium cations, embedded within the *bis*-phosphonium cations (blue and purple), viewed down the *a*-axis, and (b) similar projection showing water molecules (green) filling the interstices with the *bis*-imidazolium cation omitted. 145

Figure 6.17. Cartoon representation of ‘molecular capsule’ confined in the scaffold network built by *bis*-phosphonium cations in complex **XVI**. 145

Figure 6.18. Partial space filling for complex **XVI** showing the scaffold framework associated with orthogonally arranged *bis*-phosphonium cations (blue and purple) viewed down columns of calixarene. 146

Figure 6.19. Cartoon representation of calix[4]arene polymeric network in complex **XVII**, with the *bis*-imidazolium cation omitted for clarity. 147

Figure 6.20. (a) Partial space filling for complex **XVII** showing the gadolinium ion coordinated polymeric network of calixarenes, orientated 90^{o} with respect to each other, with the *bis*-phosphonium cations (orange) end capped by the cavitands. (b) Similar projection showing water molecules (blue) filling the interstices, with the *bis*-imidazolium cation omitted for clarity. 148

Figure 6.21. Hirshfeld fingerprint plots for *bis*-imidazolium cation, with specific contacts indicated for: (a) complex **XVI** and (b) complex **XVII**. 150

Figure 6.22. Hirshfeld fingerprint plots for water molecules, with specific contacts indicated for. (a) complex **XVI** and (b) complex **XVII**. 150

Figure 6.23. ^{1}H NMR spectra for (a) *bis*-imidazolium, (b) *bis*-imidazolium in *p*-sulfonatocalix[4]arene (1:2) and (c) *bis*-imidazolium in *p*-sulfonatocalix[4]arene with lanthanide cation, measured in D_2O (S)..152

Figure 6.24. Chemical shift changes of selected *bis*-imidazolium protons versus the *bis*-imidazolium cation at fixed calixarene concentration, measured in D_2O........153

Figure 6.25. 1D ROESY spectra of *bis*-imidazolium cation in *p*-sulfonatocalix[4]arene, acquired with a mixing time of 225 ms. The selectively excited protons (showing inverted signals) are (a) Hα, (b) Ar-H in calixarene, (c) benzyl aromatic in *bis*-imidazolium cation, (d) $H\beta_1$, (e) $H\beta_2$, (f) Hγ, (g) Ha, (h) Hb, (i) Hc, and (j) Hd...155

Figure 7.1. Components in synthesis of complex **XVIII**.....................................164

Figure 7.2. Projection down the *a*-axis with some space filling of calixarene (purple) and 3-(2-hydroxyethyl)-1-methylimidazolium cation (yellow), showing layers of phosphonium cations (orange)..165

Figure 7.3. Fingerprint plot, and front and back views of the Hirshfeld surface for 3-(2-hydroxyethyl)-1-methylimidazolium, mapped with d_{norm} and shape index…167

Figure 7.4. Stick representation showing close contacts between 3-(2-hydroxyethyl)-1-methylimidazolium and calixarene (H-bonds and C–H···π are shown as green and brown dashed lines respectively). Water molecule in close distance with the cation (inset top) and space filling showing the upper surface of the supermolecule is essentially hydrophilic (inset bottom)................................167

Figure 7.5. Fingerprint plots for (a) *p*-sulfonatocalix[4]arene and (b) [(3-methoxyphenyl) triphenyl-phosphonium..168

Figure 7.6. ^{1}H NMR spectrum for (top) 3-(2-hydroxyethyl)-1-methylimidazolium, and (bottom) 3-(2-hydroxyethyl)-1-methylimidazolium in *p*-sulfonatocalix[4]arene (1:1), measured in D_2O (S). 170

Figure 8.1. Synthesis of complexes **XIX** – **XXI**, showing the arrangement of calixarenes in the solid state structures..175

Figure 8.2. Complex **XIX** projected down the *b*-axis with some space filling of pyrrolidinium cation (blue), showing layers of phosphonium cations (green)......177

Figure 8.3. Stick representation of the supermolecules and pyrrolidinium cations in complex **XIX**. 178

Figure 8.4. Packing in complex **XX** with some space filling of pyrrolidinium cations (blue), showing layers of phosphonium cations (brown). 180

Figure 8.5. Close arrangement of the pyrrolidinium cations in the same bilayer in complex **XX**…..180

Figure 8.6. Some space filling of complex **XXI** showing some of the 1:1 supermolecules in space filling mode..182

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).........................183

Figure 8.8. ^{1}H NMR titration curve for the complexation of *p*-sulfonatocalix[4]arene and N-butyl-N-methylpyrrolidinium................................184

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. 185

Figure 9.1. Phenyl···phenyl interactions of the multiple phenyl embraces. 191

Figure 9.2. General occurrence of phenyl embraces [219]......................................193

Figure 9.3. Crystal packing in the structures of compounds **XXIIa** – **XXIXb**. 198

Figure 9.4(a). Phenyl embraces of the phosphonium cations in **off** (double arrow) and **ef** (single arrow) with the interacting phenyl rings in blue and the non-interacting in orange….. 202

Figure 9.4(b). Phenyl embraces of the phosphonium cations in **off** (double arrow) and **ef** (single arrow) with the interacting phenyl rings in blue and the non-interacting in orange….. 203

Figure 9.5. Fingerprint plots for phosphonium cations in compound **XXIIa** – **XXIXb**. 205

Figure 9.6. Bis-phosphonium cation and trifluoromethylsufonylamide anion in in compound **XXIXb**. 206

Figure 9.7. Fingerprint plots for anions in compound **XXIIa** – **XXIXb**. 208

Figure 10.1. Various functionalization for SWNTs: (A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent exohedral functionalization with surfactants, D) noncovalent exohedral functionalization with polymers, and E) endohedral functionalization [227]..213

Figure 10.2. (a) Defect-group functionalization of SWNTs with octadecylamine, (b) sidewall functionalization of SWNTs with alkyl azidoformiates and (c) hydrophilic SWNTs prepared by wrapping of the water–soluble poly (sodium 4-styrene sulfonate) around SWNTs [275, 242]……………………………………………. 215

Figure 10.3. (a) Fullerene C_{60} and (b)fullerene C_{70}. [246]......................................217

Figure 10.4. Structures of (a) [(calix[6]arene)$(C_{60})_2$] and (b)[(calix[6]arene)$(C_{70})_2$]. [271]……………………………………………………………………………222

Figure 10.5. Structures of the supramolecular complexes of C_{60} with calix[5]arenes . [274]……………………………………………………………………………223

Figure 11.1 Synthesis procedure for SWNT-*p*-sulfonatocalix[4]arene nano-composite. 229

Figure 11.2. (A) SWNT in water, and (B) SWNT-*p*-sulfonatocalix[4]arene nano-composite material in water. 229

Figure 11.3. Raman spectra of (a) pristine SWNT and (b) SWNT/*p*-sulfonatocalix[4]arene nano-composite. 231

Figure 11.4. FTIR spectra of (a) pristine SWNT, (b) SWNT/*p*-sulfonatocalix[4]arene nano-composite, and (c) *p*-sulfonatocalix[4]arene............233

Figure 11.5. Fluorescence emission (λ_{ex} = 540 nm) spectra of (1) *p*-sulfonatocalix[4]arene (6 μM, solid line), (2) pristine SWNT (0.05 wt%, dashed line) and (3) SWNT/*p*-sulfonatocalix[4]arene nano-composite (6 μM, dotted line).234

Figure 11.6. (a) TEM images showing the coating of SWNT by *p*-sulfonatocalix[4]arene, (b) carbon element mapping and (c) sulphur element mapping of the decorated SWNT with *p*-sulfonatocalix[4]arene nanoparticles....235

Figure 11.7. TGA thermogram of (1) *p*-sulfonatocalix[4]arene, (2) pristine SWNT, and (3) SWNT/*p*-sulfonatocalix[4]arene nano-composite....................................236

Figure 12.1 Structure of Brønsted acidic ionic liquid (**1**) and (**2**)..........................240

Figure 12.2 Preparation of water-soluble fullerene nano-composites. 241

Figure 12.3 Aqueous solutions of samples **A2** to **B5**..243

Figure 12.4 UV-visible spectra of (i) C_{60} (in toluene) and C_{60} nano-composites (in water); **A1** to **A5** and C_{70} (in toluene) and C_{70} nano-composites (in water); **B1** to **B5**……………………………………………………………………………...246

Figure 12.5 ^{1}H NMR spectra of C_{60} nano-composites (in D_2O, 25°C)..................248

Figure 12.6 ^{1}H NMR spectra of C_{70} nano-composites (in D_2O, 25°C)..................248

Figure 12.7 Particle size distribution graphs measured using DLS for water-soluble fullerene C_{60} nano-composites..250

Figure 12.8 Particle size distribution graphs measured using DLS for water-soluble fullerene C_{70} nano-composites..250

Figure 12.9 TEM images showing nano-particles for (i) **A1**, (ii) **A2**, (iii) **A3**, (iv) **A4** and (v) **A5** with the corresponding sulfur element mapping...........................251

Figure 12.10 TEM images showing nano-particles for (i) **B1**, (ii) **B2**, (iii) **B3**, (iv) **B4** and (v) **B5** with the corresponding sulfur element mapping. 252

List of Tables

Table 5.1. NOEs (ROESY) between guest molecules **IX**-**XI** and *p*-sulfonatocalix[4]arene in D_2O solution [strong(++), medium (+) or absence (-)]........122
Table 8.1. ^{1}H NMR titration results for complexation of *p*-sulfonatocalix[4]arene and N-butyl-N-methylpyrrolidinium in D_2O. 185
Table 9.1. Crystallographic Details for Complexes **XXIIa**-**XXIXb** 196
Table 12.1. Summary of components affording water-soluble fullerene nano-composite materials..243
Table 12.2. Summary of particle sizes measured using TEM and the Zeta potentials for the fullerene nano-composites. 249

Abbreviations

DLS	Dynamic Light Scattering
FTIR	Fourier Transform Infra Red spectroscopy
NMR	Nuclear magnetic resonance
ppm	Parts per million
SWNT	Single-walled carbon nanotube
TEM	Transmission Electron Microscope
TGA	Thermogravimetry Analysis
THF	Tetrahydrofuran
UV-Vis	Ultraviolet-visible

Acknowledgements

First and foremost I would like to thank my supervisor, Associate Professor Dr. Yatimah Alias for her guidance, encouragement and moral support which helped me in achieving all that I have during my PhD. I am grateful to my second supervisor, Professor Colin L. Raston for the opportunity to work within his research group and for his continuous support and helpful advice which have been valuable to my progress in research.

I must thank Dr. Alexandre Sobolev and Dr. Brian Skelton who has spent endless hours collecting, solving and refining my crystal structures. I would also like to acknowledge Dr. Lindsay Byrne for providing expert assistance with nuclear magnetic resonance spectroscopy. I would like to thank Dr. Mohamed Makha who has been very helpful and supportive.

I would like to express my appreciation to all the University of Malaya technical staff from the Chemistry Department and Electron Microscopy Unit for access to the analytical instruments and their valuable discussion and suggestion. I am grateful to the staff from the Centre for Microscopy, Characterisation and Analysis, The University of Western Australia for training and help in microscopy analysis.

I am also indebted to all the members of Raston research group which have made my time enjoyable and for providing valuable advice and friendship. Many thanks are due to the members of University of Malaya Centre for Ionic Liquids for their assistance and help over the years.

Special thanks are dedicated to University of Malaya for financial assistance and funding.

Lastly, I would like to convey my special appreciation to my parents and friends for their constant love and support.

Details of Publications and Abstracts

Publications

1. I. Ling, Y. Alias, M. Makha, C. L. Raston, ″Water solublisation of single-walled carbon nanotubes using *p*-sulfonatocalix[4]arene″, *New J. Chem.*, **2009**, ***33***, 1583–1587.

2. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, ″Constructing Multicomponent Materials Containing Cavitands, and Phosphonium and Imidazolium Cations″, *Cryst. Growth Des.*, **2009**, *9*, 4497–4503.

3. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, ″Calixarene C_8-imidazolium interplay as a design strategy for penetrating organic bilayers″, *CrystEngComm*, **2010**, *12*, 573–578.

4. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, ″Multi-component bilayers featuring [1-octyl-2,3-dimethylimidazolium∩*p*-sulfonatocalix[4]arene] supermolecules″, *New J. Chem.*, **2010**, *34*, 414–419.

5. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, ″*p*-Sulfonatocalix[4]arene–pyrrolidinium complexation in building multi-component layered arrays″, *Cryst. Growth Des.* **2010**, *10*, 1312–1318.

6. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, ″Lanthanoid assisted self assembly of imidazolium cations in organic bi-layers″, *CrystEngComm*, 2009, DOI: 10.1039/c000487c.

7. I. Ling, Y. Alias, A. N. Sobolev, L. T. Byrne, C. L. Raston, ″Selective binding of imidazolium cations in building multi-component layers″, *Chem. Eur. J.*, 2010, DOI: 10.1002/chem.200903320.

8. I. Ling, Y. Alias, C. L. Raston, ″Structural diversity of multi-component self assembled systems incorporating *p*-sulfonatocalix[4]arene″, *New J. Chem.*, 2010, DOI:10.1039/C0NJ00317D.

9. I. Ling, Y. Alias, A. N. Sobolev, L. T. Byrne, C. L. Raston, ″Supramolecular architecture containing end capping *bis*-imidazolium cations″, *CrystEngComm*, 2010, DOI: 10.1039/C002787A.

10. I. Ling, Y. Alias, A. N. Sobolev, C. L. Raston, "Hirshfeld surface analysis of phosphonium salts", *CrystEngComm*, 2010, DOI: 10.1039/C002832K.

11. I. Ling, Y. Alias, B. W. Skelton, C. L. Raston, ″*Exo*-cavity interplay of 3-(2-hydroxyethyl)-methylimidazolium with *p*-sulfonatocalix[4]arene in building multi-component layer″, *Aust. J. Chem.*, 2010, submitted.

Conference Abstracts:

1. I. Ling, Y. Alias and C. L. Raston. Interplay of *p*-Sulfonatocalix[4]arene with 1-Octyl-3-methylimidazolium in Building Multi-component Bilayer. *Regional Conference on Ionic Liquids 2009*. University of Malaya, Kuala Lumpur, Malaysia. 24-25th November, 2009. (Poster Presentation)

2. I. Ling, Y. Alias and C. L. Raston. Fullerene and Calixarene. *International Conference on Materials for Advanced Technologies 2009 (ICMAT 2009)*. Singapore. 28-3rd July, 2009. (Poster Presentation)

3. I. Ling, Y. Alias, M. Makha and C. L. Raston. Thin Film of Carbon Nanotube in Amphiphilic Calixarene as Charge Collectors in Conductive Electrodes for Energy Cells. *Ekspo Penyelidikan, Rekacipta & Innovasi 2009*. University of Malaya, Kuala Lumpur, Malaysia. 13-15th January, 2009. (Poster Presentation)

4. I. Ling. Interactions of *p*-Sulfonatocalixarene with SWCNT. *The17th Electron Microscopy Society Malaysia Scientific Conference (EMSM)*. Shah Alam, Selangor, Malaysia. 18-20th December, 2008. (Micrograph Competition)

5. I. Ling, Y. Alias, M. Makha and C. L. Raston. Characterization of Water-soluble *p*-Sulfonatocalix[4]arene and Single-walled Carbon Nanotube. *International Conference on Molecular Chemistry 2008*. University of Malaya, Kuala Lumpur, Malaysia. 25-27th November, 2008. (Oral Presentation)

6. I. Ling, Y. Alias and C. L. Raston. 'Molecular capsules' based on *p*-sulfonatocalix[4]arene intercalated by imidazolium and phosphonium cations. *International Conference on Molecular Chemistry 2008*. University of Malaya, Kuala Lumpur, Malaysia. 25-27th November, 2008. (Poster Presentation)

7. I. Ling, Y. Alias, M. Makha and C. L. Raston. Supramolecular complexation of fullerenes with *p*-sulfonatocalix[4]arene. International Conference on Nanoscience and Nanotechnology 2008 (NANO-SciTech 2008). Universiti

Teknologi Mara, Selangor, Malaysia. 18-21th November, 2008. (Poster Presentation)