

Development of asymmetric ammonium-based room temperature ionic liquids

A thesis submitted to The University of Manchester for the degree of

Doctor of Philosophy

In the Faculty of Engineering and Physical Sciences

2012

Hana Bashir Ali Alhanash

School of Chemistry

Contents

	page
Contents	2
List of Figures	6
List of Schemes	7
List of Spectra	9
List of Tables	11
Abstract	14
Declaration	15
Copyright statement	16
Acknowledgements	17
The author	17
Abbreviations	18
Symbols	19

1. Introduction

1.1	Introduction to ionic liquids	21
1.2	Nomenclature of ionic liquids	26
1.3	Synthesis of ionic liquids	28
1.4	Characteristic properties of ionic liquids	34
1.4.1	Melting points and thermal stabilities	34
1.4.2	Viscosity	44
1.4.3	Density	47
1.4.4	Hydrophobicity	48
1.4.5	Electrochemical properties	50
1.5	Summary of ionic liquid properties	52
1.6	Applications of ionic liquids	53

1.6.1	Ionic liquids as solvents	55
1.6.2	Ionic liquids in catalysis	59
1.6.3	Ionic liquids in electrochemistry	61
1.6.4	Ionic liquids in large scale applications	63
1.7	Aims and objectives	64
1.8	References	67

2.0 Synthesis and characterization of asymmetric aliphatic quaternary ammonium salts

2.1	Introduction	79
2.2	Synthesis and characterization of asymmetric quaternary ammonium halides	81
2.2.1	Synthesis and characterization of C1 series, N _{111R} X	81
2.2.2	Synthesis and characterization of C2 series, N _{112R} X	85
2.2.3	Synthesis and characterization of C3 series, N _{113R} X	89
2.2.4	Synthesis and characterization of C4 series, N _{114R} X	91
2.2.5	Synthesis and characterization of C6 series, N _{116R} X	97
2.3	Synthesis of completely asymmetric quaternary ammonium salts, N _{14R(14)} X	100
2.4	Melting points of asymmetric quaternary ammonium salts	105
2.5	Conclusion	109
2.6	References	111

3.0 Synthesis and characterization of fluorinated and non-aliphatic quaternary ammonium salts.

3.1	Introduction	113
3.2	Synthesis and characterization of asymmetric fluorinated quaternary ammonium salts	115
3.3	Synthesis of completely asymmetric fluorinated quaternary ammonium salt	124
3.4	Synthesis and characterization of asymmetric non-aliphatic quaternary ammonium salts, with benzyl, allyl and cyclohexyl substituents	130
3.4.1	Synthesis and characterization of dimethylbenzylalkylammonium halide series of compounds, N _{11BR} X	130
3.4.2	Synthesis and characterization of dimethylallylalkylammonium	

	Halide series of compounds, N _{11AR} X	135
3.4.3	Synthesis and characterization of dimethylcyclohexylammonium halide series of compounds, N _{11CR} X	138
3.5	Conclusion	142
3.6	References	143
4.0	Ion-exchange of asymmetric quaternary ammonium halides using fluorinated anions.	
4.1	Introduction	146
4.2	Ion-exchange of asymmetric quaternary ammonium halides with Lithium bis(trifluoromethanesulfonylimide)	147
4.3	Synthesis of the completely asymmetric quaternary ammonium bis(trifluoromethanesulfonylimide) salt	163
4.4	Synthesis of bis(perfluoroalkanesulfonylimide) potassium salts	165
4.5	Ion-exchange of asymmetric quaternary ammonium halides with potassium heptafluoroniobate(V)	173
4.6	Ion-exchange of asymmetric quaternary ammonium halides with potassium trifluoromethanesulfonate	177
4.7	Ion-exchange of asymmetric quaternary ammonium halides with hexafluorophosphate and tris(pentafluoroethyl)trifluoro phosphate	180
4.8	Ion-exchange of asymmetric non-aliphatic quaternary ammonium halides with lithium bis(trifluoromethanesulfonylimide)	185
4.9	Conclusion	188
4.10	References	189
5.0	Physical properties of developed asymmetric quaternary ammonium-based RTILs.	
5.1	Introduction	191
5.2	Thermal properties	191
5.3	Viscosity and conductivity measurements	207
5.4	Hydrophobicity	211
5.5	Density	213
5.6	Electrochemical properties	218
5.7	Conclusion	221
5.8	References	223

6.0	Experimental	
6.1	General details	226
6.2	Synthesis of asymmetric aliphatic quaternary ammonium halide salts	228
6.3	Synthesis of asymmetric quaternary ammonium halide salts with cyclohexyl, benzyl and allyl groups	233
6.4	Synthesis of completely asymmetric quaternary ammonium halide salts	237
6.5	Synthesis of fluorinated asymmetric quaternary ammonium halide salts	239
6.6	Synthesis of completely asymmetric fluorinated quaternary ammonium salt	242
6.7	Synthesis of asymmetric quaternary ammonium salts of bis(trifluoromethanesulfonylimide) anion	243
6.8	Synthesis of potassium bisperfluoroalkylsulfonylimide ($C_8F_{18}KNO_4S_2$) and potassium perfluoroalkylsulfonates	256
6.9	Synthesis of asymmetric quaternary ammonium salts containing heptafluoroniobate(V) anion	261
6.10	Synthesis of asymmetric quaternary ammonium salts of trifluoromethane sulfonate	264
6.11	Synthesis of asymmetric quaternary ammonium salts of hexafluoro phosphate and (trispentafluoro)trifluorophosphate anions	268
7.0	Conclusion and future work	
7.1	Conclusion	274
7.2	Future work	276
8.0	Appendix	
8.1	Abstract for poster presentation, Shape of Science Symposium, University of Manchester/ 05/07/2010	279
8.2	Abstract for poster presentation, 1 st international conference on Ionic Liquids in Separation and Purification Technology/Sitges, Spain 4-7/09/2011)	280
8.3	X-ray data	281

Word count: 64,082

List of figures	page
1.1 Melting points of various tributylammonium halide and trihexylalkylammonium halide salts	44
1.2 The phase behaviour of a mixture of water and a switchable hydrophilicity solvent (SHS)	50
1.3 Some applications of ionic liquids	54
2.1 Representation of the molecular structure and packing of $N_{111(10)}I$	84
2.2 Representation of the molecular structure and packing of $N_{112(18)}Br$	88
2.3 TG trace of $N_{114(14)}Br \cdot H_2O$ under Nitrogen, 10 °/min	94
2.4 TG trace of $N_{114(18)}Br \cdot H_2O$ under Nitrogen, 10 °/min	94
2.5 TG trace of $N_{1148}I$ under Nitrogen, 10 °/min	95
2.6 Representation of the molecular structure and packing of $N_{114(18)}Br \cdot H_2O$	96
2.7 Representation of the molecular structure and packing of $N_{114(12)}Br \cdot H_2O$	97
2.8 The appearance of the paste-like $N_{116(14)}Br$ salt	100
2.9 Effect of asymmetry on melting points of QA halides, $[N_{11RR}]^+$	107
3.1 Representation of the molecular structure and packing of $N_{114H}I$	118
3.2 Representation of the molecular and packing of $N_{11B(18)}Br \cdot H_2O$	134
3.3 Melting point of asymmetric quaternary ammonium non-aliphatic halides, $N_{11RR}X$	142
4.1 Representation of the molecular structure and packing of $N_{111(14)}TFSI$	151
4.2 TG chart for $N_{1128}TFSI$, under N_2 , 10 °/min rate	153
4.3 TG trace of dimethylbutyltetradecylammonium bis(trifluoromethanesulfonyl)imide $N_{114(14)}TFSI$	158
4.4 Physical appearance of $N_{114(14)}TFSI$ at r.t.	158
4.5 DSC trace for $N_{148(14)}TFSI$	164
4.6 Thermal stability trace of $N_{148(14)}TFSI$	164
4.7 DSC trace for $[N_{114(10)}], NbF_7^{2-} \cdot H_2O$	177
4.8 DSC trace for $N_{114(18)}FAP$	187
5.1 DSC trace for $N_{113(10)}TFSI$	192
5.2 DSC trace for $N_{114(10)}TFSI$	193
5.3 Melting points of non-fluorinated quaternary ammonium halide salts	194
5.4 Thermal stability trace for $N_{148(14)}TFSI$ under N_2 , 10 °/min	196
5.5 Thermal stability of some QA halide salts and their TFSI-exchanged analogues	197

5.6	Melting point and decomposition temperatures of dimethyl butyloctyl ammonium exchanged salts $N_{1148}X$ as a function of X	200
5.7	Correlation between melting points and decomposition temperatures of $N_{11R(14)}Br$ and TFSI salts	201
5.8	Comparison of 1H NMR spectra of $N_{1148}I$, $N_{1148}TFSI$ & $N_{1148}CF_3SO_3$	203
5.9	Part of 1H NMR spectrum showing different chemical shifts for different anions combined with $[N_{114(14)}]^+$	204
5.10	Part of 1H NMR spectrum showing different chemical shifts for different anions combined with $[N_{1148}]^+$	205
5.11	Viscosity Vs conductivity for asymmetric QA-TFSI RTILs	210
5.12	Conductivity Vs 1/viscosity for asymmetric QA-TFSI RTILs	210
5.13	Triphasic solution of hexane, water and $N_{111(10)}TFSI$	211
5.14	^{19}F NMR spectra of CF_3CH_2OH in D_2O and of the RTILs solubility tests in a D_2O solution containing trifluoroethanol	212
5.15	The densities of selected RTILs	213
5.16	Observed density vs calculated density (gml^{-1}) for N_{11RR} TFSI ILs	215
5.17	Experimental set up for electrochemical cell	218
5.18	Cyclic voltamogram for $N_{1148}TFSI$ at 100 mVs $^{-1}$, at a 10 μm diameter Pt microelectrode referenced to Ag pseudo reference electrode	221
5.19	Cyclic voltamogram for $N_{1168}TFSI$ at 100 mVs $^{-1}$, at a 10 μm diameter Pt microelectrode referenced to Ag pseudo reference electrode	221
5.20	Cyclic voltamogram for $N_{114(14)}TFSI$ at 100 mVs $^{-1}$, at a 10 μm diameter Pt microelectrode referenced to Ag pseudo reference electrode	221

List of schemes

1.1	Structure of "red oil" heptachlorodialuminate salt	22
1.2	Example of an eutectic mixture	22
1.3	Some common cations and anions found in ionic liquids	25
1.4	Structure of 1-alkyl-3-methylimidazolium $[C_nmim]^+$ cation	27
1.5	Five-membered heterocyclic cations of use in ionic liquids	25
1.6	Most important types of cations in ionic liquids	29
1.7	Synthesis path for the preparation of ionic liquids exemplified for an ammonium salt	29
1.8	Proposed reactions for removal of the mercury cation from water	31
1.9	Imidazolium and pyrrolidinium-cations with hexafluoroacetylacetonate anion	32
1.10	Some examples of functionalized ionic liquid cations and their uses	32
1.11	Structure of Yang's dicationic ionic liquid	33

1.12	Examples of asymmetric imidazolium ILs and their melting points	36
1.13	Structure of asymmetric trialkylsulfonium based ILs	37
1.14	Comparison of different mixed quaternary ammonium and chloroaluminate ILs and their melting points	39
1.15	Quaternary ammonium salts containing trialkyl(polyfluoroalkyl) ammonium iodides	40
1.16	Structures of the anions and cations studied by Matsumoto <i>et al.</i>	92
1.17	Structure of (fluorosulfonyl)(pentafluoroethanesulfonyl)imide	42
1.18	Synthesis of asymmetric quaternary ammonium halide salts	43
1.19	Protonation of an amidine by carbonic acid	49
1.20	The phase behaviour of a mixture of water and a switchable hydrophilicity solvent (SHS)	50
1.21	The acetylation of 1, 1, 2, 6-tetramethyl-3-isopropylindane and naphthalene in [emim]Cl-AlCl ₃ (X=0.67)	56
1.22	Demethylation of N,N-dimethylanilines with phenyl chloroformate	57
1.23	The complete synthesis of pravadoline in [bmim][PF ₆]	58
1.24	L-Proline-catalysed Aldol reactions between aromatic aldehydes and acetone in IL	60
1.25	Chlorination reaction of butane-1,4-diol in IL	63
1.26	Cations and anions used in this work	66
2.1	Synthesis of asymmetric quaternary ammonium halides	80
2.2	Asymmetric quaternary ammonium halides prepared in this study	80
2.3	Synthesis of trimethyloctylammonium iodide, N ₁₁₁₈ I	81
2.4	Synthesis of dimethylethyl-octylammonium iodide, N ₁₁₂₈ I	85
2.5	Synthesis of dimethylisopropyltetradecylammonium bromide, N ₁₁₃₍₁₄₎ Br	89
2.6	Synthesis of dimethylbutyl-octylammonium iodide, N ₁₁₄₈ I	91
2.7	Synthesis of dimethylhexyl-octylammonium iodide, N ₁₁₆₈ I	98
2.8	N-alkylation of secondary amines	101
2.9	Synthesis of completely asymmetric quaternary ammonium salt	102
3.1	Attempts to synthesise fluorinated quaternary ammonium species	115
3.2	Synthesis of completely asymmetric fluorinated quaternary ammonium salt, N _{148(C11H6F17)} I	125
3.3	Synthesis of dimethylbenzyl-octylammonium iodide, N _{11B8} I	131
3.4	Synthesis of dimethylallyl-octylammonium iodide, N _{11A8} I	136
3.5	Synthesis of dimethylcyclohexyltetradecylammonium iodide, N _{11C(14)} I	138
4.1	Biphasic synthesis of hydrophobic salts	148

4.2	Synthesis of dimethylethyl-octylammonium-bis(trifluoromethanesulfonyl)imide	152
4.3	Synthesis of dimethylbutyl-tetradecylammonium bis(trifluoromethanesulfonyl)imide, $N_{114(14)}TFSI$	157
4.4	Attempted route for the synthesis of potassium bis(nonafluorobutanesulfonyl)imide salt	166
4.5	Synthesis of potassium nonafluorobutane sulfonate, $C_4F_9SO_3K$	168
4.6	Synthesis of potassium bis(nonafluorobutanesulfonyl)imide, $[(C_4F_9SO_2)_2N]K$	169
5.1	Delocalisation of negative charge on $TFSI^-$ and $CF_3SO_3^-$ anions	203

List of spectra

2.1	1H NMR spectrum of trimethyloctylammonium iodide, $N_{1118}I$	82
2.2	1H NMR spectrum of dimethylethyl-octylammonium iodide, $N_{1128}I$	86
2.3	1H NMR spectrum of dimethylisopropyl-tetradecylammonium bromide, $N_{113(14)}Br$	90
2.4	1H NMR spectrum of dimethylbutyl-octylammonium iodide, $N_{1148}I$	92
2.5	1H NMR spectrum of dimethylhexyl-octylammonium iodide, $N_{1168}I$	98
2.6	1H NMR spectrum of methylbutyl-tetradecyl amine, $N_{14(14)}$	103
2.7	1H NMR spectrum of methylbutyl-octyl-tetradecylammonium iodide, $N_{148(14)}I$	104
3.1	1H NMR spectrum of dimethylbutylammonium iodide, $N_{114H}I$	116
3.2	1H NMR spectrum of dimethylbutyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecylammonium iodide, $N_{114(C3H6C8F17)}I$	122
3.3	^{19}F NMR spectrum of dimethylbutyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecylammonium iodide, $N_{114C3H6C8F17}I$	123
3.4	1H NMR spectrum of methylbutyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecyl amine, $N_{14(C11H6F17)}$	126
3.5	^{19}F NMR spectrum of methylbutyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecyl amine, $N_{14(C11H6F17)}$	127
3.6	1H NMR spectrum of methylbutyl-octyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecylammonium iodide, $N_{148(C11H6F17)}I$	128
3.7	^{19}F NMR spectrum of methylbutyl-octyl-1H, 1H, 2H, 2H, 3H, 3H-perfluoroundecyl ammonium iodide, $N_{148(C11H6F17)}I$	129
3.8	1H NMR spectrum of the dimethylbenzyl-octylammonium iodide,	

	$N_{1188}I$	132
3.9	1H NMR spectrum of the dimethylallyloctylammonium iodide, $N_{11A8}I$	137
3.10	1H NMR spectrum of dimethylcyclohexyltetradecylammonium bromide, $N_{11C(14)}Br$	139
4.1	Part of 1H NMR spectra of $N_{111(14)}Br$ and $N_{111(14)}TFSI$	150
4.2	1H NMR spectrum of dimethylethylloctylammonium iodide, $N_{1128}TFSI$	154
4.3	^{19}F NMR spectrum of dimethylethylloctylammonium bis(trifluoromethanesulfonyl)imide, $N_{1128}TFSI$	155
4.4	Parts of the 1H NMR spectra of $N_{1138}I$ and its exchanged $N_{1138}TFSI$ Salts	156
4.5	1H NMR spectrum of dimethylbutyltetradecylammonium bis(trifluoromethanesulfonyl)imide, $N_{114(14)}TFSI$ and part of that for $N_{114(14)}Br$	159
4.6	^{19}F NMR spectrum of dimethylbutyltetradecylammonium bis(trifluoromethanesulfonyl)imide, $N_{114(14)}TFSI$	159
4.7	Part of the 1H NMR spectrum of the halide and bistrifluorosulfonylimide salts of dimethylhexyloctylammonium cation, $[N_{1168}]^+$	162
4.8	^{19}F NMR spectrum of potassium nonafluorobutanesulfonate, $C_4F_9SO_3K$	166
4.9	^{19}F NMR spectrum of potassium bis(nonafluorobutane) sulfonylimide, $KNNf_2$	171
4.10	1H NMR spectrum of dimethylbutyltetradecylammonium bisonafluorobutanesulfonimide, $N_{114(14)}NNf_2$	172
4.11	^{19}F NMR spectrum of dimethylbutyltetradecylammonium bisonafluorobutanesulfonylimide, $N_{114(14)}NNf_2$	172
4.12	1H NMR spectrum of dimethylbutyloctylammonium heptafluoroniobate(V)	174
4.13	^{19}F NMR spectrum of dimethylbutyloctylammoniumheptafluoro niobate, $[N_{1148}]_2NbF_7$	175
4.14	1H NMR spectrum of dimethylbutyloctylammoniumtrifluoro methanesulfonate, $N_{1148}SO_3CF_3$	178
4.15	1H NMR spectrum of dimethylbutyltetradecylammonium trifluoromethanesulfonate, $N_{114(14)}SO_3CF_3$	179

4.16	^1H NMR spectrum of $\text{N}_{1148}\text{PF}_6$ and ^{19}F NMR spectrum of $\text{N}_{1148}\text{PF}_6$	182
4.17	^1H NMR (a) & ^{19}F NMR spectrum (b) of dimethylbutyloctyl ammonium trispentafluoroethyl trifluorophosphate.	183

List of tables

1.1	Melting points of selected ionic chlorides	35
1.2	Melting points for isomeric [bmim][PF ₆]	37
1.3	Melting points of some quaternary trialkyl(polyfluoroalkyl) ammonium iodides	41
1.4	Influence of different anions on the melting point of some imidazolium salts	41
1.5	Melting points of various quaternary ammonium salts (°C)	43
1.6	Viscosities of some common solvents at 25 °C	46
1.7	Viscosities of various 1-N-butyl-3-methyl imidazolium, [bmim] at 20 °C	47
1.8	Some of the ionic liquids used in the reaction depicted in scheme 1.21 and their yields	57
2.1	Elemental analysis of C1 series, $\text{N}_{111}\text{R}\text{X}$	83
2.2	Bond lengths and angles of $\text{N}_{111(10)}\text{I}$	83
2.3	Elemental analysis of C2 series, $\text{N}_{112}\text{R}\text{X}$	87
2.4	Selected bond lengths and angles of $\text{N}_{112(18)}\text{Br}$	88
2.5	Elemental analysis of C3 series, $\text{N}_{113}\text{R}\text{X}$	91
2.6	Elemental analysis of C4 series, $\text{N}_{114}\text{R}\text{X}$	93
2.7	Selected bond lengths and angles of $\text{N}_{114(18)}\text{Br}\cdot\text{H}_2\text{O}$	96
2.8	Elemental analysis of C6 series, $\text{N}_{116}\text{R}\text{X}$	99
2.9	Elemental analysis of tertiary amine, $\text{N}_{14(14)}$	103
2.10	Elemental analysis for the completely asymmetric quaternary ammonium salt, $\text{N}_{148(14)}\text{I}$	105
2.11	Effect of symmetry for quaternary ammonium bromide salts on their melting points	106
2.12	Asymmetry vs melting point (°C) for the $\text{N}_{11\text{RR}}'\text{X}$ quaternary halides (X= Br, I)	107
2.13	Melting points for [bmim]PF ₆ and [pmim]PF ₆ salts	108
2.14	Melting points for symmetric quaternary ammonium bromide salts	109
3.1	Elemental analysis for $\text{N}_{114}\text{H}\text{I}$	117
3.2	Selected bond lengths and bond angles for $\text{N}_{114}\text{H}\text{I}$	119
3.3	Elemental analysis for products of some hydrofluoroalkyl iodides	

	with Me ₂ BuN and Bu ₃ N	120
3.4	Elemental analysis for products from reaction of C3-spacer (Rfl) with Me ₂ BuN, MeiPrN and Bu ₃ N	121
3.5	Elemental analysis of the completely asymmetric fluorinated amine, N _{14C11H6F17}	127
3.6	Elemental analysis and melting points for the benzyl series, N _{11BR} X	133
3.7	Selected bond lengths and bond angles for the benzyl series, N _{11B(18)} Br.H ₂ O	135
3.8	Elemental analysis and physical states for the allyl series, N _{11AR} X	137
3.9	Elemental analysis and physical states for the cyclohexyl series, N _{11CR} X	140
3.10	Melting points of the non-aliphatic QA halides	141
4.1	Elemental analysis, mp of N ₁₁₁₈ I and trimethylalkylammonium bis(trifluoromethanesulfonyl)imide salts	149
4.2	Selected bond lengths and angles of N ₁₁₁₍₁₄₎ TFSI	152
4.3	Elemental analysis of N _{112R} TFSI	154
4.4	Melting points, appearance and elemental analysis data the halide and TFSI salts of [N ₁₁₃₈] ⁺	156
4.5	Melting points, appearance and elemental analysis of the iodide and TFSI salts of [N ₁₁₃₍₁₀₎] ⁺	157
4.6	Melting points of N ₁₁₄₍₁₄₎ X salts	158
4.7	Physical properties and elemental analysis of exchanged C4 series N ₁₁₄₍₁₄₎ TFSI	160
4.8	Physical appearance and elemental analysis of the dimethylhexyloctylammonium-TFSI, N ₁₁₆₈ TFSI, its iodide analogue and N ₁₁₆₍₁₀₎ TFSI	162
4.9	A comparison between melting points of some quaternary ammonium iodides and TFSI analogues	163
4.10	Elemental analysis and melting points of N ₁₄₈₍₁₄₎ TFSI	165
4.11	Elemental analysis of the isolated potassium nonafluorobutane sulfonate, C ₄ F ₉ SO ₃ K	166
4.12	Elemental analysis of potassium perfluorooctylsulfonate, C ₈ F ₁₇ SO ₃ K	167
4.13	Melting points and elemental analysis for the isolated nonaflates	168
4.14	Elemental analysis of potassium bis(nonafluorobutane sulfonylimide), C ₈ F ₁₈ KNO ₄ S ₂ (KNNf ₂)	170

4.15	Elemental analysis for $N_{114(14)}NNf_2$	171
4.16	Physical properties and elemental analysis of asymmetric quaternaryammonium heptafluoroniobates	176
4.17	Physical states and elemental analysis of quaternary ammoniumtrifluoromethanesulfonate	180
4.18	Elemental analysis and physical properties of dimethylbutylalkylammoniumhexafluorophosphate, $N_{114R}PF_6$	181
4.19	Elemental analysis and physical properties of $N_{114R}FAP$ salts	184
4.20	Melting points of $N_{114R}PF_6$ and $N_{114R}FAP$ salts	185
4.21	Physical properties and elemental analysis of non-aliphatic quaternary ammonium bis(trifluoromethanesulfonylimides)	186
5.1	Melting points of non-fluorinated quaternary ammonium salts, $N_{11RR}X$	194
5.2	A comparison of the melting points of some TFSI salts	195
5.3	Comparison of thermal stabilities of some novel TFSI-RTILs and their halide analogues	198
5.4	Physical properties of dimethylbutyloctylammonium-based ionic liquids, $N_{1148}X$ with different anions	199
5.5	Liquid range and onset decomposition temperature of selected TFSI-RTILs	201
5.6	Liquid range and physical properties of PF_6 and FAP-exchanged salts	206
5.7	Viscosities and conductivities of developed RTILs	209
5.8	Densities at 19 °C of asymmetric quaternary ammonium RTILs and derived molar volumes	214
5.9	Densities at 19 °C of non-aliphatic quaternaryammonium RTILs	215
5.10	Densities, estimated molar volumes and viscosities of $N_{11R(10)}$ TFSI series	216
5.11	Comparison of observed density with that calculated using two Different methods	217
5.12	Electrochemical windows of selected TFSI-RTILs	219

**Development of asymmetric quaternary ammonium-based room temperature
ionic liquids.**

Hana Bashir Ali Alhanash

Thesis submitted for the degree of Doctor of Philosophy
The University of Manchester
2012

Abstract

Ionic liquids (ILs) are salts with a melting point lower than 100 °C. Room temperature ionic liquids (RTILs) are a subset of these salts which are liquid at room temperature. Chapter one surveys the historical development of RTILs and their applications, concentrating in particular on quaternary ammonium-based systems. A series of asymmetric quaternary ammonium halide salts formulated as $N_{11RR'}X$ (where R = methyl, ethyl, propyl, butyl, hexyl, allyl, benzyl and cyclohexyl, R' = octyl, decyl, tetradecyl and octadecyl, X = I or Br) and $N_{14R(14)}I$ (where R = allyl, propyl, octyl and decyl) have been prepared and characterised. Introduction of asymmetry into the quaternary ammonium salts is shown to have a profound influence on their melting points and has been investigated as a primary step for the development of RTILs. Attempts to introduce fluorinated alkyl chains into the cation based on $Rf(CH_2)_nX$ compounds was successful when $n = 3$, but when $n = 2$, $RfCH=CH_2$ and $N_{11RH}X$ resulted.

Anion exchange using a range of fluorinated anions (including sulfonate, PF_6^- , $P(C_2F_5)_3F_3^-$ (FAP), heptafluoroniobates) resulted in 42 new RTILs. The TFSI⁻ anion is found to be the most promising candidate, and it led to the development of 21 new stable, hydrophobic room temperature ionic liquids. Introduction of asymmetry into the anion, e.g. replacing PF_6^- with FAP⁻ also lowers the melting points of these quaternary ammonium salts.

Investigation of the properties of these new ionic liquids showed that they are thermally stable ($T_d > 400$ °C) with wide liquid ranges (over 420 °C), relatively low viscosity, high conductivity and wide electrochemical windows (> 4 V). Some physical properties were found to be related directly to the chain-lengths of the substituent groups in the cation. The X-ray crystal structures of $N_{112(18)}Br$, $N_{114(18)}Br \cdot H_2O$, $N_{114}I$, $N_{11B(18)}Br \cdot H_2O$, $N_{111(10)}I$ and $N_{111(14)}TFSI$ are reported.

Declaration

No portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Signature

Date

Copyright statement

The author of this thesis (including any appendices and/or schedules to this thesis) owns certain copyright or related rights in it (the “Copyright”) and she has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

Copies of this thesis, either in full or in extracts and whether in hard or electronic copy, may be made **only** in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

The ownership of certain Copyright, patents, designs, trade marks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the thesis, for example graphs and tables (“Reproductions”), which may be described in this thesis, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions cannot and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

Further information on the conditions under which disclosure, publication and commercialisation of this thesis, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy (see <http://documents.manchester.ac.uk/DocuInfo.aspx?DocID=487>), in any relevant Thesis restriction declarations deposited in the University Library, The University Library’s regulations (see <http://www.manchester.ac.uk/library/aboutus/regulations>) and in The University’s policy on presentation of Theses

Acknowledgements

I would first like to thank 'god' for making me reach to this level!

I would like to thank my supervisor Dr. Alan K. Brisdon who gave me the opportunity to work in such an interesting topic and for his continuous guidance and encouragement throughout my research and writing up period. Many thanks to Dr Robin Pritchard for solving crystal structures and Martin Jennings and the microanalysis lab for running my microanalysis and for training on the DSC. Many thanks for Antony Thomas for his continuous assistance.

I would like to thank my entire family for their constant support, my parents whose belief and faith in me, gave me self-reliance to continue my studies, above all my husband and children whom, put up with the long hours and busy weekends, especially my husband for his support and assistance at all times.

Thanks for my sisters and brothers and very special thanks for my sister Fatma, whose assistance helped me to overcome many research and writing up difficulties and was always there for me, to support me and drive me through the good and bad times, wish her and my husband the best in their viva as well. Finally many thanks for the Libyan government for their funding.

The Author

The author completed her first degree and Masters in the University of Tripoli/Libya, gaining an MSc degree in inorganic Chemistry, graduating in 1998. Since October 2008 the author has worked under the supervision of Dr. Alan Brisdon at The University of Manchester working towards a PhD thesis. The author worked as a researcher in the Industrial Research Centre/ Tripoli since 1988.

Abbreviations

A	allyl group
B	benzyl group
C	cyclohexyl group
AAIL	amino acid-based ionic liquids
RTILs	room temperature ionic liquids
TFSI	bis(trifluoromethanesulfonylimide)
TSAC	(trifluoromethylsulfonyl)acetamide
BF ₄	tetrafluoroborate
PF ₆	hexafluorophosphate
TSIL	task-specific ionic liquids
S ₁₁₁	trimethylsulfonium
FTA	fluorosulfonyltrifluoromethanesulfonylimide.
FPFSI	fluorosulfonyl(pentafluoroethanesulfonyl)imide
Me	methyl
Et	ethyl
Bu	butyl
Hex	hexyl
Oct	octyl
(FH) _n F	fluorohydrogenate
N(CN) ₂	dicyanamide
VOCs	volatile organic solvents
DMF	dimethylformamide
DMSO	dimethylsulfoxide
HPLC	high performance liquid chromatography
BASIL	biphasic acid scavenging utilizing ionic liquids
EW	electrochemical window
IFP	Institut francais du petrole
DCM	dichloromethane
PS-TPP	polymer support triphenylphosphine
DIAD	diisopropylazo-carboxylate
THF	tetrahydrofuran
DABCO	1,4-diazobicyclo[2,2,2]octane
KNNf ₂	potassium bis(nonafluorobutanesulfonylimide)
FAP	tris(pentafluoroethyl)trifluorophosphate
DSC	differential scanning calorimetry
TG	thermogravimetric analysis

IL	ionic liquid
TETDP	trihexyltetradecylphosphonium
QA	quaternary ammonium

Symbols

ΔG_{fus}	Gibbs free energy of fusion
r	radius
K	Boltzman constant
T	absolute temperature
γ	surface tension
η	viscosity
T_c	crystallization temperature
T_d	decomposition onset temperature
T_m	melting point
T_g	glass transition temperature
V_m	molecular volume

1. Introduction

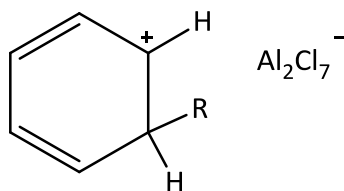
- 1.1. Introduction to ionic liquids
- 1.2. Nomenclature of ionic liquids
- 1.3. Synthesis of ionic liquids
- 1.4. Characteristic Properties of ionic liquids
 - 1.4.1. Melting points and thermal stabilities
 - 1.4.2. Viscosity
 - 1.4.3. Density
 - 1.4.4. Hydrophobicity
 - 1.4.5. Electrochemical properties
- 1.5. Summary of ionic liquid properties
- 1.6. Applications of ionic liquids
 - 1.6.1. Ionic liquids as solvents
 - 1.6.2. Ionic liquids in catalysis
 - 1.6.3. Ionic liquids in electrochemistry
 - 1.6.4. Ionic liquids in large scale applications
- 1.7. Aims and objectives
- 1.8. References

1.1. Introduction to ionic liquids

An ionic liquid is a salt which consists entirely of positively and negatively charged ions, just as sodium chloride (NaCl) does, but with a melting temperature below the boiling point of water (100 °C).^[1] Room temperature ionic liquids (RTILs) are a subgroup of these salts and are defined as materials which are liquids at or below room temperature. Ionic liquids are known by a number of synonyms in the literature, such as: “room temperature molten salts”, “low temperature molten salts”, “ambient temperature molten salts” and “liquid organic salts”.

A major distinction between ionic liquids and conventional molten salts, is that ionic liquids generally contain organic, rather than inorganic cations.^[1] As such ionic liquids avoid the worst disadvantage of molten salts, such as having to work at high temperatures and their highly viscous and corrosive nature. Furthermore, because they are often composed of organic ions they offer the possibility of almost limitless variation. As the complexity and size of the ions change, so does the melting point of the derived ionic liquid. For example, the melting point of NaCl is 803 °C whereas that of imidazolium chloride is only 80 °C, as a crystalline structure is energetically not favoured and the salt becomes an ionic liquid.

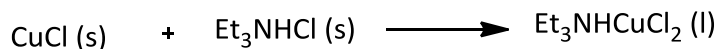
The first ionic liquid to be documented was “red oil” observed in the mid-19th century, during Friedel-Crafts reactions. At first this by-product could not be characterised. However, once NMR spectroscopy became widely used, Atwood of the University of Missouri, characterised the “red oil” as a heptachlorodialuminate complex of the formula shown in Scheme 1.1, which is a stable intermediate in the Friedel-Crafts reaction.^[2]



Scheme 1.1. Structure of “red oil” heptachlorodialuminate salt.

Subsequently simple alkylammonium nitrates, such as ethylammonium nitrate, $[\text{C}_2\text{H}_5\text{NH}_3]\text{NO}_3$, (formed by the reaction of ethylamine with concentrated nitric acid) with a melting point of $12\text{ }^\circ\text{C}$, were discovered in the early 20th century during world war I, when looking for new explosives.^[3] Despite this early discovery of an organic-based ionic liquid, most attention was paid to the molten and eutectic salts those days. In 1948, electrodeposition of aluminium with an N-alkylpyridinium halide was patented.^[4] Later, in 1951, Hurley and Weir reported that room temperature ionic liquids (RTILs) could be prepared by mixing and warming 1-ethylpyridinium chloride with anhydrous aluminium chloride, these liquids were the first to be used as solutions for electroplating of aluminium.^[5]

In the 1960's, Yoke of Oregon State University discovered what is known nowadays as 'Eutectic mixtures'. He reported that mixing copper(I) chloride with alkylammonium chloride, both being solids, resulted in a liquid at room temperature as shown in Scheme 1.2.^[6]



Scheme 1.2. Example of an eutectic mixture.

These eutectic mixtures were able to maintain similar reactions to those known to occur in their chloroaluminate analogues.

In the 1970s and 1980s, Osteryoung *et al.*^[7,8] and Hussey *et al.*,^[9a,10,11] carried out extensive research on organo-chloride/aluminium chloride ambient temperature ionic liquids. The authors used these chloroaluminate melts for the investigation of transition metal complexes in non-aqueous polar solvents. The tetraalkylammonium-chloroaluminate class of ionic liquids has been widely studied since the late 1970's. Despite the necessity to handle these materials under an inert atmosphere, the chloroaluminate(III) ionic liquids are extraordinary powerful solvents for kerogen, C₆₀ and many polymers.^[12]

Chloroaluminate-based ionic liquids, based on a mixture of organic chlorides and aluminium chlorides are commonly referred to as the first generation of room temperature ionic liquids. These ionic liquids are tremendously moisture sensitive and their handling requires an environment with exclusion of moisture. Therefore, the use of such ionic liquids is limited and they cannot be used in open environments or for general applications. Despite this, the chloroaluminate ionic liquids have been studied for many years as solvents and catalysts for organic reactions.^[2] Since these ionic liquid systems exhibit high electrical conductivity, enlarged electrochemical window and enhanced thermal stability compared with traditional molecular solvents, they were initially used as electrolytes in high energy batteries that were sealed and therefore had no contact with the atmosphere.

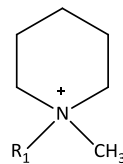
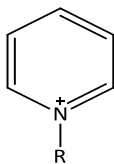
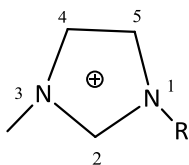
In the 1990's a new class of ionic liquids was described, based on 1-ethyl-3-methylimidazoliumtetrafluoroborate, which were less sensitive to moisture than the chloroaluminates.^[13] Thus, the first air and moisture stable imidazolium-based ionic liquid with either tetrafluoroborate or hexafluorophosphate anions was reported in 1992 by Wilkes and Zaworotko. These hexafluorophosphate and tetrafluoroborate ionic liquids showed better stability in air than the chloroaluminates, although in some cases their

decomposition at high temperature in the presence of water gave off the corrosive acid HF.^[14] This drawback spurred on research towards other fluorinated anions but with the fluorine bonded to a carbon atom, since the C-F bond is inert to hydrolysis, thus anions such as trifluorosulfonate, CF_3SO_3^- and bis(trifluoromethanesulfonyl)imide, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, TFSI⁻ were marketed. The first TFSI-containing ionic liquids were reported in 1995 by Koche *et al.*^[15]

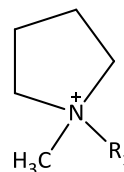
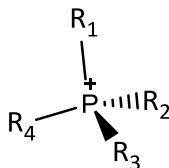
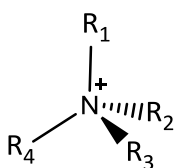
Since then, the number of papers on ionic liquids increased significantly in various fields of chemistry. A significant increase in the number of patents has also occurred, for example in the decade 1996-2006 the number of patents published increased from less than ten, in 1996, to more than 240 in the year 2006.^[16]

Modern RTILs are most likely to consist of nitrogen-, sulfur- and phosphorus-containing organic cations coupled with large organic or inorganic anions.^[3] Examples include, tetraalkylammonium, $[\text{R}_4\text{N}]^+$, aromatic amines, (pyridinium, imidazolium), saturated amines (piperidinium, pyrrolidinium), sulfonium-based $[\text{R}_3\text{S}]^+$ and phosphonium-based $[\text{R}_4\text{P}]^+$ systems. The combination of these bulky cations with inorganic anions such as AlCl_4^- , NO_3^- , PF_6^- and BF_4^- , dicyanoamide $[\text{N}(\text{CN})_2]^-$ and organic ions such as $[\text{C}_4\text{F}_9\text{SO}_3]^-$, $[\text{CF}_3\text{CO}_2]^-$, $[\text{N}(\text{CF}_3\text{SO}_2)_2]^-$, $[\text{CF}_3\text{CONCF}_3\text{SO}_2]^-$ and $[\text{C}(\text{CF}_3\text{SO}_2)_3]^-$ leads to a large number of ionic liquids that provide considerable flexibility in the ability to tailor their physical and chemical properties for a specific application. Scheme 1.3 shows some common cations and anions used in ionic liquids.

Cations:



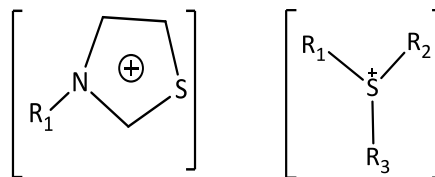
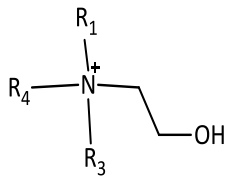
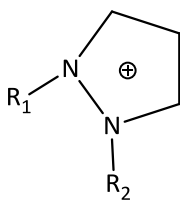
1-alkyl-3-methylimidazolium *N*-alkylpyridinium *N*-alkyl-*N*-methyl piperidinium



Ammonium

Phosphonium

N-alkyl-*N*-methylpyrrolidinium

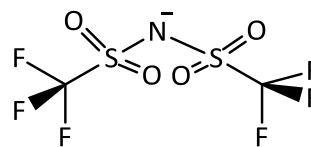
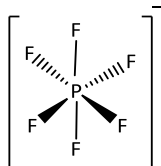
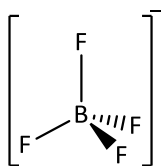


1,2-dialkylpyrazolium

Cholinium

N-alkylthiazolium Trialkylsulfonium

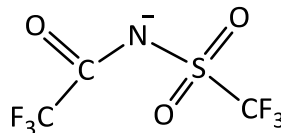
Anions:



Tetrafluoroboro

Hexafluorophosphate

Bis(trifluoromethanesulfonyl)imide



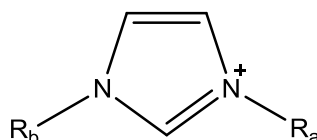
2,2,2-trifluoro-*N*-(trifluoromethanesulfonyl)acetamide.

Scheme 1.3. Some common cation and anions found in ionic liquids.

1.2 Nomenclature of ionic liquids

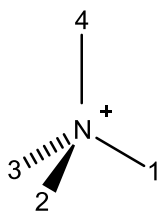
Because many ionic liquids are composed of complex organic molecules, a number of accepted shorthand names have been developed to identify ionic liquids. This includes for the imidazolium-based systems:

abim =



Where a and b refer to the first letter of the R_a and R_b carbon chain length names for example butyl, methyl imidazolium is abbreviated to bmim.

For quaternary ammonium systems shorthand of the type N_{1234}^+ is used, where the subscripts denote the chain length of each of the 4 alkyl chains of the quaternary ammonium cation.



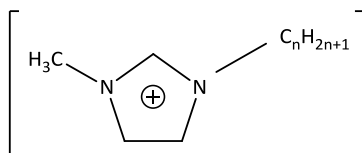
N_{1234}^+ = methylethylpropylbutylammonium.

Generally speaking, ionic liquids are composed of large asymmetric imidazolium or quaternary ammonium systems; comparatively small and symmetric ions tend not to form RTILs. These are coupled with large anions, which can either be symmetric, such as hexafluorophosphate or tetrafluoroborate, or less symmetric, such as bis(trifluoromethanesulfonyl)

imide (TFSI⁻) or amides. The TFSI⁻ anion forms ionic liquids with many cations, except for the small symmetric quaternary ammonium [R₄N]⁺ systems. However the asymmetric amide, TSAC⁻, [CF₃CONSO₂CF₃]⁻ can form RTILs with even small symmetric quaternary ammonium ions such as the tetraethylammonium cation, [N₂₂₂₂]⁺.^[16]

These, so-called second generation, room temperature ionic liquids considerably expanded the range of applications to which room temperature ionic liquids could be applied. This was because the second generation room temperature ionic liquids shared the advantages of their predecessors but also remain stable when exposed to water and air.^[12,2,18] These systems included salts based upon poorly nucleophilic anions such as [BF₄]⁻, [PF₆]⁻, [CF₃CO₂]⁻, [CF₃SO₃]⁻ etc (Scheme 1.3), although low melting point salts based on other cations such as complex polycationic amines,^[19] and heterocyclic-containing drugs^[20,21] have also been prepared.

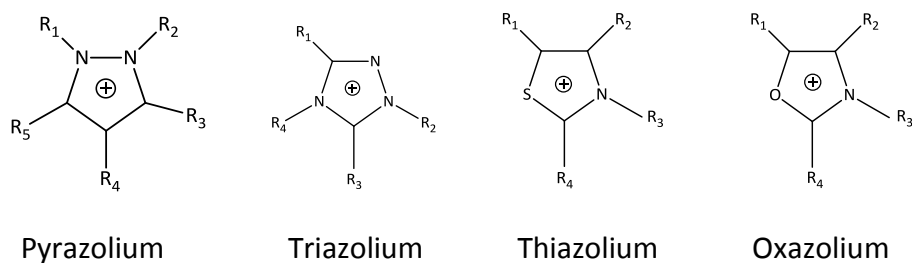
Many of the most commonly used ionic liquids are based around the 1-alkyl-3-methylimidazolium cation, shown in Scheme (1.4) especially the 1-ethyl-3-methylimidazolium, [emim]⁺ and 1-butyl-3-methylimidazolium, [bmim]⁺ cations.



Scheme 1.4. Structure of 1-alkyl-3-methylimidazolium [C_nmim]⁺ cation.

Imidazolium-based ionic liquids are the most versatile used ionic liquids in industrial applications due to their low volatility and viscosity.^[22-24,9a] They are used both as solvents and catalysts.^[25-30]

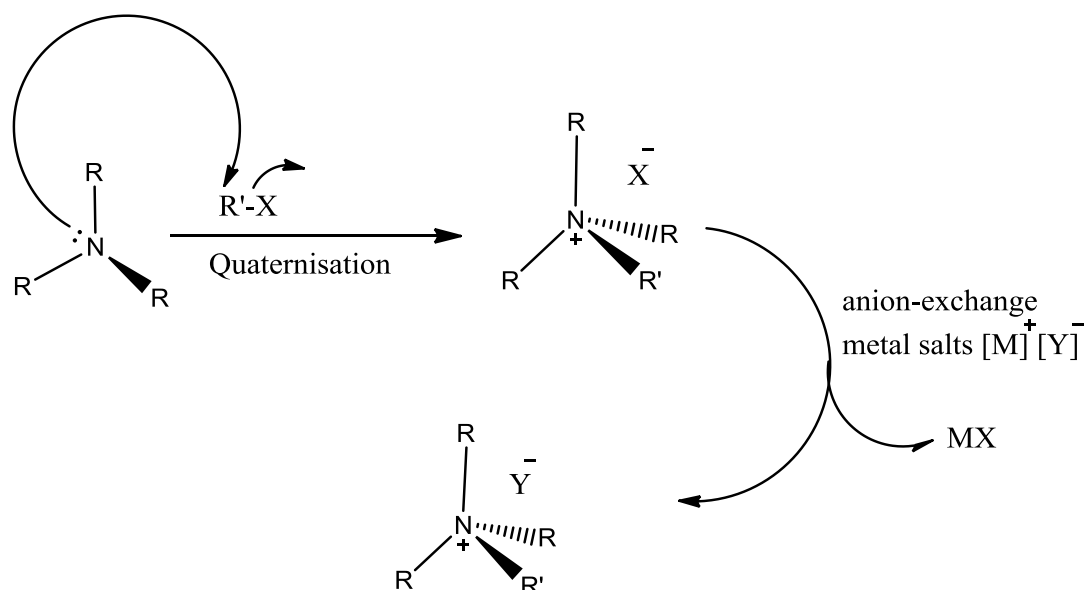
Scheme 1.5 shows some alternatives to the popular imidazolium cations including pyrazolium,^[31] triazolium,^[32] thiazolium^[26,33] and oxazolium.^[34]



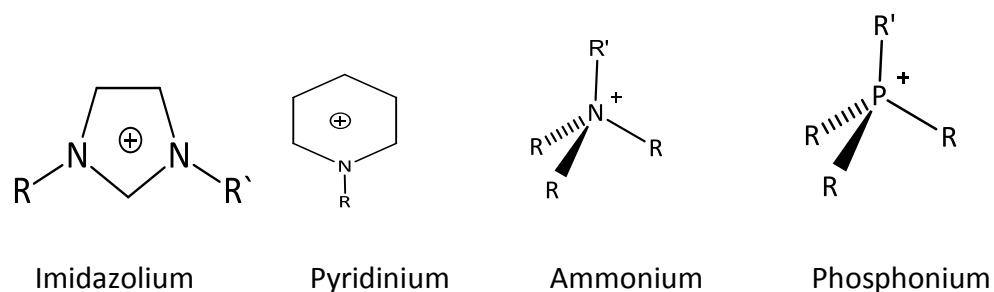
Scheme 1.5. Five-membered heterocyclic cations of use in ionic liquids taken, from ref [35].

1.3 Synthesis of Ionic Liquids

Generally ionic liquids are synthesized in two steps. The initial step is quaternisation (Scheme 1.6) of an amine or phosphine, for example, to form the cation.^[3] The most important reported cation types are shown in scheme (1.7).



Scheme 1.6. Synthesis path for the preparation of ionic liquids exemplified for an ammonium salt.



Scheme 1.7. Most important types of cations in ionic liquids.

This reaction occurs by nucleophilic attack by the amine onto the electron deficient carbon-centre directly bonded to the halide leaving group (X). The R-X bond is broken causing the formation of the quaternary salt. Quaternisation is then followed by an ion-exchange step, in which the halide is replaced with a larger anion as shown in Scheme 1.6.

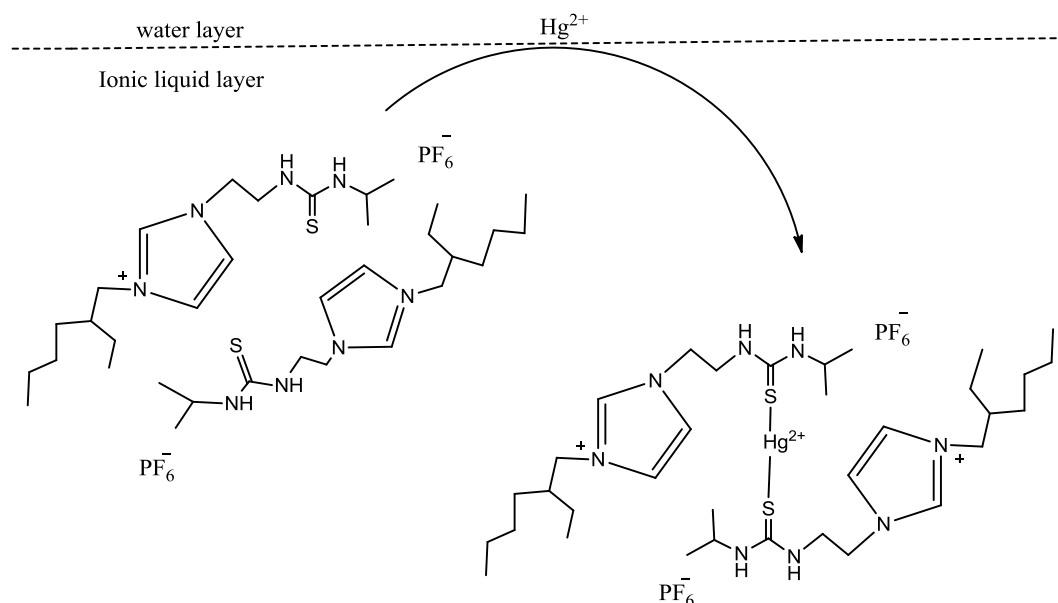
In some cases the desired cation is commercially available at reasonable cost, this is most often as the halide salt, e.g. 1-butyl 3-methylimidazolium chloride, [bmim]Cl, [R₄N]Cl or [R₄P]Cl, thus only the anion exchange step is required.

Quaternisation reactions in principle are extremely simple: the amine (or phosphine) is mixed with the desired alkylating agent, possibly without the need of a solvent, and the mixture is then heated and stirred (Scheme 1.6).^[1] This general technique can be applied to a wide range of substrates, including other amines such as pyridine,^[36] isoquinoline,^[37] 1,8-diazabicyclo[5,4,0]-7-undecene,^[38] 1-methylpyrrolidine,^[39] and trialkylamines,^[40] as well as for phosphines.^[41] The reaction temperature and time are very dependent on the alkylating agent employed, chloroalkanes require longer time being least reactive and iodoalkanes take a shorter time being the most reactive, the bulk and donating ability of the alkyl chain is also another factor to take into consideration.

There are also other possible routes for the synthesis of ionic liquids, such as that previously described for ethylammonium nitrate. One of these, which has been reported recently by the Abbott Group, involves the addition of a simple amide to AlCl₃ resulting in the formation of ionic liquids of the type [AlCl₂.nAmide]⁺AlCl₄⁻.^[42] In addition to their ease of preparation, these compounds showed lower sensitivity to water than other aluminium-containing ionic liquids and had physical properties similar to their quaternary ammonium-based ionic liquid analogues.

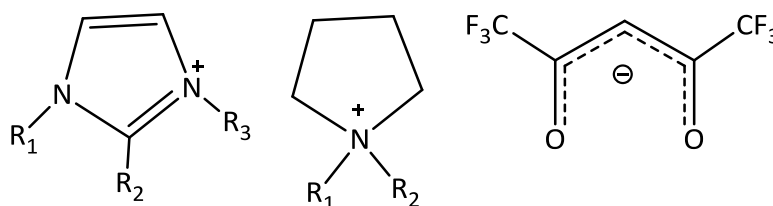
The synthesis of imidazolium-based ionic liquids using a household microwave oven is reported by Varma *et al.*^[43] The authors reported that this solventless, quick method (it requires only a few minutes) was suitable for the preparation of imidazolium-based ionic liquids with longer alkyl chain substituents giving reaction yields reaching up to 94 %.

Due to the ability to fine-tune the different functionalities of an ionic liquid (in either the cation or anion or both) it is found that the properties of the resulting ionic liquid can be varied to make them suitable for specific applications, such as in electrochemistry, separations, synthesis and catalysis. These ionic liquids are called task-specific ionic liquids (TSIL). In 2001, Rogers *et al.* were the first to report the use of task specific ionic liquids, based on derivatised imidazolium-based cations with task specific functionality (thiourea, thioether and urea) combined with PF_6^- anion.^[44] In this study the authors reported the use of electron-rich functional groups as ligands that have the ability to form complexes with heavy metal ions and sequester them in the IL phase, focusing on the removal of toxic heavy metal ions such as Cd(II) and Hg(II) from aqueous solutions as shown in Scheme 1.8. The derived imidazolium-based ionic liquids with functional groups acted both as hydrophobic solvent and metal ion extractant in liquid/liquid separation.



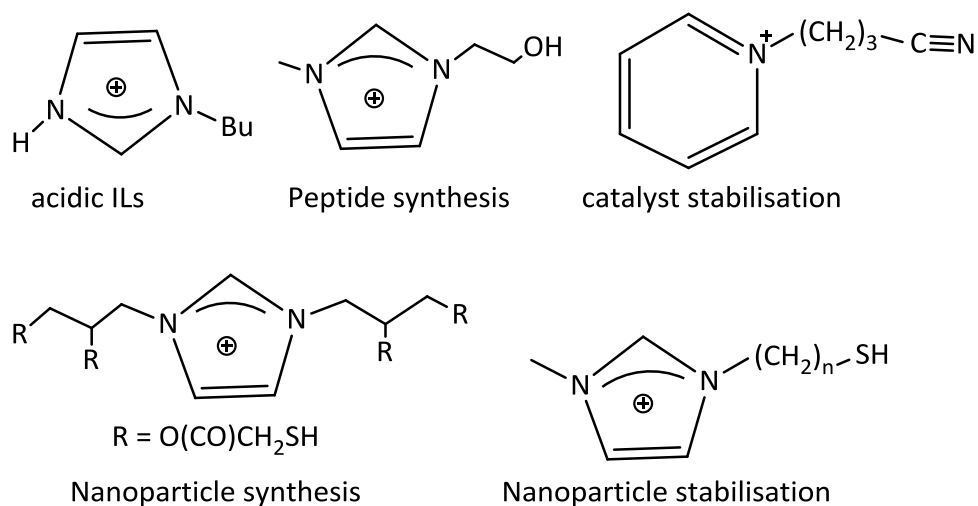
Scheme 1.8. Proposed reactions for removal of the mercury cation from water, taken from ref [44].

Nockemanns *et al.* developed new ionic liquids, where the anion forms a complex with a metal, based on hexafluoroacetylacetonate systems combined with imidazolium and pyrrolidinium cations (Scheme 1.9).^[45] These ionic liquids were suitable for the extraction of rare metal ions, such as neodymium from electronic scrap by forming a complex with the anion.



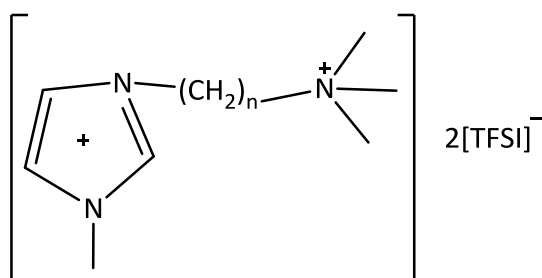
Scheme 1.9. Imidazolium and pyrrolidinium-cations with hexafluoroacetylacetonate anion, taken from reference [45].

Below are some other examples of functionalised ionic liquids, with TFSI⁻ or BF₄⁻, counterions, which were developed for specific applications, mainly in catalysis (Scheme 1.10).



Scheme 1.10. Some examples of functionalised ionic liquid cations and their uses, taken from ref [46].

In addition to the monocationic ionic liquids, ionic liquids consisting of two cations or 'dicationic' ionic liquids have also been reported. Yang *et al.* reported the synthesis of dicationic ionic liquids of the formula (MICnN₁₁₁-TFSI₂), where MI is the imidazolium cation, N₁₁₁ represents the trimethyl ammonium cation and Cn (n = 2, 5) is a spacer linking the two cations together, as shown in Scheme 1.11.^[47]



Spacer length n = 2, 5.

Scheme 1.11. Structure of Yang's dicationic ionic liquid.

Fascinatingly, the authors reported that increasing the spacer length from n = 2 to n = 5 reduced the melting point significantly and increased the thermal stability of the ionic liquid. The ionic liquid with the C5-spacer is a liquid at room temperature with a glass transition temperature, T_g , of -53 °C, whilst the C2-spacer compound was a solid with a melting point of 133 °C. Due to the useful properties of (MIC5N₁₁₁-TFSI₂), the authors suggested that this ionic liquid could be used as a promising additive in lithium secondary batteries. A similar tendency has been reported by Anderson *et al.* for analogous imidazolium-based and pyrrolidinium-based dicationic ionic liquids combined with four different anions (Br⁻, BF₄⁻, PF₆⁻ and TFSI⁻) where the increase in spacer length lowered the melting point.^[48] The spacer length varied from (n = 3 to 12 carbons). The melting points decreased in the order Br⁻ > PF₆⁻ > BF₄⁻ > TFSI⁻. Some interesting findings for this class of ionic liquids

is their high thermal stability and liquid range, which is higher than those of the more conventional monocationic ionic liquids, this enables them to be used in a wide variety of applications. For example, the liquid range for one of the pyrrolidinium-based dicationic ionic liquid, C9(mpy)₂-TFSI, (1-methylpyrrolidinium dication with a C9 spacer) is from -4 to > 400 °C. The density of these dicationic ionic liquids decreased with increase in the spacer length.

Armstrong *et al.* have further suggested that dicationic ionic liquids have another advantage over the monoatomic analogues, in that their properties are more tunable to a greater extent.^[49]

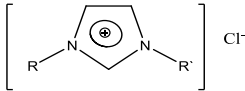
1.4. Characteristic Properties of ILs

1.4.1. Melting Points and thermal stabilities.

The key parameter for the assessment of an ionic liquid is, by definition, its melting point. Both the structure and chemical composition of the cations and anions contribute to the melting points of ionic liquids. Melting points of compounds are determined in a large part by the strength of their crystal lattice. This is controlled by three factors, intermolecular forces, molecular symmetry and conformational degrees of freedom of molecules.^[50] Comparisons of the melting points of different chloride salts clearly illustrate the influence of the cation. High melting points are characteristic for alkali metal chlorides, whereas chlorides with large organic cations melt at much lower temperatures (Table 1.1).

It has been reported that cations that produce low melting points are generally bulky organic species with low symmetry,^[18] which result in weak intermolecular interactions^[11] and an efficient distribution of charge in the cation.^[51]

Table 1.1. Melting points of selected ionic chlorides.^[3]

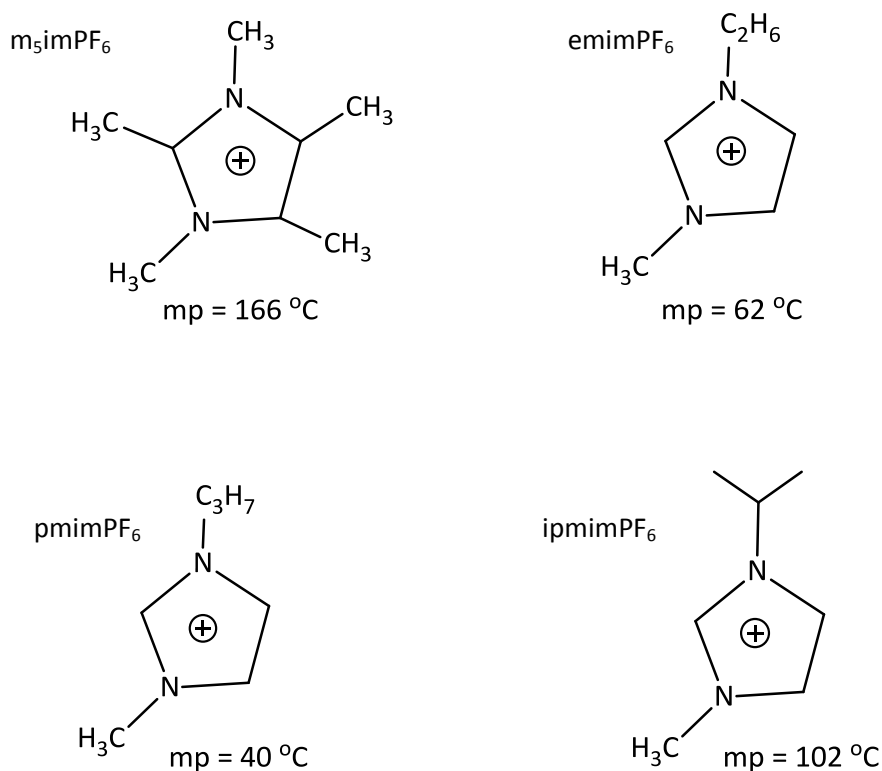
Salt	mp (°C)
NaCl	803
KCl	772
 $\left[\begin{array}{c} \text{R}-\text{N} \quad \text{N}-\text{R}' \\ \diagup \quad \diagdown \\ \text{C} \\ \diagdown \quad \diagup \\ \text{R}-\text{N} \quad \text{N}-\text{R}' \end{array} \right]^+ \text{Cl}^-$	$\text{R} = \text{R}' = \text{CH}_3$ ([mmim]Cl)
	125
	$\text{R} = \text{CH}_3, \text{R}' = \text{C}_2\text{H}_5$ ([emim]Cl)
	87
	$\text{R} = \text{CH}_3, \text{R}' = \text{n-butyl}$ ([bmim]Cl)
	65

This can be understood on the basis that such ions would cause a distortion from ideal close-packing of the ions in the solid state lattice, resulting in a reduction in the lattice energy and a depression of the melting point. Further reductions in melting points are possible by selecting an anion in which there is considerable charge delocalization which tends to decrease interionic interactions e.g. bistrifluoromethanesulfonyl imide or polyfluoro- β -diketonate.

The melting point of ILs has also been related to the symmetry of its ions.^[52] For example, the melting points of *N*-butylpyridinium ([Nbupy]⁺) salts^[53] are 100 °C higher than those of their 1-ethyl-3-methylimidazolium ([C₂mim]⁺) analogues which has been ascribed to the fact that [Nbupy]⁺ is more symmetric (it has a mirror plane) than [C₂mim]⁺, which has only C₁ symmetry.^[18]

Huddleston *et al.* reported that asymmetry in the imidazolium-based cation, [C_n(C₁im)]⁺, where n = 4, 6 and 8 depressed the melting point, whereas for n > 8 an increase in the melting point resulted, the authors described this as owing to the formation of a bilayer-type structure resulting from an inter-chain hydrophobic packing effect, i.e. hydrophobicity increases with increase in chain length (n) of the alkyl substituents.^[54] Ngo *et al.* reported that introducing asymmetry in imidazolium-based cations, significantly reduced

the melting temperature, examples are shown in Scheme 1.12 all with hexafluorophosphate (PF_6^-) as the counter ion.^[55]



Scheme 1.12. Examples of asymmetric imidazolium ILs and their melting points.

The highest melting point was for the more symmetric cation (C_{2v}), m₅imPF₆, (166 °C) and the lowest was pmimPF₆, 40 °C, due to the greater degrees of freedom and asymmetry provided in the larger linear *n*-propyl chain while the isopropyl containing material shows a melting point higher than its *n*-propyl isomer and the emimPF₆.

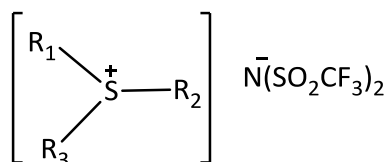
However, it was reported that an increase in the degree of branching within an alkyl chain of the imidazolium ring raises the melting point, this reflects the changes in the efficiency of the crystal packing due to the decrease in the free rotation volume, and the atom density is increased (Table 1.2).

Table 1.2. Melting Points for isomeric [bmim]PF₆.^[1]

N(1)-Substitution	Melting point (°C)
n-butyl ([bmim])	6
s-butyl ([bmim])	83
t-butyl ([bmim])	159

*[bmim]= butylmethylimidazolium

Fang *et al.* found that reducing the symmetry of the cations of trialkylsulfonium based ionic liquids reduced the melting points (Scheme 1.13).^[56]



Scheme 1.13. Structure of asymmetric trialkylsulfonium based ILs.

R₁ = CH₃, C₂H₅, R₂ = CH₃, C₂H₅, R₃ = CH₃, n-C₃H₇, n-C₄H₉, n-C₅H₁₁.

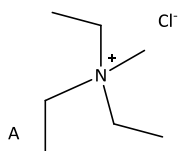
The authors studied the influence of the introduction of asymmetry in sulfonium-based TFSI ionic liquids on their melting points for three different series, S_{11R}TFSI (R = 1-5), S_{22R}TFSI (R = 1, 3, 4, 5) and S_{12R}TFSI (R = 3, 4, 5). All the S_{11R}TFSI and S_{22R}TFSI salts possessed melting points lower than their symmetric analogues, S₁₁₁TFSI (mp 44 °C) and the S₂₂₂TFSI (mp -14 °C), in each series as the linear alkyl chain (R) increases the melting point decreased reaching -60 °C, whereas the melting point of the S_{12R}TFSI series all showed melting temperature below -60 °C. This is explained by the authors that the asymmetry disrupts ideal close-packing of the ions and therefore lowers the melting point.

Krossing *et al.* proposed an explanation of why these salts are liquids based on the Gibbs free energy of fusion (Δ G_{fus}).^[57] According to their work, the

authors concluded that as the bulkiness and conformational flexibility of the ions increase, the lattice enthalpies get smaller and the entropy changes get larger, both of which support melting such that they observed a negative ΔG_{fus} for all the investigated ionic liquids at ambient conditions.

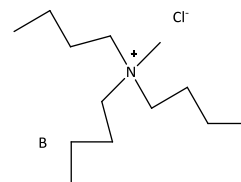
MacFarlane *et al.*,^[40,58-60] reported the aliphatic quaternary ammonium cations which have relatively short (C_1 - C_4) alkylchains could not easily form a RTIL. However, Angell *et al.*^[61,62] and Matsumoto *et al.*^[63-65a] claimed that some asymmetric and short chain aliphatic quaternary ammonium cations with a methoxyethyl or methoxymethyl group on the nitrogen atom formed ionic liquids below room temperature. Busi *et al.* reported quaternary ammonium salts of the type $R_2R'_2N^+X^-$ where R = methyl or ethyl, R' = alkyl groups with different carbon lengths ranging from 2 to 9, X = Br or I.^[65b] Their physical properties ranged from crystalline powders through sticky powders and microcrystalline gels and by increasing the chain length on the alkyl group there was a decrease in the melting points. The measured melting points ranged from 45 °C for the salt ($N_{1166}I$) to 175 °C for $N_{1133}I$ and some such as $N_{1133}Br$, $N_{2244}Br$ and $N_{2244}I$, showed no melting points before reaching the decomposition temperature of the salt.

Kim *et al.* attempted to lower the melting point of quaternary ammonium based ionic liquids by using longer alkyl chains on the quaternary ammonium ion to increase charge delocalization and also substituted one aliphatic alkyl group with a benzyl group (Scheme 1.14).^[66a]



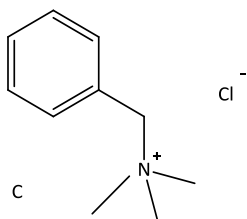
Triethylmethyammoniumchloride,

278 °C



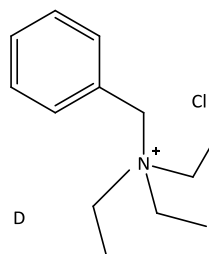
Tributylmethyammoniumchloride,

105 °C



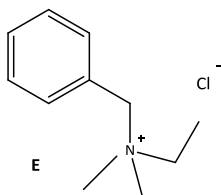
Benzyltrimethylammoniumchloride,

55 °C



Benzyltriethylammoniumchloride,

66 °C



Benzyl dimethylethylammoniumchloride, 13 °C

Scheme 1.14. Structural comparison of quaternary ammonium chloroaluminate ILs and their MPs ($N = 0.55$) for starting materials BTMACl, BTEACl, and BDMEACl.^[66a]

The benzyl substituted quaternary ammoniumchloroaluminate ionic liquids showed a significant decrease in the melting point compared to the quaternary aliphatic ammonium chloride.

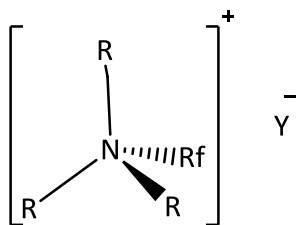
The authors interpreted these melting points in the following way: Compound D has a higher melting point than compound C due to charge delocalization. This result implies that there are other factors to the melting point. A high

degree of symmetry increases the melting point of the salts because of the ease of packing/crystallization, also, when comparing the ethyl and butyl groups in A and B, the benzyl group is more effective in disrupting symmetry.

Karna *et al.* also reported new quaternary ammonium salts with the TFSI anion, of the type $N_{11RR}TFSI$ (R = benzyl, *p*-methoxybenzyl) and $N_{RRR(ROR)}TFSI$ (R = aliphatic chains of 2-5 carbons length, ROR = $CH_3CH_2OCH_2CH_2-$).^[66b] The authors stated that the salts with the benzyl and *p*-methoxybenzyl substituents are solids whereas the aliphatic ammonium salts with the ether group were liquids with low melting points, except for $N_{333(ROR)}TFSI$ which is a room temperature solid with a melting point 58 °C.

Quaternary ammonium salts have been known as molten salts for a long time, Gordon and SubbaRao reported the synthesis of a series of bromide, chlorate and tetraphenylborate salts of the isomers of *n*-tetrapentylammonium salts where the chain lengths of the alkyl substituents are varied in such a way that the total number of carbons in the cationic species was always twenty.^[67] The authors reported that lowering the symmetry in the cation resulted in decreasing the melting point.

A series of water and thermally stable low-melting salts based on quaternary trialkyl(polyfluoroalkyl) ammonium cations have been synthesized as well (Scheme 1.15 and Table 1.3).^[68]



$R = n\text{-C}_3\text{H}_7, n = \text{C}_4\text{H}_9, i\text{-C}_8\text{H}_{17}$

$R_f = (\text{CF}_2)_x\text{CF}_3, x = 3, 7, 9$ $Y = \text{N}(\text{CF}_3\text{SO}_2)_2, \text{CF}_3\text{SO}_3, \text{C}_3\text{F}_7\text{CO}_2$.

Scheme 1.15. Quaternary ammonium salts containing polyfluoroalkyl groups, taken from ref [68].

Table 1.3 Melting points of some quaternary trialkyl(polyfluoroalkyl) ammonium iodides.^[68]

R	Rf	mp °C
<i>n</i> -C ₄ H ₉	CF ₃ (CF ₂) ₃	82
<i>n</i> -C ₄ H ₉	CF ₃ (CF ₂) ₇	91
<i>i</i> -C ₈ H ₁₇	CF ₃ (CF ₂) ₃	22
<i>i</i> -C ₈ H ₁₇	CF ₃ (CF ₂) ₇	20
<i>i</i> -C ₈ H ₁₇	CF ₃ (CF ₂) ₉	18

Besides the cation, the anion has a great influence on the melting point of the resulting ionic liquid. Table 1.4 shows the melting points of different salts with the 1-ethyl-3-methylimidazolium, [emim] cation, in most cases, as the size of the anion increases (whilst maintaining the same charge) the melting point decreases.

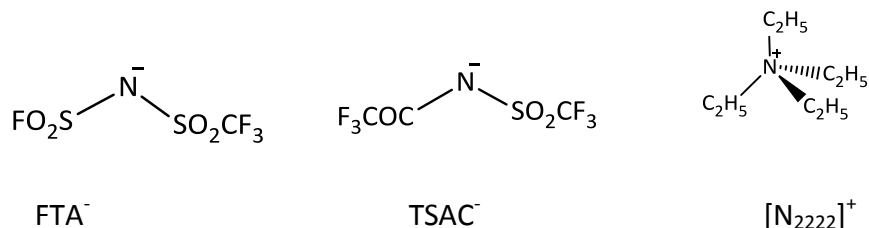
Table 1.4 Influence of different anions on the melting point of imidazolium salts.^[3]

Imidazolium salt	mp °C
[emim]Cl	87
[emim]NO ₂	55
[emim]NO ₃	38
[emim]AlCl ₄	7
[emim]BF ₄	6*
[emim]CF ₃ SO ₃	-9
[emim]CF ₃ CO ₂	-14

*= T_g (Glass transition temperature)

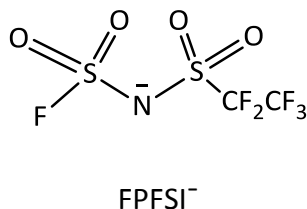
Asymmetry in the anion results in a remarkable change in the melting point as well. For example Zhou *et al.* and others^[69,70] prepared hydrophobic ionic liquids based on perfluoroalkyltrifluoroborate anions of general formula [emim]RfBF₃ (Rf = C₂F₅, *n*-C₃F₇ and *n*-C₄F₉) and [PY_{R,ROR}]C₂H₅BF₃ (R = C₃H₇, C₄H₉, C₅H₁₁, C₆H₁₃, C₆H₁₅; ROR = CH₃OCH₂, CH₃O(CH₂)₂, C₂H₅O(CH₂)₂, CH₃O(CH₂)₂OCH₂)₂ and observed that the melting points of the salts containing the lower symmetry anions [RfBF₃] and [C₂H₅BF₃] are lower than the corresponding [emim]BF₄ and [PY_{R,ROR}]BF₄ salts.

Matsumoto *et al.* have also reported that asymmetric amide anions such as $[(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})\text{N}]^-$ (TSAC⁻)^[65] and $[(\text{CF}_3\text{SO}_2)(\text{C}_2\text{F}_5\text{SO}_2)\text{N}]^-$ (C₁C₂⁻)^[70] reduce the melting point of ionic liquids when combined with aliphatic ammonium cations. Indeed both fluorosulfonyltrifluoromethanesulfonylimide $[(\text{FSO}_2)(\text{CF}_3\text{SO}_2)\text{N}]^-$ (FTA⁻) and trifluorosulfonyltrifluorocarbonylimide $[(\text{CF}_3\text{SO}_2)(\text{CF}_3\text{CO})\text{N}]^-$ (TSAC⁻) are the only anions to form ILs with the small sized symmetric tetraethylammonium cation ($[\text{N}_{2222}]^+$), N₂₂₂₂FTA has a melting point of 8 °C and N₂₂₂₂TSAC has a melting point of 21 °C (Scheme 1.16 shows the structure of TSAC⁻ and FTA⁻ and the cation reported).



Scheme 1.16. Structures of the anions and cations studied by Matsumoto *et al.*

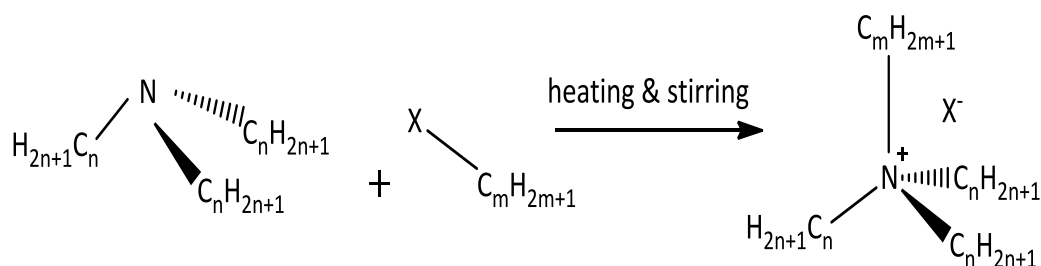
More recently, Liu *et al.* reported synthesis of a novel asymmetric anion, an isomer of TFSI, as shown in Scheme 1.17 (fluorosulfonyl) (pentafluoroethanesulfonyl)imide, (FPFSI⁻) which had a great influence on depressing the melting point when combined with various cations, quaternary ammonium, imidazolium, pyrrolidinium and piperidinium systems were reported and resulted in a new family of hydrophobic ionic liquids.^[71]



Scheme 1.17. Structure of (fluorosulfonyl)(pentafluoroethanesulfonyl) imide, taken from ref [71]

This new family of ionic liquids displayed low melting points, low viscosities, good thermal stabilities and wide electrochemical windows. This is the third anion to form a RTIL when combined with the small sized and highly symmetric, tetraethylammonium, $[N_{2222}]^+$ cation. For example, the melting point of N_{2222} FPFSI is 6 °C compared to its TSFI analogue, N_{2222} TSFI, which has a melting point of 105 °C.

Previously work in our group has also investigated the effects of asymmetry. The synthesis and characterization of a series of asymmetric tetraalkylammonium ionic liquids of general formula $(R_3R^+NX^-)$ (Scheme 1.18) was undertaken. The melting points of the resulting salts were reported, as shown in table 1.5.^[72a]



Where $n = 2, 4, 6$ or 8 , $m = 8, 10, 14, 18$ and $X = \text{Br}$ or I .

Scheme 1.18. Synthesis of asymmetric quaternary ammonium halide salts.

Table 1.5. Melting points of various quaternaryalkylammonium halide salts (°C).

	Octyliodide	Decylbromide	Tetradecylbromide	Octadecylbromide
NEt_3	94-97	110-115	93-98	86-90
NBu_3	72-76	22	21	64-67
NHexyl_3	67-73	-18*	-23*	42-45
NOctyl_3	95-98	101-105	51-54	43

* = T_g (Glass transition temperature)

The author concluded that introducing asymmetry into the quaternary ammonium salts has a considerable impact on the melting point, i.e. by reducing the symmetry of the ammonium cation the melting points of the corresponding salts are decreased. This effect of the degree of asymmetry is illustrated in figure 1.1.

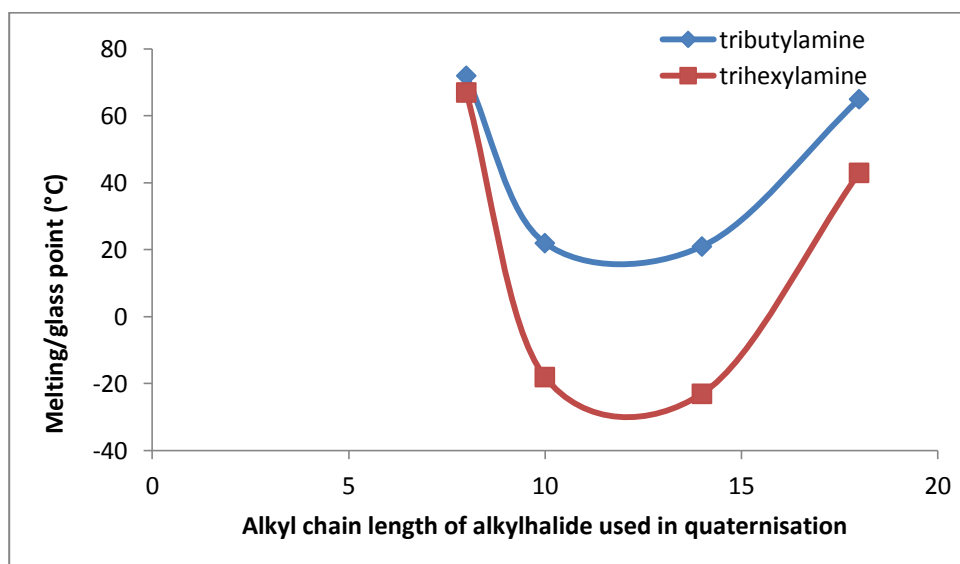


Figure 1.1. Melting points of various tributylalkylammonium halide and trihexylalkylammonium halide salts.^[72a]

1.4.2. Viscosity

One of the drawbacks of ILs is their high viscosity, this is especially important in the field of electrochemistry since this significantly lowers the conductivity and mobility of the ions. In the literature several models have been developed to account for ion mobility in molten salts, one of which is the 'hole' theory.^[72b]

This theory assumes that 'cavities' or 'holes' of different sizes arise on melting an ionic material, where the hole radius, r (*ca.* 1.5-2.5 Å) is related to the liquid's surface tension (γ), as shown in equation (1).

$$4\pi(r^2) = 3.5KT/\gamma. \quad (1)$$

K = Boltzman constant

T = Absolute temperature

In the case of molten salts, the average hole-sizes are larger than the average ion sizes, accordingly, the ability of smaller ions to move into these holes is relatively easy, and the liquids are mobile. However, in room temperature ionic liquids, where the temperature is lower, the cavity size is smaller, this coupled with the larger ion size means that the viscosity of room temperature ionic liquids is higher than that of the molten salts and conventional solvents.

The viscosity of ionic liquids is similar to that of oils, about 1-3 orders of magnitude greater than those of common molecular solvents^[73] (Table 1.6) and their viscosities range from 10 mPa.s to about 500 mPa.s at room temperature. Among the ionic liquids reported, the least viscous ionic liquids (< 45 mPa.s at 25 °C) are the imidazolium-based ionic liquids, typically based on the [emim] cation, combined with anions such as TFSI⁻ (28 mPa.s),^[74] [F(HF)_{2.3}]⁻ (4.8 mPa.s), [AlCl₄]⁻ (18 mPa.s), [Al₂Cl₇]⁻ (14 mPa.s), [N(CN)₂]⁻ (17-21 mPa.s), TSAC⁻ (25 mPa.s) and [BF₄]⁻ (37-43 mPa.s). However, most of these ionic liquids are of limited use because of the unsuitability of their anions in particular applications, for example, the dicyanoamide anion exhibits coordinating ability which may lead to deactivation of a catalyst in organic reactions and is electrochemically unstable, the chloroaluminates are moisture sensitive and the fluorohydrogenate is unstable chemically and thermally.

Table 1.6. Viscosities of some common solvents at 25 °C.

Solvent	η [mPa.s]
acetone	0.306
benzene	0.604
ethylene glycol	16.1
glycerol	1500
water	0.894
castor oil	985
sulphuric acid	24.2

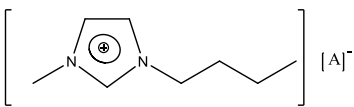
<http://en.wikipedia.org/wiki/viscosity>

Low viscosity ionic liquids have been successfully prepared by Zhang *et al.* by combining four amino acid anions, glycine, L-alanine, β -alanine and valine with small quaternary ammonium cations of the type $[R_3R^+N]^+$ and $[R_4N]^+$.^[75] The viscosities ranged from 29-283 mPa.s which are much lower than for the amino acid derived ionic liquids reported by Ohno *et al.*,^[76] for which the viscosity of phosphonium and imidazolium cations ranged from 520 - 4180 mPa.s.

More recently, in 2012 Matsumoto *et al.*^[77] reported the synthesis of ionic liquids with very low viscosities and very high conductivities based on the sulfonium cation, (S_{111} , S_{112} , S_{122} , S_{222} where the 1 and 2 subscripts refer to methyl and ethyl groups respectively e.g. S_{111} stands for trimethylsulfonium) combined with fluorohydrogenate anion ($(FH)_nF^-$) $n = 1.9, 2.0$, with the lowest viscosity (7.8 mPa.s) recorded for $S_{111}(FH)_{1.9}F$ at 25 °C. These ionic liquids possessed higher viscosities than their imidazolium homologues, for example $[emim](FH)_{2.3}F$ (4.8 mPa.s), and lower viscosities than their pyrrolidinium analogues, $EMPyr(FH)_{2.3}F$ (*N*-ethyl-*N*-methylpyrrolidinium fluorohydrogenate), 11.5 mPa.s. Based on the authors interpretations, this is explained as, an increase in the van der Waals interactions increases the viscosity while the increase in conformational degrees of freedom will decrease the viscosity of an ionic liquid.

On the other hand Wasserscheid *et al.* reported that the alkyl chain lengthening in the anion leads to an increase in the viscosity of ionic liquids as shown in table 1.7 when comparing imidazolium-based cation [bmim] systems with different anions. The author's interpretation was based on two factors, the affinity of forming H-bonding and the strength of van der Waals interactions, explaining that the $n\text{-C}_4\text{F}_9\text{SO}_3^-$ and $n\text{-C}_3\text{F}_7\text{COO}^-$ possessed stronger van der Waals interactions compared to their smaller sized analogues resulting in higher viscosity values.

Table 1.7. Viscosities of various 1-*N*-butyl-3-methyl imidazolium[bmim] salts at 20 °C.^[3]

	Anion, [A] ⁻	η [mPa.s]
	CF ₃ SO ₃ ⁻	90
	<i>n</i> -C ₄ F ₉ SO ₃ ⁻	373
	CF ₃ COO ⁻	73
	<i>n</i> -C ₃ F ₇ COO ⁻	182
	(CF ₃ SO ₂) ₂ N ⁻	52

In contrast to monocationic ionic liquids, dicationic ionic liquids have higher viscosities, for example the pyrrolidinium-based dicationic ionic liquid, C9(mpy)₂-NTf₂, (1-methylpyrrolidinium dication with a C9 spacer) have viscosity values ranging from 240 to 2500 mPa.s at 30 °C.^[48]

1.4.3. Density

Density is one of the most often measured properties of ILs, probably because nearly every application requires knowledge of the material density. Ionic liquids in general are denser than water with values ranging from 1 to 1.6 g/ml and their densities decrease with an increase in the length of the alkyl chain on the cation. For example, in ionic liquids composed of substituted imidazolium cations and the CF₃SO₃⁻ anion, the density decreases from 1.39 g/ml for [emim]⁺ to 1.33 g/ml for [eeim]⁺ (1-ethyl-3-

ethylimidazolium) to 1.29 g/ml for [bmim]⁺ and 1.27 g/ml for [beim]⁺ (1-butyl-3-ethyl imidazolium).^[1]

However, there are some ionic liquids that possess densities lower than 1 g/ml, such as those based on dicyanoamide anion, [N(CN)₂]⁻ when combined with pyrrolydinium cations, for example [PrMePy][N(CN)₂]⁻, [BuMePy][N(CN)₂]⁻, [HexMePy][N(CN)₂]⁻ have densities of 0.92, 0.94 and 0.92 g/ml respectively.^[17]

The densities of ionic liquids are also affected by the anions. Anions with higher molecular weight increase the density of the ionic liquid for a specific cation.

1.4.4. Hydrophobicity

ILs can generally be divided into two groups according to their solubility in water. Hydrophobicity can often be modified by a suitable choice of anion, an example, [bmim]BF₄ is completely miscible with water while its PF₆⁻ salt is not, which make them each suitable for different applications. Fluorinated anions such as TFSI⁻, TSAC⁻ usually form hydrophobic ionic liquids. For example, the water-immiscible (hydrophobic) IL such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF₆]) and 1-decyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([dmim][TFSI]) were used in glassy carbon electrodes as films and on carbon ceramics because of their hydrophobicity.^[78,79]

Matsumoto *et al.* reported a new family of hydrophobic ionic liquids, by combining large 1,3-dialkylimidazolium and small quaternary ammonium cations with the perfluoroalkyltrifluoroborates, ([RfBF₃])⁻, Rf = CF₃, C₂F₅, *n*-C₃F₇, *n*-C₄F₉) where they described the anion as weakly coordinating and more resistant to hydrolysis than their BF₄⁻ analogues due to their hydrophobicity.^[50]

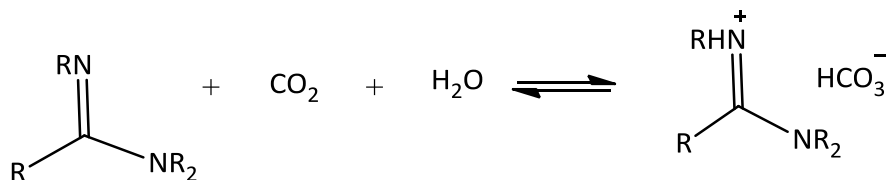
A new asymmetric fluorinated anion, has also been introduced by Liu *et al.*, the (fluorosulfonyl)(pentafluoroethanesulfonyl)imide (FPFSI⁻) that resulted in hydrophobic RTILs when combined with quaternary ammonium, imidazolium, pyrrolidinium and pyridinium cations.^[71]

The other type of IL is the water-miscible (hydrophilic) ILs such as [bmim][BF₄], which can also form electrochemically active films on glassy carbon that can be used in aqueous media.^[80]

Papaiconomou *et al.* reported that the pyridinium-based ionic liquids show lower miscibility in water than their imidazolium analogues and as the alkyl chain length on the anion increases hydrophobicity of the ionic liquid increases.^[81]

Amino acid derived imide anions of the formula, (CF₃SO₂NH-CH(R)COOCH₃), R = CH₃, CH(CH₃)₂, CH₂CH(CH₃)₂, alanine, valine and leucine respectively have been introduced as anionic components of ionic liquids, resulting in hydrophobic room temperature ionic liquids, with the imidazolium and phosphonium-based cations.^[76] Asymmetric phosphonium ionic liquids which are highly fluorinated have been reported to be suitable for developing new superhydrophobic coatings.^[82]

Interestingly, some ionic liquids showed switchable hydrophilicity (fig. 1.2). Jessop *et al.* reported that *N,N,N'*-tributylpentanamidine had reversible miscibility with water (Scheme 1.19), in air this IL had low solubility in water but was completely miscible in water under a CO₂ atmosphere (1 Bar).^[83]



Scheme 1.19. Protonation of an amidine by carbonic acid.

The authors utilised these solvents for the extraction of organic materials, such as soya bean oil, without the need for distilling the solvent from the product.

In the presence of both water and carbon dioxide, the amidine is protonated by carbonic acid, forming a water soluble bicarbonate salt. (Figure 1.2).

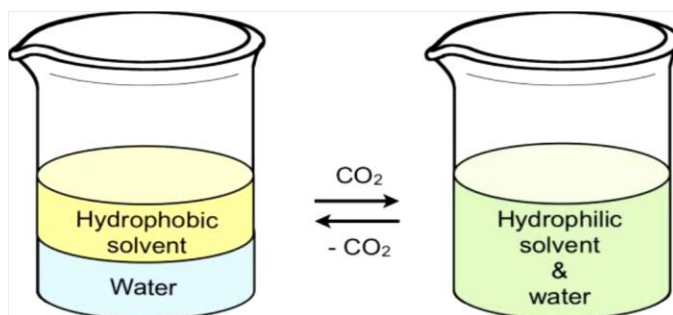


Figure 1.20. The phase behaviour of a mixture of water and a switchable hydrophilicity solvent (SHS), taken from ref [83].

High purity hydrophobic RTILs composed of *N*-methyl-*N*-alkylpyrrolidinium cations and perfluoroalkylsulfonylimide anions were synthesised by Giovanni *et al.*, suitable for electrochemical applications such as high-voltage super capacitors and lithium batteries,^[84] photochemistry, catalysis^[85] and electrosynthesis.

1.4.5. Electrochemical properties

Conductivity is a measure of the number of charge carriers and their mobility. Ionic liquids have relatively good ionic conductivities, compared to the best conventional organic solvents but have lower conductivity values compared to concentrated aqueous solutions of ionic salts. Because ionic liquids are composed only of ions, their conductivities are expected to be high,

unfortunately this is not the case. This may be explained due to a reduction in the number of charge carriers, sometimes because of ion aggregation or ion pairing, as well as reduced mobility of the large constituent ions of the ionic liquid.^[86] MacFarlane *et al.* reported that there is a trend in the conductivity values for a given anion, the imidazolium-based systems showed the highest conductivity followed by those containing the pyrrolidinium ion and the lowest were those based on tetralkylammonium systems. The authors rationalised this due the planarity of the cationic core, which gave the imidazolium ring a higher conductance than the tetrahedral arrangement of the alkyl groups in the quaternary ammonium systems, while the pyrrolidinium-containing ionic liquids possess an intermediate geometry and conductivity values. The pyrrolidinium ring approaches planarity, but due to its substituents above and below the ring its mobility is restricted.^[39]

Lewandowski reported that the imidazolium-based ionic liquids possess a higher conductivity than the ammonium-based systems with an average value of 10 mScm^{-1} , typically [emim]BF₄ has a conductivity of 14 mScm^{-1} . Whereas ionic liquids based on the pyrrolidinium or piperidinium ions possess lower conductivity in the range of $1\text{-}2 \text{ mScm}^{-1}$.^[87] The highest conductivity of 131 mScm^{-1} at 25°C for S₁₁₁(FH)_{1.9}F was reported recently by Matsumoto *et al.*^[77]

In 2009, Ohno *et al.* synthesised novel translucent thermotropic gels by mixing different ionic liquids together, one of which is an amino acid-based ionic liquid (AAIL), e.g. mixing ([P₄₄₄₄]⁺[amino acid]⁻ + [bmim]⁺TFSI⁻ (where amino acid = the anions of alanine, valine and lysine).^[88] These gels showed relatively high conductivity, are handled easily and turn into liquids when heated.

The electrochemical window is an important property and plays a key role in using ionic liquids in electrodeposition of metals and semiconductors. The electrochemical window is defined as the electrochemical potential range

over which the electrolyte is neither reduced nor oxidised at an electrode. It is well established that the electrodeposition of elements and compounds in water is limited by its low electrochemical window of only ~ 1.2 V. By comparison, ionic liquids, have significantly larger electrochemical windows e.g. 4.15 V for [bmim]PF₆ at a platinum electrode, and 4.10 V for [bmim]BF₄ at a glassy carbon electrode.^[89]

1.5. Summary of Ionic Liquid Properties

As described in the previous sections, ionic liquids are attractive as potential solvents for a number of reasons:

- They are generally colourless liquids with relatively low viscosities.
- They exhibit very low vapour pressures under ambient conditions and thus are effectively non-volatile.
- Being composed of two parts, there is a greater synthetic flexibility than is available for single component molecular solvents.
- Ionic liquids have been found that are good solvents for a broad spectrum of inorganic, organic and polymeric materials as well as gases; they are immiscible with numerous organic solvents and are sometimes immiscible with each other. Thus, applications in process intensification and as non-aqueous polar alternatives in biphasic systems are possible.
- In addition to their physical properties, they may be readily prepared from commercially available reagents. It is also now possible to source ionic liquids from a number of suppliers in a range of different qualities. This is particularly important in catalysis, where trace impurities can make a huge difference to the outcome of a reaction.
- Many ionic liquids involving fully quaternised nitrogen cations are non-flammable, this combined with very low or negligible vapour pressures has significant implications for health and safety concerns.^[35] Their non-volatility allows ionic liquids to be used in high vacuum systems without any loss and

permits a range of separation techniques such as distillation or sublimation of products and by-products, which are not possible using traditional low-boiling organic solvents. The non-flammability of ILs is particularly valuable when they are used as solvents for exothermic reactions.

1.6. Applications of Ionic Liquids

Due to their unique properties, ionic liquids have become one of the most important research targets in chemistry, physics, engineering and material science and technology.^[90] Their remarkable solvation capacity towards a variety of materials, inorganic, organic, organometallic and gas molecules, their lack of detectable vapour pressure, under normal conditions, high thermal stabilities and wide liquid range indicate a great potential for replacement of volatile organic solvents (VOCs) in synthetic chemical processes where the latter are considered as a source of environmental pollution problems. This allows ILs to be excellent candidates for industrial applications compared to volatile organic solvents. Organic solvents have been used for several centuries, and obviously occupy most of the solvent market in industry. However by comparing the properties of ionic liquids and organic solvents, it could be anticipated that industry may be a suitable environment for the use of ionic liquids.^[16]

Ionic liquids are viewed as a remarkable class of solvents and have been studied extensively in various applications such as electrochemistry, chemical synthesis, catalysis, liquid-liquid separation,^[12,2,91,44,92-97] and as media for organic and inorganic reactions.^[90,98,99] This has led to novel applications of RTILs in chemical sensors,^[100,101] dye-sensitised solar cells,^[102,103] batteries,^[104] as energetic materials,^[105] thermal fluids,^[106] hydraulic fluids,^[107] lubricants,^[108] ionogels,^[109] novel ion selective sensors^[101] anticancer agents,^[110] stationary phases in gas chromatography^[48] nuclear waste

treatment,^[111-114] and as flame-retarding additives in Li batteries.^[115] Ionic liquid gels were found to have good biocompatibility with enzymes, proteins and even living cells. The range of applications are summarised in the following diagram:^[16]

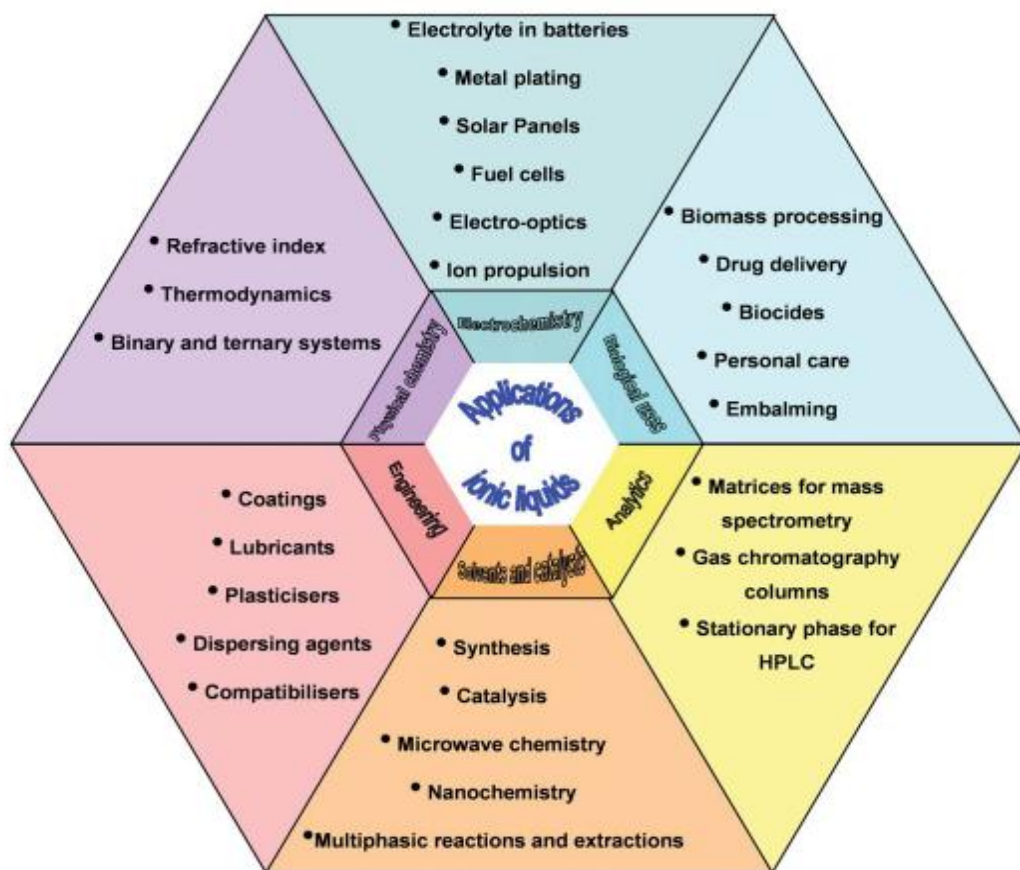


Fig.1.3. Some applications of ionic liquids taken from reference [16].

A number of specific applications of ionic liquids will be given in the remainder of this chapter.^[16]

1.6.1 Ionic liquids as solvents

The major enduring problems facing chemical industries and academia are the persistent dependence on enormous volumes of noxious, dangerous, combustible and environmentally harmful organic solvents. Problems related to the separation of these volatile solvents from reaction mixtures and their handling and recycling are encountered in addition to the need of high expenses accordingly.

Ionic liquids have been generating increasing interest over the last decade.^[1] Much of this interest is centred on their possible use as “greener” alternatives to volatile organic solvents as well as their use to improve the rate, specificity and yield of the reactions. Ionic liquids have the tendency to imitate the performance of dipolar aprotic solvents and subsequently can be used as green solvents in a wide range of reactions, replacing DMF and DMSO volatile solvents.^[95]

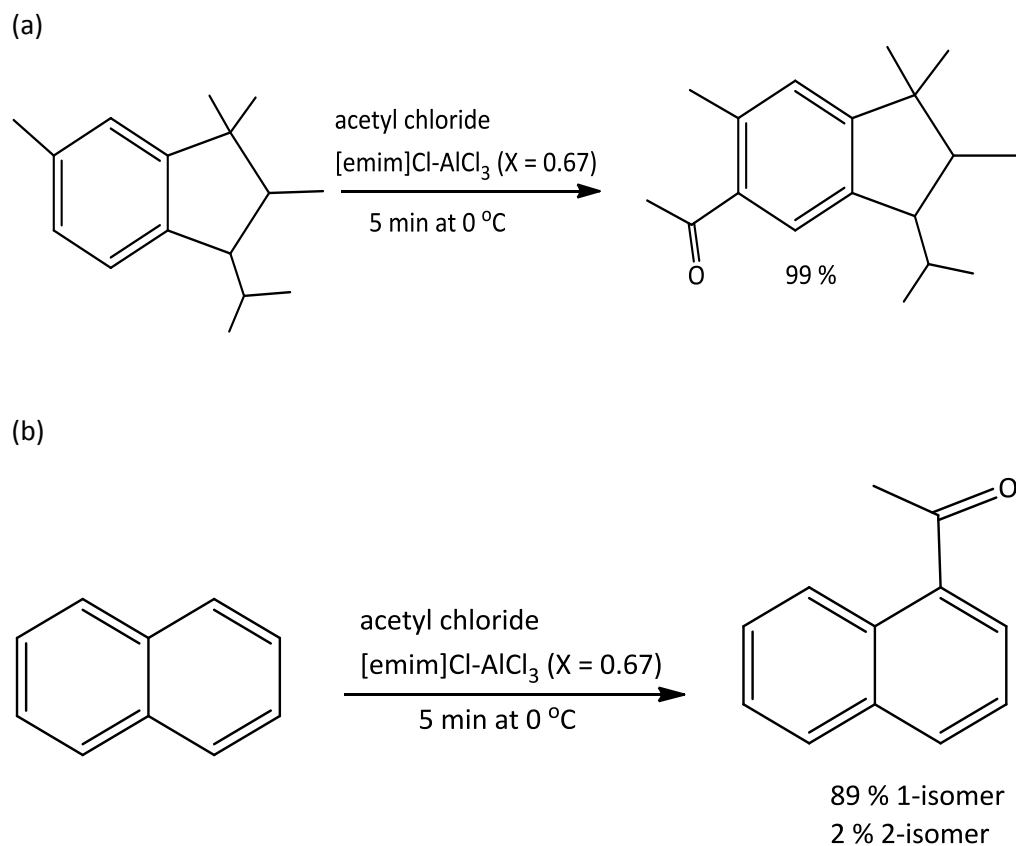
Higher yields and selectivities were observed in some Diels-Alder reactions on using ionic liquids as solvents, in contrast to those found with the best conventional organic solvents,^[116-118] [bmim]BF₄ has been found to be an excellent solvent for such reactions.^[116,117] Heck reactions could also be performed in a triphasic liquid system, [Bmim]PF₆, water and cyclohexane.^[27]

In the field of analytical chemistry, ionic liquids are used in many applications such as liquid/liquid separations,^[119] as additives in HPLC,^[120,121] electrolytes in electrochemical electrophoresis,^[122,123] and as stationary phases in gas liquid chromatography.^[124,48]

The fundamental aspect that ionic liquids hold is their wide liquidus range.^[1] The liquidus range is the temperature range between the melting point and the boiling point of solvents. No molecular solvents can match the liquidus range of ionic liquids, and only a few liquid polymers come near to doing so.

A few examples for the use of ionic liquids as solvents are shown below:-

The fragrance molecules of great commercial importance are traseolide® (5-acetyl-1,1,2,6-tetramethyl-3-isopropylindane) and tonalid® (6-acetyl-1,1,2,4,4,7-hexamethyltetralin), which are synthesized using Friedel-Crafts acylation in the chloroaluminate(III) ionic liquid, [emim]Cl-AlCl₃ in high yields (Scheme 1.21).^[12]

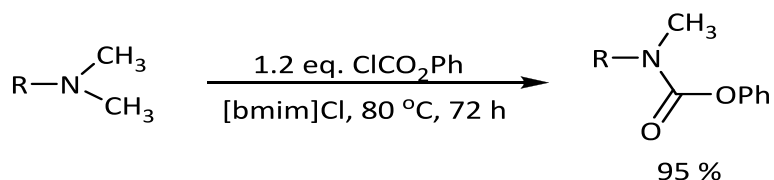


Scheme 1.21. The acetylation of 1,1,2,6-tetramethyl-3-isopropylindane (a) and naphthalene (b) in [emim]Cl-AlCl₃.^[125]

Where X represents the mole fraction of AlCl₃ in the tetrachloroaluminate(III) ionic liquid, {X(AlCl₃)}.

Isomerization and cracking reactions occur rapidly in the same ionic liquid as well.^[12] A typical example is the conversion of polyethylene to a mixture of gaseous alkanes having general formula (C_nH_{2n+2} , $n = 3 - 5$). The advantage of these systems is that in the chloroaluminate (III) ionic liquids reaction occurs at a much lower temperature, 90 °C, rather than that used in conventional solvents, 300 – 1000 °C.^[126]

Togo *et al.* reported demethylation (Scheme 1.22) of *N,N*-dimethylanilines using different reaction solvents, and under solventless conditions and confirmed that reactivity significantly depends on the reaction solvent involved (see Table 1.8) with the best solvent, [bmim]Cl showing the highest reaction yield.^[9b]

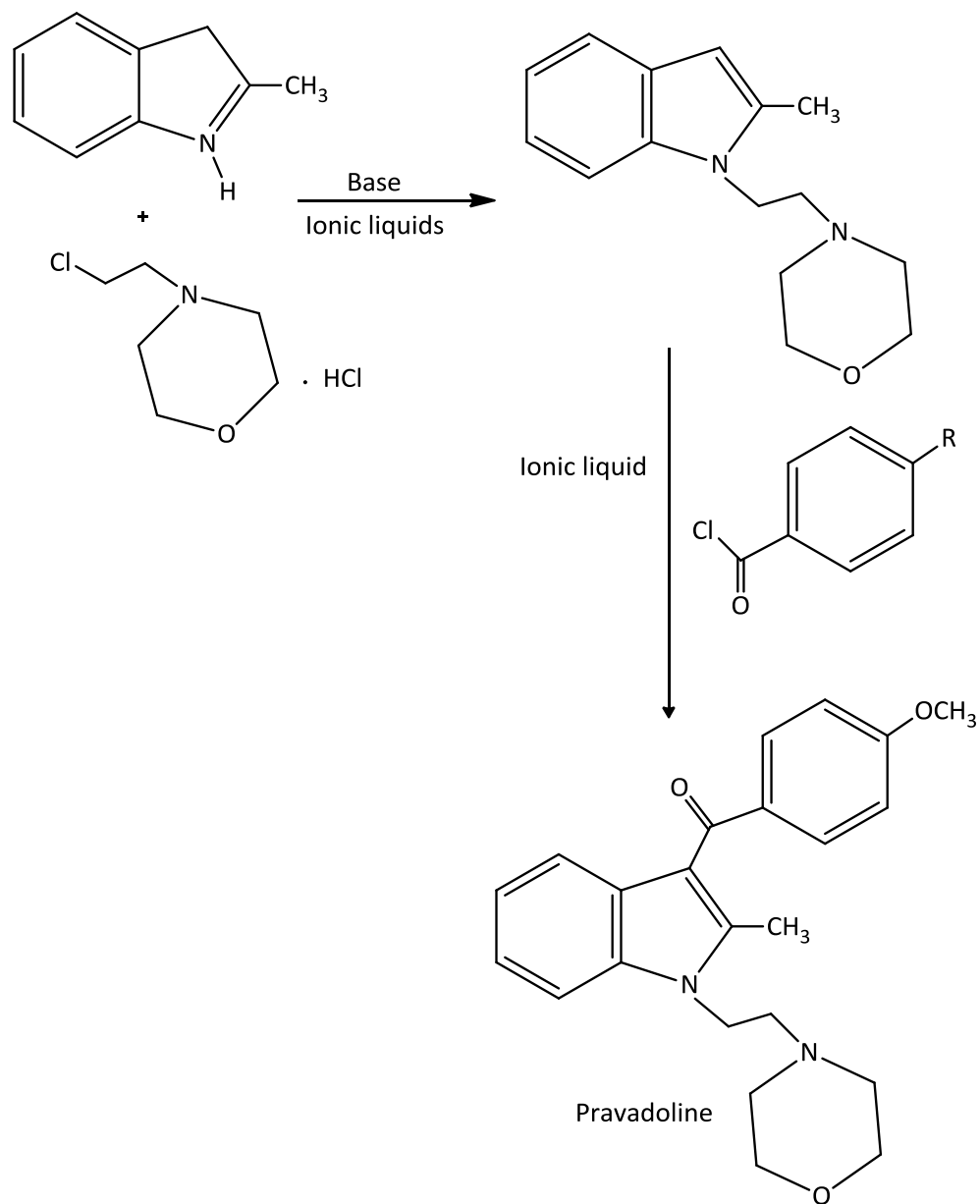


Scheme 1.22 Demethylation of *N,N*-dimethylanilines with Phenyl Chloroformate, taken from ref [9b].

Table 1.8. Some of the ionic liquids used in the reaction depicted in scheme 1.22 and their yields.

solvent	Yield %	solvent	Yield %
MeCN	24	[bmim]Br	80
solvent free	25	[bmpy]TFSI	49
[bmpy]PF ₆	64	[bmpy]PF ₆	64
[bmim]BF ₄	69	[bmim]Cl	95

Pharmaceutically the complete synthesis of pravadoline in the imidazolium-based ionic liquid, [bmim]PF₆, by combining Fiedel-Crafts and displacement reaction has been reported (Scheme 1.23).^[12]



Scheme 1.23. The complete synthesis of pravadoline in [bmim]PF₆, taken from ref [12].

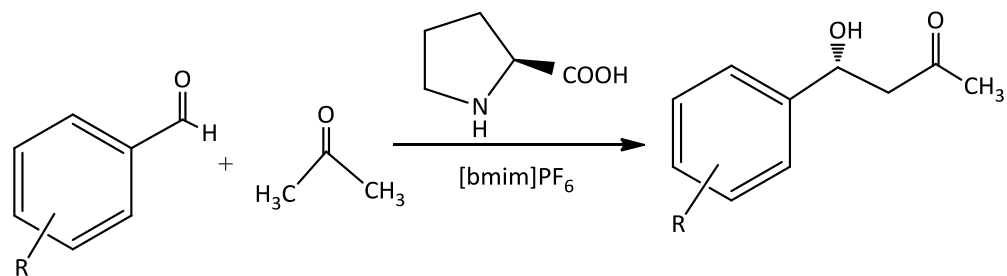
Abbott *et al.* showed that eutectic mixtures of urea with choline chloride in a 2:1 ratio, resulting in liquids that had unusual properties suitable for the use as ambient temperature solvents which are strongly influenced by hydrogen bonding.^[21] This eutectic mixture possessed a freezing point (12 °C) lower than its constituents, choline chloride, mp 302 °C, and urea, mp 133 °C resulting from the hydrogen bonding interactions between the chloride ion and urea molecules.

1.6.2. Ionic liquids in catalysis

Investigations into catalytic reactions using ionic liquids have been performed for more than 35 years. In 1986, Wilkes *et al.* were the first to report the use of ionic liquids (imidazolium chloroaluminates) as catalysts in Friedel-Crafts acylation.^[127] However, extensive interest in a broad range of stoichiometric and catalytic reactions has seen a dramatic growth of published papers in this area.

Ionic liquids supported with many catalysts and reagents resulted in improved reaction yields and selectivities in many important reactions.^[128,129] In France at the IFP (Institut français du pétrole), based on the investigations of ionic liquid ternary system, ([bmim]Cl-AlCl₃-EtAlCl₂), Chauvin and co-workers found that chloroaluminate ionic liquids are good solvents for dimerisation of linear olefins using Ni catalysts. Where, the reaction products can be easily separated by simple decantation, since they are not soluble in the ionic liquid, and showed higher yields and selectivity of the required dimers compared to the traditional solvent and solventless systems.

Kotrusz *et al.* reported the possibility of using the ionic liquid, [bmim]PF₆ in proline-catalysed Aldol reactions (scheme 1.24), giving good product yields with suitable enantioselectivities even when using smaller amounts of catalyst (1-5 %) from that used originally, about 30 %.^[130]



Scheme 1.24. L-Proline-catalysed Aldol reactions between aromatic aldehydes and acetone in an IL, taken from ref [130].

Recently Lee *et al.* reported that rare earth triflate (eg. Sc(OTf)₃) catalyst activity increases in the presence of ionic liquids. For example, the Diels-Alder reaction of 1,4-naphthoquinone with 1,3-dimethylbutadiene proceeded effectively in [bmim]PF₆ or [bmim]SbF₆ in the presence of 0.2 mol % Sc(OTf)₃, in contrast to the identical reaction in dichloromethane which is very slow.^[131a] Moreover, reactions that did not proceed at all in conventional solvents and water, such as the Sc(OTf)₃-catalysed Friedel-Crafts alkylation of benzene with hexane, could surprisingly proceed smoothly at room temperature in ionic liquids such as [bmim]PF₆ and [bmim]SbF₆.

Ionic liquids are also used in biocatalysis. Enzymes are catalysts that accelerate large numbers of organic reactions under a wide-range of conditions but are limited by their solubility.^[131b] Enzymes work well in water and non-polar solvents, leaving a large-gap in the solubility for enzyme-catalysed reactions. This gap is filled by the use of ionic liquids and supercritical fluids. Enzymes not only tolerated these solvents but were stable showing in some cases higher activity than in the conventional solvents.

ionic liquids such as 1,3-dialkylimidazolium and *N*-alkylpyridinium-based combined with hexafluorophosphate, tetrafluoroborate and bis(trifluoromethanesulfonyl)imide have been used in biocatalysis since 2008.^[132-134]

A typical example is the transesterification of *N*-acetyl-L-phenylalanine ethyl ester with 1-propanol in the presence of α -chymotrypsin in [bmim]PF₆ and [omim]PF₆.^[135]

A detailed review on this topic can be found in the review published 2007, by Rantwijk and Sheldon.^[136]

1.6.3. Ionic liquids in electrochemistry

Due to their exceptional properties such as broad electrochemical window, and reasonable conductivity, ionic liquids are widely used in electrochemistry. They provide media for metal electrodepositions, such that many metals and alloys that were previously handled only in high temperature molten salts, can currently be deposited in ionic liquids.^[86] Lipsztajn *et al.*, were the first to report the electrodeposition of lithium in chloroaluminate ionic liquids.^[137] Since then many papers have been published on metal deposition in ionic liquid systems.^[14,138-140] Aluminium deposition in imidazolium-based and pyridinium-based chlorides mixed with AlCl₃ are to date the most commonly studied.^[5,141,142] Besides deposition of aluminium, other metals such as zinc,^[143] copper,^[144] cobalt,^[145] indium,^[146,147] tin^[143] and antimony^[148,137] have been deposited in chloroaluminate ionic liquids.

It was reported that metal deposition occurs only in chloroaluminate ionic liquids that were Lewis acids and when the mole fraction of AlCl₃ is greater than (0.5).^[14] Furthermore, investigations on the morphology and speciation of aluminium deposition in chloroaluminate-based ionic liquids has been reported by Abbott *et al.* for the system bmimCl–AlCl₃–toluene–LiCl.^[149] The

authors studied the mechanism of growth and morphology using a number of different techniques including atomic force microscopy, ^{27}Al NMR spectroscopy and scanning electron microscopy to determine the effect of addition of diluents (toluene) and electrolyte (LiCl), where both toluene and LiCl were found to affect the morphology of the electrodeposited aluminium.

Scrosati *et al.* reported that processes that are unfeasible in water baths may be possible in ionic liquids, with an improvement in the quality and morphology of the deposits formed. These include the direct electroplating of aluminium and perhaps even magnesium, in addition to many other metals with a deposition potential incompatible with the decomposition of water. Aluminium electrodeposition in ionic liquids nowadays has advanced adequately and it is suggested that it will be produced commercially on a large scale in industry within the coming few years.^[150]

The quaternary ammonium-based ionic liquids of the type NR_4X , R = methyl, ethyl, propyl and butyl and $\text{X} = \text{ClO}_4^-$, BF_4^- , PF_6^- and CF_3SO_3^- , such as $\text{N}_{2222}\text{BF}_4$, are the most commonly used supporting electrolytes in electrochemistry due to their good stability. Whereas their less symmetric analogues, also have high electrochemical stability at *ca.* 6 V along with a lower melting point.^[17]

Raabe *et al.*^[151] have reported the use of symmetric quaternary ammonium salts with large fluorinated alkoxyaluminates, $[\text{NR}_4]^+[\text{Al}(\text{OC}(\text{R}_f)_3)_4]^-$ for electrochemical applications. The authors also reported that these salts provided undisturbed anion environments since the anions are weakly coordinating and this allowed a reliable determination of ion volume for the anion.

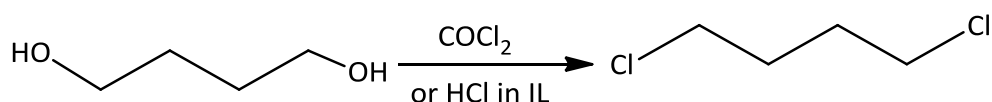
Long-chain quaternary ammonium salts of higher symmetry of the type $[\text{N}_{1\text{RRR}}]^+$ (where R = 16, 18 and 20) are used in the construction of anion-selective electrodes (ISE), acting as the ion-sensing ligands.^[152] In this study it has been observed that increasing the length of the R group has showed

significant improvement in chloride ion selectivity as compared to the conventional quaternary cation normally used, $[N_{1(12)(12)(12)}]^+$.

1.6.4. Ionic Liquids in Large Scale Applications

Ionic liquids are leaving many academic labs and finding their way into a wide variety of industrial applications, below are a few examples of commercialised processes involving ionic liquids:

In 2009 BASF in Germany implemented the BASIL process (Biphasic Acid Scavenging Utilizing Ionic Liquids), for the production of alkoxyphenylphosphines. This is based on replacing the acid scavenger triethylamine with 1-methylimidazole in the course of reaction, where the latter results in the formation of a discrete layer of 1-methylimidazolium chloride instead of solid triethylammonium chloride, which is difficult to separate at this stage. Furthermore BASF demonstrated that hydrogen chloride in ionic liquids can replace the poisonous gas phosgene in the chlorination reaction of butane-1,4-diol to form 1,4-dichlorobutane in high purity and excellent yield (scheme 1.25).^[17]



Scheme 1.25 Chlorination reaction of butane-1,4-diol in IL.

BASF have found a new technology for cellulose dissolution. Cellulose is reported to dissolve in pure ionic liquids (imidazolium-based ILs) without the use of conventional volatile organic solvents, for example, 0.3 g of powdered cellulose fully dissolved in 10 grams of [bmim]Cl containing 0.99 g 1-methylimidazole when heated at 95 °C for 48 minutes.^[153]

Degussa is a company producing a new range of paints which are more environmentally friendly, by reducing the use of the normal volatile solvents. Degussa includes small amounts of ionic liquids as additives in their paints, which act as secondary dispersing agents which results in an improvement of the finishing and appearance properties.^[154,155]

IFP (Institut français du pétrole) was the first company to operate an ionic liquid pilot plant.^[16] The use of chloroaluminate(III) ionic liquids as solvents for nickel-catalysed dimerisation (Dimersol/ Difasol) reactions have been developed at the IFP, decreasing the expense which was involved in separating products from the catalyst. The dimerisation process of alkenes, typically propenes and butenes, is widely used in industry with 25 plants worldwide, which produce *ca.* 1×10^6 tonnes-annually. Ionic liquids have shown increased catalytic activity towards higher degrees of polymerization.^[95]

Air Products and Technology use ionic liquids in the transport of poisonous gases such as arsines and phosphines and have found this to be a much safer route for their transport.^[16] The reactive gases are complexed in the ionic liquids and stored at sub-atmospheric pressures in 2.2 Litre cylinders, instead of the normal pressurized cylinders. For example, phosphine (PH_3) is stored in ionic liquids such as $[\text{C}_n\text{mim}][\text{Cu}_2\text{Cl}_3]$ or $[\text{C}_n\text{mim}][\text{Cu}_2\text{Br}_3]$ and then simply removed from the cylinder by applying vacuum.

1.7. Aims and Objectives

The most commonly used ILs are those based on the aromatic cations such as the imidazolium, pyrrolidinium or pyridinium systems. A number of symmetric quaternary ammonium and phosphonium-based ionic liquids have also been extensively studied, but few papers have been published on the asymmetric aliphatic quaternary ammonium-based ionic with long alkyl chains.

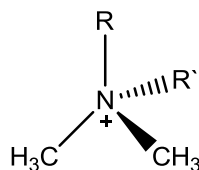
Based on a survey of published work it appears that generally quaternary ammonium ILs, ahead of the more common imidazolium ILs produce larger liquid/liquid electrochemical window (Ews).^[72a]

This work aims to synthesis new hydrophobic ionic systems containing asymmetric ammonium cations combined with fluorinated anions. Followed by the investigation of their physical properties such as melting point, miscibility with water, electrochemical stabilities, viscosity, conductivity and thermal properties, these form the basis of the work reported in chapters 2-5.

A summary of the cationic and anionic species used in this research is shown below in Scheme (1.26).

Cation and Anion structures used in this work.

Cations:

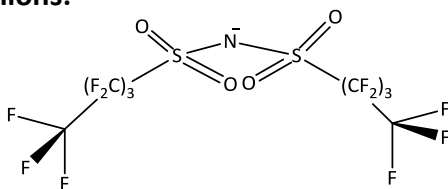


$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}, \text{CH}_2=\text{CHCH}_2,$

$\text{PhCH}_2, \text{C}_6\text{H}_{11}, \text{C}_7\text{H}_6\text{F}_9, \text{C}_{11}\text{H}_6\text{F}_{17}.$

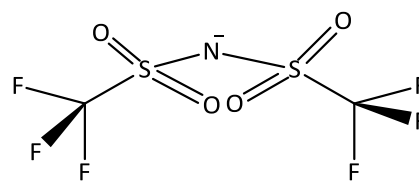
$R' = \text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{14}\text{H}_{29}, \text{C}_{18}\text{H}_{37}.$

Anions:



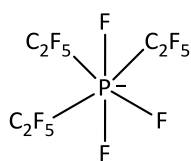
bis(nonfluorobutanesulfonyl)

imide, NNf_2



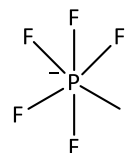
bis(trifluoromethanesulfonyl)

imide, TFSI.

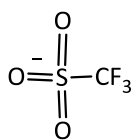


tris(pentafluoroethyl)trifluoro

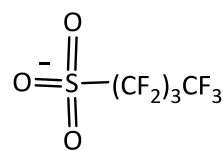
phosphate, FAP.



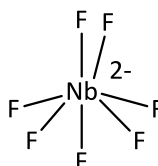
hexafluorophosphate, PF_6^- .



trifluoromethanesulfonate, CF_3SO_3^-



nonafluorobutanesulfonate, $\text{C}_4\text{F}_9\text{SO}_3^-$.



heptafluoronioate, NbF_7^{2-}

Scheme 1.26. Cations and anions used in this work.

1.8 References

1. P. Wasserscheid, T. Welton, *Ionic liquids in synthesis*, Wiley-VCH, Weinheim-New York, 2002.
2. J. S. Wilkes, *Green Chemistry*, 2002, **4**, 73.
3. P. Wasserscheid, W. Kevin, *Angew. Chem. Int. Ed.*, 2000, **39**, 3772.
4. F. H. Hurley, *US Patent*, 1948, US 2446331 19480803.
5. F. H. Hurley and T. P. Weir, *J. Electrochem. Soc.*, 1951, **98**, 207.
6. J. T. Yoke, J. F. Weiss, G. Tollin, *Inorg. Chem.*, 1963, **2**, 1210.
7. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, *J. Am. Chem. Soc.*, 1975, **97**, 3264.
8. J. Robinson, R.A. Osteryoung, *J. Am. Chem. Soc.*, 1979, **101**, 323.
9. (a) J. S. Wilkes, J. A. Levisky, R. A. Wilson, C. L. Hussey, *Inorg. Chem.*, 1982, **21**, 1263. (b) S. Imoria, H. Togo, *Synlett*, 2006, 2629.
10. T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, P. D. Armitage, *Inorg. Chem.*, 1983, **22**, 2099.
11. D. Appleby, C. L. Hussey, K. R. Seddon and J.E. Turp, *Nature*, 1986, **323**, 614.
12. M. J. Earle, K. R. Seddon, *Pure Appl. Chem.*, 2000, **72**, 1391.
13. J. S. Wilkes, M. J. Zaworotko, *Chem. Commun.*, 1992, 965.
14. F. Endres, S. Zein El-Abedin, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2101.
15. V. R. Koch, C. Nanjundiah, G. B. Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, 1995, **142**, L116.
16. N. V. Plechkovo, K. R. Seddon, *Chem. Soc. Rev.*, 2008, **37**, 123.
17. M. Galinski, A. Lewandowski, I. Stepniak, *Electrochimica Acta*,

2006, **51**, 5567.

- 18.** K. R. Seddon, *J. Chem. Tech. Biotechnol.*, 1997, **68**, 351.
- 19.** S. I. Lall, D. Mancheno, S. Castro, V. Behaj, J. L. I. Cohen, R. Engel, *Chem. Commun.*, 2000, 2413.
- 20.** J. H. Davis, K. J. Forrester, T. Merrigan, *Tetrahedron Lett.*, 1998, **39**, 8955.
- 21.** A. P. Abbott, G. Capper, D. L. Davies, R. Rasheed, V. Tambyrajah, *Chem. Commun.*, 2003, 70.
- 22.** E. R. Shepard, H. A. Shonle, *J. Am. Chem. Soc.*, 1947, **69**, 2269.
- 23.** B. K. M. Chan, N. H. Chang, M. R. Grimmett, *Aust. J. Chem.* 1977, **30**, 2005.
- 24.** F. Ricciardi, W. A. Romanchick, M. M. Joullie, *Polym. Lett. Ed*, 1983, **21**, 633.
- 25.** T. Welton, *Coord. Chem. Rev.* 2004, **248**, 2459.
- 26.** M. Deetlefs, H. G. Raubenheimer, M. W. Esterhuysen, *Catal. Today*, 2002, **72**, 29.
- 27.** A. J. Carmichael, M. J. Earle, J. D. Holbrey, P. B. Mc-Cormac, K. R. Seddon, *Org. Lett.*, 1999, **1**, 997.
- 28.** L. Xu, W. Chen, J. Xiao, *Organometallics*, 2000, **19**, 1123.
- 29.** J. P. Canal, T. Ramnial, D. A. Dickie, J. A. C. Clyburne, *Chem. Commun.*, 2006, 1809.
- 30.** S. Liu, T. Fukuyama, M. Sato, I. Ryu, *Synlett*, 2004, 1814.
- 31.** Y. Abu-Lebdeh, P. J. Alarco, M. Armand, *Angew. Chem. Int. Ed.* 2003, **42**, 4499.
- 32.** Y. R. Mirzaei, B. Twamley, J. M. Shreeve, *J. Org. Chem.*, 2002, **67**, 9340.

33. J. H. Davis, K. J. Forrester, T. Merrigan, *Tetrahedron Lett.*, 1999, **40**, 1621.
34. V. R. Koch, C. Nanjundiah, R. T. Carlin, *International Patent Appl.* WO 9702252, 1997.
35. S. A. Forsyth, J. M. Pringle, and D. R. MacFarlane, *Aust. J. Chem.* 2004, **57**, 113.
36. C. M. Gordon, J. D. Holbrey, A. R. Kennedy, K. R. Seddon, *J. Mater. Chem.*, 1998, **8**, 2627.
37. A. V. Visser, J. D. Holbrey, R. D. Rogers, *Chem. Commun.*, 2001, 2484.
38. T. Kitazume, F. Zulfiqar, G. Tanaka, *Green Chem.*, 2000, **2**, 133.
39. D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B*, 1999, **103**, 4164.
40. J. Sun, M. Forsyth, D. R. MacFarlane, *J. Phys. Chem. B*, 1998, **102**, 8858.
41. C. J. Bardaric, A. Downard, C. Kennedy, A. J. Robertson, Y. Zhou, *Green Chem*, 2003, **5**, 143.
42. H. M. A. Abood, A. P. Abbott, A. D. Ballantyne, K. S. Ryder, *Chem. Commun.*, 2011, **47**, 3523.
43. R. S. Varma, V. V. Namboodiri, *Pure and Applied Chem.*, 2001, **73**, 1309.
44. A. E. Visser, R. P. Swattoski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H Davis and R. D Rogers, *Chem. Commun.*, 2001, 135.
45. H. Mehdi, K. Binnemanns, K. Van Hecke, L. Van Meervelt, P. Nockemann, *Chem. Commun.*, 2010, **46**, 234.
46. Z. Fei, T. J. Geldbach, D. Zhao, and P. J. Dyson, *Chem. Eur. J.* 2006, **12**, 2122.

47. Z. Zhang, H. Zhou, L. Yang, K. Tachibana, K. Kamijima, J. Xu, *Electrochimica Acta*, 2008, **53**, 4833.
48. J. L. Anderson, R. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.* 2005, **127**, 593.
49. T. Payagala, J. Huang, Z. S. Breitbach, P. S. Sharma, and D. W. Armstrong, *Chem. Mater.*, 2007, **19**, 5848.
50. Z. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.*, 2005, **11**, 752.
51. R. T. Carlin, H. C. De Long, J. Fuller, P.C. Trulove, *J. Electrochem. Soc.*, 1994, **141**, L73.
52. H. Matsumoto, N. Terasawa, T. Umecky, S. Tsuzuki, H. Sakaebe, *Chemistry Letters*, 2008, **37**, 10.
53. D. Xiao, L. G. Hines, R.A. Bartsch and E. L. Quitevis, *J. Phys. Chem. B*, 2009, **14**, 113.
54. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
55. H. L. Ngo, K. LeCompte, L. Hargens, A. B. McEwen, *Thermochimica Acta*, 2000, 97.
56. S. Fang, L. Yang, C. Wei, C. Peng, K. Tachibana, K. Kamijima, *Electrochem. Commun.*, 2007, **9**, 2696.
57. I. Krossing, J. M. Slattery, C. Daguene, P. J. Dyson, A. Oleinikova, H. Weingartner, *J. Am. Chem. Soc.*, 2006, **128**, 13427.
58. J. Sun, D. R. MacFarlane, M. Forsyth, *Ionics*, 1997, **3**, 356.
59. J. Sun, M. Forsyth, D. R. MacFarlane, *Molten salt forum*, 1998, **5-6**, 585.
60. D. R. MacFarlane, J. Sun, J. Golding, P. Meakin, M. Forsyth,

- Electrochim. Acta*, 2000, **45**, 1271.
61. E. I. Cooper, C. A. Angell, *Solid State Ionics*, 1986, **18-19**, 570.
62. W. X. Emanuel, I. Cooper, C. A. Angell, *J. Phys. Chem.*, 2003, **107**, 6170.
63. H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, *Chem. Lett.*, 2000, 922.
64. H. Matsumoto, H. Kageyama, Y. Miyazaki, *Chem. Lett.* 2001, 182.
65. (a) H. Matsumoto, H. Kageyama, Y. Miyazaki, *Chem. Commun.* 2002, 1726. (b) S. Busi, M. Lahtinen, H. Mansikkamäki, J. Valkonen, K. Rissanen, *J. of Solid State Chem.*, 2005, **178**, 1722.
66. (a) K. Kim, C. M. Lang, P. A. Kohl, *J. Electrochem. Soc.*, 2005, **152**, E56. (b) M. Karna, M. Lahtinen, J. Valkonen, *J. of Mol. Struct.*, 2009, **922**, 64.
67. J. E. Gordon, G. N. SubbaRao, *J. Am. Chem. Soc.*, 1978, **100**, 7445.
68. H. Xue, J. M. Shreeve, *Eur. J. Inorg. Chem.*, 2005, 2573.
69. Z. B. Zhou, M. Takeda, M. Ue, *J. Fluorine Chem.*, 2004, **125**, 471.
70. H. Matsumoto, H. Sakaebe, K. Tatsumi, M. Kikuta, E. Ishiko, M. Kono, *J. Power Sources*, 2006, **160**, 1308.
71. K. Liu, Y. Zhou, H. Han, S. Zhou, W. Feng, J. Nie, H. Li, X. Huang, M. Armand, Z. Zhou, *Electrochimica Acta*, 2010, **55**, 7145.
72. (a) Ph.D Thesis, A. D. Ballantyne (2008) University of Manchester, School of Chemistry. (b) A.P. Abbott, *Chem. Phys. Chem.*, 2004, **5**, 1242.
73. P. Hapiot and C. Lagrost, *Chem. Rev.*, 2008, **108**, 2238.

74. Z. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.*, 2004, **10**, 6581.
75. H. Yu, Y. Wu, Y. Jiang, Z. Zhou, Z. Zhang, *New J. Chem.*, 2009, **33**, 2385.
76. K. Fukumoto, H. Ohno, *Chem. Commun.*, 2006, 3081.
77. R. Taniki, K. Matsumoto, R. Hagiwara, *Electrochemical and Solid-State Letters*, 2012, **15**, F13.
78. S. F. Wang, T. Chen, Z. L. Zhang, X. C. Shen, Z. X. Lu, D. W. Pang, K. Y. Wong, *Langmuir*, 2005, **21**, 9260.
79. E. Rozniecka, G. Shul, J. Sireix-Plenet, L. Gaillon, M. Opallo, *Electrochem. Commun.*, 2005, **7**, 299.
80. P. Yu, Y. Q. Lin, L. Xiang, L. Su, J. Zhang, L. Q. Mao, *Langmuir*, 2005, **21**, 9000.
81. N. Papaiconomou, J. Salminen, J. Lee, J. M. Prausnitz, *J. Chem. Eng. Data*, 2007, **52**, 833.
82. J. J. Tindale and P. J. Ragona, *Chem. Commun.*, 2009, 1831.
83. P. G. Jessop, I. Phan, A. Carrier, S. Robinson, C. J. Durr and J.R. Harjani, *Green Chem.*, 2010, **12**, 809.
84. B. Giovanni, *J. Electrochem. Soc.*, 2006, **153**, A1685.
85. D. Zhao, M. Wu, Y. Kou, E. Min, *Catalysis Today*, 2002, **74**, 157.
86. H. Liu, Y. Liu, J. Li, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1685.
87. A. Lewandowski, A. S'widerska-Mocek., *J. Of power sources* 2009, **194**, 601.
88. J. Kagimoto, N. Nakamura, T. Kato and H. Ohno, *Chem. Commun.*, 2009, 2405.
89. U. Shroder, J. D. Wadhawan, R. G. Compton, F. Marken, P. A. Z.

- Suarez, C. S. Consorti, R.F. de Souza and J. Dupont, *New J. Chem.*, 2000, **24**, 1009.
90. R. D. Rogers, K. R. Seddon *Ionic liquids IIIB; Fundamentals, Progress and opportunities. Transformations and Processes*, ACS Symposium Series, Vol. 902, American Chemical Society, Washington DC, 2005.
91. J. G. Huddleston, H. D. Willauer, R. P. Swattoski, A. E. Visser, R. D. Rogers, *Chem. Commun.*, 1998, 1765.
92. P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168.
93. J Fuller, A. C. Breda, and R. T Carlin, *J. Electroanal. Chem.*, 1998, **29**, 459.
94. T. Welton, *Chem. Rev.*, 1999, 2071.
95. J. D. Holbrey, and K. R. Seddon, *Clean Products and Processes*, 1999, **1**, 223.
96. A. G. Fadeev, and M. M. Meagher, *Chem. Commun.*, 2001, 295.
97. C. M. Gordon, A. J. McLean M. J. Muldoon and I. R. Dunkin *American Chemical Society*, 2002, 428.
98. J. F. Wishart, E. W. Castner, *J. Phys. Chem. B* 2007, **111**, 4639.
99. R. D. Rogers, G. A. Voth, *Acc. Chem. Res.* 2007, **40**, 1077.
100. X. Jin, L. YU, D. Garcia, R. X. Ren, X. Zeng, *Anal. Chem.*, 2006, **78**, 6980.
101. D. Wei, A. Ivaska, *Anal. Chim. Acta*, 2008, **607**, 126.
102. W. Peng, S. M. Zakeeruddin, E. Ivan, M. Gratzel, *Chem. Commun.*, 2002, 2972.

103. K. Fredlin, M. Gorlov, H. Petterson, A. Hagfeldt, L. Kloo, G. Boschloo, *J. Phys. Chem. C*, 2007, **111**, 13261.
104. H. Nakagawa, S. Izuchi, K. Kuwana, T. Nukuda, Y. Aihara, *J. Electrochem. Soc.*, 2003, **150**, A695.
105. M. Smiglak, A. Melten, R. D. Rogers, *Acc. Chem. Res.* 2007, **40**, 1182.
106. M. E. Van Valkenburg, R. L. Vaughn, M. Williams, J. S. Wilkes, *Thermochim. Acta*, 2005, **425**, 181.
107. W. Gu, H. Chen, Y.-C. Tung, J.-C. Meiners, S. Takayama, *Appl. Phys. Lett.*, 2003, **90**, 033505/1.
108. J. Sane, F. J. Carrion, M.-D. Bernudez, G. Martinez-Nicolas *Tribol. Lett.*, 2006, **21**, 121.
109. J. Le Bideau, P. Gaveau, S. Bellayer, M.-A Neouze, A. Vioux, *Phys. Chem. Chem. Phys.*, 2007, **9**, 5419.
110. V. Kumar, S. V. Malhotra, *Bioorg. Med. Chem. Letters*, 2009, **19**, 4643.
111. H. Luo, S. Dai, P. V. Bonnesen, *Anal. Chem.*, 2004, **76**, 2773.
112. H. Luo, S. Dai, P. V. Bonnesen, A. C. Buchanan III, J. D. Holbrey, N. J. Bridges, R. D. Rogers, *Anal. Chem.*, 2004, **76**, 3078.
113. P. Y. Chen and C. L. Hussey, *Electrochim. Acta*, 2005, **50**, 2533.
114. T. Tsuda and C. L. Hussey, *Electrochem. Soc. Interf.*, 2007, 42.
115. J. Choia, Y. Sunb, E. Shimc, B. Scrosatid, D. Kima, *J. Electrochimica Acta*, 2011, **56**, 10179.
116. M. J. Earle, P. B. McCormac, K. R. Seddon, *Green Chem.*, 1999, **1**, 23.
117. T. Fischer, T. Sethi, T. Welton, J. Woolf, *Tetrahedron Lett.*,

- 1999, **40**, 793.
- 118.** D. A. Jaeger, C. E. Tucker, *Tetrahedron Lett.*, 1989, **30**, 1785.
 - 119.** S. Carda-Broch, A. Berthod, D. W. Armstrong, *Anal. Bioanal. Chem.*, 2003, **375**, 191.
 - 120.** C. F. Poole, B. R. Kersten, S. S. J. Ho, M. E. Coddens, K. J. Furton, *J. Chromatogr.*, 1986, 407.
 - 121.** S. K. Poole, P. H. Shetty, C. F. Poole, *Anal. Chim. Acta*, 1989, 241.
 - 122.** E. G. Yanes, S. R. Gratz, A. M. Stalcup, *Analyst*, 2000, **125**, 1919.
 - 123.** E. G. Yanes, S. R. Gratz, M. J. Baldwin, S. E. Robinson, A. M. Stalcup, *Anal. Chem.*, 2001, **73**, 3838.
 - 124.** D. W. Armstrong, L. He, Y.S. Liu, *Anal. Chem.*, 1999, **71**, 3873.
 - 125.** C. J. Adams, M. J. Earle, G. Roberts, K. R. Seddon, *Chem. Commun.*, 1998, 2097.
 - 126.** R. W. J. Westerhout, J. Waanders, J. A. M. Kuipers, W.P. Van Swaaij, *Ind. Eng. Chem. Res.*, 1988, **37**, 2293.
 - 127.** J. A. Boon, J. A. Levisky, J. L. Pflug, and J. S. Wilkes, *J. Org. Chem.*, 1986, **51**, 480.
 - 128.** R. Šebesta, I. Kmentová, Š. Toma, *Green Chem.*, 2008, **10**, 484.
 - 129.** W. Miao, T. H. Chan, *Acc. Chem. Res.*, 2006, **39**, 897.
 - 130.** P. Kotrusz, I. Kmentová, B. Gotov, Š. Toma, E. Solčániová, *Chem. Commun.*, 2002, 2510.
 - 131.** (a) J. W. Lee, J. Y. Shin, Y. S. Chun, H. B. Jang, C. E. Song, and S. Lee, *Acc. Chem. Res.*, 2010, **43**, 985. (b) S. Cantone, U. Hanefeld and A. Basso, *Green Chem.*, 2007, **9**, 954.
 - 132.** S. G. Cull, J. D. Holbrey, V. Vargas-Mora, K. R. Seddon, G. J. Lye, *Biotechnol. Bioeng.*, 2000, **69**, 227.

- 133.** M. Erbedinger, A. J. Mesiano, A. J. Russell, *Biotechnol. Prog.* 2000, **16**, 1129.
- 134.** R. M. Lau, F. Van Rantwijk, K. R. Seddon, R. A. Sheldon, *Org. Lett.*, 2000, **2**, 4189.
- 135.** J. A. Laszlo and D. L. Compton, *Biotechnol. Bioeng.*, 2001, **75**, 181.
- 136.** F. V. Rantwijk and R. A. Sheldon, *Chem. Rev.*, 2007, **107**, 2757.
- 137.** M. Lipsztajn and R. A. Osteryoung, *Inorg. Chem.*, 1985, **24**, 716.
- 138.** A. P. Abbott and K. J. McKenzie, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4265.
- 139.** F. Endres, S. Zein El Abedin, A. Y. Saad, E. M. Moustafa, N. Borissenko, W. E. Price, G. G. Wallace, D. R. MacFarlane, P. J. Newman, A. Bund, *Phys. Chem. Chem. Phys.*, 2008, **10**, 2189.
- 140.** H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, New York, 2005.
- 141.** G. E. McManis, A. N. Fletcher, D. E. Bliss and M. H. Miles, *J. Electroanal. Chem.*, 1985, **190**, 171.
- 142.** W. H. Safranek, W. C. Schickner and C. L. Fraust, *J. Electrochem. Soc.*, 1952, **99**, 53.
- 143.** W. R. Pitner and C. L. Hussey, *J. Electrochem. Soc.*, 1997, **144**, 3095.
- 144.** B. J. Tierney, W. R. Pitner, J. A. Mitchell, C. L. Hussey and G. R. Stafford, *J. Electrochem. Soc.*, 1998, **145**, 3110.
- 145.** R. T. Carlin, P. C. Trulove and H. C. De Long, *J. Electrochem. Soc.*, 1996, **143**, 2747.
- 146.** J. S. Y. Liu and I. W. Sun, *J. Electrochem. Soc.*, 1997, **144**, 140.

- 147.** M. K. Carpenter, *J. Mater. Res.*, 1994, **9**, 2584.
- 148.** D. A. Habboush and R. A. Osteryoung, *Inorg. Chem.*, 1984, **23**, 1726.
- 149.** A. P. Abbott, F. Qiu, H. M. A. Abood, M. R. Ali and K. S. Ryder, *Phys. Chem. Chem. Phys.*, 2010, **12**, 1862.
- 150.** M. Armand, F. Endres, D. R. MacFarlane, H. Ohno and B. Scrosati, *Nature materials*, 2009, **8**, 621.
- 151.** I. Raabe, K. Wagner, K. Guttsche, M. Wang, M. Gratzel, G. Santiso-Quinones, and I. Krossing., *Chem. Eur. J.*, 2009, **15**, 1966.
- 152.** S. Ozawa, H. Miyagi, Y. Shibata, N. Oki, T. Kunitake and W. E. Keller., *Anal. Chem.*, 1996, **68**, 4149.
- 153.** M. Matthias, S. Veit, *PCT Int. Appl.*, 2006, WO 2006 108861.
- 154.** A. Hoff, C. Jost, A. Prodi-Schwab, F. G. Schmidt and B. Weyershausen, *Degussa Science Newsletter*, 2004, **9**, 10.
- 155.** B. Weyershausen and K. Lehmann, *Green Chem.*, 2005, **7**, 15.

2. Synthesis and Characterisation of Asymmetric Aliphatic Quaternary Ammonium Salts.

- 2.1** Introduction
- 2.2** Synthesis and characterization of asymmetric quaternary ammonium halides.
 - 2.2.1.** Synthesis and characterization of C1 series, $N_{111}R^+X^-$.
 - 2.2.2.** Synthesis and characterization of C2 series, $N_{112}R^+X^-$.
 - 2.2.3.** Synthesis and characterization of C3 series, $N_{113}R^+X^-$.
 - 2.2.4.** Synthesis and characterization of C4 series, $N_{114}R^+X^-$.
 - 2.2.5.** Synthesis and characterization of C6 series, $N_{116}R^+X^-$
- 2.3** Synthesis of completely asymmetric quaternary ammonium salts, $N_{14R(14)}^+I^-$.
- 2.4** Melting points of asymmetric quaternary ammonium salts.
- 2.5** Conclusion.
- 2.6** References.

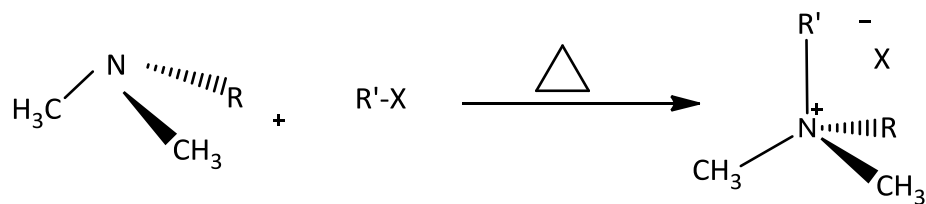
2.1 Introduction

Saturated quaternary ammonium salts (QA) have attracted attention in recent years, especially those combined with electronically stable anions, such as $[(CF_3SO_2)_2N]^-$, since these ionic systems have much larger electrochemical windows than the more popular 1,3-dialkylimidazolium-based ionic liquids.^[1-5] This fluoroanion combines low symmetry, good flexibility and a weakly coordinating nature, all of which are beneficial to lowering the melting point and viscosity of ionic liquids.^[2,3,4,6]

In this work a series of asymmetric quaternary ammonium halide salts are prepared as the cationic components of room temperature ionic liquids. They are composed of three different alkyl chain lengths (CH_3 , R and R') and form series of compounds of the type C1 $[N_{111R'}]^+X^-$, C2 $[N_{112R'}]^+X^-$, C3 $[N_{113R'}]^+X^-$, C4 $[N_{114R'}]^+X^-$ and C6 $[N_{116R'}]^+X^-$ and the completely asymmetric quaternary ammonium iodides in which four different alkyl chains are incorporated, $[N_{14R(14)}]^+I^-$ (R = propyl, octyl, decyl and allyl). The limited introduction of asymmetry into quaternary ammonium salts of the type $[NR_3R']X$ has previously been shown to have a profound influence on their melting points and has been investigated as a primary step for the development of room temperature ionic liquids.^[7]

These asymmetric quaternary ammonium systems, $[NMe_2RR']X$ have been synthesized by heating equimolar quantities of the asymmetric amine $((CH_3)_2RN)$ and an alkyl halide ($R'-X$) (scheme 2.1).

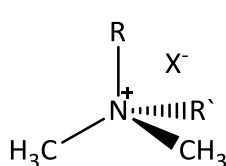
All of the salts were prepared solvent free, in a Schlenk tube which was sealed and heated in an oil bath at 90 °C. Reactions of the shorter chain amines, such as trimethylamine, dimethylethylamine and dimethylisopropylamine were completed after 48 hours. While reactions of dimethylbutylamine and dimethylhexylamine were completed after 72 hours.



$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}$ $R' = \text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{14}\text{H}_{29}, \text{C}_{18}\text{H}_{37}$ $X = \text{Br}$ or I .

Scheme 2.1. Synthesis of asymmetric quaternary ammonium halides.

The products obtained at this stage possessed a range of physical states, ranging from solids to pastes and liquids. All solid products were washed thoroughly with hexane, filtered and air dried, apart from the dimethylethylammonium halides, which were hygroscopic and were filtered and dried under vacuum. The liquid products were washed 6 times with hexane and the remaining solvent removed under vacuum with gentle heating, whereas the pastes were very difficult to purify. The synthesis of the quaternary ammonium salts is explained in detail in the experimental section (chapter 6). Scheme 2.2 shows the prepared asymmetric quaternary ammonium halides (cationic species).



$R = \text{CH}_3, \text{C}_2\text{H}_5, \text{CH}(\text{CH}_3)_2,$
 $\text{C}_4\text{H}_9, \text{C}_6\text{H}_{13}.$
 $R' = \text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{14}\text{H}_{29},$
 $\text{C}_{18}\text{H}_{37}.$
 $X^- = \text{Br}^-, \text{I}^-.$

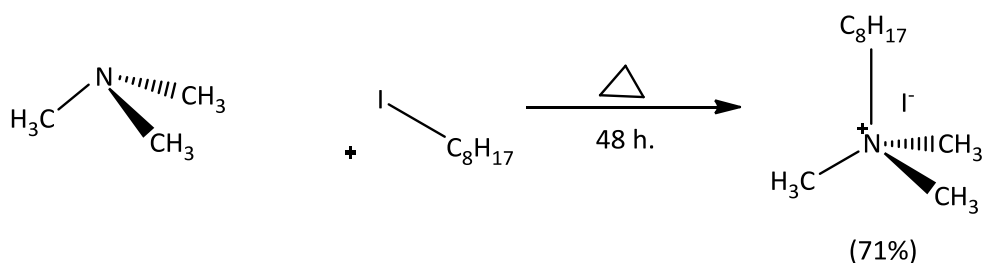
Scheme 2.2. Asymmetric quaternary ammonium halides prepared in this study.

All products were characterized by ^1H NMR spectroscopy and elemental analysis, in addition to the measurement of their melting points and their thermal stabilities using TG/DTA and DSC.

2.2 Synthesis and characterization of asymmetric aliphatic quaternary ammonium halides.

2.2.1. Synthesis and characterization of C1 series, N₁₁₁₈X.

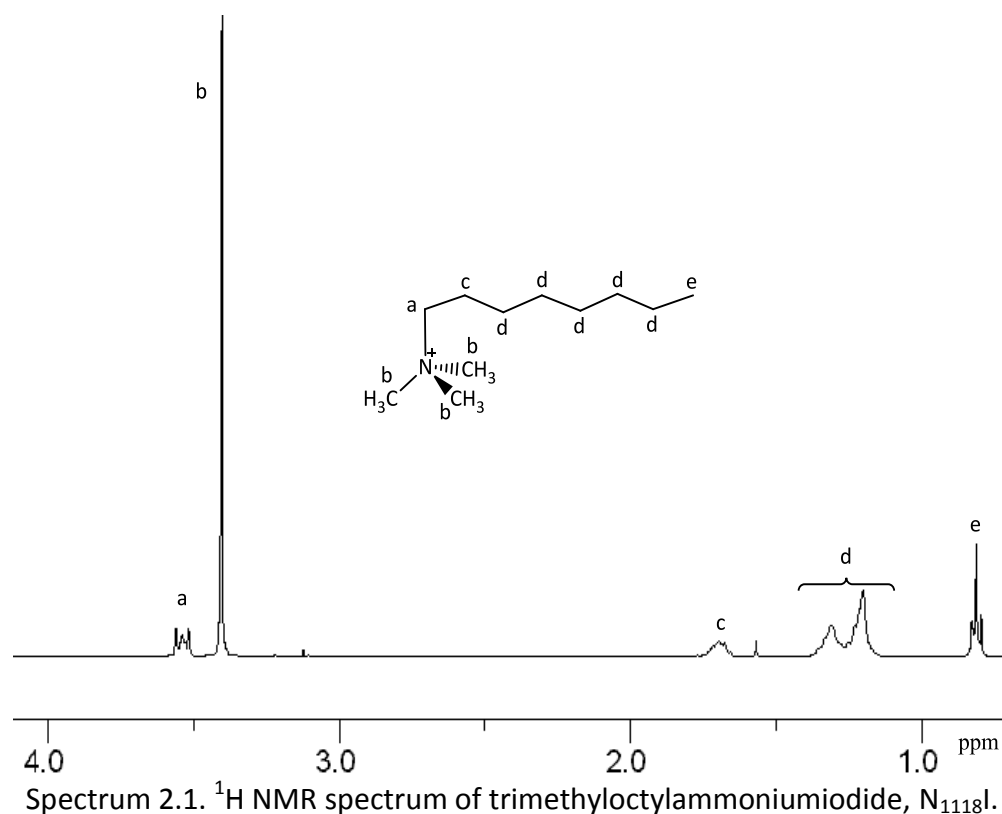
The reaction of trimethylamine (Me₃N) with octyliodide resulted, after workup, in solid N₁₁₁₈I (scheme 2.3). These reactions were performed to compare the melting points of these products with the more asymmetric quaternary ammonium salts, all products were solids at this stage.



Scheme 2.3. Synthesis of trimethyloctylammonium iodide, N₁₁₁₈I.

The ¹H NMR spectrum of trimethyloctylammoniumiodide (spectrum 2.1) shows five sets of peaks. The resonance at $\delta = 3.54$ ppm (a) is a second order multiplet resulting from the CH₂ group adjacent to the ammonium centre.

The resonance at $\delta = 3.4$ (b) is a singlet that arises from the three chemically equivalent methyl groups adjacent to the nitrogen centre. The beta CH₂ group on the octyl chain appears as a resonance at $\delta = 1.7$ ppm (c), this is a broad peak, presumably due to coupling to the two adjacent CH₂ groups. The rest of the CH₂ groups appear as multiplets over the shift range $\delta = 1.2$ -1.3 ppm (d). This is likely to be due to the overlapping of 5 CH₂ peaks in similar chemical environments which would all have a large number of couplings involved in their resonances. Again this is commonly seen in all the ammonium halide ions.



The terminal CH_3 group resonates at $\delta = 0.81$ ppm (e), appearing as a triplet due to coupling to the adjacent CH_2 protons. Confirmation of the identity of the products was by elemental analysis where satisfactory figures were obtained, see table 2.1. Similar procedures were performed by reacting trimethylamine with a series of longer chain alkyl halides such as 1-iododecane, 1-bromotetradecane and 1-bromooctadecane to complete the C1 series, all of which showed relatively high purity as shown in below table 2.1.

Crystals were grown from a layered solution of DCM / hexane for one of the C1 series which were suitable for X-ray diffraction studies, trimethyldecylammonium iodide ($\text{N}_{111(10)}\text{I}$).

Table 2.1. Elemental analysis of C1 series, N_{111R}X.

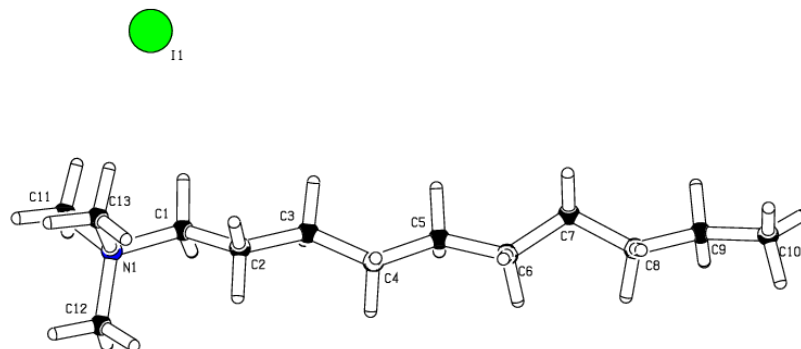
Sample identity	Elemental analysis					
	Theoretical %			Found %		
	C	H	N	C	H	N
N ₁₁₁₈ I	44.13	8.76	4.68	44.19	9.00	4.57
N ₁₁₁₍₁₀₎ I	47.69	9.24	4.28	47.90	9.48	4.25
N ₁₁₁₍₁₄₎ Br	60.68	11.39	4.16	60.78	11.71	4.15
N ₁₁₁₍₁₈₎ Br	64.24	11.82	3.57	64.07	12.17	3.53

Fig 2.1 shows a representative view of the molecule with atomic numbering as illustrated. Selected bond lengths (Å) and angles (°) are given in table 2.2. The unit cell parameters are: monoclinic, space group P21, $a = 5.75(15)$, $b = 7.44(19)$, $c = 18.83(6)$ Å, $\alpha = 90$, $\beta = 92.55(13)$, $\gamma = 90^\circ$, $V = 804.1(4)$ Å³.

Table 2.2 bond lengths and angles of N₁₁₁₍₁₀₎I.

Bond	Length(Å)	Angle	Angle (°)
N1-C1	1.506(6)	C1-N1-C11	105.6(4)
N1-C11	1.476(6)	C1-N1-C12	114.4(8)
N1-C12	1.465(7)	C1-N1-C13	108.4(9)
N1-C13	1.467(7)	C11-N1-C12	114.8(8)
C13-H13...I1	3.848(6)	C11-N1-C13	101.4(9)
		C12-N1-C13	111.3(4)

(a)



(b)

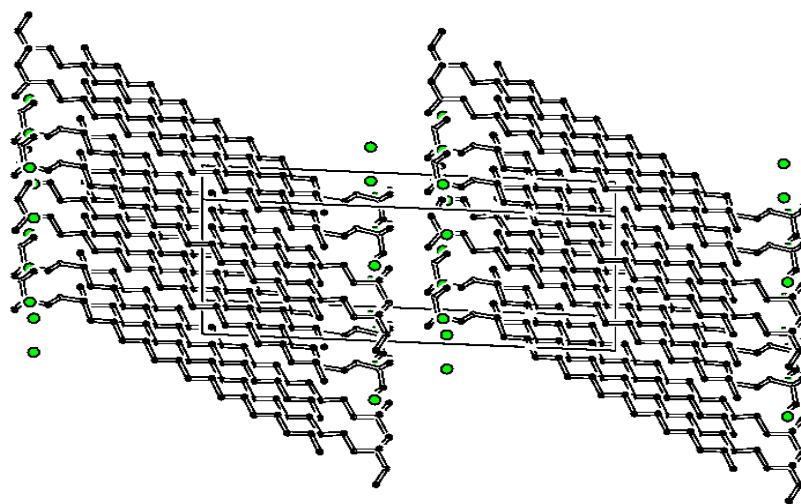


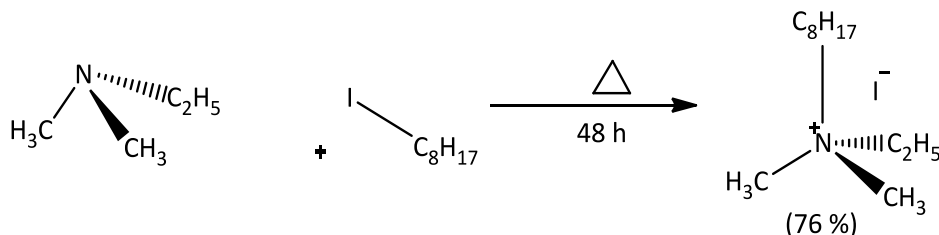
Figure 2.1. Representation of the molecular structure (a) and packing (b) of $N_{11(10)}I$.

There is one unique molecule contained within the unit cell, the C-N bond lengths lie between 1.465(7) and 1.506(6) Å, where the Me-N bond lengths are all similar 1.465(7) – 1.476(6) Å whilst that of the decyl chain-N bond is larger 1.506(6) Å. The C-N-C bond angles range from 101.4(9) – 114.8(8).

The crystal structure viewed along the b axis, fig 2.1, shows the packing of the molecules parallel to each other in a head to tail arrangement. This arrangement is similar to that of the dimethylbutyldodecylammonium bromide monohydrate where alkyl chains are packed in bilayers parallel to each other.^[8a]

2.2.2. Synthesis and characterization of C2 series, N_{112R}X.

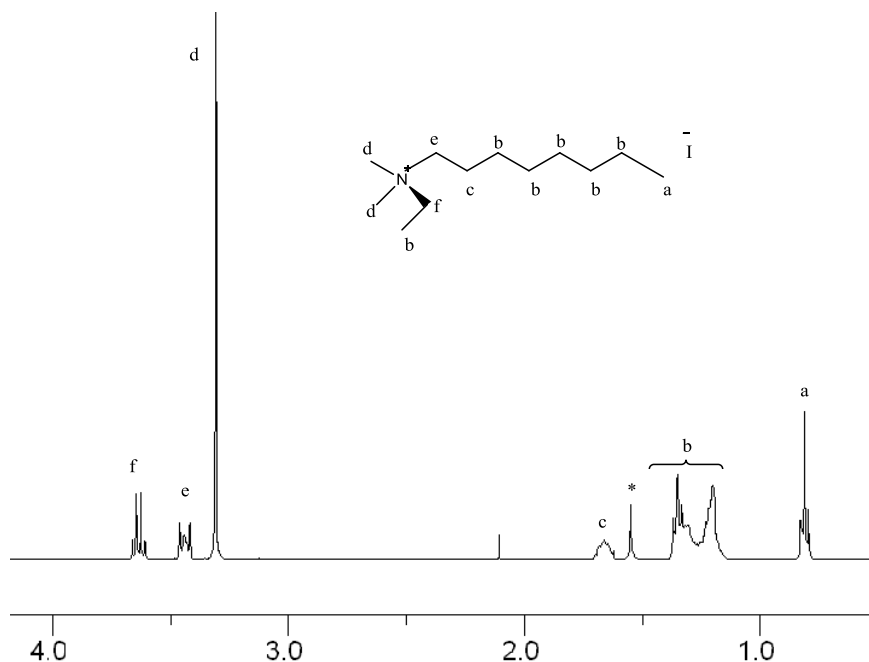
Similarly, the reaction of dimethylethylamine with octyliodide resulted, after workup, in solid N₁₁₂₈I (scheme 2.4), which was found to be hygroscopic as evidenced by the change in appearance of the solid.



Scheme 2.4. Synthesis of dimethylethyloctylammonium iodide, N₁₁₂₈I.

The ¹H NMR spectrum of the product (spectrum 2.2) shows a number of peaks. The resonance at 3.31 ppm of relative intensity six (labeled d) is a singlet and corresponds to the two methyl groups of the ammonium cation, the chemical shift value for these methyl protons is significantly higher than that of the corresponding CH₃ group on the octyl chain (δ = 0.81 ppm labelled a) due to being adjacent to the formally positively charged quaternary nitrogen centre. The resonance at δ 3.63 ppm (f) which appears as a quartet is

due to the CH₂ group of the ethyl chain adjacent to the nitrogen atom (NCH₂CH₃) which couples with the CH₃ group.



Spectrum 2.2. ¹H NMR spectrum of dimethylethyl-octylammonium iodide, N₁₁₂₈I (*= water).

The CH₂ group adjacent to the nitrogen centre on the octyl chain resonates at δ 3.44 ppm (e) and appears as a second order multiplet. The β-CH₂ group of the octyl chain resonates at δ 1.66 ppm (c) appearing as a broad multiplet. The rest of the CH₂ groups of the octyl chain and the CH₃ group of the ethyl chain overlap and appear as a multiplet in the range δ = 1.2 – 1.35 ppm (b). The resonance at δ = 1.55 ppm (*) is due to the presence of water as mentioned earlier arising from the hygroscopic nature of the product and impurities in CDCl₃.

A similar procedure was performed by reacting dimethylethylamine with a series of longer chain alkyl halides such as 1-iododecane, 1-bromotetradecane and 1-bromooctadecane to complete the C2 series, in each case resulting in hygroscopic white solids. Assignment of the ¹H NMR spectra of the C2 series of salts showed the anticipated peaks and indicated that the products were

relatively pure, which is confirmed by their elemental analysis, as shown in table 2.3.

Crystals suitable for X-ray diffraction were successfully grown from a DCM/hexane layered solution of one of the C2 series, the compound $N_{112(18)}Br$, which crystallises in the space group P-1. The unit cell parameters are: triclinic, space group P-1, $a = 10.66(7)$, $b = 8.43(7)$, $c = 26.57(3)$ Å, $\alpha = 84.73(3)$, $\beta = 94.4(3)$, $\gamma = 88.04^\circ$, $V = 2367.9(4)$ Å³. Its molecular structure (a) and packing (b) is shown in fig 2.2 and selected bond lengths (Å) and angles ($^\circ$) are given in table 2.4.

There are two molecules contained within the unit cell. The molecules show alternate head-to-tail stacking of the hydrocarbon chains forming parallel layers. The geometry around the nitrogen is distorted tetrahedral with three C-N distances almost the same ($1.53(2) - 1.54(2)$ Å) while the fourth is slightly shorter ($1.47(2)$ Å), (CNC angles lie between $105.5(12)$ and $114.0(13)^\circ$), as shown in table 2.4.

Table 2.3. Elemental analysis of C2 series, $N_{112R}X$.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$N_{1128}I$	solid	45.99	9.01	4.47	45.23	9.12	4.30
$N_{112(10)}I$	solid	49.24	9.45	4.10	49.38	9.91	4.01
$N_{112(14)}Br$	solid	61.68	11.51	4.00	61.83	12.16	3.93
$N_{112(18)}Br$	solid	64.98	11.91	3.45	65.08	12.89	3.32

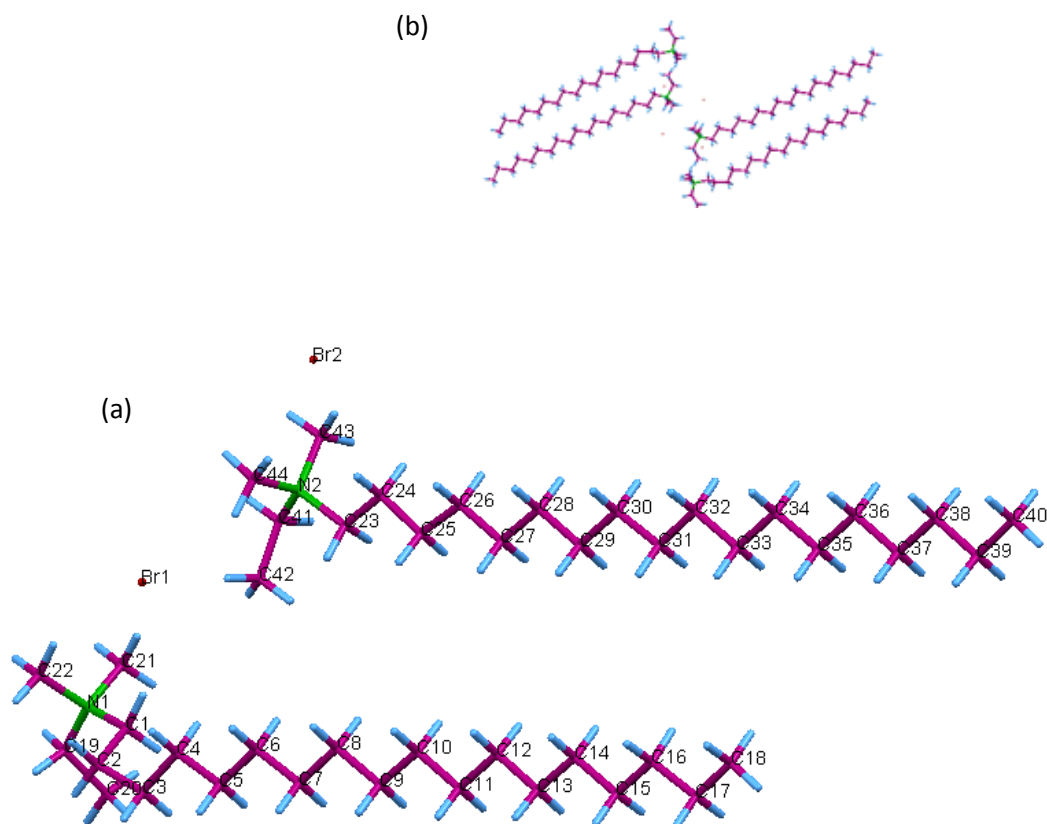


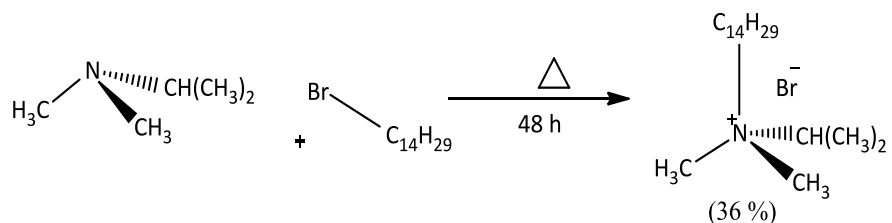
Figure 2.2. Representation of the molecular structure (a) and packing (b) of $N_{112(18)}Br$.

Table 2.4. Selected bond lengths and angles of $N_{112(18)}Br$.

Bond	Length (Å)	Angle	Angle (°)
N1-C1	1.54(2)	C1-N1-C19	114.0(13)
N1-C19	1.47(2)	C1-N1-C21	105.5(12)
N1-C21	1.53(2)	C1-N1-C22	109.4(13)
N1-C22	1.53(2)	C19-N1-C21	111.8(13)
C21-H21B....Br(1)	3.854(16)	C19-N1-C22	108.3(13)
C21-H21C....Br(2)	3.642(16)	C21-N1-C22	107.7(12)
C22-H22B.....Br(2)	3.667(16)		

2.2.3. Synthesis and characterization of C3 series, N_{113R}X.

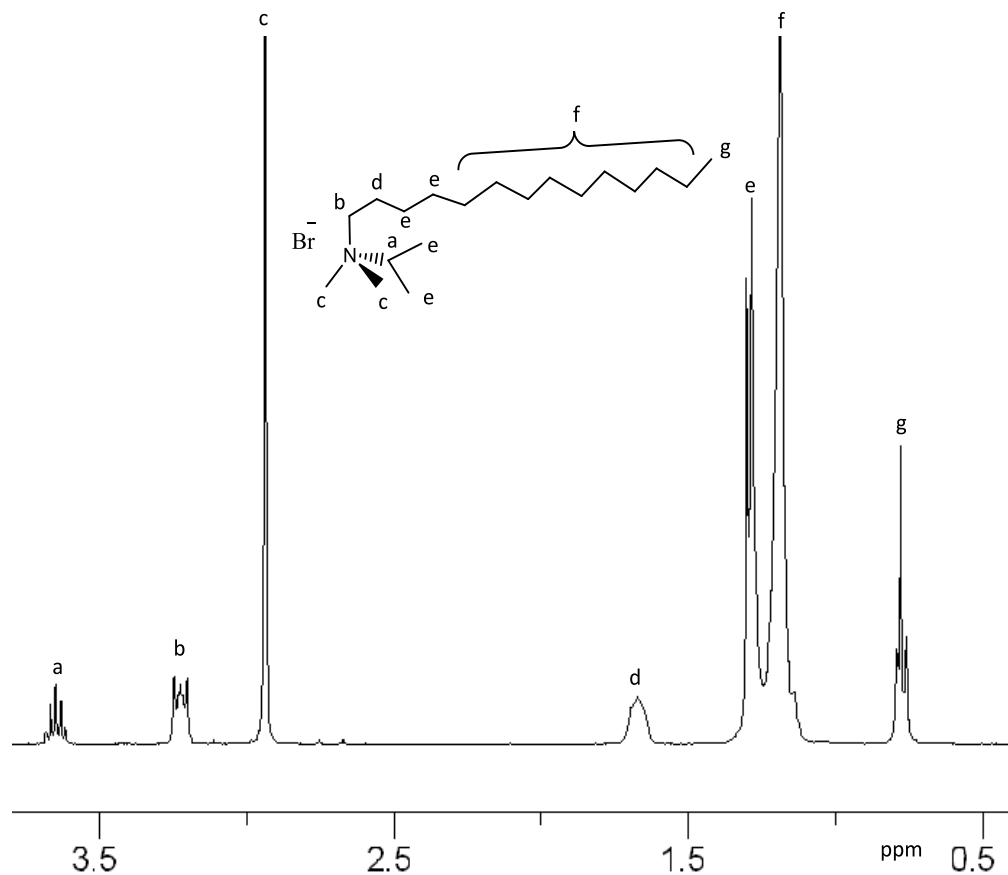
The reaction of dimethylisopropylamine with tetradecylbromide resulted, after workup, in a solid product, dimethylisopropyltetradecylammonium bromide (scheme 2.5).



Scheme 2.5. Synthesis of dimethylisopropyltetradecylammonium bromide, N₁₁₃₍₁₄₎Br.

The ¹H NMR spectrum of dimethylisopropyltetradecyl ammonium bromide is shown in spectrum 2.3. The resonance at δ = 3.65 ppm (a) arises from the CH proton of the isopropyl group, the signal being a septet, with a coupling constant of 6.6Hz, due to coupling to the six protons of the two adjacent CH₃ groups. The resonance at δ = 3.22 ppm (b) is a second order multiplet resulting from the complex overlapping of the CH₂ on the tetradecyl chain adjacent to the ammonium centre. This type of signal is common in all dimethylisopropylalkylammonium halides.

The beta CH₂ group on the tetradecyl chain resonates at δ = 1.67 ppm (d). This is a broad singlet presumably, due to the coupling of the adjacent CH₂ groups broadening the signal. This is seen for all of the ammonium salts.



Spectrum 2.3. ^1H NMR spectrum of dimethylisopropyltetradecylammonium bromide, $\text{N}_{113(14)}\text{Br}$.

The resonance at $\delta = 1.29$ ppm (e) is a doublet ($J = 6.6$ Hz) and so is assigned to the methyl groups on the isopropyl chain. The rest of the CH_2 groups on the chain are observed to overlap with this signal and are seen as a broad signal at $\delta = 1.19$ ppm (f).

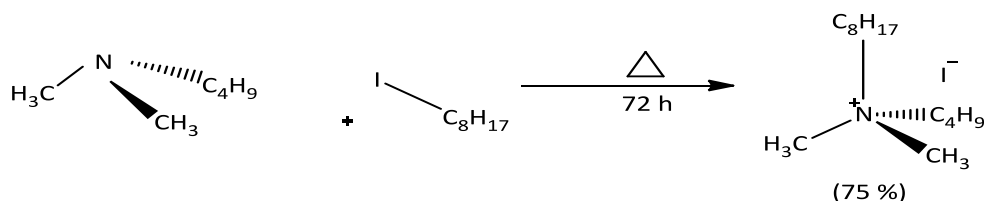
The CH_3 group at the end of the tetradecylammonium chain resonates at $\delta = 0.78$ ppm (g) giving a triplet arising from the coupling due to the adjacent CH_2 group. The methyl groups directly bound to the ammonium centre resonate at $\delta = 2.94$ ppm (c). A complete C3 series have been synthesized, their ^1H NMR data show that they are relatively pure and this is also shown from the elemental analysis where the calculated values are consistent with those found (table 2.5).

Table 2.5. Elemental analysis of C3 series, N_{113R}X.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₃₈ I	solid	47.69	9.24	4.28	47.63	10.02	4.27
N ₁₁₃₍₁₀₎ I	solid	50.68	9.65	3.94	50.71	10.05	3.83
N ₁₁₃₍₁₄₎ Br	solid	62.60	11.62	3.84	61.97	11.93	3.17
N ₁₁₃₍₁₈₎ Br	solid	65.67	11.99	3.33	64.93	12.32	2.86

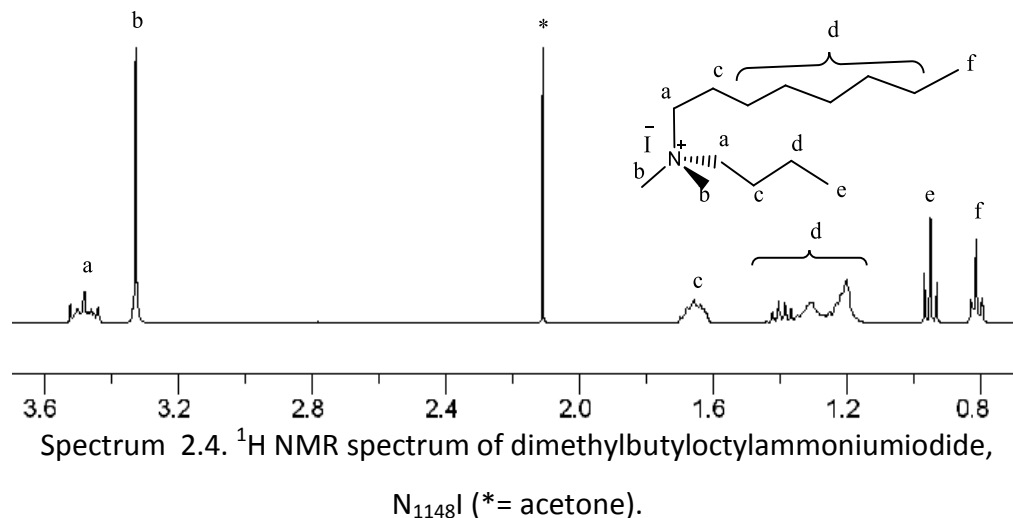
2.2.4. Synthesis and characterization of C4 series, N_{114R}X.

A typical example of the third type of asymmetric quaternary ammonium halide that has been prepared is dimethylbutyloctylammoniumiodide, N₁₁₄₈I which is synthesised in a similar manner to those stated above but was found to require a longer reaction time (scheme 2.6).



Scheme 2.6. Synthesis of dimethylbutyloctylammonium iodide, N₁₁₄₈I.

The reaction of dimethylbutylamine with 1-iodooctane, after workup, resulted in a yellow solid the ¹H NMR spectrum of which is shown in spectrum 2.4.



The resonance at $\delta = 3.48$ ppm (a) is a second order multiplet resulting from the complex overlapping of the signals due to the $\alpha\text{-CH}_2$'s of the butyl and octyl groups adjacent to the nitrogen (NCH_2).

The resonance at $\delta = 3.32$ ppm of relative intensity six (b) is a singlet and corresponds to the two methyl groups of the ammonium cation, the chemical shift value for these methyl groups is significantly higher than that of the corresponding CH_3 group on the octyl chain ($\delta = 0.81$ ppm (f)) and butyl chain ($\delta = 0.95$ ppm (e)) due to being adjacent to the positively charged nitrogen centre.

The beta CH_2 protons of both the octyl and butyl chain overlap, being observed at $\delta = 1.65$ ppm (c) as a broadened signal. This is commonly seen for the ammonium salts.^[7] The other CH_2 nuclei appear as multiplets in the shift range of $\delta = 1.21\text{--}1.39$ ppm (d). These are multiplets due to overlapping of 6 CH_2 signals, 5 from the octyl chain and one from the butyl chain, each of which are in only slightly different chemical environments.

The CH_3 group on the end of the butyl chain resonates at $\delta = 0.95$ ppm (e) appearing as a triplet signal due to the coupling to the adjacent CH_2 protons, this CH_3 group resonates at a slightly higher chemical shift value than that of

the CH₃ group of the octyl chain $\delta = 0.81$ ppm due to the relative proximity of the CH₃ group to the ammonium centre. Again this signal is a triplet which arises due to coupling to the adjacent CH₂ protons. The NMR data is confirmed by the elemental analysis data which shows consistent values to those calculated (table 2.6).

Table 2.6. Elemental analysis of C4 series, N_{114R}X.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₄₈ I	solid	49.24	9.45	4.10	48.79	9.51	4.06
N ₁₁₄₍₁₀₎ I	solid	52.01	9.83	3.79	51.82	10.01	3.75
N ₁₁₄₍₁₄₎ Br.H ₂ O	solid	60.57	11.70	3.53	60.45	11.77	3.52
N ₁₁₄₍₁₈₎ Br.H ₂ O	solid	63.67	12.03	3.10	63.87	12.25	3.06

Based on the elemental analyses the longer chain quaternary salts where (R = C₁₄H₂₉, C₁₈H₃₇) show the presence of water molecules. In addition to this the TG curves for N₁₁₄₍₁₄₎Br (fig. 2.3) and N₁₁₄₍₁₈₎Br (fig. 2.4) showed a weight loss at an early stage of heating before their decomposition temperature, which is attributed to the loss of a water molecule.

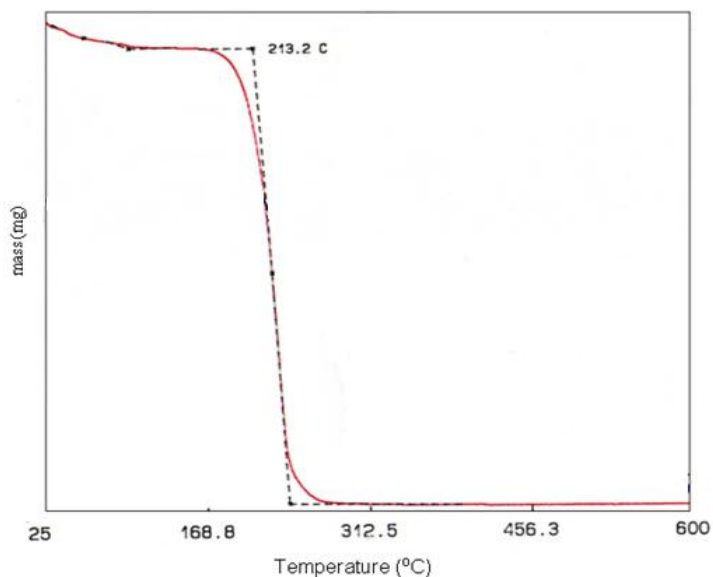


Figure 2.3. TG trace of $N_{114(14)}Br \cdot H_2O$, under nitrogen and 10 °C/min heating rate.

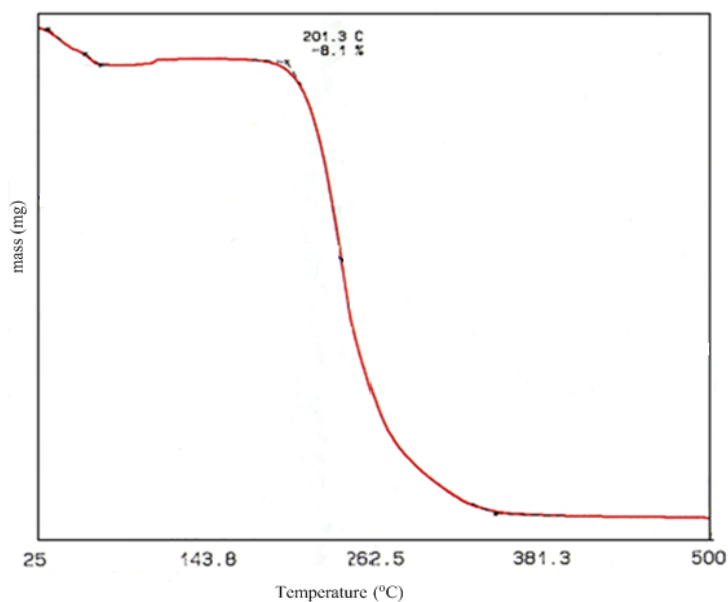


Figure 2.4. TG trace of $N_{114(18)}Br \cdot H_2O$, under nitrogen and 10 °C/min heating rate.

This behaviour is not present in the other non-hydrated quaternary ammonium halides which showed no weight loss until they reach their decomposition temperature as shown in fig. 2.5.

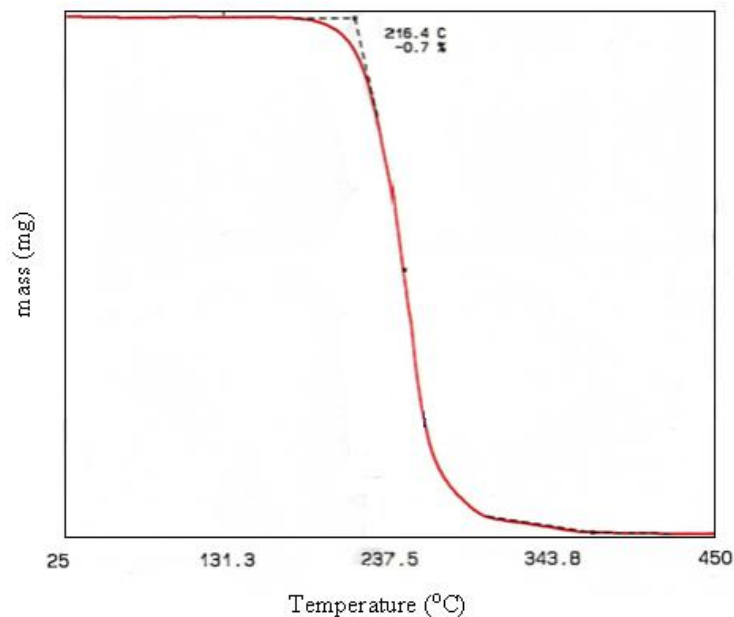


Figure 2.5. TG trace of N₁₁₄₈I working conditions: under nitrogen and 10 °C/min heating rate.

It has been reported by Kazarian *et al.* based on IR studies that water-insoluble ionic liquids tend to absorb water from the atmosphere, and are mostly present in the ‘free’ state, bonded via hydrogen bonding with different anions such as PF₆⁻, CF₃SO₃⁻ and TFSI⁻.^[8b]

We could successfully grow crystals suitable for single crystal X-ray diffraction studies of the hydrated long chain quaternary ammonium salt, N₁₁₄₍₁₈₎Br.H₂O from a layered solution of dichloromethane/hexane. The unit cell parameters are: triclinic, space group P-1, $a = 8.1021(8)$, $b = 8.5773(9)$, $c = 20.4765(18)$ Å, $\alpha = 95.096(8)$, $\beta = 90.729(8)$, $\gamma = 110.255(10)^\circ$, $V = 1328.3(2)$ Å³.

A representation of the molecule with atomic labeling is shown in fig 2.6. Selected bond distances and angles are listed in table 2.7.

The molecules are packed in bilayers with a head to tail arrangement. Hydrogen bonds are formed between two water molecules and two bromide anions forming a diamond-shaped motif with a Br...O distance of 3.358(4) Å.

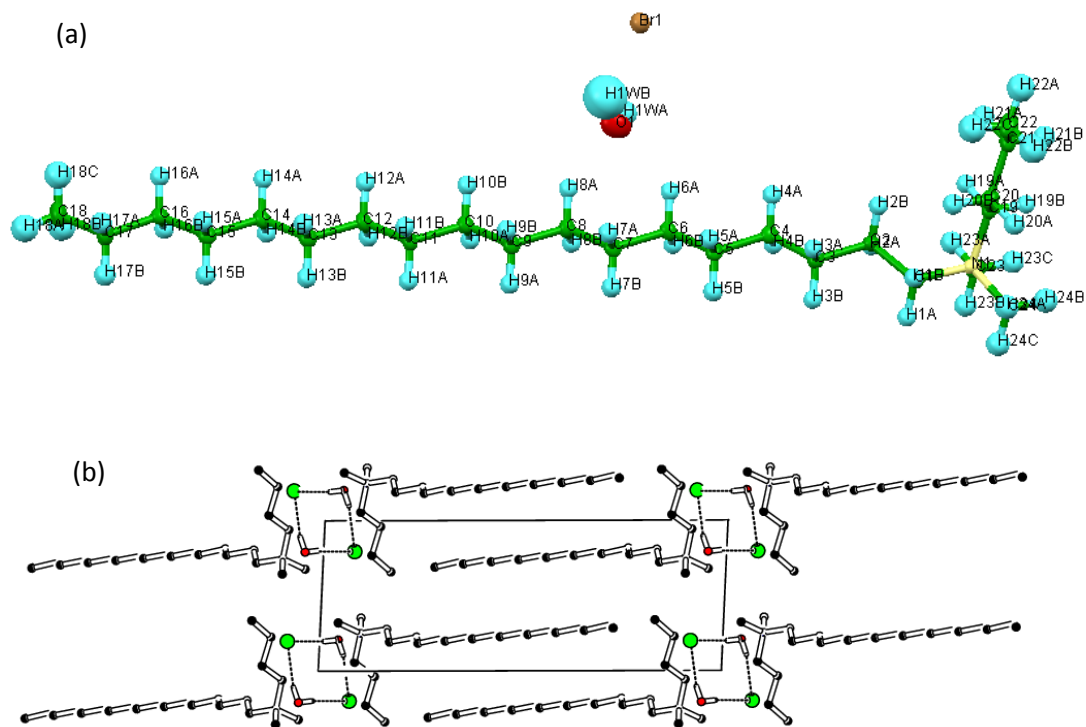


Figure 2.6. Representation of the molecular structure (a) and packing (b) of $N_{114(18)}Br.H_2O$ (alkyl hydrogens removed for clarity).

Table 2.7 Selected bond lengths and angles of $N_{114(18)}Br$.

bond	Bond Length (Å)	Angle	Angle (°)
N1-C1	1.513(5)	C1-N1-C19	113.1(3)
N1-C19	1.515(5)	C1-N1-C23	110.4(3)
N1-C23	1.507(5)	C1-N1-C24	108.2(3)
N1-C24	1.506(5)	C19-N1-C23	106.9(3)
C23-H23B...Br	3.788(4)	C19-N1-C24	107.9(3)
C24-H24C...Br	3.771(4)	C23-N1-C24	107.9(3)
		N1-C1-C2	117.0(5)

Taga *et al.* have also reported the presence of water molecule in the salt of dimethylbutyldodecylammonium bromide, $N_{114(12)}Br.H_2O$ as shown in fig. 2.7.^[8a] The authors reported a bilayer packing of the molecules with average C-N and C-C distances of 1.504 and 1.501 Å respectively. The dodecyl and butyl chains have a zig-zag arrangement and an isolated anionic group is

formed via hydrogen bonding between the bromide ions and water molecules with a Br $\cdots$ H bond distance of 3.414(1) Å.

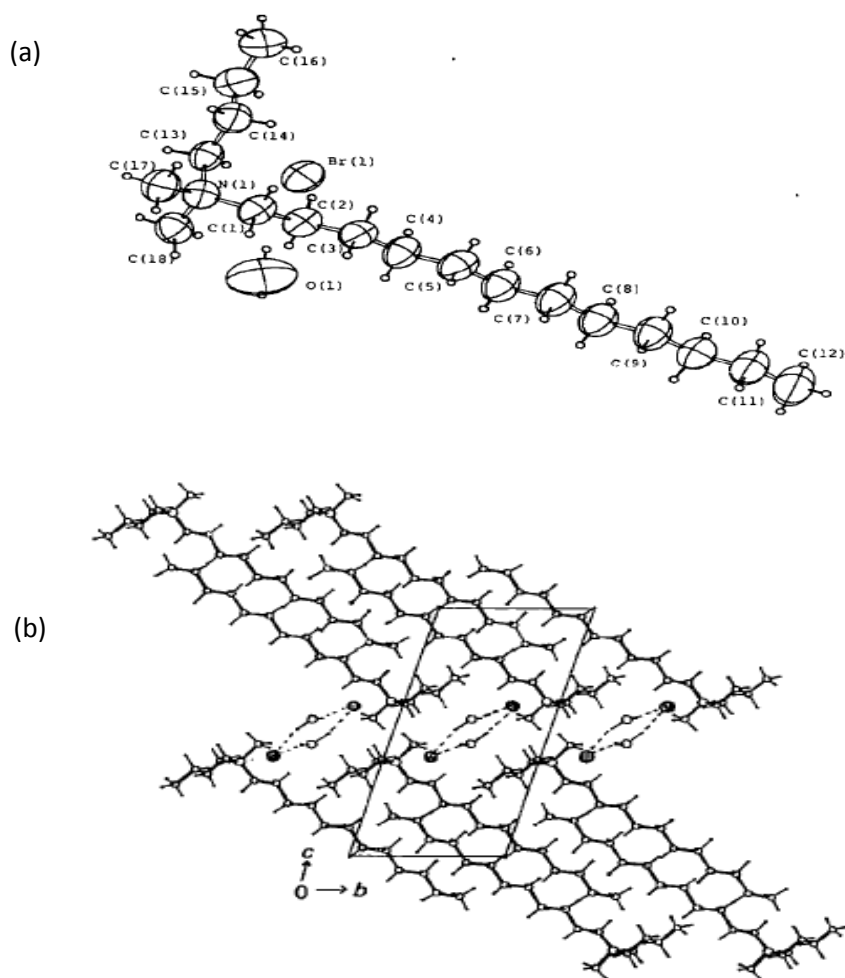
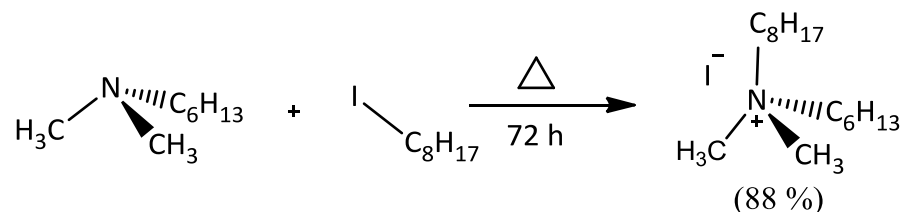


Figure 2.7. Representation of the molecular structure (a) and packing (b) of $N_{114(12)}Br \cdot H_2O$, taken from reference [8a].

2.2.5. Synthesis and characterization of C₆ series, $N_{116R}X$.

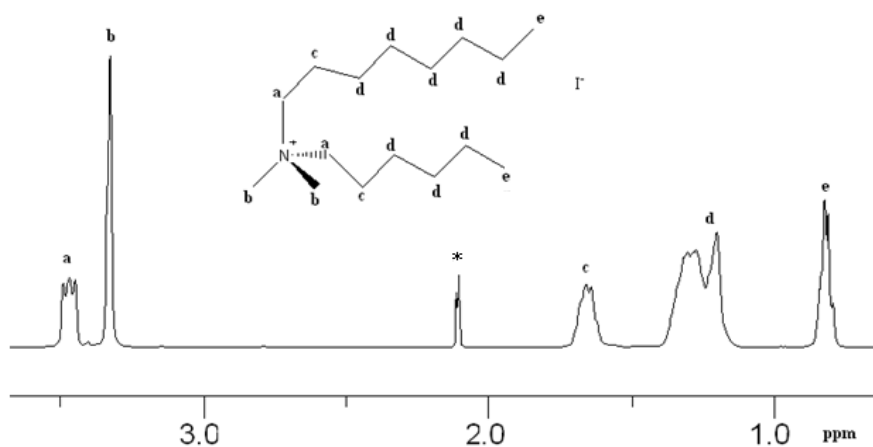
The C₆ series of quaternary ammonium halides were prepared in a similar manner to that of the above quaternary salts. A typical example is the reaction of dimethylhexylamine with 1-iodooctane (scheme 2.7), which after workup, resulted in a liquid in excellent yield. This is unusual at this stage of reaction, all the other aliphatic series prepared so far gave solid products at

this stage. This liquid had a honey-like colour and texture. Difficulties were encountered in purifying this product due to its very high viscosity. The product was washed with hexane six times and finally the remaining solvent was pumped off under vacuum with gentle heating.



Scheme 2.7. Synthesis of dimethylhexyloctylammonium iodide, N₁₁₆₈I.

The ¹H NMR spectrum of dimethylhexyloctylammoniumiodide (spectrum 2.5) shows a number of peaks. This spectrum shows a slight difference in the signals for the terminal CH₃ groups on the octyl and hexyl chains, these tend to overlap, appearing as a broad multiplet at $\delta = 0.81$ ppm (e) with relative intensity six, since both CH₃ groups are in almost the same environment. This wasn't the case with the butyl substituent analogues, where the two terminal CH₃ environments are sufficiently different appearing as two separate triplets.



Spectrum 2.5. ¹H NMR spectrum of dimethylhexyloctylammoniumiodide, N₁₁₆₈I (* = acetone).

The two α -CH₂ groups on both the hexyl and octyl chains adjacent to the nitrogen centre resonate at $\delta = 3.46$ ppm (a), this appears as a second order multiplet resulting from the complex overlap of the CH₂ groups.

The singlet at $\delta = 3.32$ ppm (b) is due to the CH₃ groups on the nitrogen centre. The two β -CH₂ groups on the hexyl and octyl resonate at $\delta = 1.64$ ppm (c). Again the ¹H NMR spectra of the longer chain ammonium salts show that the two CH₂ resonances tend to overlap. This is because the CH₂ groups arising from both the hexyl and the octyl chains are in very similar chemical environments.

The ¹H NMR spectrum shows that the product is of relatively high purity and this is confirmed by its elemental analysis (table 2.8).

Table 2.8. Elemental analysis of C6 series, N_{116R}X.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₆₈ I	liquid	52.01	9.83	3.79	51.67	10.09	3.79
N ₁₁₆₍₁₀₎ I	liquid	54.38	10.15	3.53	54.33	10.82	3.59

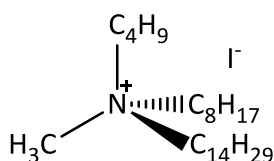
The longer chain halide salts (N₁₁₆₍₁₄₎)Br and N₁₁₆₍₁₈₎Br were paste-like materials and were very difficult to purify, and were therefore not studied further (see fig 2.8).



Fig 2.8. The appearance of the paste-like, $N_{116(14)}Br$ salt at r.t.

2.3. Synthesis of completely asymmetric quaternary ammonium salt, $N_{14R(14)}X$.

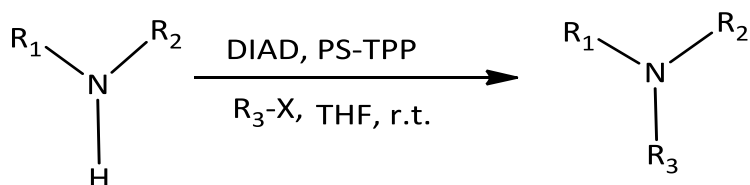
In addition to the asymmetric quaternary ammonium series mentioned earlier, fully asymmetric quaternary aliphatic ammonium halides, $N_{14R(14)}I$, see below, were prepared from the reaction of an asymmetric amine with an alkyl halide.^[9]



The first step in preparing the completely asymmetric quaternary ammonium salts, was to synthesise the asymmetric amine ($N_{14(14)}$).

Several methods were investigated for the synthesis of asymmetric tertiary amines but were unsuccessful. One attempt was that reported by Kurosu *et al.* which was based on the secondary amine alkylation with polymer-support

triphenylphosphine (PS-TPP) and diisopropylazo-carboxylate (DIAD) in THF at room temperature as shown in scheme 2.8.^[10]



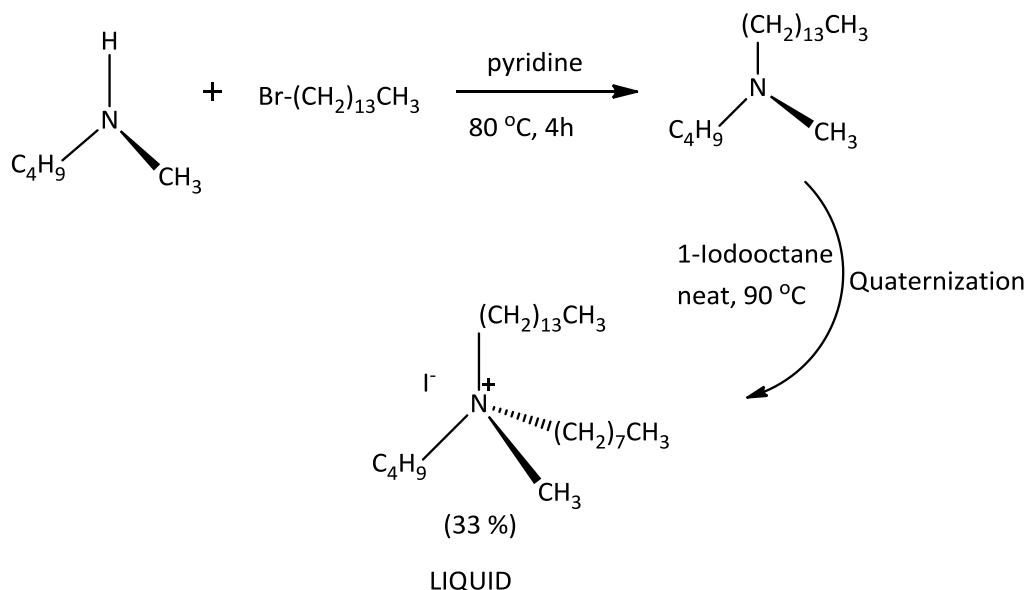
Scheme 2.8. N-alkylation of secondary amines reported by, Kurosu *et al.* [10].

In our attempts the actual combination of secondary amine and the alkylating agent was different from that reported but under the same working conditions. Ethyliodide was added dropwise to a suspension of the methylbutylamine (1.0 mmol), PS-TPP (~3.0 mmol/g) and DIAD (1.5 mmol) in THF, the mixture was stirred for 12 h at room temperature. A yellow liquid was isolated but from the NMR data, the reaction seems to be unsuccessful, the expected peaks were not observed in the ¹H NMR spectrum.

Another unsuccessful attempt was based on the alkylation of a secondary amine with an alkyl halide in the presence sodium hydroxide acting as hydrogen halide acceptor reported by Limanov *et al.*, followed by acetylation using AcOH and Ac₂O to separate the secondary amines from the tertiary amines.^[11] Extraction with dilute hydrochloric acid, then treatment with ether to remove impurities, followed by the adjustment of the pH to 9-10 and finally extraction with ether, resulted in a yellowish-grey liquid which showed no signals corresponding to the amine in the proton NMR.

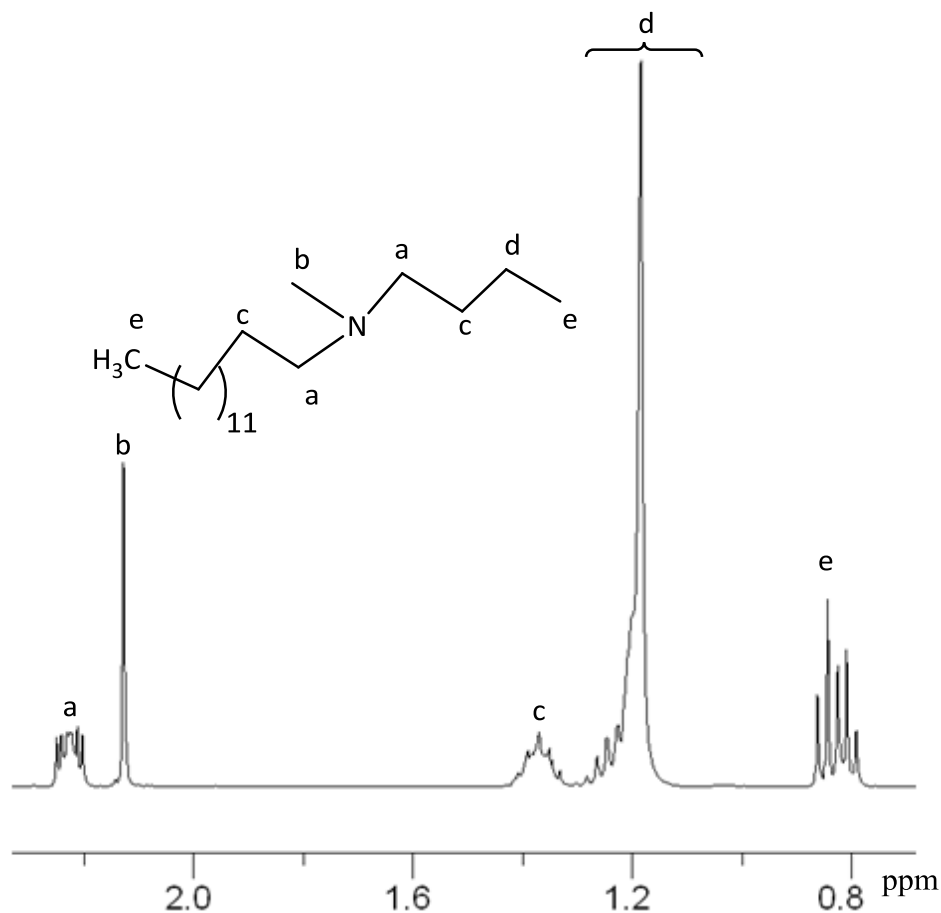
Eventually a successful procedure was investigated, this was achieved by reacting methylbutylamine with 1-bromotetradecane (scheme 2.9) in the presence of pyridine, after workup, resulting in a yellow oily liquid (N₁₄₍₁₄₎) as detailed in the experimental section, reported by Tanaka *et al.*^[9] The ¹H NMR spectrum of methylbutyltetradecylamine, N₁₄₍₁₄₎ (spectrum 2.6) shows five

different signals. The resonance at $\delta = 2.22$ ppm (a) is a second order multiplet resulting from the complex overlapping of the α -CH₂ groups of the butyl and tetradecyl chains. The methyl group on the nitrogen centre shows a singlet at $\delta = 2.13$ ppm (b).



Scheme 2.9. Synthesis of completely asymmetric quaternary ammonium salt.

The beta CH₂ of the octyl and tetradecyl chains appear as a single resonance at $\delta = 1.37$ ppm (c). This is a broad peak, presumably due to coupling to the two adjacent CH₂ groups. The remainder of the CH₂ groups appear as multiplets over the shift range $\delta = 1.18$ - 1.24 ppm (d). This is due to the overlapping of 12 CH₂ peaks (11 of the tetradecyl chain and 1 of the butyl chain) all in rather similar chemical environments which would all have a large number of couplings involved in their resonances and so appears as a broad signal. The terminal CH₃ groups resonate at $\delta = 0.83$ ppm (e), appearing as a multiplet due to the overlapping of the two triplet signals.



Spectrum 2.6. ^1H NMR spectrum of methylbutyltetradecyl amine, $\text{N}_{14(14)}$.

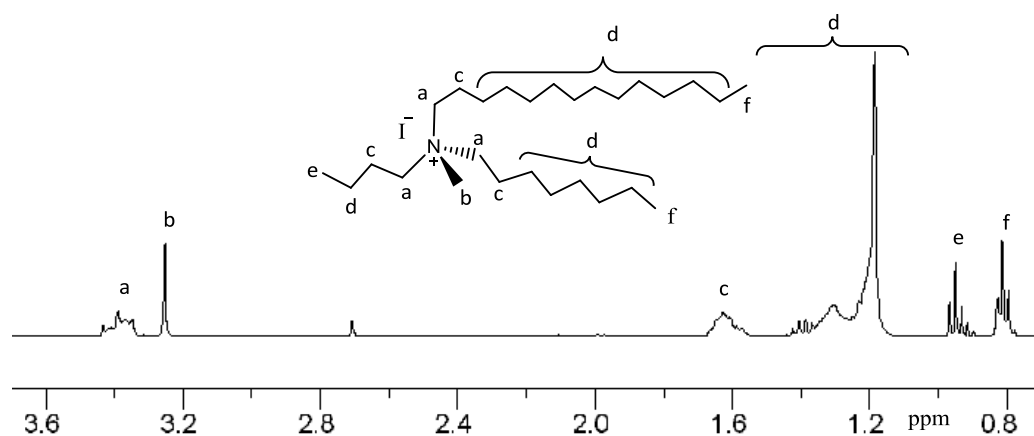
The ^1H NMR spectrum shows that the isolated tertiary amine is of high purity and this is supported by its elemental analysis as shown in table 2.9.

Table 2.9. Elemental analysis of tertiary amine, $\text{N}_{14(14)}$.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$\text{N}_{14(14)}$	liquid	80.47	14.58	4.94	79.99	14.64	5.31

The tertiary amine is then quaternised using different alkyl iodides (R-I, R= propyl, octyl, decyl and allyl) groups. On quaternising the asymmetric amine, $N_{14(14)}$ with 1-iodooctane, methylbutyloctyltetradecylammonium iodide, $N_{148(14)}I$ was isolated as an oily liquid. The 1H NMR spectrum of the completely asymmetric quaternary aliphatic ammonium iodide is shown in spectrum 2.7, this shows all the anticipated peaks.

The resonance at $\delta = 3.38$ (a) ppm is a second order multiplet that arises from the complex overlapping of the 3 α -CH₂ groups. The methyl resonance on the nitrogen centre gives a singlet at 3.25 ppm (b). The three beta CH₂ groups resonate at 1.63 ppm (c) which appears as a broad multiplet arising from the overlapping of the beta CH₂ groups on the butyl, octyl and tetradecyl chains due to them having similar chemical environments.



Spectrum 2.7. 1H NMR spectrum of methylbutyloctyltetradecylammonium iodide, $N_{148(14)}I$.

The rest of the CH₂ groups appear as multiplets over the shift range $\delta = 1.18$ -1.4 ppm (d). This is due to the overlapping of 17 CH₂ peaks (11 of the tetradecyl chain, 5 of the octyl chain and 1 of the butyl chain) in similar chemical environments which would all have a large number of couplings. The terminal CH₃ group on the octyl chain resonates at $\delta = 0.94$ ppm (e) appearing

as a triplet signal due to coupling to the adjacent CH₂ protons, this CH₃ group resonates at a slightly higher chemical shift value than that of the terminal CH₃ of the tetradecyl chain $\delta = 0.82$ ppm (f) due to its relative proximity to the ammonium centre. The ¹H NMR spectrum indicated that the product is of high purity and this is verified by the elemental analysis (table 2.10), where the calculated figures closely match those found.

All of the completely asymmetric quaternary ammonium salts isolated were liquids possessing relatively low melting points.

Table 2.10. Elemental analysis for the completely asymmetric salts, N_{14R(14)}I.

Sample identity	Melting point	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₄₈₍₁₄₎ I	11	61.91	11.17	2.68	62.28	10.97	2.96
N ₁₃₄₍₁₄₎ I	-22	58.24	10.67	3.09	59.77	10.43	2.71
N ₁₄₍₁₀₎₍₁₄₎ I.H ₂ O	-21	61.12	11.33	2.46	60.70	10.41	2.77
N _{14A(14)} I.2H ₂ O	16	54.18	10.34	2.87	54.13	9.46	3.35

2.4. Melting points of asymmetric quaternary ammonium salts.

Our prime interest in this work is the combination of ions that result in low melting point ionic liquids, near or below room temperature. It is well known that this characteristic property of ionic liquids varies with the choice of anion and cation. The structure of an ionic liquid directly impacts upon its properties, especially its melting point and liquidus range.

These halide salts are often referred to as ionic liquid precursors since they are used as starting materials for the metathesis to other ionic liquids via the reaction of a metal salt of the desired anion. Generally, melting points of organic salts are related to the symmetry of the ions: increasing symmetry in

the ions increases melting points, by permitting more efficient ion-ion packing in the crystal lattice.^[9,12] Conversely, a reduction in the symmetry of the ions causes a distortion from ideal close-packing of the ionic species in the solid state lattice, resulting in a reduction in the lattice energy, and depression of melting points. Table 2.11 shows the effect of symmetry on melting point for some reported aliphatic quaternary ammonium bromide salts, where the cation N_{abcd} has 4 linear alkyl substituents, the total length of which are 20 carbons, so the masses remain the same.

Table 2.11.^[12] Effect of symmetry for quaternary ammonium bromide salts on their melting point.

Cation ($[N_{abcd}]^+Br^-$)	Melting point °C
N_{5555}	101
N_{6644}	83
N_{8444}	67

After synthesizing the asymmetric quaternary ammonium halides and purifying them to a satisfactory degree the major concern was the determination of their melting points and a comparison of the influence introducing asymmetry has on their melting points. Melting points were measured using the traditional capillary tube method and the DSC technique. A significant decrease in the melting point was observed with increase in asymmetry as shown in table 2.12. This is illustrated by the completely asymmetric quaternary ammonium iodides which are liquids at room temperature with a melting point lower than all of those stated in table 2.12, $N_{148(14)}I$ mp = 11, $N_{143(14)}I$ mp = -22, $N_{14allyl(14)}I \cdot 2H_2O$ mp = 16, $N_{14(10)(14)}I \cdot H_2O$ mp = -21 °C.

The melting points ranged from 208 °C to below room temperature (fig. 2.9). All of the quaternary ammonium halides obtained showed melting points

lower than that of the completely symmetric quaternary ammonium halide ($N_{1111}Br$) which is above 300 °C.^[12]

Table 2.12. Asymmetry Vs melting point (°C) for the $N_{11RR'}X$ quaternary halides (X = Br, I).

R \ R'	octyl	decyl	tetradecyl	octadecyl
Me	131	128	109	109
Et	111	109	101	110
iPr	196	205	206	206
Bu	92	56	52	75
Hex	liquid@rt	Liquid@rt	Paste-like	Paste-like

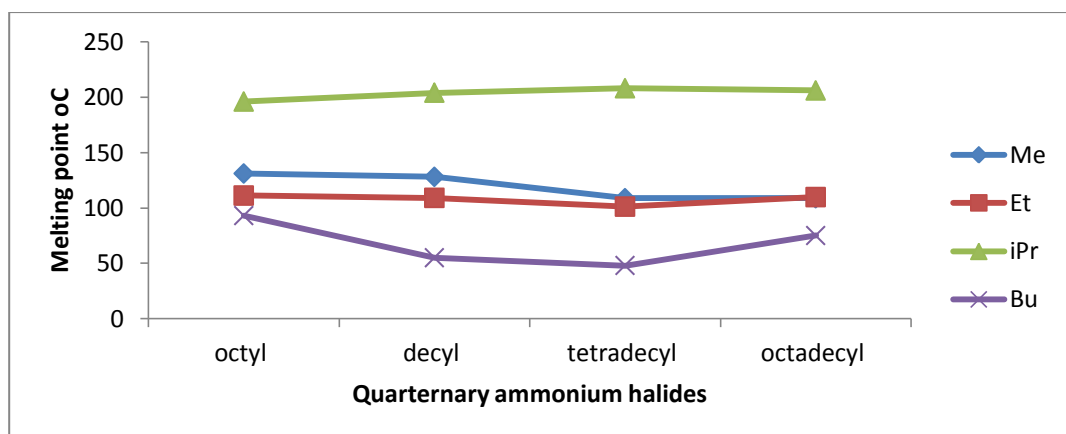


Figure 2.9. Effect of asymmetry on melting points of QA halides, $[N_{11RR'}]^+$.

Increasing the chain length of one of the chains in the sequence octyl, decyl, tetradecyl and octadecyl reduces the melting point to 131, 128, 109 and 109 °C respectively.

Similarly, by replacing one of the methyl groups with a longer chain length in the parent amine to C_2 , C_3 , C_4 or C_6 , resulted in changes in the observed melting points. However, some less obvious trends were observed. The C_3 series showed higher melting points than the C_1 series, unlike the other series which showed a depression in the melting points as expected, as did the C_6

series to the point that these were liquids at room temperature. The C₁ series were expected to give the highest melting points because of their smaller size but this wasn't the case. Infact, the isopropyl series (C₃) showed unexpectedly high melting points. This may be explained due to the branching in the isopropyl chain (unfortunately the *n*-propyldimethylamine is not commercially available). It has been reported that the degree of branching, influences the efficiency of the crystal packing as the free rotation volume decreases and atom density is increased ^[12]

A similar trend has been reported for isomeric-alkyl substituted imidazolium salts, [pmim]PF₆ as shown in table 2.13, i.e the melting point increased with the degree of branching in the alkyl substituent. ^[12]

Table 2.13. Melting Points for [bmim]PF₆ and [pmim]PF₆ salts. ^[12]

N(1)-Substitution	Melting point (°C)
n-butyl ([bmim])	6
s-butyl ([bmim])	83
t-butyl ([bmim])	159
n-propyl ([pmim])	40
i-propyl ([pmim])	102

*[bmim]= butylmethylimidazolium, [pmim]= pentylmethylimidazolium

Whereas increasing the linear alkyl chain length in symmetric quaternary salts decreased their melting points (table 2.14) up to a certain length $n = 8$, for $n > 8$ there is a gradual increase in melting point with increasing chain length. ^[12] Aguirre *et al.* reported that an increase in the linear alkyl chain substituents increases the Van der Waals interaction energy and thus the melting point.

Moreover, the replacement of the hydrogen atom in the C2 position by a methyl group in the imidazolium ionic liquids increases its melting point.^[13]

Therefore, both the ion symmetry and the alkyl substitution on the cationic species appear to influence the efficient packing of ions in a crystalline lattice.

Table 2.14. Melting points for symmetric quaternaryalkylammonium bromide salts.^[12]

Cation	Melting point °C
[Me ₄ N]	>300
[Et ₄ N]	284
[Bu ₄ N]	121-128
[Hex ₄ N]	99-100
[Oct ₄ N]	95-98

Introduction of asymmetry into quaternary ammonium halides has a profound influence on their respective melting points (fig 2.9), Since the completely asymmetric quaternary iodides N_{14R(14)}I are liquids at room temperature. A similar trend has been reported by Gordon *et al.*^[14] working in the area of molten salts, who noted that lowering the symmetry of the cation effectively lowers the melting point, for example the melting point of N₅₅₅₅Br is 101 °C while N₃₄₅₈Br is a liquid at room temperature but their work seemed to stop at this point, no further articles have appeared since 1978.

2.5. Conclusion

The introduction of asymmetry into quaternary ammonium halides was found to have a considerable influence on their relevant melting points making it a potential route in the development of RTILs.

Asymmetric quaternary ammonium salts were established by reacting asymmetric amines (N_{11R}, R = 1, 2, 3, 4, 6) with a range of alkyl halides (R'X), defined as C1, C2, C3, C4 and C6 series according to the amine used in addition to the completely asymmetric ammonium iodides of the formula

(N_{14R(14)}I, R = propyl, octyl, decyl and allyl). The melting points of the isolated salts decreased as the linear alkyl chain length increased.

The most promising series are the butyl (C4) and hexyl (C6) series which showed low melting points compared to the smaller analogues in addition to the completely asymmetric quaternary ammonium iodides. All the butyl series showed melting points below 100 °C, and are classified as ionic liquids whereas the hexyl series and the completely asymmetric quaternary ammonium iodide are liquids at room temperature which is unusual at this stage of synthesis. It is usually necessary for the halide to be exchanged by larger anions to obtain RTILs.

In contrast to this, the branched alkyl chains (isopropyl (C3) series) in quaternary ammonium halides elevated the melting point of the salts predominantly in agreement to that reported in literature.^[12] Almost all salts were highly pure and could be prepared with high yields.

2.6. References

1. D. R. MacFarlane and M. Forsyth, *Adv. Matter.*, 2001, **13**, 957.
2. J. Sun, M. Forsyth, D.R. MacFarlane, *J. Phys. Chem. B* 1998, **102**, 8858.
3. D. R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *J. Phys. Chem. B* 1999, **103**, 4164.
4. H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, *Chem. Lett.* 2000, 922.
5. S. Forsyth, J. Golding and D. R. MacFarlane and M Forsyth, *Electrochim. Acta*, 2001, **46**, 1753.
6. H. Sakaebō and H Matsumoto, *Electrochem. Commun.*, 2003, **5**, 594.
7. A. D. Ballantyne, Ph.D thesis, (2008), University of Manchester.
8. (a) T. Taga, Y. Miwa and K. Machida, *Acta Cryst.* 1990, **C46**, 293. (b) L. Cammarata, S. G. Kazarian, P. A. Salter and T. Welton, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5192.
9. M. Tanaka, A. Rastogi, G. N. Toepfferwein, R. A. Riggelman, N. M. Felix, J. J. de Pablo and C. K. Ober., *Chem. Mater.* 2009, **21**, 3125.
10. M. Kurosu, S. S. Dey and D. C. Crick, *Tetrahedron Letters*, 2006, **47**, 4871.
11. V.E. Limanov, N.V. Myazina, and I.M. Tsivrova, Translated from *Khimikofarmatsevticheskii Zhurnal*, 1990, **24**, 36.
12. T. Welton, P. Wasserscheid, *Ionic liquids in Synthesis*, 2nd edition Wiley-VCH, Weinheim New York, 2002.
13. C. L. Aguirre, L. A. Cisternas, J. O. Valderrama, *Int. J. Thermophys.*, 2012, **33**, 34.
14. J. E. Gordon and G.N. Subba Rao, *J. Am. Chem. Soc.*, 1978, **100**, 7445.

3. Synthesis and Characterisation of fluorinated and non-aliphatic quaternary ammonium salts.

3.1 Introduction

3.2 Synthesis and characterization of asymmetric fluorinated quaternary ammonium salts.

3.3 Synthesis of completely asymmetric fluorinated quaternary ammonium salt

3.4 Synthesis and characterization of asymmetric non-aliphatic quaternary ammonium salts with benzyl, allyl and cyclohexyl substituents.

3.4.1. Synthesis and characterization of dimethylbenzylalkylammonium halide series of compounds, N_{11BR}X.

3.4.2. Synthesis and characterization of dimethylallylalkylammonium halide series of compounds, N_{11AR}X.

3.4.3. Synthesis and characterization of dimethylcyclohexylammonium halide series of compounds, N_{11CR}X.

3.5. Conclusion

3.6. References.

3.1 Introduction

The melting points of ionic liquids are influenced by the size and shape of the ions resulting in changes in their lattice energy. It has been demonstrated that large asymmetric ions result in lowering the melting point. Since the asymmetric aliphatic quaternary ammonium iodides studied in chapter 2 are claimed to possess remarkably low melting points further reactions were performed to introduce different groups such as the benzyl, allyl, cyclohexyl and fluorinated groups on the nitrogen centre to investigate the effect they had on the melting points compared to the asymmetric aliphatic quaternary ammonium salts. Whilst it is common for anions in ionic liquids to be fluorinated, such as TFSI^- , BF_4^- , PF_6^- there are relatively few reports on fluorinated cations. Commercially there is a limited number of fluorinated amines to use in our reaction, those that are available are perfluorinated amines such as tris(perfluorobutyl)amine but they show no substantial basic properties, so are not suitable for preparing quaternary ammonium salts.^[1]

Yagupol'ski *et al.* in 1980 reported the synthesis of quaternary ammonium salts with fluorinated cations of the type, $[\text{MeR}_2\text{N}(\text{CF}_3)]^+\text{BF}_4^-$.^[2] These salts showed a wide range of melting points from 265 °C ($\text{R} = \text{CH}_3$) to 53 °C for dimethyltrifluoromethyl-p-chloro phenylammonium tetrafluoroborate.

In 1989, Nogami *et al.* reported the quaternisation of 1,4-diazabicyclo[2.2.2.]octane (DABCO) with long-chain poly- and perfluoroalkyl halides, such as $\text{CF}_3(\text{CF}_2)_9\text{CH}_2\text{Br}$ and $\text{CF}_3(\text{CF}_2)_7\text{I}$ to form solid compounds of the type $[\text{R}_f\text{-DABCO-R}_f]\text{X}_2$ and $[\text{R}_f\text{-DABCO-R}]\text{X}_2$.^[3]

There are, however, reports of quaternary ammonium salts containing fluorinated chains possessing spacer units of the type $\text{R}_f(\text{CH}_2)_n-$ ($n = 2, 3, 5$). Thus, the quaternisation of R_3N , $\text{R} = \text{Bu}$, Oct with $\text{I}(\text{CH}_2)_2(\text{CF}_2)_n\text{CF}_3$, ($n = 3, 7, 9$) is reported to give the quaternary ammonium iodides $[\text{R}_3\text{N}(\text{CH}_2)_2(\text{CF}_2)_n\text{CF}_3]\text{I}$ in *ca.* 80 % yield.^[4] Interestingly, the authors reported that there is relatively

little effect on the physical properties of the ammonium salt on changing the fluorine-containing alkyl chain. Thus, the salts $[\text{Oct}_3\text{N}(\text{CH}_2)_2(\text{CF}_2)_n\text{CF}_3]\text{I}$ ($n = 3, 7, 9$) were reported to be room temperature ionic liquids, all of which possess melting points within the range 18-22 °C, whilst the *n*-Bu analogues melt at temperatures between 82-91 °C.

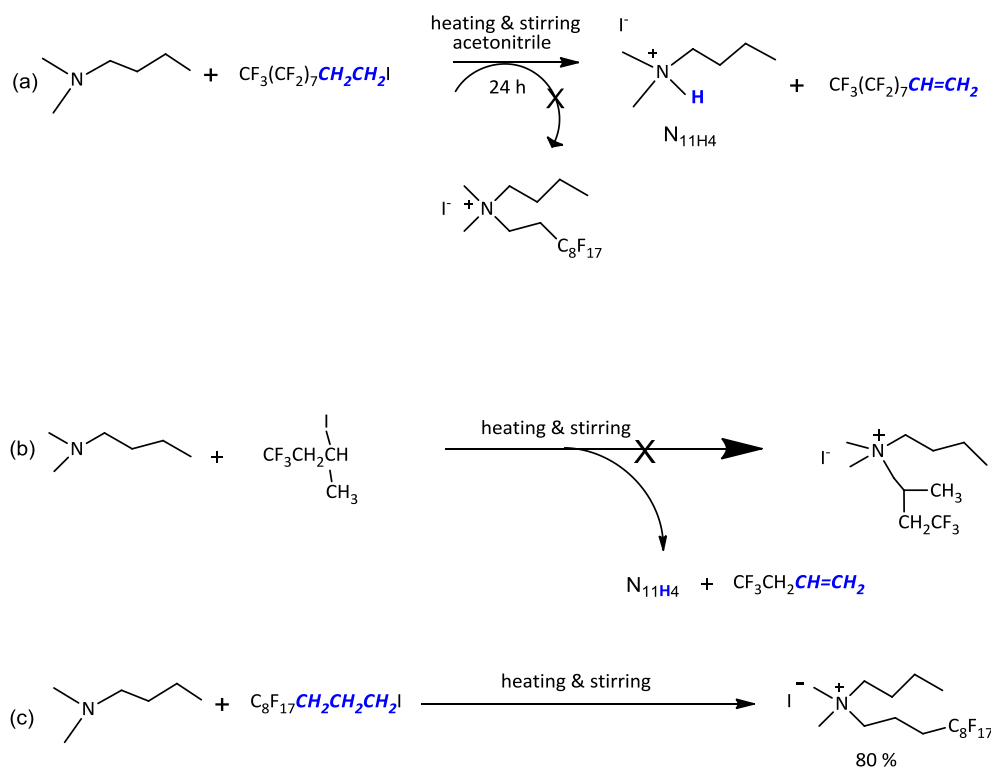
More recently in 2010, Gladysz *et al.* reported the use of fluorous quaternary ammonium salts of the type $[\{\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_5\}_3\text{N}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3]\text{I}$ including both $-(\text{CH}_2)_2$ and $-(\text{CH}_2)_5$ spacer units for phase transfer catalysis.^[5]

A number of quaternary ammonium systems containing a $-\text{CH}_2\text{CH}_2\text{CH}_2-\text{R}_f$ group have been reported previously; these include the synthesis of $[\text{C}_8\text{F}_{17}(\text{CH}_2)_3\text{NBu}_3]\text{F}$, a fluorous analogue of tetra *n*-butylammonium fluoride (TBAF),^[6] fluoroalkyl-containing compounds such as $[\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_3\text{NR}_3]\text{I}$ ($\text{R} = \text{Me}, \text{Et}$) with biological activity,^[7] and solvents for electrochemical deposition.^[8]

However, in each of these cases the degree of asymmetry around the nitrogen centre is low. We, and others, have previously reported that by reducing the symmetry of the constituent ions the melting point of an ionic liquid is generally lowered. This is, in part, because of the influence that the size and shape of the ions have on the packing arrangement and hence lattice energy. Since the reported fluorous ammonium iodides described above are claimed to possess low melting points we sought to increase the degree of asymmetry around the nitrogen centre by studying the reaction of $\text{I}(\text{CH}_2)_m(\text{CF}_2)_n\text{CF}_3$ ($m = 2, 3; n = 3, 7$) with asymmetric amines such as *i*-PrMe₂N or *n*-BuMe₂N, in doing so we have identified some inconsistencies with some of the previously reported studies.

3.2 Synthesis and characterization of asymmetric fluorinated quaternary ammonium salts

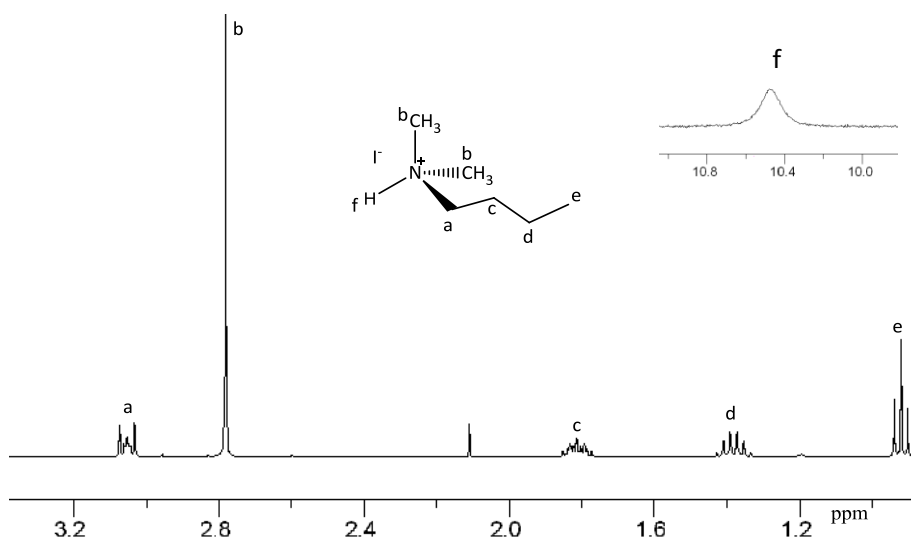
Several attempts were made to introduce fluorine in the cationic species of an ionic liquid using similar methods to those outlined in chapter 2. A typical example is the reaction of dimethylbutyl amine, Me_2BuN , with 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide, $\text{ICH}_2\text{CH}_2\text{R}_f$ ($\text{R}_f = \text{C}_8\text{F}_{17}$) performed by heating the two materials together in a sealed Shlenk tube at both temperatures 90 and 150 °C for 24 hours, giving a white solid (mp 120.7 °C) (scheme 3.1(a)).



Scheme 3.1. Attempts to synthesise fluorinated quaternary ammonium species.

The ^1H NMR spectrum of the product of reaction 3.1(a) is shown in spectrum 3.1. It showed that the CH_2CH_2 spacers of the perfluoroiodide are not present in the product, however peaks consistent with the presence of butyl and

methyl groups (1.00, 1.46, 1.89, 2.81 and 3.06 ppm) are observed all of which show a shift from those of the starting amine, (0.85, 1.25, 1.37 and 2.14 ppm) suggesting that quaternisation has occurred but without incorporation of the fluorinated chain. This was supported by the fluorine NMR spectrum that showed no significant signals due to the expected fluoroalkyl chain. However, an additional signal appeared as a broad singlet (f) at 10.47 ppm in the proton NMR spectrum, integrating to a single proton, suggesting the presence of hydrogen directly bonded to the nitrogen centre, signifying that the product contained the $\text{Me}_2\text{BuNH}^+ [\text{N}_{11}\text{H}_4]^+$ cation.



Spectrum 3.1 ^1H NMR spectrum of dimethylbutylammonium iodide, N_{114}H .

The elemental analysis values were also inconsistent with $[\text{n-BuMe}_2\text{NCH}_2\text{CH}_2(\text{CF}_2)_7\text{CF}_3]\text{I}$, but suggest that $[\text{n-BuMe}_2\text{NH}]\text{I}$ might have been formed instead, as shown in table 3.1. This would be consistent with the additional signal in the proton NMR spectrum.

Furthermore, crystals suitable for X-ray diffraction were successfully grown

from a DCM/hexane layered solution of the solid product. Its molecular structure is shown in fig 3.1 and selected bond lengths (Å) and angles (°) are given in table 3.2 confirming that $[n\text{-BuMe}_2\text{NH}]\text{I}$ had been formed. The unit cell parameters are: trigonal, space group R-3, $a = 36.558(8)$, $b = 36.558(8)$, $c = 7.828(8)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 120^\circ$, $V = 9060(12)$ Å³.

Table 3.1 Elemental analysis for $\text{N}_{114}\text{H}\text{I}$.

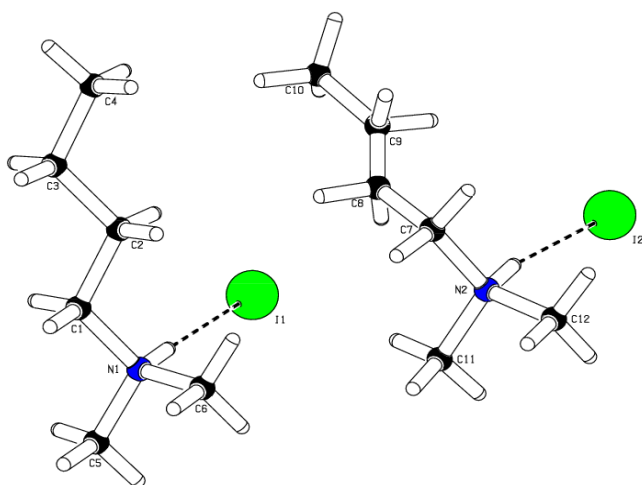
Sample identity	Elemental analysis					
	Theoretical %			Found %		
	C	H	N	C	H	N
$\text{N}_{114}\text{H}\text{I}$	31.44	7.04	6.11	31.95	6.10	5.01
$\text{N}_{114}(\text{CH}_2)_2(\text{CF}_2)_7\text{CF}_3\text{I}$	28.44	2.84	2.07	31.95	6.10	5.01

The crystal structure data shows that there are two unique molecules contained within the unit cell, both show similar features around the nitrogen centre, the C-N bond lengths lie between 1.50(2) and 1.52(3) Å, whilst the C-N-C bond angles range from 109.4(13) – 114.(13). One of the carbon atoms, C(9), of the butyl chain in the second molecule shows some disorder, whilst the other molecule does not. It is clear from this data that, in agreement with the spectroscopic data, $[\text{Me}_2\text{BuNH}]^+\text{I}^-$ has been formed.

Classical hydrogen bonds are formed between each N-H unit and an iodide with $\text{H}\cdots\text{I}$ distances of 3.458(15) and 3.463(15) Å with a near linear arrangement of the N-H $\cdots$ I fragment.

The packing diagram, fig. 3.1(b), viewed down the c -axis, shows that a micellar-like structure is adopted, in that all the butyl chains point towards each other such that at the four corners of the unit cell micelles are generated, with two more contained within the cell. This is composed of six sets of alternating residues 1 and 2, with the iodides sitting above and below the quaternary nitrogen centre.

(a)



(b)

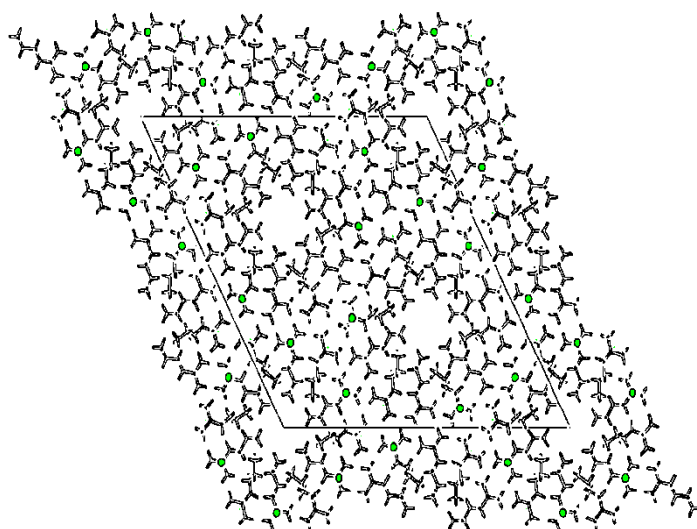


Figure 3.1 Representation of the molecular structure (a) and packing (b) of N_{114HI} .

In this way channels are generated parallel to the *c*-direction which in total constitute *ca.* 7.5% of the cell volume. Interestingly, a search of the crystallographic database shows that there are no crystal structures of other

dimethylalkylammonium halides (H-systems) with which to make a direct comparison.

Table 3.2 Selected bond lengths and bond angles for N₁₁₄Hl.

Bond	Length (Å)	Angle	Angle (°)
N1-C1	1.51(2)	C1-N1-C5	111.5(13)
N1-C5	1.50(3)	C1-N1-C6	111.7(15)
N1-C6	1.51(2)	C5-N1-C6	110.4(14)
N1-H1	0.93	C1-N1-H1	108.0
N2-C7	1.50 (2)	C5-N1-H1	107.0
N2-C11	1.52(3)	C6-N1-H1	108.0
N2-C12	1.52 (2)	C7-N2-C11	114.0(13)
N2-H2	0.93	C7-N2-C12	112.0(14)
N1-H1...I1	3.458(15)	C11-N2-C12	109.4(13)
		C11-N2-H2	107.0
		C12-N2-H2	107.0
		C7-N2-H2	107.0

However, for well known cationic surfactants, such as hexadecyltrimethylammonium bromide the longer alkyl chains are found to lie parallel to each other, rather than forming the micellar-like arrangement observed here.^[9]

In addition to solid [BuMe₂NH]I being generated, a liquid product was also formed, the ¹⁹F NMR spectrum of which showed the presence of a CF₃ group and CF₂ signals. The ¹H NMR spectrum of this liquid displayed two second-order signals in the ratio 1:2 at 5.75 and 5.91 ppm. These data are assigned to heptafluoro-1-decene by comparison with previously published NMR data.^[10] Thus, the reaction between neat Me₂BuN and ICH₂CH₂C₈F₁₇ at 80 °C results in [*n*-BuMe₂NH]I and CH₂=CHC₈F₁₇.

When similar reactions are performed using the shorter chain C2-spacer fluorinated alkylhalide, ICH₂CH₂R_f (R_f = C₆F₁₃) and the secondary fluorinated alkylhalide, 3-iodo-1,1,1-trifluorobutane, CH₃CHICH₂CF₃, the formation of

quaternary ammonium salts of the type $[R_2R'NH]I$ and $RfCH=CH_2$ also predominates (scheme 3.1 (b)). Table 3.3 shows the elemental analysis along with the reaction system involved.

Table 3.3. Elemental analysis for products of some hydrofluoroalkyl iodides with Me_2BuN & Bu_3N , and calculated values in parenthesis for possible quaternary products.

System	% C	% H	% N	mp (°C)
$BuMe_2N + I(CH_2)_2(CF_2)_5CF_3$ $[BuMe_2N(CH_2)_2(CF_2)_5CF_3]I$ $[BuMe_2NH]I$	31.95 (29.22) (31.44)	6.10 (3.33) (7.04)	5.01 (2.44) (6.11)	116-118
$BuMe_2N + I(CH_2)_2(CF_2)_7CF_3$ $[BuMe_2N(CH_2)_2(CF_2)_7CF_3]I$ $[BuMe_2NH]I$	30.63 (28.44) (31.44)	5.16 (2.84) (7.04)	4.31 (2.07) (6.11)	116-117
$Bu_3N + I(CH_2)_2(CF_2)_7CF_3$ $[Bu_3N(CH_2)_2(CF_2)_7CF_3]I$ $[Bu_3NH]I$	45.66 (34.78) (45.99)	9.18 (4.12) (9.01)	4.44 (1.84) (4.47)	103 ¹¹ 97
$BuMe_2N + CH_3CHICH_2CF_3$ $[BuMe_2NCH(CH_3)CH_2CF_3]I$ $[BuMe_2NH]I$	31.86 (35.39) (31.44)	7.14 (6.24) (7.04)	6.02 (4.13) (6.11)	111-114

These findings are interesting, in that the reaction of tri(*n*-butyl)amine with perfluorobutylethyl iodide $ICH_2CH_2(CF_2)_3CF_3$ has been reported by Shreeve *et al.* to give the fluorinated quaternary ammonium iodide, $[N_{444}(CH_2CH_2(CF_2)_4)]I$.^[4] However, in our case, reacting tri(*n*-butyl)amine (or dimethylbutyl amine) with $ICH_2CH_2(CF_2)_7CH_3$ resulted in tributylammonium iodide, $N_{444}HI$ or dimethylbutylammonium iodide, $N_{114}HI$ respectively. In addition reacting dimethylbutyl amine with the secondary fluorinated alkyl halide, $CH_3CHICH_2CF_3$ also lead to the same product, $N_{114}HI$. Table 3.3 shows the reactions undertaken, in an attempt to prepare a fluorinated quaternary ammonium iodide and their elemental analyses.

On moving to a fluorinated halide with a C3-spacer a successful quaternisation reaction occurred resulting in isolation of the expected fluorinated cationic

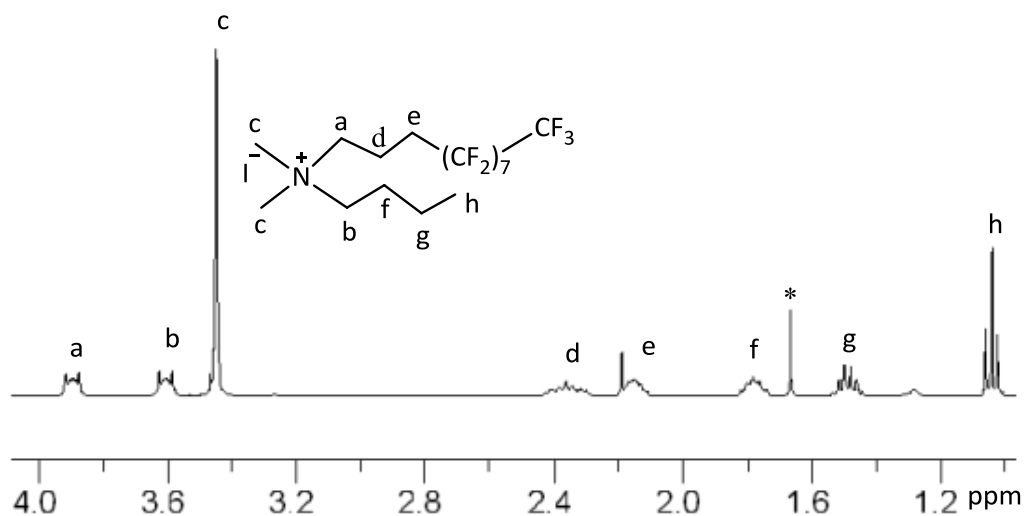
species Scheme 3.1 (b)).^[6a] For example, treating dimethylbutylamine with 1-iodo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-heptadecafluoro undecane in acetonitrile in a sealed Shlenk tube at 150 °C (scheme 3.1) over 24 hours yielded, after workup, a solid, for which elemental analysis figures consistent with [BuMe₂N(CH₂)₃(CF₂)₇CF₃]I were obtained (table 3.4).

Table 3.4 Elemental analysis for products from reaction of C3-spacer (Rfl) with Me₂BuN, Me₂*i*PrN and Bu₃N.

System	% C	% H	% N	mp °C
Me ₂ BuN + I(CH ₂) ₃ (CF ₂) ₇ CF ₃ [Me ₂ BuN(CH ₂) ₃ (CF ₂) ₇ CF ₃]I	30.13 (29.61)	2.88 (3.07)	2.08 (2.03)	167(dec)
Me ₂ <i>i</i> PrN + I(CH ₂) ₃ (CF ₂) ₇ CF ₃ [Me ₂ <i>i</i> PrN(CH ₂) ₃ (CF ₂) ₇ CF ₃]I	28.75 (28.44)	3.12 (2.84)	2.50 (2.07)	183 (dec)
Bu ₃ N + I(CH ₂) ₃ (CF ₂) ₇ CF ₃ [Bu ₃ N(CH ₂) ₃ (CF ₂) ₇ CF ₃]I	36.03 (35.70)	4.41 (4.30)	1.91 (1.81)	83-86
Me ₂ BuN + I(CH ₂) ₃ (CF ₂) ₃ CF ₃ [Me ₂ BuN(CH ₂) ₃ (CF ₂) ₃ CF ₃]I	32.31 (31.90)	4.38 (4.33)	3.13 (2.86)	140-142
Me ₂ <i>i</i> PrN + I(CH ₂) ₃ (CF ₂) ₃ CF ₃ [Me ₂ <i>i</i> PrN(CH ₂) ₃ (CF ₂) ₃ CF ₃]I	30.54 (30.31)	3.87 (4.03)	3.29 (2.95)	>190(dec)

In this case the proton NMR spectrum showed the presence of peaks corresponding to the alkyl groups on the starting amine, shifted to higher frequency (spectrum 3.2). In addition, resonances for the three CH₂ spacer groups were observed at 2.16, 2.36 and 3.9 ppm denoted as (e), (d) and (a) in spectrum 3.2, also shifted to higher frequency compared with the starting iodide (2.02, 2.23 and 3.18 ppm).

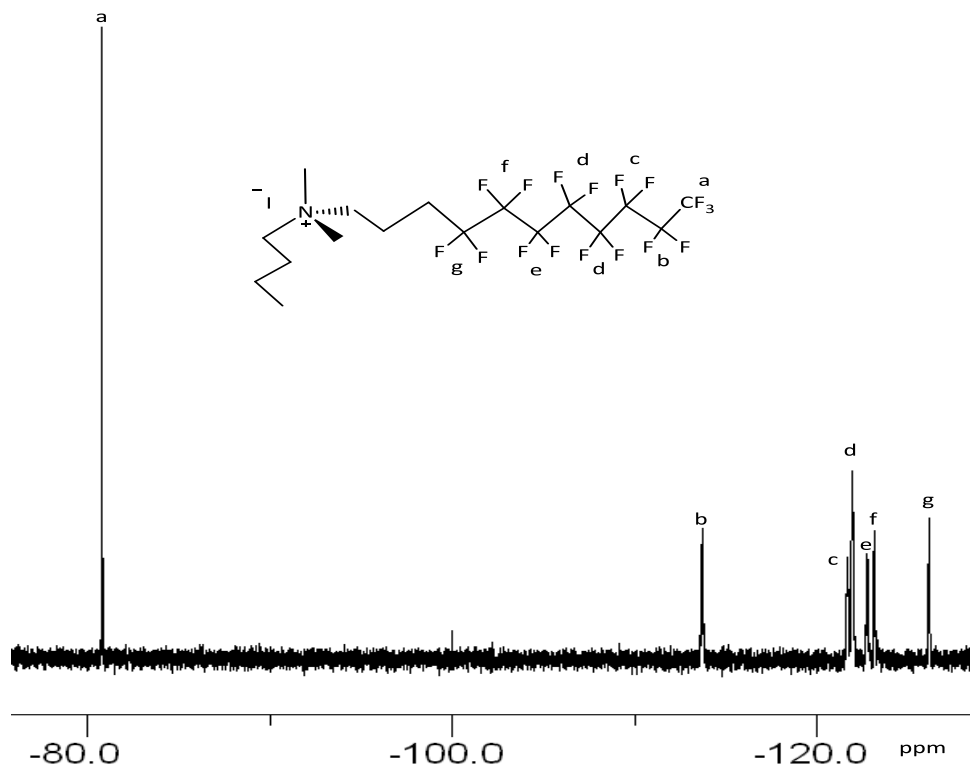
The resonance at $\delta = 1.04$ ppm (h) appearing as a triplet is due to the terminal methyl protons on the butyl chain coupling to the adjacent CH₂ protons.



Spectrum 3.2 ^1H NMR spectrum of dimethylbutyl-1H,1H,2H,2H,3H,3H-perfluoroundecylammonium iodide, $\text{N}_{114}(\text{CH}_2)_3(\text{CF}_2)_7\text{CF}_3\text{I}$. (*=water impurity in CDCl_3)

The CH_2 next to the terminal methyl group on the butyl chain is observed as a multiplet at $\delta = 1.48$ ppm (g). The $\beta\text{-CH}_2$ on the butyl chain appears as a broad multiplet at $\delta = 1.78$ ppm (f). The singlet at $\delta = 3.44$ ppm (c) arises from the methyl protons directly bonded to the nitrogen centre. The CH_2 group adjacent to the nitrogen centre on the butyl chain resonates at δ 3.6 ppm (b) and appears as a second order multiplet.

The ^{19}F NMR spectrum showed the expected peaks (spectrum 3.3); the CF_3 signal appears as a triplet at $\delta = -80.77$ ppm (a) due to the coupling to the adjacent CF_2 group.



Spectrum 3.3. ^{19}F NMR spectrum of dimethylbutyl 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecylammonium iodide, $\text{N}_{114}(\text{CH}_2)_3(\text{CF}_2)_7\text{CF}_3\text{I}$.

The multiplet at $\delta = -113.68$ ppm (b) arises from the CF_2 next to the terminal CF_3 . The rest of the signals at c, d, e, f, g integrate in the ratio 2:4:2:2:2 and are assigned to CF_2 groups where the two middle CF_2 groups are almost in the same chemical environments so their signals overlap.

These elemental analysis data obtained from the reactions between Bu_3N , *i*-PrMe₂N with $\text{I}(\text{CH}_2)_3(\text{CF}_2)_7\text{CF}_3$ and BuMe_2N and *i*-PrMe₂N with $\text{I}(\text{CH}_2)_3(\text{CF}_2)_3\text{CF}_3$ are summarised in table 3.4.

From the data presented in tables 3.3 and 3.4 it is clear that the 2-spacer fluorinated groups, $-\text{CH}_2\text{CH}_2\text{Rf}$ did not quaternise with the amines we investigated, and this may be due to the fact that the $-\text{CH}_2\text{CH}_2$ spacer is insufficiently long to insulate the electron withdrawing effects of the

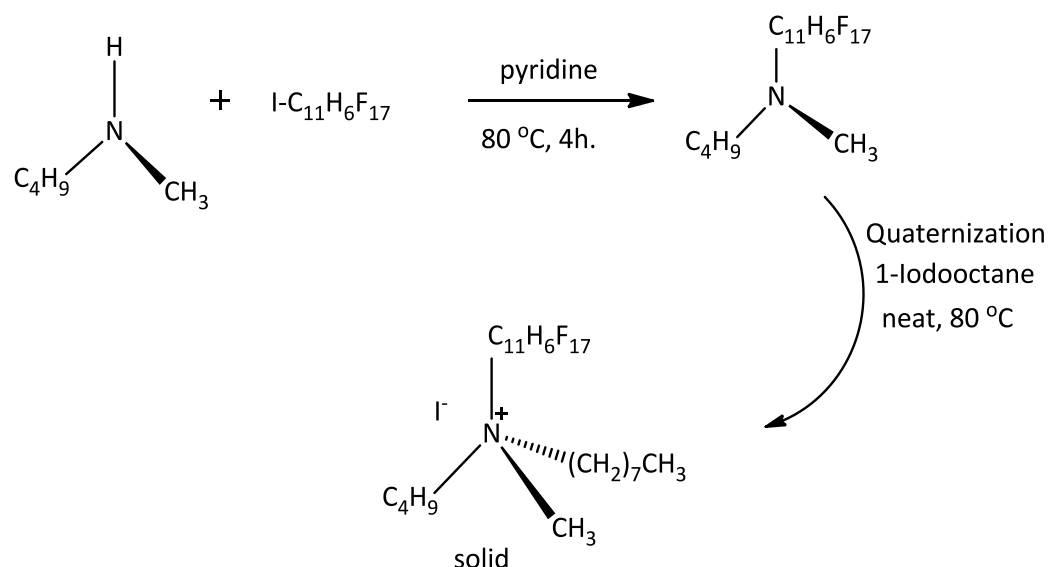
fluorines, so the CH₂ protons are acidic and deprotonation and elimination of HI occurs instead. That HI reacts with the amine to give the observed H-containing quaternary systems shown in table 3.3. Whereas the 3-spacer groups formed the anticipated quaternised salts. A similar effect was reported by Hope *et al.* on the P-Se coupling constants in trisarylphosphine selenides possessing fluoroalkyl chain with different spacer groups.^[6b] The authors reported that an additional CH₂ group in the spacer affords better insulation of the phosphorus atom from the electronic properties of the perfluoroalkyl groups.

Introducing fluorinated groups on the cation unfortunately resulted in solids of high melting points, which are not consistent with the aim of our work. A similar observation has been reported by Le *et al.* for the TFSI exchanged ammonium-based ionic liquids with smaller alkyl groups (with three methyl groups and a butyl group terminally fluorinated).^[6c] By replacing the terminal methyl group of the butyl chain around the nitrogen with a CF₃ one induced the elevation of melting point. For example, the melting point of the fluorinated salt is 90 °C whereas that of the N₁₁₁₄TFSI is only 17 °C, this increase in melting point is claimed by the authors possibly arising from hydrogen bonds to the fluorine of the CF₃ group.

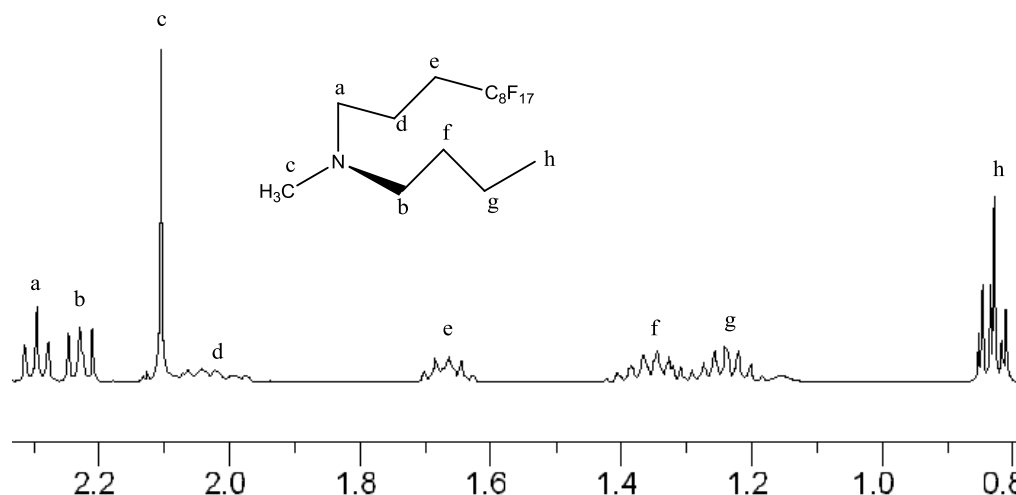
3.3. Synthesis of completely asymmetric fluorinated quaternary ammonium salt.

In addition to the above mentioned fluorinated quaternary ammonium salts, a completely asymmetric fluorinated quaternary ammonium salt was prepared by first synthesizing an asymmetric amine^[12] (N₁₄(C₁₁H₆F₁₇)), by reacting methylbutylamine with 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl iodide (scheme 3.2) as detailed in the experimental section. The ¹H NMR spectrum of the asymmetric amine is shown in spectrum 3.4.

The ^1H NMR spectrum of methylbutyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl amine (spectrum 3.5) shows eight different peaks. The resonance at $\delta = 2.31$ ppm (a) is a triplet resulting from the $\alpha\text{-CH}_2$ group of the fluorinated chain and the multiplet at $\delta = 2.24$ ppm (b) arises from the $\alpha\text{-CH}_2$ on the butyl chain. The methyl group on the nitrogen centre appears as a singlet at $\delta = 2.12$ ppm (c).



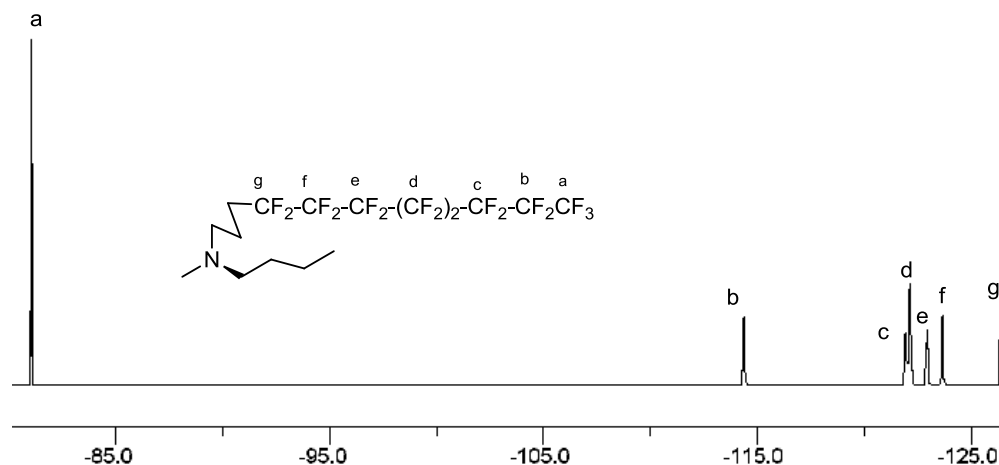
Scheme 3.2. Synthesis of completely asymmetric fluorinated quaternary ammonium salt, $\text{N}_{148}(\text{C}_{11}\text{H}_6\text{F}_{17})\text{I}$.



Spectrum 3.4 ^1H NMR spectrum of methylbutyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl amine, $\text{N}_{14}(\text{C}_{11}\text{H}_6\text{F}_{17})\cdot$

The other CH_2 groups of the fluorinated chain appear as broad multiplets at $\delta = 2.03$ ppm (d) and at $\delta = 1.68$ ppm (e). The β - CH_2 group of the butyl chain appears as a broad multiplet at $\delta = 1.36$ ppm (f). The remaining CH_2 group of the butyl chain gives a broad multiplet at $\delta = 1.25$ ppm (g). The terminal CH_3 group resonates at $\delta = 0.84$ ppm (h), appearing as a triplet due to the coupling to the adjacent CH_2 group.

The ^{19}F NMR spectrum 3.5 shows the anticipated peaks; the CF_3 resonance appears at $\delta = -80.74$ ppm (a) as a triplet due to coupling to the adjacent CF_2 group, the multiplet at $\delta = -113.48$ ppm (b) arises from the CF_2 next to the CF_3 and is assigned on the basis of its coupling constant.



Spectrum 3.5 ^{19}F NMR spectrum of methylbutyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl amine, $\text{N}_{14}(\text{C}_{11}\text{H}_6\text{F}_{17})$.

The rest of the CF_2 resonances, labeled as c, d, e, f, g integrate as 2:4:2:2:2 where the two middle CF_2 groups of the chain are almost in the same chemical environment so their signals overlap. The isolated asymmetric fluorinated amine seems to be pure and this is supported by its elemental analysis as shown in table 3.5.

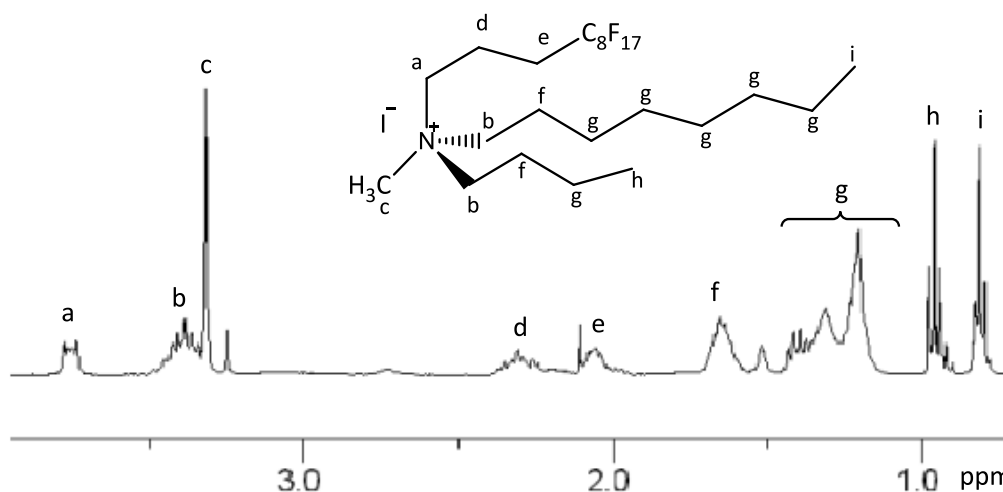
Table 3.5. Elemental analysis of the completely asymmetric fluorinated amine, $\text{N}_{14}\text{C}_{11}\text{H}_6\text{F}_{17}$.

Sample identity	Elemental analysis					
	Theoretical %			Found %		
	C	H	N	C	H	N
$\text{N}_{14}\text{C}_{11}\text{H}_6\text{F}_{17}$	35.09	3.32	2.56	35.71	3.08	2.98

On quaternising the fluorinated asymmetric amine with 1-iodooctane, a yellow sticky solid, $\text{N}_{148}(\text{C}_{11}\text{H}_6\text{F}_{17})\text{I}$ was isolated with relatively high melting point, 97 °C. This may be the only completely asymmetric quaternary ammonium salt bearing a fluorinated group to be reported to date. In contrast the completely asymmetric non-fluorinated iodides such as that we

have prepared are liquids at room temperature with melting points below 16 °C.

The ^1H NMR spectrum of the asymmetric fluorinated quaternary ammonium iodide is shown in spectrum 3.6, this shows all the anticipated peaks.

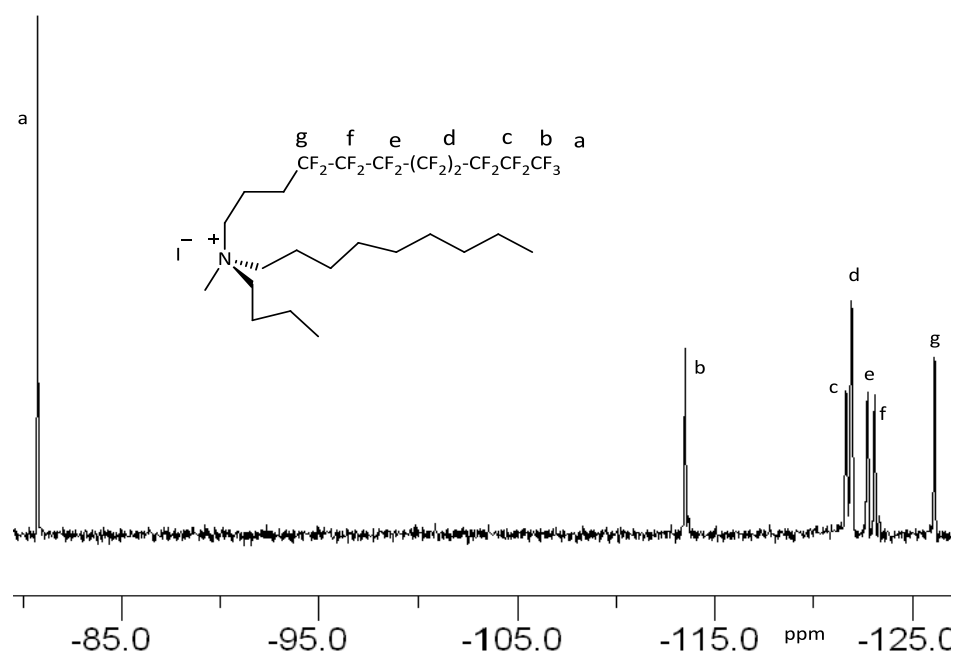


Spectrum 3.6 ^1H NMR spectrum of methylbutyloctyl-1H,1H,2H,2H,3H,3H-perfluoroundecyl ammonium iodide, $\text{N}_{148}(\text{C}_{11}\text{H}_6\text{F}_{17})\text{I}$.

The resonance at $\delta = 3.76$ ppm (a) is a second order multiplet that arises from the complex overlapping of the $\alpha\text{-CH}_2$ groups on the fluorinated chain, this shows a higher chemical shift than its analogues on the butyl and octyl chains due to the effect of fluorine. The $\alpha\text{-CH}_2$ groups on the octyl and butyl chains overlap due to their similar chemical environments giving a broad multiplet at $\delta = 3.38$ ppm (b). The resonance for the methyl group on the nitrogen centre is observed as a singlet at $\delta = 3.31$ ppm (c). The two CH_2 groups on the fluorinated chain resonate at $\delta = 2.30$ ppm (d) and $\delta = 2.05$ ppm (e) both of which appear as broad multiplets. The $\beta\text{-CH}_2$ groups of the butyl and octyl chains appear as a broad multiplet at $\delta = 1.64$ ppm (f), arising from the overlapping of the two signals due to them being in a similar chemical environment. The rest of the CH_2 groups appear as multiplets over the shift

range $\delta = 1.2\text{--}1.4$ ppm (g). These correspond to the overlapping of 6 CH₂ peaks (5 of the octyl chain and 1 of the butyl chain) in similar chemical environments which would all have a large number of couplings.

The terminal CH₃ group on the butyl chain resonates at $\delta = 0.96$ ppm (h) appearing as a triplet signal due to coupling to the adjacent CH₂ protons. This CH₃ group resonates at a slightly higher chemical shift value than that of the terminal CH₃ of the octyl chain, $\delta = 0.81$ ppm (i), presumably due to its relative proximity to the ammonium centre.



Spectrum 3.7. ¹⁹F NMR spectrum of methylbutyloctyl-1H,1H,2H,2H,3H,3H-perfluoroundecyl ammonium iodide, N₁₄₈(C₁₁H₆F₁₇)I.

The ¹⁹F NMR spectrum (spectrum 3.7) shows a triplet at $\delta = -80.74$ ppm (a) due to coupling of the CF₃ to the adjacent CF₂ group. Resonance (b) at $\delta = -113.48$ ppm is a multiplet arising from the CF₂ group next to the terminal CF₃. The rest of the CF₂ groups, c, d, e, f, g integrate as 2:4:2:2:2, where the

two middle CF₂ groups are almost in the same chemical environments so their signals overlap.

Finally on investigating the formation of fluorinated quaternary ammonium salts it has been observed that the reactions of RfCH₂CH₂CH₂I with R₂R'N yields salts of the type [R₂R'N(CH₂)₃Rf]I, all of which possess high melting points. Interestingly this showed almost an inverse relationship to their aliphatic analogues in terms of melting point. There is no correlation between the degree of asymmetry around the nitrogen centre and lowering the melting point in fluorinated cations. As is clear from the table 3.4 that the fluorinated salt with the higher symmetry [Bu₃N(CH₂)₃(CF₂)₇CF₃]I showed the lowest observed melting point.

In contrast performing similar reactions with a shorter spacer unit –CH₂CH₂– resulted in a quaternary ammonium salt of the type [R₂R'NH]I and RfCH=CH₂. These products presumably arise from a competitive deprotonation of acidic protons by the amine.

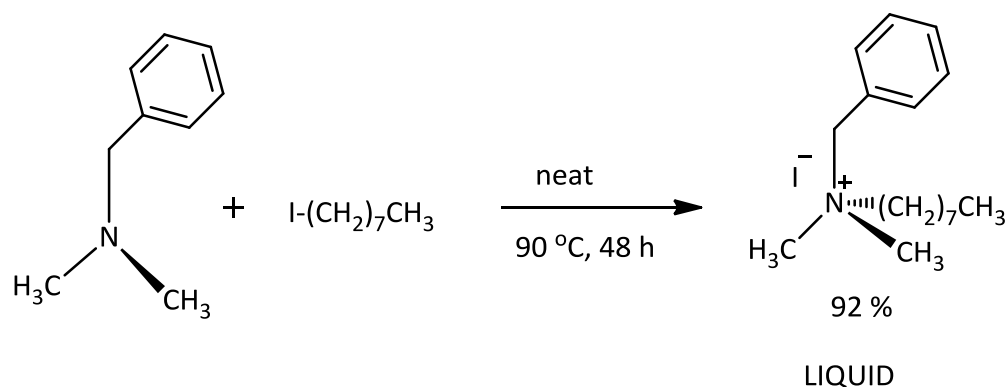
3.4. Synthesis and characterization of asymmetric non-aliphatic quaternary ammonium salts with benzyl, allyl and cyclohexyl substituents.

3.4.1. Synthesis and characterization of dimethylbenzylammonium halide series of compounds, N_{11BR}X.

Since the introduction of fluorinated groups did not result in a reduction in the melting points of the quaternary ammonium halides, asymmetric quaternary ammonium salts with benzyl substituents were synthesized following a similar procedure to that described in chapter 2. A typical example is the reaction of dimethylbenzylamine with 1-iodooctane at 90 °C for 48 hours, which after cooling and workup resulted in dimethylbenzyloctylammonium iodide as a viscous liquid with a honey-like colour and texture (scheme 3.3) with excellent yield. This is unusual at this stage of the reaction sequence, since apart from

dimethylhexyloctylammoniumiodide, dimethylhexyldecylammoniumiodide and the completely asymmetric iodides the previously isolated quaternary halide products were solids.

The liquid samples, especially the viscous ones, were very difficult to purify and had to be washed many times with hexane followed by removal of residual solvent under vacuum with gentle heating for a longer time than the solid samples, sometimes requiring continuous pumping over 24h or even more to remove the solvent completely.



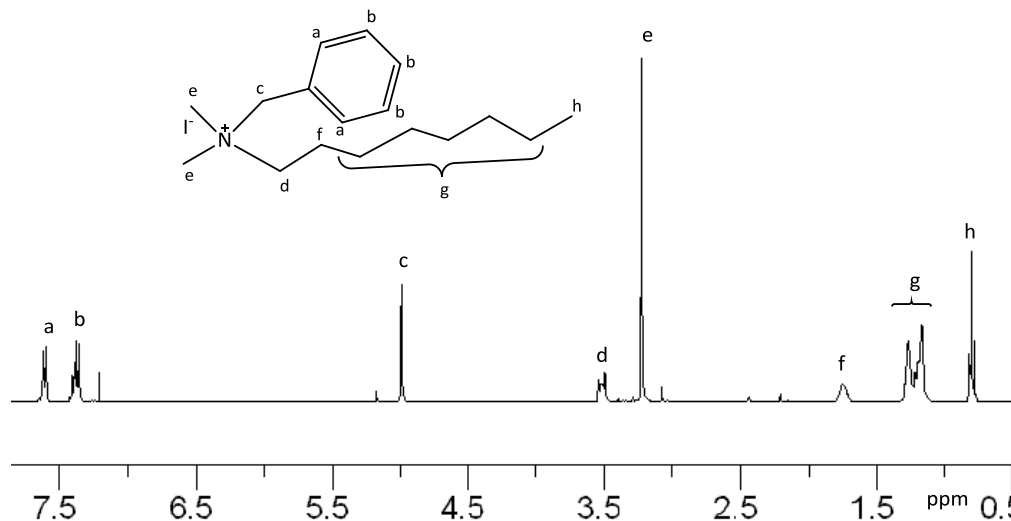
Scheme 3.3. Synthesis of dimethylbenzyloctylammonium iodide, N_{11B8I}.

The ¹H NMR spectrum of dimethylbenzyloctylammonium iodide (spectrum 3.8) shows all the anticipated peaks. The resonances at $\delta = 7.61$ ppm (a) and $\delta = 7.39$ ppm (b) are multiplets that arise from the aromatic ring protons integrating in a 2:3 ratio.

The singlet at $\delta = 4.99$ (c) arises from the benzyl group attached directly to the ammonium centre. While the α -CH₂ on the octyl group appears as a second order multiplet at $\delta = 3.51$ ppm (d). The methyl groups attached to the ammonium centre resonate at $\delta = 3.22$ ppm (e); this is a singlet.

The β -CH₂ nuclei of the octyl group appear as a broad multiplet at $\delta = 1.75$ ppm (f). The rest of the CH₂'s resonate over the chemical shift range of

$\delta = 1.17$ to 1.26 ppm (g). These appear as broad multiplets due to the overlapping of 5 CH_2 peaks which would have a large amount of coupling. The terminal CH_3 group of the octyl chain appears as a triplet at $\delta = 0.79$ ppm (h).



Spectrum 3.8. ^1H NMR spectrum of the dimethylbenzylammonium iodide, $\text{N}_{11}\text{B8I}$.

Similar reactions were performed with the longer chain alkyl halides, 1-iododecane also resulted in a viscous liquid with a consistency similar to that of the honey. Whilst, 1-bromotetradecane and 1-bromooctadecane, on reaction with dimethylbenzylamine resulted in solid products but with relatively low melting points, 48 and 65 $^{\circ}\text{C}$ respectively. Table 3.6 shows the melting points and the elemental analyses of the benzyl series, N_{11}BRX .

It was observed that the longer-chain quaternary ammonium salts tend to pick up water. This is shown from their elemental analyses and their TG curves, which show a weight loss at an early stage of the heating step prior to its decomposition temperature, corresponding to water loss. Confirmation subsequently came from the X-ray crystal structures.

Table 3.6. Elemental analysis and melting points for the benzyl series, N_{11BR}X.

Sample identity	mp (°C)	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N _{11B8} I	-19*	54.38	8.06	3.73	54.46	8.60	3.79
N _{11B(10)} I	-21*	56.55	8.50	3.47	57.00	8.56	3.63
N _{11B(14)} Br.H ₂ O	48	64.15	10.31	3.25	64.09	10.18	3.24
N _{11B(18)} Br.H ₂ O	65	66.62	10.78	2.88	67.75	10.48	2.93

* = T_g (glass transition temperature)

Crystals were successfully grown from a layered dichloromethane/hexane solution for the hydrated quaternary ammonium salt dimethylbenzyl octadecylammonium bromide, N_{11B(18)}Br.H₂O. The molecular structure and atomic numbering for N_{11B(18)}Br.H₂O is illustrated in fig. 3.2. The unit cell parameters are: triclinic, space group P-1, a = 8.1882(1), b = 8.8075(1), c = 21.7792(5) Å, α = 89.773(1), β = 98.888(1), γ = 114.941(1)°, V = 1403.80(4) Å³.

The packing diagram, fig. 3.2, shows the long alkyl chains lie in a head-to-tail arrangement parallel to each other rather than forming the micellar-like arrangement that was observed with the N_{11H4}I quaternary salt. The bromide ions and water molecules form an isolated anionic group in a square arrangement similar to what has been reported in the crystal structure of N₁₁₄₍₁₂₎Br.H₂O.^[13]

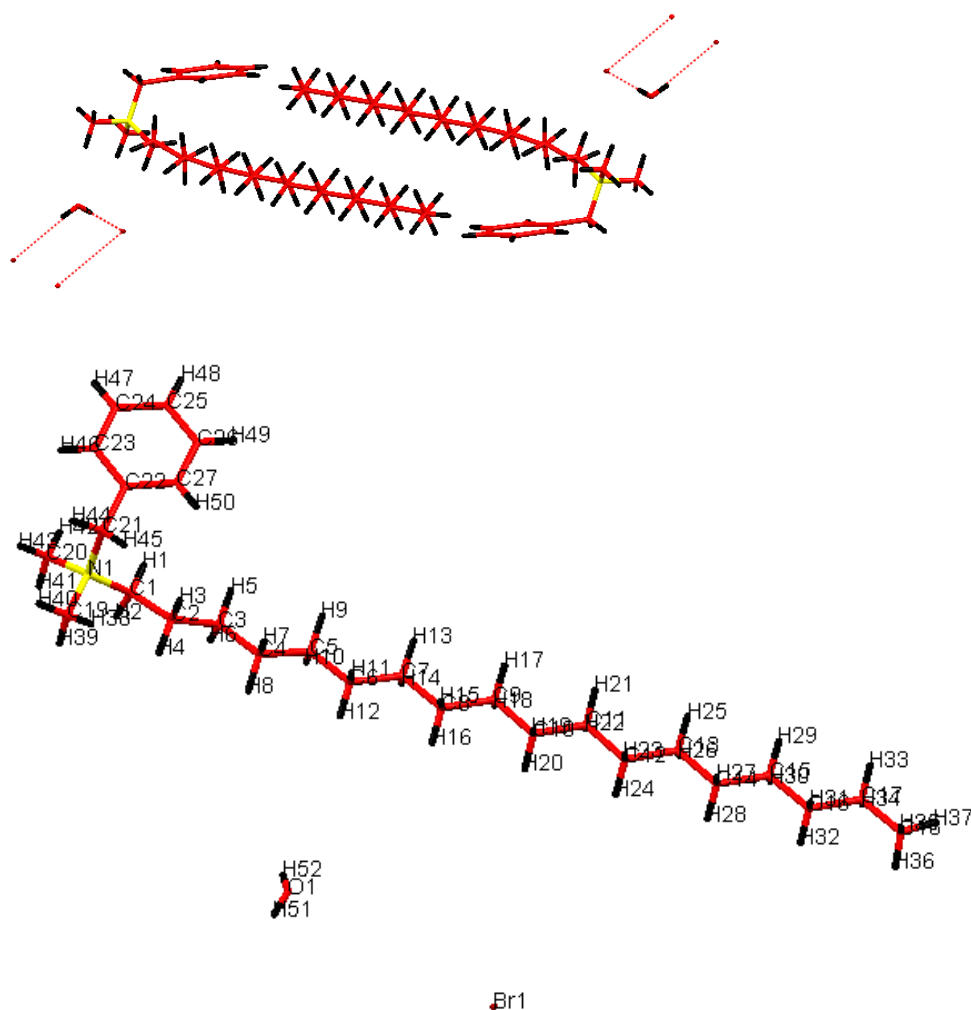


Figure 3.2 Representation of the molecular structure and packing of $N_{11B(18)}Br.H_2O$

The aromatic rings are stacked parallel to each other with a Cg-Cg distance of 5.45 Å and with a slippage of 0.83 Å. Selected bond lengths (Å) and angles (°) are listed in table 3.7. The structure confirms the presence of a water molecule in this product.

Table 3.7. Selected bond lengths and bond angles for N_{11B(18)}Br.H₂O.

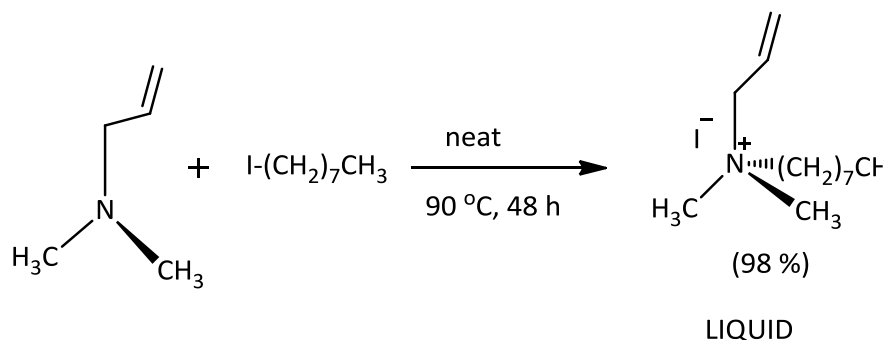
Bond	Length (Å)	Angle	Angle (°)
N1-C1	1.522(3)	C1-N1-C21	113.03(15)
N1-C19	1.507(3)	C19-N1-C21	107.78(16)
N1-C20	1.506(3)	C20-N1-C21	109.54(16)
N1-H21	1.537(2)	C19-N1-C1	110.16(16)
O1-H51	0.73 (3)	C20-N1-C1	107.85(16)
O1-H52	0.83(4)	C20-N1-C19	108.39(16)
		H51-O1-H52	110(4)

* H51 & H52 are hydrogens of the water molecules.

There is a single unique molecule contained within the unit cell. The C-N bond lengths lie between 1.506(3) and 1.537(2) Å, whilst the C-N-C bond angles range from 107.78(16) to 113.03(15)° with a slight backbone curvature in the C18 chain. A similar curvature has been reported by Hodorowicz *et al.* for the hydrated salts *N*-benzyl-*N,N*-dimethylalkylammonium bromides, where the alkyl group is octyl, nonyl and decyl, studied for the modification of natural clays (Na-montmorillonite).^[14]

3.4.2. Synthesis and characterization of dimethylallylammonium halide series of compounds, N_{11AR}X.

Quaternary asymmetric ammonium salts with non-aliphatic groups were further synthesized by the reaction of dimethylallyl amine with the alkyl halides, RX, used previously where R = C₈H₁₇, C₁₀H₂₁, C₁₄H₂₉, C₁₈H₃₇. A typical example is the neat reaction of dimethylallylamine with 1-iodooctane in a sealed Schlenk tube with heating at 90 °C for 48 h (scheme 3.4). Dimethylallyloctylammonium iodide resulted as a viscous liquid in relatively excellent yield. Surprisingly, again this is a liquid at this stage, a similar trend was observed with the benzyl series where dimethylbenzyloctylammonium iodide and dimethylbenzyldecylammonium iodide were liquids at room temperature.

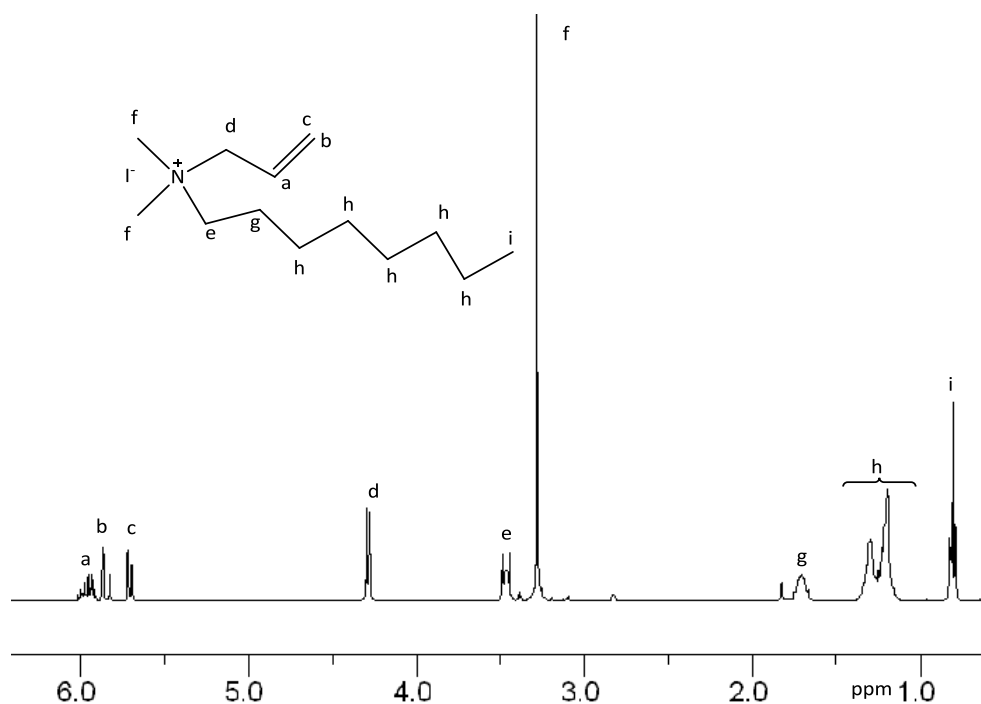


Scheme 3.4. Synthesis of dimethylallyloctylammonium iodide, N_{11A8}I.

The dimethylallyl -tetradecyl and -octadecyl ammonium bromides are solids with relatively low melting points, 64 and 86 °C respectively. The ¹H NMR spectrum shows all the expected peaks (spectrum 3.9). The β-CH group on the allyl group appears as a multiplet at δ = 5.96 ppm (a) which arises from coupling to the adjacent CH₂ protons. While the terminal CH₂ on the allyl groups give rise to two individual multiplet peaks (b & c) because the protons (b) and (c) are in slightly different chemical environments.

The doublet peak at δ = 4.29 ppm (d) is due to the α-CH₂ adjacent to the nitrogen centre coupling to a CH proton on the allyl group. The α-CH₂ protons on the octyl chain appear as a second order multiplet at δ = 3.47 ppm (e).

The resonance at δ = 3.28 ppm (f) is a singlet that arises from the chemically equivalent methyl protons adjacent to the ammonium centre. The beta CH₂ group on the octyl chain appears as a resonance at δ = 1.71 ppm (g), this is a broad peak, presumably due to coupling to the two adjacent CH₂ groups. The rest of the CH₂ groups appear as multiplets over the shift range δ = 1.19 - 1.29 ppm (h). This is due to the similar chemical environments of the 5CH₂ groups. Again this is commonly seen in many of the others ammonium halides. The terminal CH₃ group resonates at δ = 0.8 ppm (i), appearing as a triplet due to coupling to the adjacent CH₂ protons.



Spectrum 3.9. ^1H NMR spectrum of the dimethylallyloctylammonium iodide, $\text{N}_{11\text{A}8}\text{I}$.

The ^1H NMR spectrum shows that the product is relatively pure and this is supported by its elemental analysis, as shown in table 3.8.

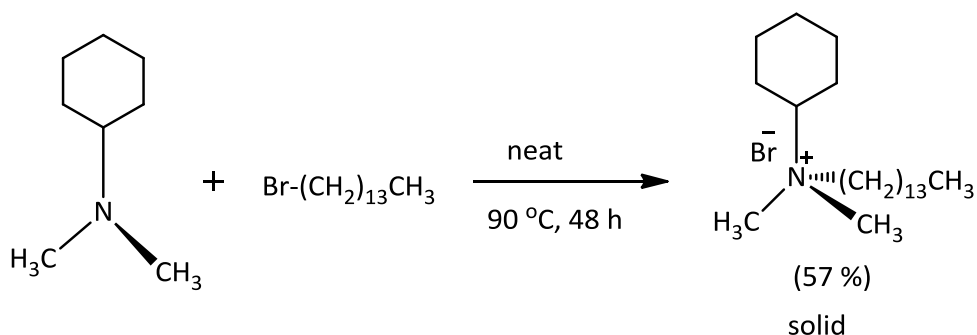
Table 3.8. Elemental analysis and physical states for the allyl series, $\text{N}_{11\text{AR}}\text{X}$.

Sample identity	mp ($^{\circ}\text{C}$)	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$\text{N}_{11\text{A}8}\text{I}$	-24*	47.98	8.68	4.31	47.52	8.55	4.25
$\text{N}_{11\text{A}(10)}\text{I}$	30	50.97	9.13	3.97	50.67	9.11	3.82
$\text{N}_{11\text{A}(14)}\text{Br}$	64	62.95	11.13	3.87	62.25	11.14	3.92
$\text{N}_{11\text{A}(18)}\text{Br}$	86	65.98	11.57	3.35	65.69	11.68	3.41

* = T_g (glass transition temperature)

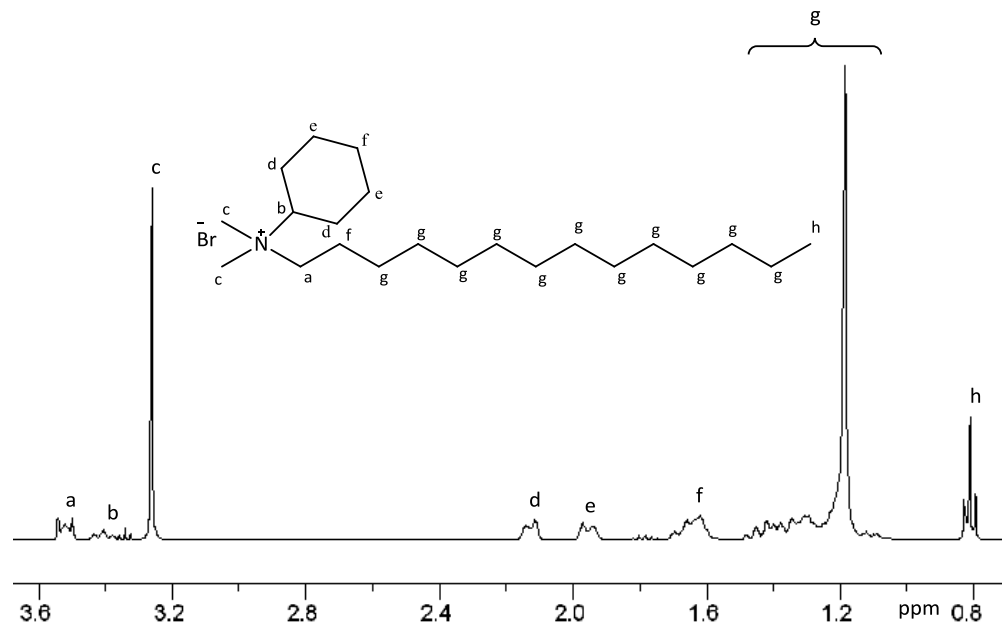
3.4.3. Synthesis and characterization of dimethylcyclohexylammonium halide series of compounds, N_{11CR}X.

The final series of compounds to have been synthesized included a cyclic but saturated cyclohexyl group using the same alkylhalides as previously. These were prepared in a similar way to that described earlier, but all of the products were found to be solids unlike those with allyl and benzyl substituents. For example, the reaction of dimethylcyclohexylamine with 1-bromotetradecane resulted in dimethylcyclohexyltetradecylammonium-bromide as a white solid (scheme 3.5).



Scheme 3.5 Synthesis of dimethylcyclohexyltetradecylammonium iodide, N_{11C(14)}Br.

All products were characterized using ¹H NMR spectroscopy and elemental analysis. The ¹H NMR (spectrum 3.10) showed the anticipated peaks.



Spectrum 3.10. ^1H NMR spectrum of dimethylcyclohexyltetradecyl ammoniumbromide, $\text{N}_{11}\text{C}(14)\text{Br}$.

The peak at $\delta = 3.52$ ppm (a) is a second order multiplet arising from the α - CH_2 group of the tetradecyl chain adjacent to the nitrogen centre. The CH group on the cyclohexyl group bonded directly to the nitrogen centre resonates at $\delta = 3.41$ ppm (b) integrating to a single proton. The two equivalent methyl groups attached directly to the nitrogen appear as a singlet at $\delta = 3.26$ ppm (c).

The remaining cyclohexyl protons resonate at $\delta = 2.12$ ppm (d), 1.95 ppm (e), integrating as two protons each, at $\delta = 1.63$ ppm (f) integrating as one proton, which overlaps the signal of the β - CH_2 on the tetradecyl chain. While the rest of the CH_2 's and the other 5 cyclohexyl protons resonate over the range of 1.18-1.41 ppm (g) due to the overlapping of 11 CH_2 groups and the cyclohexyl protons. The terminal CH_3 signal appears as a triplet at $\delta = 0.81$ ppm (h) due to its coupling to the adjacent CH_2 on the tetradecyl chain.

All of the cyclohexyl series showed similar ^1H NMR spectra and all showed that the products were of high purity. The elemental analysis provided further confirmation, with the found values being consistent with those calculated. Table 3.9 shows the elemental analysis of the cyclohexyl series.

Table 3.9. Elemental analysis and physical states of dimethylcyclohexylammonium halide series of compounds, N_{11}CRX .

Sample identity	mp (°C)	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$\text{N}_{11}\text{C}_8\text{I}$	144	52.29	9.33	3.81	51.55	9.77	3.75
$\text{N}_{11}\text{C}_{(10)}\text{I}$	147	54.66	9.69	3.54	54.73	9.47	3.62
$\text{N}_{11}\text{C}_{(14)}\text{Br}$	136	65.30	11.47	3.46	65.13	11.65	3.22
$\text{N}_{11}\text{C}_{(18)}\text{Br}$	137	67.78	11.82	3.04	67.27	11.83	2.71

A significant decrease in the melting points was observed in the series prepared with non-aliphatic group substituents except for the cyclohexyl series. Where the octyl and decyl quaternary salts of the dimethyl -benzyl and -allyl series were liquids, this is not the case with the aliphatic series apart from the hexyl series and the completely asymmetric salts. The cyclohexyl series were all solids at room temperature and with relatively high melting points.

Table 3.10 shows the melting point or glass transition temperatures of the different quaternary salts with non-aliphatic substituents (B = benzyl, A = allyl and C = cyclohexyl groups).

Table 3.10. Melting points of the non-aliphatic QA halides.

Sample Identity	Melting point or glass transition (°C)
N _{11B8} I	-19*
N _{11B(10)} I	-21*
N _{11B(14)} Br.H ₂ O	48
N _{11B(18)} Br.H ₂ O	65
N _{11A8} I	-24*
N _{11A(10)} I	30
N _{11A(14)} Br	63-65
N _{11A(18)} Br	86
N _{11C8} I	144
N _{11C(10)} I	147
N _{11C(14)} Br	135-138
N _{11C(18)} Br	135-140

* = T_g (glass transition temperature)

Figure 3.3. shows that there is a significant decrease in the melting point of the allyl and benzyl substituted quaternary ammonium salts investigated, all of these being ionic liquids with melting points below 100 °C and some are room temperature ionic liquids even as the halide salts, R= octyl or decyl see table 3.10.

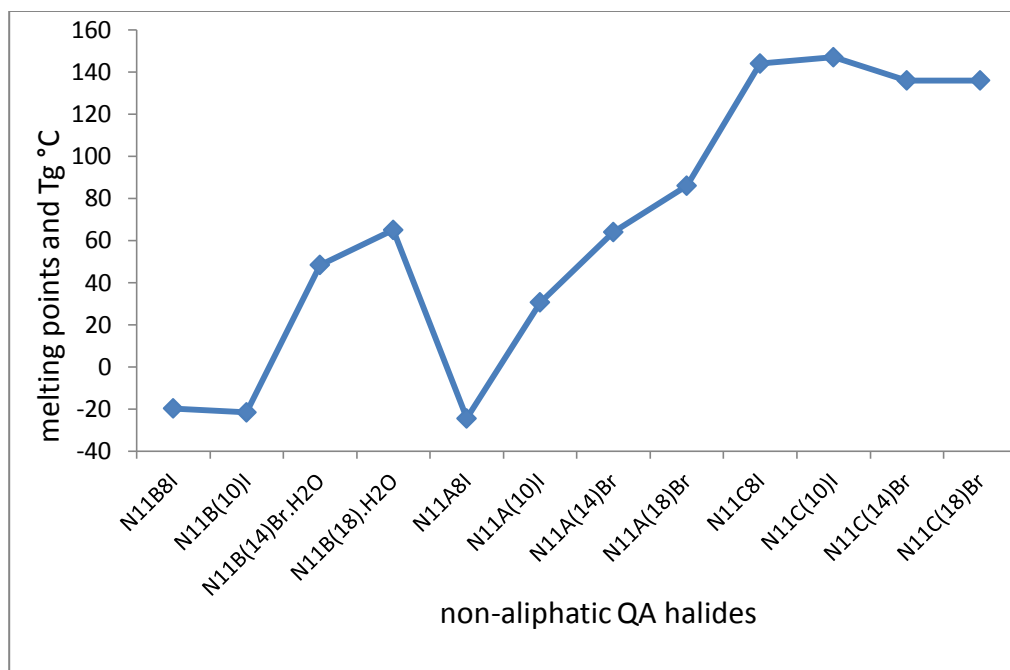


Figure 3.3. Melting points of asymmetric quaternary ammonium non-aliphatic halides, $N_{11RR}X$.

Whereas the cyclohexyl substituted quaternary ammonium halides possessed higher melting points and all are solids at room temperature.

3.5. Conclusion

In conclusion, one can say that introducing allyl and benzyl groups in quaternary ammonium salts reduced the melting point appreciably and may be considered as promising precursor halides for the development of room temperature ionic liquids. In contrast the cyclohexylquaternary ammonium halides possessed high melting points exceeding all of those of the aliphatic quaternary ammonium halides discussed in chapter 2 apart from the quaternary halides of the C3 series. Whilst the fluorinated asymmetric quaternary halides were all solids and possessed high melting points, making them not suitable for the development of room temperature ionic liquids.

3.6. References

1. R.N. Haszeldine, *J. Chem. Soc.*, 1951, 102.
2. L.M. Yagupol'skii, N.V. Kondratenko, G. N. Timofeeva, M.I. Dronkina, Yu. L. Yaguposl'skii, *J. Org. Chem. USSR*, 1980, **16**, 2139.
3. T. Terada, T. Nogami and Y. Shiota, *Bull. Chem. Soc. of Jpn*, 1989, **62**, 2793.
4. O. D. Gupta, P. D. Armstrong and J. M. Shreeve, *Tetrahedron Lett.*, 2003, **44**, 9367.
5. D. Mandal, J. A. Gladysz, *Tetrahedron*, 2010, **66**, 2793.
6. (a) S. Fustero, A. G. Sancho, J. L. Acena and J. F. Sanz-Cervera, *J. Org. Chem.* 2009, **74**, 6398. (b) D. J. Adams, J. A. Bennett, D. Duncan, E. G. Hope, J. Hopewell, A. M. Stuart, A. J. West, *Polyhedron*, 2007, **26**, 1505. (c) M. L. P. Le, F. Alloin, P. Strobel, J-C. Leprêtre, C. Pérez del Valle, P. Judeinstein, *J. Phys. Chem. B*, 2010, **114**, 894.
7. J.B. Nivet, R. Bernelin, M. Le Blanc, J.G. Reiss, *Eur. J Med. Chem*, 1992, **27**, 891.
8. P. N. Bartlett, D. C. Cook, M. W. George, J. Ke, W. Levason, G. Reid, W. Sub and W. Zhanga, *Phys. Chem. Chem. Phys.*, 2010, **12**, 492.
9. A. R. Campanelli and L. Scaramuzza, *Acta. Crystolgr., Sect C*, 1986, **42**, 1380.
10. C. J. Pouchert, J. Behrike, The Aldrich Library of ^{13}C & ^1H FT NMR Spectra, Spectrum 149C Vol. 1, 1993.
11. C. R. Witschonke and C. A. Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2472.
12. M. Tanaka, A. Rastogi, G. N. Toepperwein, R. A. Riggelman, N. M. Felix, J. J. de Pablo and C. K. Ober., *Chem. Mater.*, 2009, **21**, 3125.

13. T. Taga, Y. Miwa and K. Machida, *Acta Cryst.*, 1990, C46, 293.
14. M. Hodorowicz, K. Stadnicka, J. Czapkiewicz, *J. colloidal interface Sci.*, 2005, **290**, 76.

4. Ion-exchange of asymmetric quaternary ammonium halides using fluorinated anions.

- 4.1** Introduction.
- 4.2** Ion-exchange of asymmetric quaternary ammonium halides with bis(trifluoromethanesulfonylimide) lithium salt.
- 4.3** Synthesis of the completely asymmetric quaternary ammonium bis(trifluoromethanesulfonylimide) salt.
- 4.4** Synthesis of bis(perfluoroalkanesulfonylimide) potassium salts.
- 4.5** Ion-exchange of asymmetric quaternary ammonium halides with potassium heptafluoroniobate(V).
- 4.6** Ion-exchange of asymmetric quaternary ammonium halides with potassium trifluoromethanesulfonate.
- 4.7** Ion-exchange of asymmetric quaternary ammonium halides with hexafluorophosphate and tris(pentafluoroethyl)trifluorophosphate.
- 4.8** Ion-exchange of asymmetric non-aliphatic quaternary ammonium halides with lithium bis(trifluoromethanesulfonylimide).
- 4.9** Conclusion.
- 4.10** References.

4.1. Introduction

Along with modification of the cation, the anion size and geometry has an important influence on the melting points of salts. Generally speaking, as the size of the ions increases, the melting point of the salt decreases. For example, comparing the melting points of the chlorides of group 1 elements from Na to Cs the melting points decrease from 803 to 646 °C as the size of the cation increases.^[1a] On the other hand as the size of the anion increases, the melting point decreases. For example comparing the melting points of the sodium halide salts going from F⁻ to I⁻, the melting points of the sodium salts decreases from 995 to 660 °C.^[1b] A similar effect is observed when comparing the melting points of the anion-substituted salts of sodium, from Cl⁻ to BF₄⁻ to PF₆⁻ to AlCl₄⁻, the melting points of sodium salts decreases from 803 to 185 °C.^[1a]

As described in chapter 1, there is particular interest in ionic liquids that contain large fluorine-containing cations. Indeed in 1998 a U.S. patent made claims relating to a vast number of “hydrophobic ionic liquids” with pyridinium, pyridazinium, pyrimidinium, pyrazinium, imidazolium, pyrazolium, thiazolium, oxazolium and triazolium cores, many of which have fluorine-containing cations.^[2]

The authors concluded that when the cation and/or the anion is fluorinated, the hydrophobic ionic liquids of invention have certain additional special properties, including :

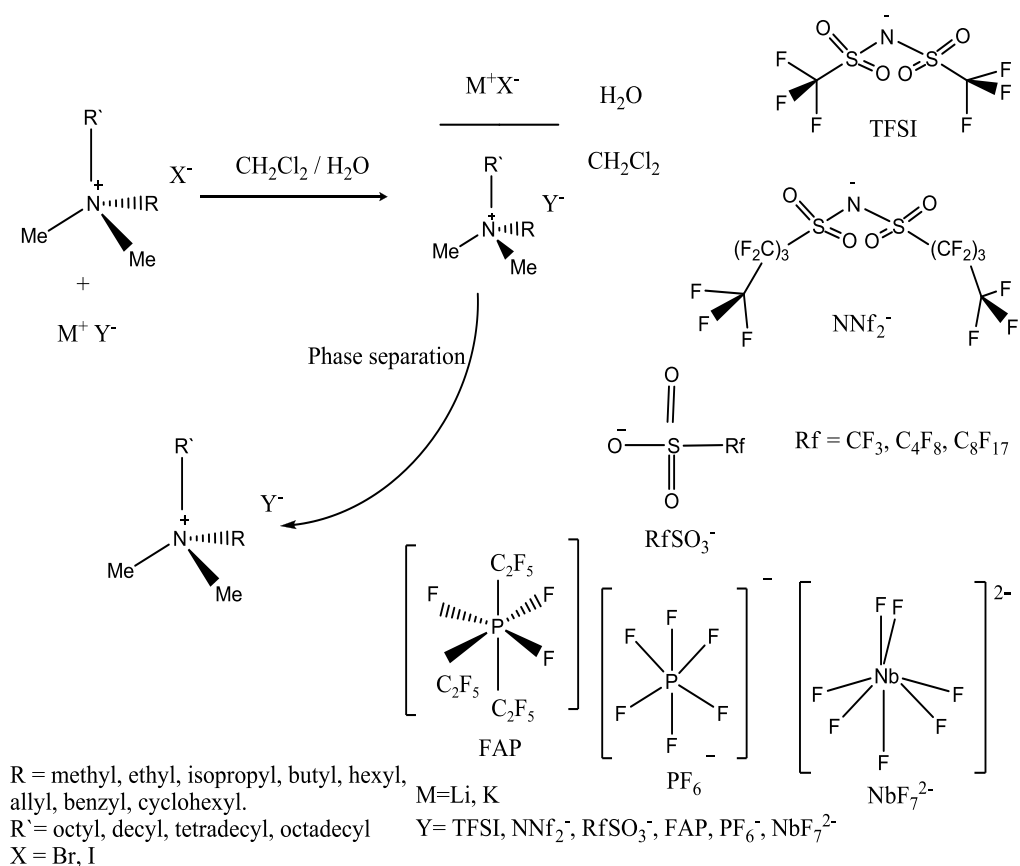
1. Inertness to organic solvents and oxidizing agents.
2. Resistance to corrosive acids and bases.
3. Resistance to extremes of temperature and pressure.

For this reason the ion-exchange of the quaternary ammonium halides to introduce fluorine-containing anions was undertaken. Ion-exchange reactions were performed using fluorine-containing anions such as

trifluoromethanesulfonate, bis(trifluoromethanesulfonyl)imide, bis(nonfluorobutanesulfonyl)imide, and heptafluoroniobate, hexafluorophosphate and tris(pentafluoroethyl)trifluorophosphate (FAP).

4.2. Ion-exchange of asymmetric quaternary ammonium halides with bis(trifluoromethanesulfonylimide) lithium salt.

A number of synthetic methods for carrying out ion-exchange reactions have been presented in the literature, the method used here was based on that described by Seddon *et al.*^[3] Scheme 4.1 shows the principle behind this process. The exchange reaction was carried out at room temperature by mixing a slight excess of the alkali metal salt of the fluorinated anion e.g., Li[(CF₃SO₂)₂N], K[(C₄F₉SO₂)₂N], KSO₃CF₃, KC₄F₉SO₃, KC₈F₁₇SO₃, K₂NbF₇, KPF₆ and KP(C₂F₅)₃F₃ (FAP) with the quaternary ammonium halide in a 1:1 water and dichloromethane solution, with constant stirring for 24 hours. The ion-exchanged ammonium salt was found to be preferentially soluble in the organic layer while the alkali metal halide, M⁺Y⁻, salt is preferentially soluble in water and so resides in the aqueous layer. Thus, the individual salts can be isolated by simple phase separation. The desired product was then washed with deionised water and passed through a purification column, consisting of celite, silica and activated charcoal, to remove any impurities and decolorize the product. The solution of the purified products was dried with MgSO₄, followed by removal of the solvent under vacuum to yield the products as clear oils, which depending on their melting point, either remained as liquids or ultimately solidified.



Scheme 4.1. Biphasic synthesis of hydrophobic salts.

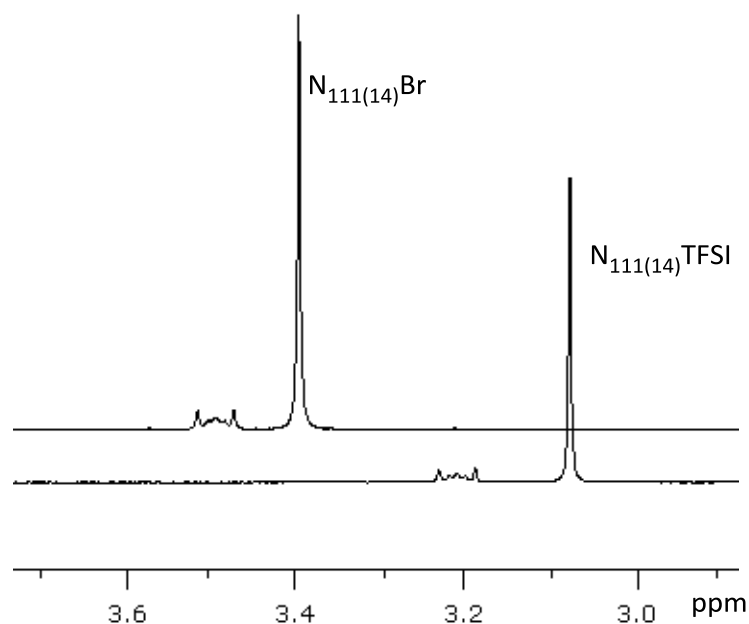
Preliminary reactions were carried out using the LiTFSI salt with all of the asymmetric quaternary ammonium halides. Ion-exchange on the more symmetric quaternary ammonium salt, e.g. trimethyloctylammoniumiodide with the LiTFSI resulted in a salt with a low melting point, below room temperature. The product $\text{N}_{1118}\text{TFSI}$, is a clear and non-viscous liquid with a relatively low mp (3.2 °C) compared to that reported for the symmetric quaternary ammonium bis(trifluoromethanesulfonyl)imide, $\text{N}_{1111}\text{TFSI}$ having a melting point of 133 °C.^[4] The ^1H NMR spectrum showed the appropriate peaks of the anticipated product with slightly lower chemical shifts of the methyl and $\alpha\text{-CH}_2$ groups, compared with the starting halide salt as observed in all other series. Table 4.1 shows the physical appearance, melting point and

elemental analysis of trimethyloctylammonium iodide and its corresponding bistrifluoromethylsulfonylimide salts, N₁₁₁₈I and N_{111R}TFSI. The melting points for liquid samples being determined by Differential Scanning Calorimetry (DSC).

Table 4.1. Elemental analysis, mp of N₁₁₁₈I and trimethylalkylammonium bistrifluoromethylsulfonylimide salts.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₁₈ I	131	44.13	8.76	4.68	44.19	9.00	4.57
N ₁₁₁₈ TFSI	3	34.50	5.80	6.19	34.78	5.72	6.34
N ₁₁₁₍₁₀₎ TFSI	14	37.49	6.30	5.83	37.73	6.31	6.06
N ₁₁₁₍₁₄₎ TFSI	55	42.52	7.14	5.22	42.83	7.27	5.12
N ₁₁₁₍₁₈₎ TFSI	58	46.60	7.83	4.73	49.68	8.39	3.93

The exchange of the longer chain trimethylalkylammonium halides such as trimethyltetradecylammonium bromide, mp 109 °C, resulted in a solid product with a low melting point, mp 55 °C (table 4.1). Both the ¹H and ¹⁹F NMR spectra and the elemental analysis verify the resulting product is of high purity and once again due to the exchange lower proton chemical shift values are observed for the methyl groups and the α CH₂ groups coordinated to the nitrogen centre (spectrum 4.1), this behaviour is seen in all the exchanged TFSI salts.



Spectrum 4.1 Part of ^1H NMR spectra of $\text{N}_{111(14)}\text{Br}$ & $\text{N}_{111(14)}\text{TFSI}$.

Crystals suitable for X-ray crystallography could be successfully grown from a layered DCM/hexane solution of the more symmetric ionic liquid, trimethyltetradecylammoniumbis(trifluoromethane)sulfonylimide, $\text{N}_{111(14)}\text{TFSI}$. The unit cell parameters are: monoclinic, space group $\text{P}2_1/\text{c}$, $a = 24.02(6)$, $b = 8.38(2)$, $c = 13.17(3)$ Å, $\alpha = 90$, $\beta = 96.87(10)$, $\gamma = 90^\circ$, $V = 2361.00(11)$ Å³. The molecular structure of $\text{N}_{111(14)}\text{TFSI}$ is shown in fig 4.4 (a). The packing diagram, fig 4.1 (b) shows that molecules are packed in bilayers parallel to each other. Table 4.2 lists selected bond lengths and bond angles of $\text{N}_{111(14)}\text{TFSI}$.

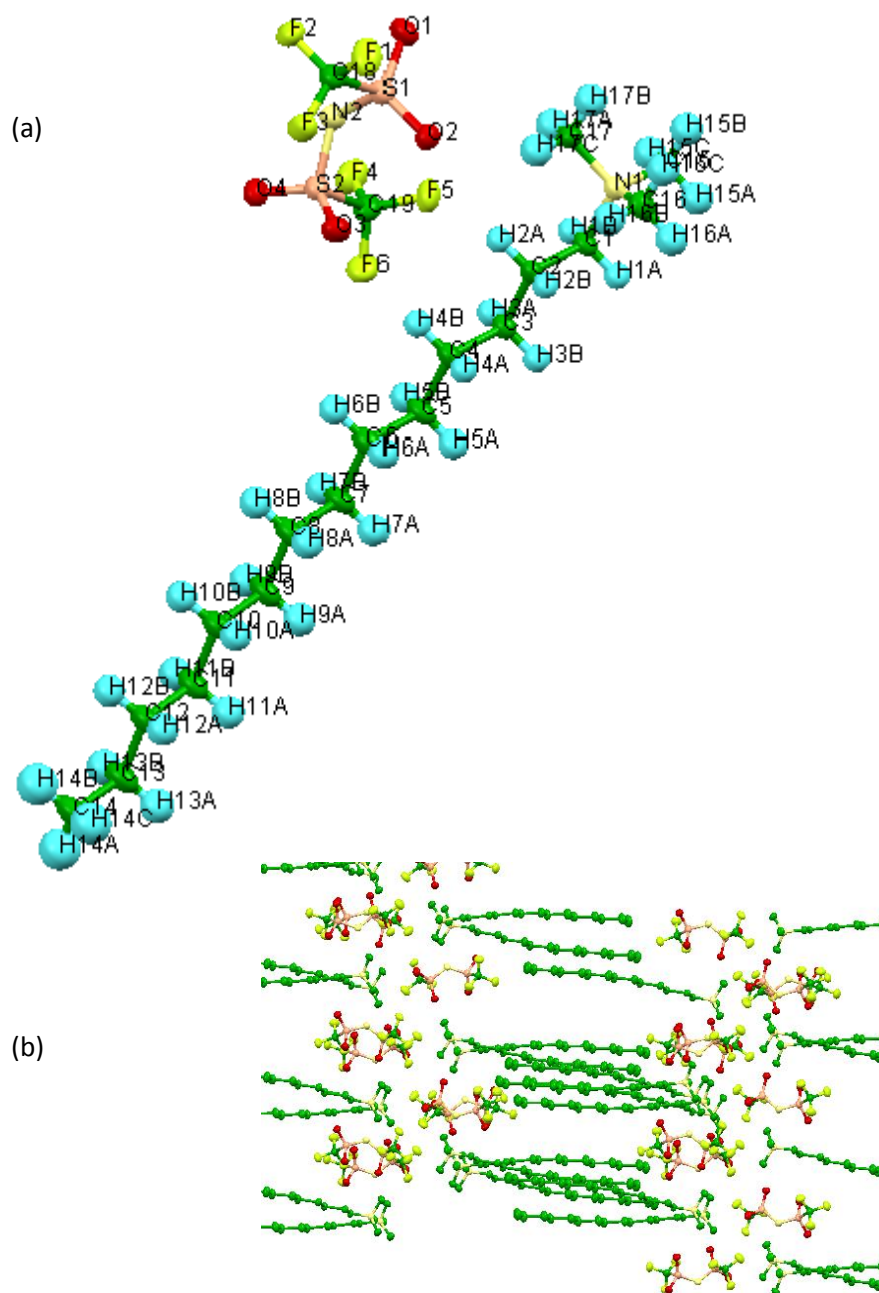
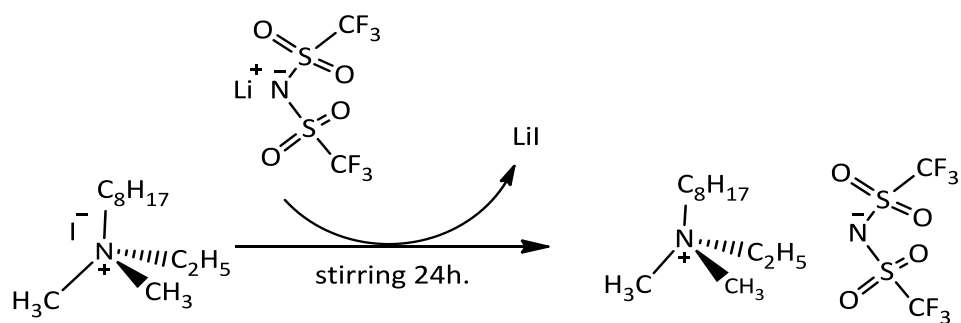


Figure 4.1. Perspective molecular structure (a) and packing (b) of N₁₁₁₍₁₄₎TFSI (hydrogens removed for clarity).

Table 4.2. Selected bond lengths and angles of N₁₁₁₍₁₄₎TFSI.

Bond	Length (Å)	Bond	Length (Å)
N1-C1	1.518(5)	N1-C16	1.488(5)
N1-C15	1.507(5)	N1-C17	1.489(5)
Angle	Angle (°)	Angle	Angle (°)
C1-N1-C15	108.0(3)	C16-N1-C15	108.3(3)
C1-N1-C17	111.2(3)	S1-N2-S2	123.9(2)
C15-N1-C16	110.9(3)	O2-S1-O1	118.77(18)
C16-N1-C17	109.8(3)	O2-S1-N2	115.66(18)
C17-N1-C15	108.5(3)	O1-S1-N2	109.68(19)
O4-S2-N2	108.27(19)	O2-S1-C18	104.78(19)
O3-S2-N2	116.33(18)	O1-S1-C18	103.48(18)
O4-S2-C19	104.7(2)	N2-S1-C18	102.10(19)
O3-S2-C19	104.6(2)	O4-S2-O3	118.98(18)
N2-S2-C19	101.62(19)		

Similarly, the reaction of dimethylethyl-octylammonium iodide with lithium bis(trifluoromethanesulfonyl)imide, (scheme 4.2) resulted in a nice clear RTIL, N₁₁₂₈TFSI with high thermal stability, > 380 °C (fig 4.2).



Scheme 4.2. Synthesis of dimethylethyl-octylammonium-bis(trifluoromethane sulfonyl)imide, N₁₁₂₈TFSI.

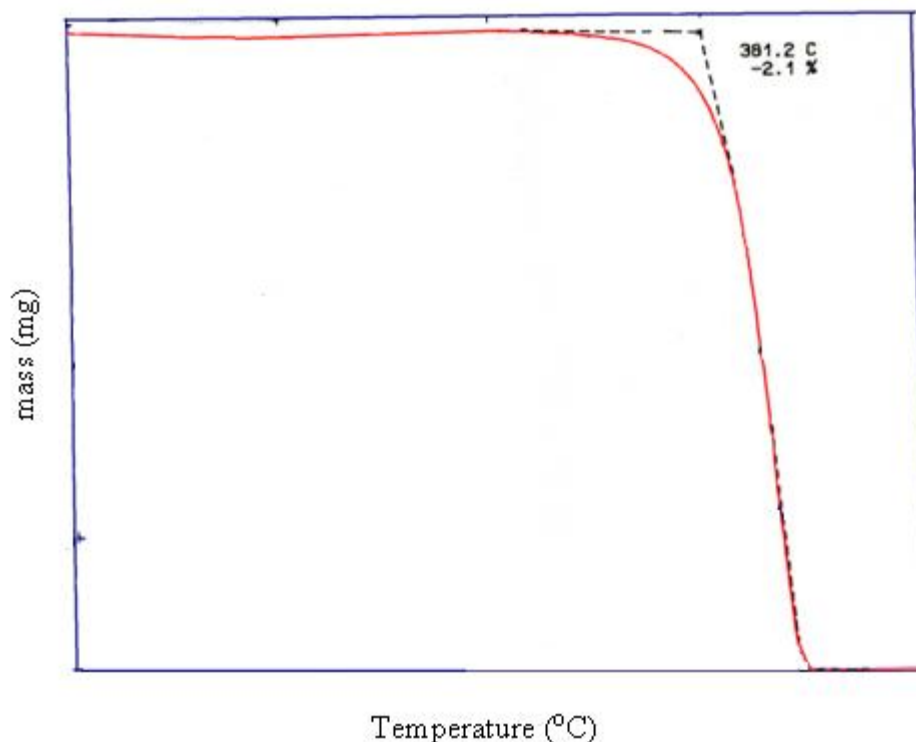


Figure 4.2. TG chart of N₁₁₂₈TFSI, under nitrogen and 10 °C/min heating rate.

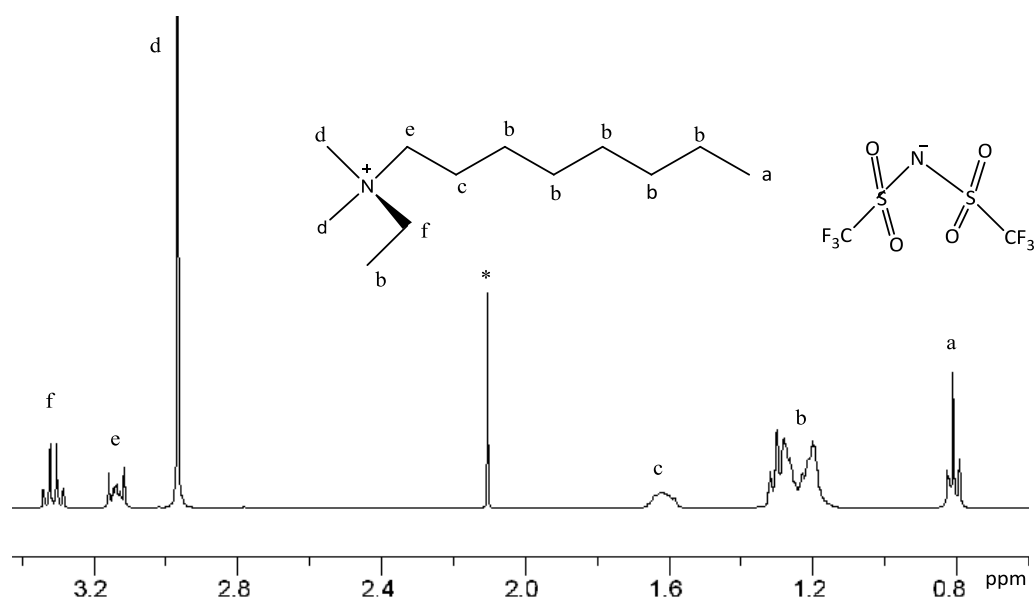
Initial indications from the ¹H NMR spectrum (spectrum 4.2) show that the product is obtained in relatively high purity and the ¹⁹F NMR spectrum (spectrum 4.3) shows the anticipated single peak corresponding to the CF₃ group. This is further verified by the elemental analysis, as shown in table 4.3.

The ¹H NMR spectrum of the RTIL N₁₁₂₈TFSI, (spectrum 4.2) shows a number of peaks. The resonance at $\delta = 3.3$ ppm (f) of relative intensity two, is a quartet ($J = 7.36$ Hz), assigned as the CH₂ group of the ethyl group. The resonance at $\delta = 3.14$ ppm (e) is a second order multiplet due to the α -CH₂ group adjacent to the nitrogen centre. The influence of the anion on the cation can be seen in the ¹H NMR spectrum which shows a shift in this peak position compared to that of the ammonium halide salt ($\delta = 3.44$ ppm).

Table 4.3. Elemental analysis of N_{112R}TFSI.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₂₈ TFSI	-25*	36.04	6.05	6.01	36.04	6.34	6.15
N ₁₁₂₍₁₀₎ TFSI	-22*	38.85	6.53	5.67	38.90	6.94	5.53
N ₁₁₂₍₁₄₎ TFSI	41	43.62	7.33	5.09	43.67	7.75	4.98
N ₁₁₂₍₁₈₎ TFSI	65	47.50	7.98	4.62	48.04	8.46	4.43

* = T_g (glass transition temperature)

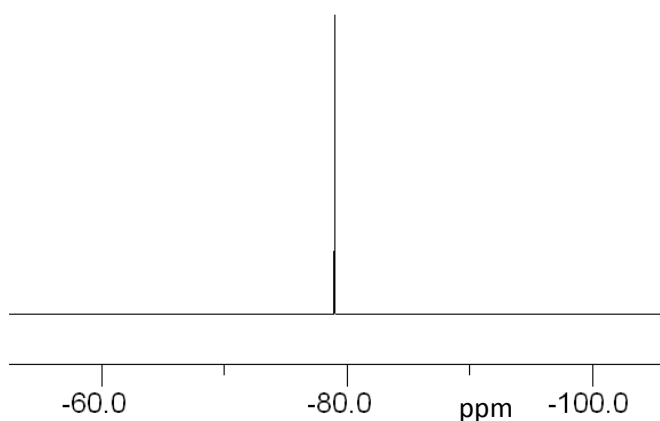


Spectrum 4.2. ¹H NMR spectrum of dimethylethyloctylammoniumiodide N₁₁₂₈TFSI. (*=water impurity in CDCl₃)

The resonance at $\delta = 2.96$ ppm (d) of relative intensity six is a singlet arising from the two methyl groups of the ammonium cation, the chemical shift for these methyl groups is lower than that of the parent halide ($\delta = 3.31$ ppm) because of the influence of the anion on the cation. This is observed in all of the exchanged products.

The β -CH₂ group on the octyl chain resonates at $\delta = 1.61$ (c) and appears as a multiplet. The other CH₂ resonances appear as a broad multiplet in the chemical shift range of $\delta = 1.19 - 1.3$ ppm (b), this is due to the overlapping of five CH₂ groups and the CH₃ group of the ethyl chain. The terminal CH₃ group of the octyl chain resonates at $\delta = 0.81$ ppm (a).

The ¹⁹F NMR spectrum (spectrum 4.2) shows a single peak at $\delta = -78.91$ ppm due to the CF₃ group of the TFSI anion.



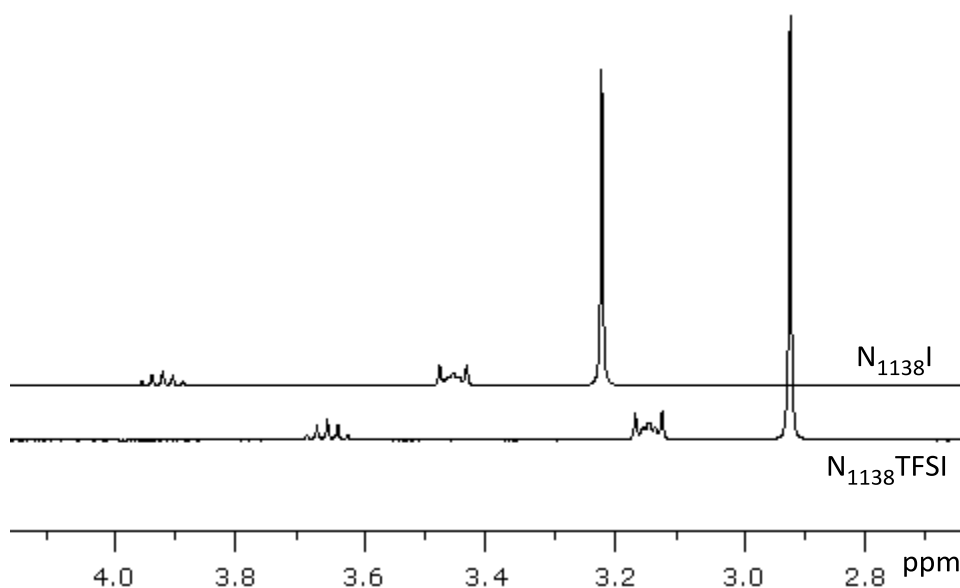
Spectrum 4.3. ¹⁹F NMR spectrum of dimethyethyloctylammonium bistrifluoromethanesulphonylimide, N₁₁₂₈TFSI.

Exchanging the iodide of dimethylisopropyloctylammonium iodide (N₁₁₃₈I, mp. 196 °C) with the TFSI anion resulted in a clear RTIL. The ¹H NMR of the resulting RTIL showed all the expected peaks with a slight change in the chemical shift values of the CH₃ groups (N-CH₃) and the α CH₂ groups (N-CH₂) of the ammonium centre compared to that of the parent halide as expected (spectrum 4.4). It is obvious that the compound has been obtained in high purity due to the excellent correlation of the elemental analysis data (table 4.4).

Table 4.4. Melting points, appearance and elemental analysis data of the halide and TFSI salts of $[N_{1138}]^+$.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$N_{1138}I$	196	47.69	9.24	4.28	47.63	10.02	4.27
$N_{1138}TFSI$	-30*	37.49	6.30	5.83	37.54	6.22	5.85

* = T_g (glass transition temperature)



Spectrum 4.4. Parts of the 1H NMR spectra of $N_{1138}I$ and its exchanged $N_{1138}TFSI$ salt.

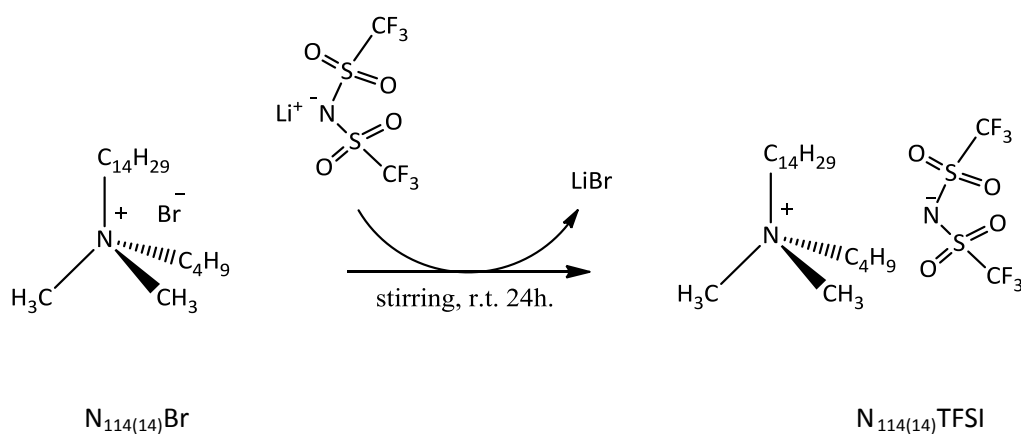
In the same manner exchanges of the longer quaternary ammonium halides of the C3 series showed a significant depression in the melting point compared to their halide salts, The $N_{113(10)}TFSI$ showed a depression in melting point of more than 200 °C as shown in table 4.5.

Table 4.5 Melting points, appearance and elemental analysis data of the iodide and TFSI salts of $[N_{113(10)}]^+$.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$N_{113(10)}I$	202-204	50.68	9.65	3.94	50.71	10.05	3.83
$N_{113(10)}TFSI$	-2	40.14	6.74	5.51	39.80	6.87	5.24

Similarly the TFSI-exchanged dimethylisopropyloctadecylammonium ($N_{113(14)}TFSI$) and dimethylisopropyloctadecylammonium ($N_{113(18)}TFSI$) salts were solids with melting points 34 and 57 °C respectively, lowered by more than 150 °C compared with their parent halide analogues as shown in chapter 2.

Further exchanges in the C4 series were performed. A typical example is the combination of the quaternary ammonium halide salt with the lowest melting point in the C4 series, dimethylbutyltetradecylammonium bromide $N_{114(14)}Br$, with LiTFSI (scheme 4.3) from which a nice clear RTIL, $N_{114(14)}TFSI$, was obtained (fig 4.4), with high thermal stability > 370 °C (fig 4.3).



Scheme 4.3. Synthesis of dimethylbutyltetradecyl ammonium bistrifluoromethanesulfonylimide, $[N_{114(14)}]TFSI$.

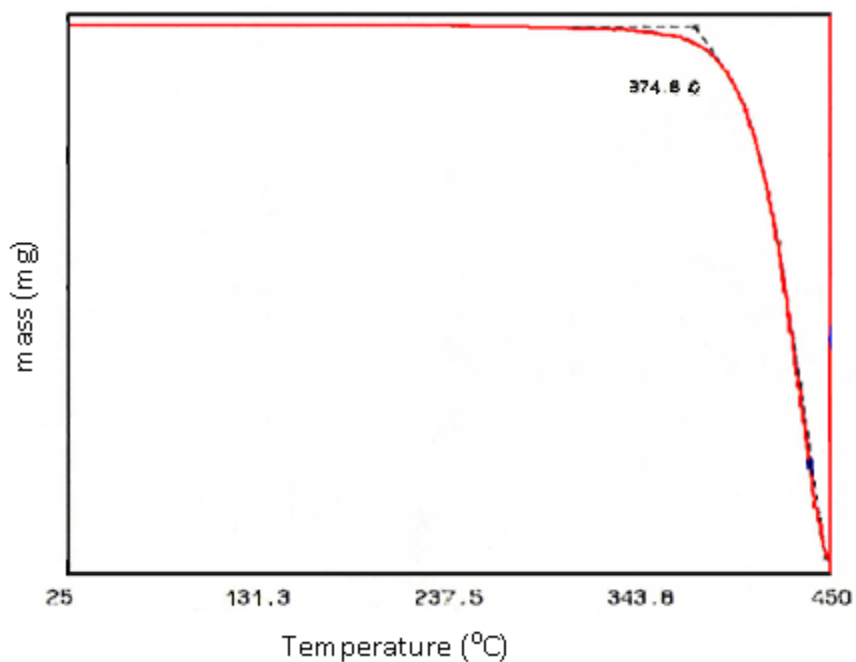


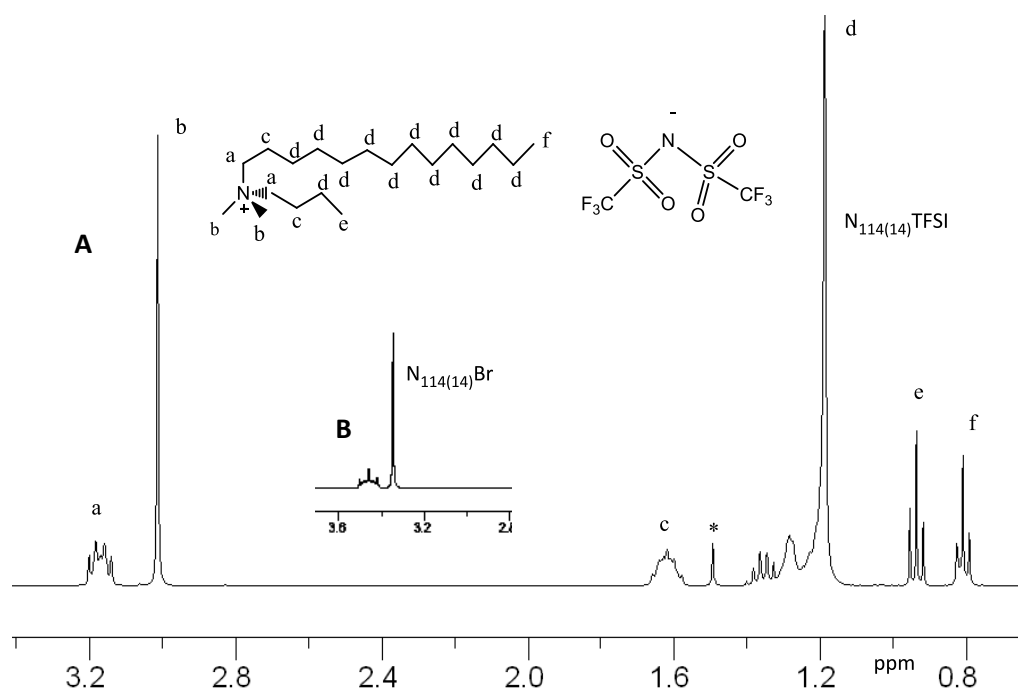
Figure 4.3 TG thermogram $N_{114(14)}TFSI$ under nitrogen and 10 °C/min heating rate.

Initial indications from the 1H NMR spectra (spectrum 4.5) show that the products are present in relatively high purity and the ^{19}F NMR spectrum (spectrum 4.6) shows the anticipated peak corresponding to the CF_3 group. This is further verified by the elemental analysis as shown in table (4.7).

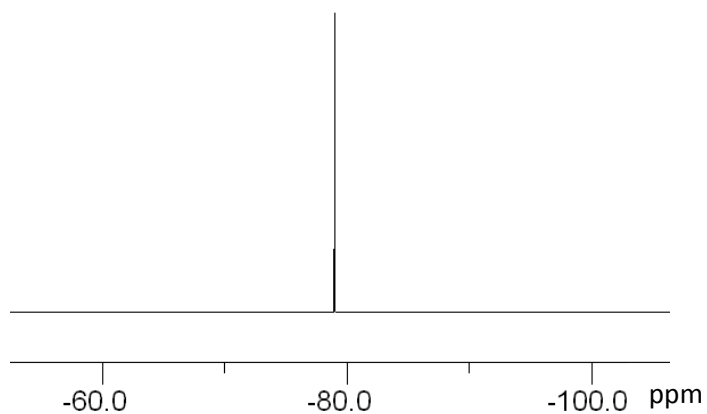


Figure 4.4. Physical appearance of $N_{114(14)}TFSI$.

Table 4.6. mp of $N_{114(14)}X$ salts	
Anion (X^-)	$[N_{114(14)}]^+$
Br^-	52 °C
TFSI	9 °C



Spectrum 4.5. ^1H NMR spectrum of dimethybutyltetradecyl ammonium bistrifluoromethylsulphonylimide, $\text{N}_{114(14)}\text{TFSI}$ (A) and part of that for $\text{N}_{114(14)}\text{Br}$ (B). (* = water impurity in CDCl_3)



Spectrum 4.6. ^{19}F NMR spectrum of dimethybutyltetradecyl ammonium bistrifluoromethylsulphonylimide, $\text{N}_{114(14)}\text{TFSI}$.

The ^1H NMR spectrum of the RTIL $\text{N}_{114(14)}\text{TFSI}$, (spectrum 4.5A) shows a number of peaks one of which at 1.5 ppm (*) may be assigned to water as an

impurity in CDCl_3 . The resonance at $\delta = 3.0$ ppm (b) of relative intensity six is a singlet due to the two methyl groups of the ammonium cation, the chemical shift value for these methyl groups is slightly lower than that of the parent halide ($\delta = 3.34$ ppm) because of the influence of the anion (TFSI) on the cation.

The resonance at $\delta = 3.1$ ppm (a) is a second order multiplet resulting from the complex overlapping of the signals due to the two α CH_2 groups adjacent to the ammonium centre. The influence of the anion on the cation can be seen in the ^1H NMR spectrum 4.5 B which shows a shift in this peak position compared to that of the ammonium halide salt ($\delta = 3.46$ ppm).

The two beta CH_2 groups, one on the butyl group and the other on the tetradecyl chain overlap and show a resonance at $\delta = 1.62$ ppm (c), these appear as a broad multiplet.

The rest of the CH_2 groups appear as a broad multiplet in the shift range of $\delta = 1.18$ - 1.3 ppm (d). This is due to the overlapping of signals from 12 CH_2 groups, 11 from the tetradecyl group and one from the butyl group.

The CH_3 group on the end of the butyl chain resonates at $\delta = 0.93$ ppm (e) giving a triplet signal due to the coupling to the adjacent CH_2 protons. Again the CH_3 group on the tetradecyl chain resonates at $\delta = 0.81$ ppm (f) giving a triplet signal due to the coupling to the adjacent CH_2 protons.

The ^{19}F NMR spectrum (spectrum 4.6) shows a single peak at $\delta = -78.89$ ppm due to the CF_3 group of the TFSI anion.

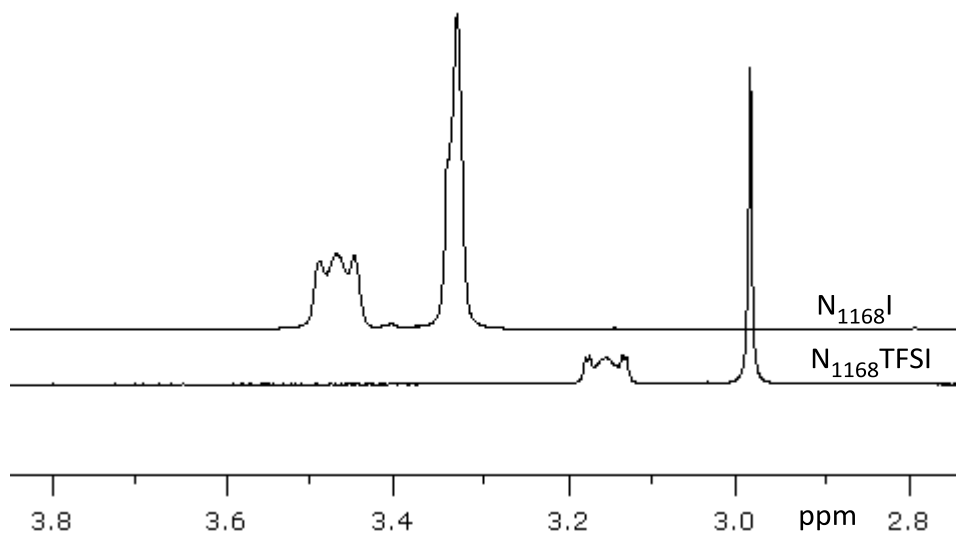
These exchanges resulted in either RTILs or solids with a melting point below 100°C and a significant depression in the melting point compared to that of their original halides, table 4.7 shows the elemental analysis of the C4 exchanged salts.

Table 4.7. Physical properties and elemental analysis of exchanged C4 series $N_{114(14)}$ TFSI.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N_{1148} TFSI	-24*	38.85	6.53	5.67	38.73	6.69	6.17
$N_{114(10)}$ TFSI	-25*	41.36	6.95	5.36	41.19	7.38	5.23
$N_{114(14)}$ TFSI	9	45.65	7.67	4.84	45.71	8.00	4.76
$N_{114(18)}$ TFSI	34	49.19	8.26	4.42	48.21	8.29	4.18

* = T_g (glass transition temperature)

Further exchanges were done on the C_6 series as well. The quaternary ammonium halide salt $N_{1168}I$ is already a liquid. This halide salt is a very viscous liquid with the consistency and colour of honey, but after the exchange with LiTFSI a clear, colourless, less viscous liquid was obtained N_{1168} TFSI. This is a relatively thermally stable RTIL, having a decomposition temperature of more than 380 °C. The 1H NMR spectrum shows the same signals as that of the ammonium halide, but with slightly lower chemical shift values for the CH_3 groups ($N-CH_3$) and the α CH_2 groups ($N-CH_2$) of the ammonium centre compared to that of the parent halide (spectrum 4.7).



Spectrum 4.7. Part of the ^1H NMR spectrum of the halide and bistrifluoromethylsulphonylimide salts of dimethylhexyloctylammonium cation, $[\text{N}_{1168}]^+$.

The ^1H NMR spectrum shows that the product is pure and this is confirmed by the elemental data which gave an excellent correlation to that expected (Table 4.8).

Table 4.8. Physical appearance and elemental analysis of dimethylhexyloctylammonium-TFSI, its iodide analogue and $\text{N}_{116(10)}\text{TFSI}$.

Sample identity	mp ($^{\circ}\text{C}$)	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N_{1168}I	-	52.01	9.83	3.79	51.67	10.09	3.79
$\text{N}_{1168}\text{TFSI}$	-23*	41.36	6.95	5.36	41.25	7.18	5.39
$\text{N}_{116(10)}\text{TFSI}$	-82	43.62	7.33	5.09	43.62	7.49	5.27

* = T_g (glass transition temperature)

Exchanging the halides with the TFSI anion in the asymmetric ammonium salts resulted in a significant depression in the melting point compared to that of the parent halides to give either RTILs or solids with a melting point below 100 °C. Table 4.9 shows the influence of anion exchange on the melting points.

Table 4.9 A comparison between melting points of some quaternary ammonium iodides and TFSI analogues.

Sample identity	Melting point °C	Sample identity	Melting point °C
N ₁₁₁₍₁₀₎ I	128	N ₁₁₁₍₁₀₎ TFSI	-37
N ₁₁₃₍₁₀₎ I	204	N ₁₁₃₍₁₀₎ TFSI	-2
N ₁₁₄₍₁₀₎ I	55	N ₁₁₄₍₁₀₎ TFSI	-25
N ₁₁₂₍₁₀₎ I	109	N ₁₁₂₍₁₀₎ TFSI	- 22*
N ₁₁₆₍₁₀₎ I	-23*	N ₁₁₆₍₁₀₎ TFSI	-82

* = T_g (glass transition temperature)

More than 20 novel RTILs were prepared based on aliphatic long chain asymmetric alkylammonium quaternary salts N_{11RR}X from the exchange reaction using the bistrifluoromethylsulfonylimide lithium salt, with relatively high purity and this is supported by their elemental analysis as shown in the preceding tables. These are the first to be reported, only the smaller asymmetric alkylammonium quaternary salts have been reported.^[4b,4c,7] Even the exchange with the least asymmetric quaternary ammonium halides (N₁₁₁₈I, N₁₁₁₍₁₀₎I) with the TFSI anion resulted in RTILs.

4.3. Synthesis of the completely asymmetric quaternary ammonium bis(trifluoromethanesulfonylimide) salt.

The completely asymmetric aliphatic quaternary ammonium bis(trifluoromethanesulfonyl)imide, the first to be reported with > 20 carbon

atoms in total, was a room temperature ionic liquid and interestingly had one of the lower melting points ($-58\text{ }^{\circ}\text{C}$) of all the exchanged TFSI salts (fig 4.5). This is a very promising result, in addition to this it possessed one of the highest thermal stabilities for the ionic liquids studied in this research with a decomposition onset of $394\text{ }^{\circ}\text{C}$ (fig. 4.6). The elemental analysis of the completely asymmetric salt is in good agreement with that calculated as shown in table 4.10.

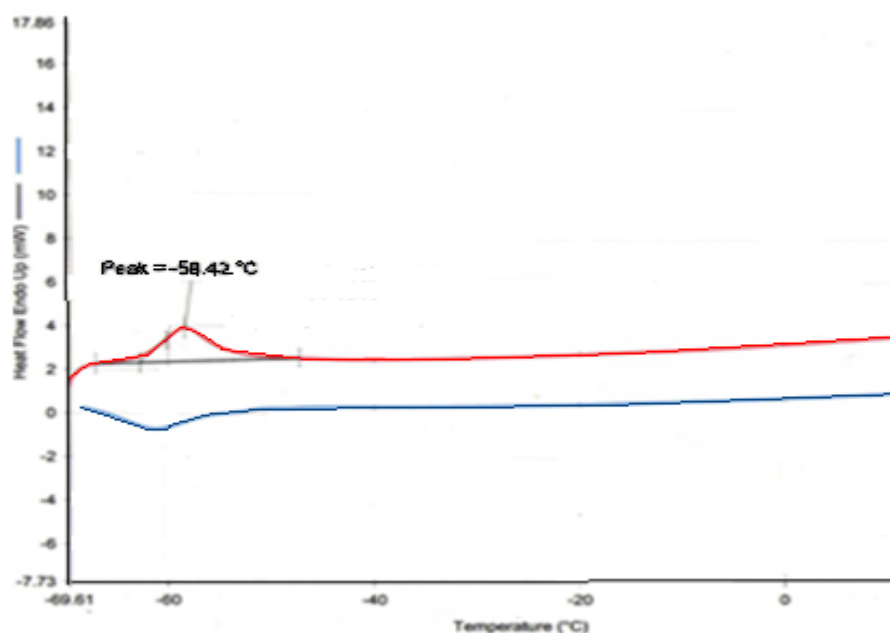


Figure 4.5. DSC trace for $\text{N}_{148(14)}\text{TFSI}$.

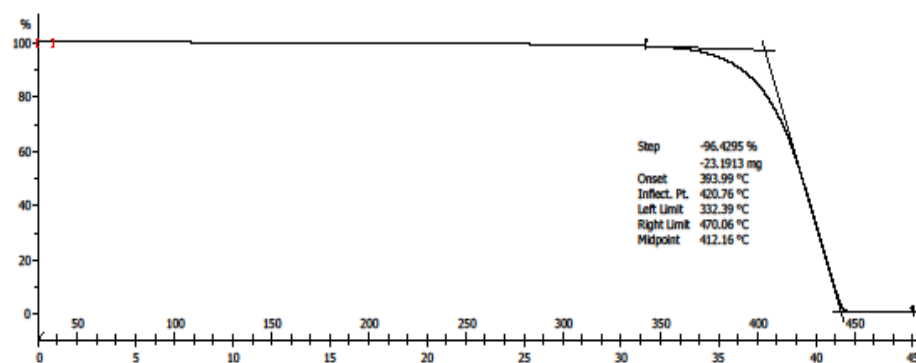


Figure 4.6. TG trace of $\text{N}_{148(14)}\text{TFSI}$, under nitrogen and $10\text{ }^{\circ}\text{C}/\text{min}$ heating rate.

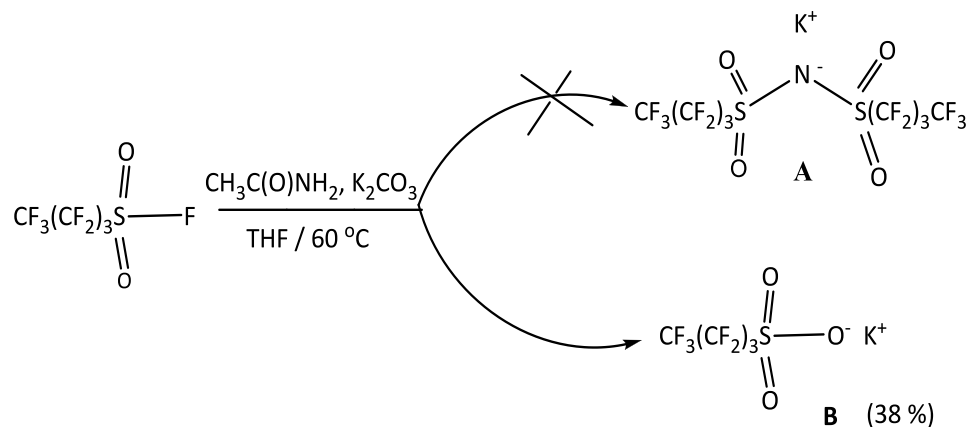
Table 4.10. Elemental analysis and melting points of N₁₄₈₍₁₄₎TFSI.

Sample identity	mp (°C)	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₄₈₍₁₄₎ TFSI	-58	51.54	8.64	4.14	51.12	8.60	4.68

Since the bis(trifluoromethanesulfonyl)imide appears to be a promising anion, which resulted in a number of RTILs and significantly reduced the melting points of the salts, compared with the parent quaternary ammonium halides, attempts were made to extend the fluorinated chain in the anion to see if this lowered the melting point even further. It was therefore decided to prepare the bis(nonafluorobutanesulfonylimide) potassium salt.

4.4. Synthesis of bis(perfluoroalkanesulfonyl)imide potassium salts.

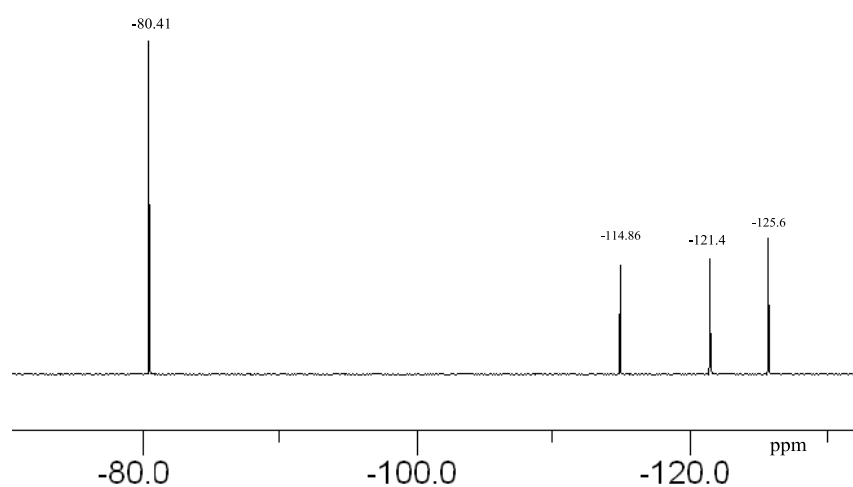
An attempt was made to extend the length of the fluorinated chain in the anion, using the one pot reaction reported by Sogabe *et al.* for the synthesis of potassium perfluoroalkylsulfonylimides directly from trifluoroacetamide using the sulfonylating reagent, nonafluorobutane-1-sulfonyl fluoride or perfluorooctane-1-sulfonyl fluoride, in the presence of potassium carbonate.^[5] When this reaction was carried out, as described, (scheme 4.4) a white crystalline material was obtained along with evolution of a gas. The ¹⁹F NMR spectrum of the solid (spectrum 4.8) showed the 4 signals of the appropriate 3 CF₂ groups, (δ = -125.6 ppm, -121.4 ppm and -114.9 ppm) and the CF₃ group (δ = - 80.41 ppm) as expected. However the elemental analysis data (table 4.11), showed no presence of nitrogen, and the carbon : sulfur ratio was 4:1. This suggests that the reaction has not proceeded as described, and instead C₄F₉SO₃K (**B**) might have been prepared. Indeed, the elemental analysis figures are consistent with this formulation (table 4.11).



Scheme 4.4. Attempted route for the synthesis of potassium bisnonafluorobutanesulfonylimide salt.

Table 4.11. Elemental analysis of the isolated potassium nonafluorobutane sulfonate, $C_4F_9SO_3K$.

Sample identity	Elemental analysis							
	Theoretical %				Found %			
	C	H	N	S	C	H	N	S
$C_4F_9SO_3K$	14.20	0	0	9.46	13.97	0	0	9.46



Spectrum 4.8. ^{19}F NMR spectrum of potassium nonafluorobutane sulfonate.

A similar outcome was observed in the attempted synthesis of the potassium bisperfluorooctylsulfonylimide salt using the reported synthetic route, instead potassium perfluorooctylsulfonate resulted as a major product. The ^{19}F NMR spectrum showed signals for the 7 CF_2 groups $\delta = -128.1$ ppm (CF_2), -124.3 ppm (CF_2), -123.4 , (CF_2)₃, -121.7 ppm, (CF_2), -109 ppm (CF_2) and the CF_3 ($\delta = -83.3$ ppm) group as expected. This is also supported by the elemental analysis as shown in table 4.12.

Table 4.12 Elemental analysis of potassium perfluorooctylsulfonate, $\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$.

Sample identity	Elemental analysis							
	Theoretical %				Found %			
	C	H	N	S	C	H	N	S
$\text{C}_8\text{F}_{17}\text{SO}_3\text{K}$	17.84	0	0	5.94	17.88	0	0	5.75

Interestingly, the original paper provided elemental analysis figures for what they claim to be $(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NK}$ which were not consistent with that expected, found: [C (17.30 %), N (2.17 %) whereas expected: C (18.85 %), N (1.37 %)]. However, the authors have probably interpreted their product based on the ^{19}F NMR which will obviously show the peaks expected.

Despite the isolated compound not being that originally sought, the product is a long-chain fluorinated salt and so ion-exchange reactions were performed using the potassium nonafluorobutane-1-sulfonate with two of our quaternary ammonium salts, dimethylbutyltetradecylammonium bromide and dimethylhexyloctylammonium iodide.

The reaction of both the dimethylbutyltetradecylammonium bromide (mp 48°C) and the dimethylhexyloctylammonium iodide with the potassium nonafluorobutylsulfonate resulted initially in a liquid that crystallised gradually on cooling. Both resulting solids had a melting point higher than

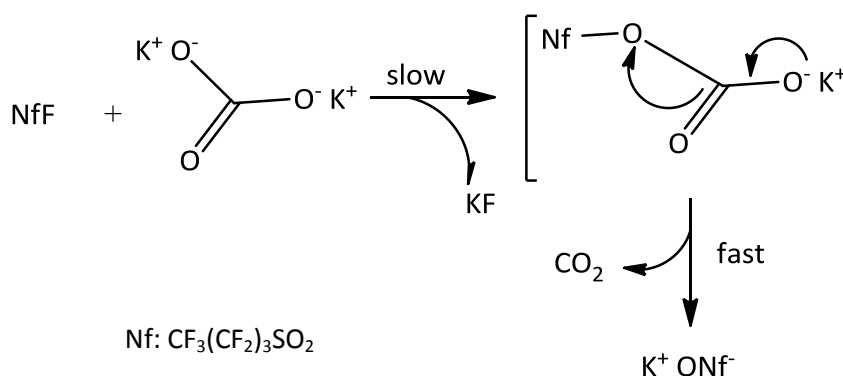
their original parent halides and exceeding 100 °C which is an exceptional case to the exchanged TFSI-products table 4.13.

Table 4.13. Melting points and elemental analysis for the isolated nonaflates.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₄₍₁₄₎ C ₄ F ₉ SO ₃	111	48.22	7.42	2.34	48.48	7.61	2.31
N ₁₁₆₈ C ₄ F ₉ SO ₃	139	44.34	6.70	2.59	44.33	6.81	2.50

On the other hand these salts showed high thermal stabilities, 340.8 and 325.5 °C for N₁₁₄₍₁₄₎C₄F₉SO₃ and N₁₁₆₈C₄F₉SO₃ respectively. Although there are some differences in the melting points, there does not appear to be a systematic correlation between anion or cation and the melting point.

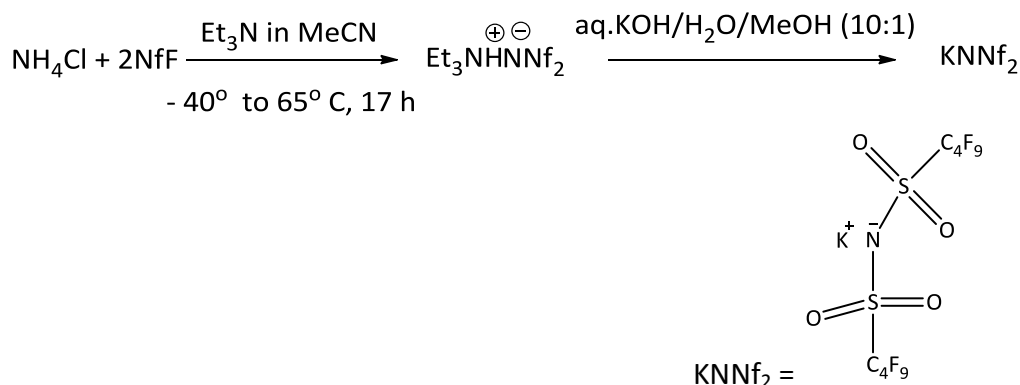
Interestingly S. K. Quek *et al.* have reported that on following the method described by Sogabe *et al.*, they ended up with the same product, potassium nonafluoro-1-butane sulfonate and not the bis-substituted potassium salt as intended (scheme 4.5).^[6] The authors suggested a mechanism for the production of the sulfonate route and developed a new protocol to circumvent the difficulties caused by using K₂CO₃.



Scheme 4.5. Synthesis of potassium nonafluorobutane sulfonate, C₄F₉SO₃K.

Ammonium chloride (NH₄Cl) and triethylamine (Et₃N) were used instead of the potassium carbonate which is compatible with sulfonyl fluoride in acetonitrile as shown in scheme 4.6.

In this way we could successfully prepare the desired potassium salt of bis(nonfluorobutanesulfonylimide), (K[(C₄F₉SO₂)₂N]),^[6] as described in detail in the experimental section (Chapter 6) in a two step reaction (scheme 4.6).



Scheme 4.6. Synthesis of potassium bis(nonafluorobutanesulfonyl)imide, (C₄F₉SO₂)₂NK.

This method is reported in the literature using the relatively inexpensive sulfonylating reagent, nonafluorobutane-1-sulfonyl fluoride in the presence of ammonium chloride and triethylamine to give the intermediate Et₃NH⁺NNf₂⁻ as a tawny crystalline solid. The ¹H NMR spectrum of the intermediate showed peaks as previously reported, a triplet at δ = 1.24 ppm due to the resonance of the CH₃ groups, a quartet at δ = 3.1 ppm due to the CH₂ groups and the NH resonates at δ = 7.19 ppm appearing as a broad singlet.

The ¹³C NMR spectrum also shows two peaks consistent with those reported, one appearing at δ = 8.4 ppm due to the methyl (CH₃) carbon and the other at δ = 47.0 ppm due to the methylene (CH₂) carbon. Finally the ¹⁹F NMR spectrum showed the appropriate peaks, at δ = -126.17 ppm, due to the α-CF₂ that is adjacent to the nitrogen, the second β-CF₂ group resonates at

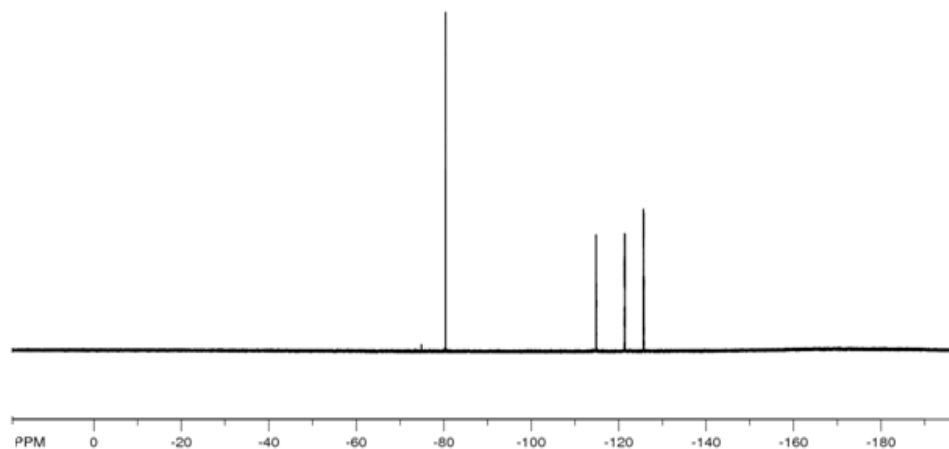
$\delta = -121.3$ ppm appearing as a complex multiplet. The third CF_2 group is observed as a complex multiplet at $\delta = -113.0$ ppm and the terminal CF_3 resonance is found at $\delta = -81.05$ ppm appearing as a triplet of triplets.

The white crystalline solid, KNNf_2 (mp 341.7°C) was then precipitated by the addition of a solution of the $\text{Et}_3\text{NH}^+\text{NNf}_2^-$ in MeOH dropwise to a solution of KOH with vigorous stirring, followed by thorough washing with cold deionised water and addition of CH_3Cl . The ^{19}F NMR spectrum (spectrum 4.9) of the product showed the anticipated peaks at $\delta = -125.77$ ppm, a triplet is observed due to the CF_2 adjacent to the nitrogen atom. The $\beta\text{-CF}_2$ resonates at $\delta = -121.07$ ppm and appears as a multiplet. The third CF_2 group resonates at $\delta = -113.36$ ppm and finally the CF_3 group resonates at $\delta = -80.39$ ppm. Both the NMR spectra and the melting point of the salt are consistent with those reported and the elemental analysis figures agree with those calculated (table 4.14).

Table 4.14. Elemental analysis of potassium bis(nonafluorobutane sulfonylimide), $(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NK}$, (KNNf_2).

Sample identity	mp $^\circ\text{C}$	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NK}$	341	15.51	0	2.26	15.51	0	2.45

After the identification of the potassium salt, ion-exchange reactions were performed with two of the quaternary ammonium salts, dimethylbutyl tetradecylammonium bromide (melting point 48°C) and dimethyl hexyloctylammonium iodide (liquid at room temperature). The reaction of both the dimethylbutyltetradecylammonium bromide and dimethyl hexyloctylammonium iodide with the potassium bis(nonafluorobutanesulfonylimide) resulted initially in liquids that crystallized gradually on cooling.

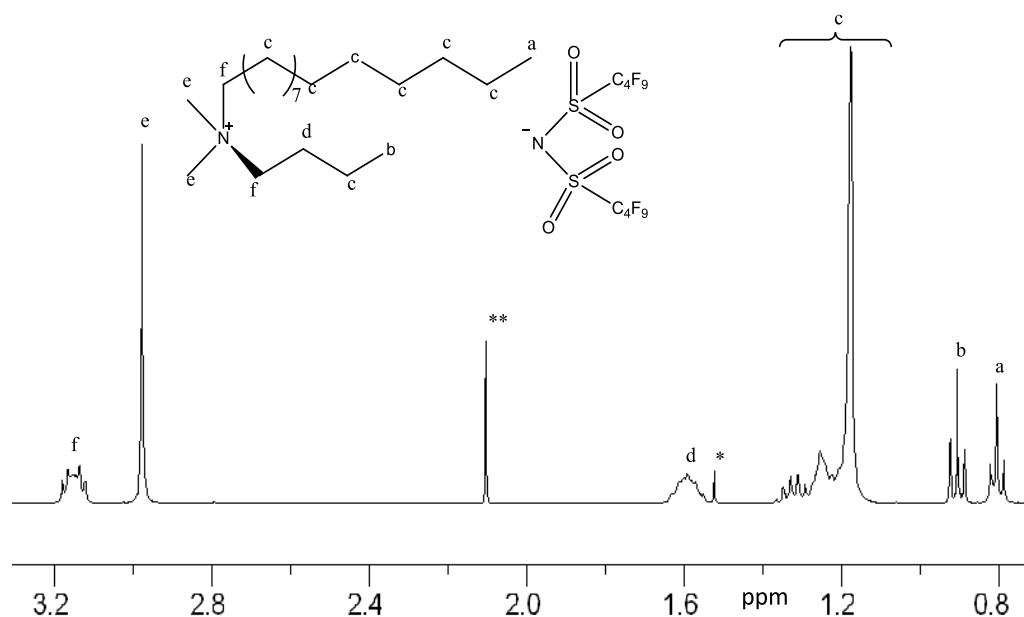


Spectrum 4.9. ^{19}F NMR spectrum of potassium bis(nonafluorobutane sulfonyl)imide, KNNf_2 ($(\text{C}_4\text{F}_9\text{SO}_2)_2\text{NK}$).

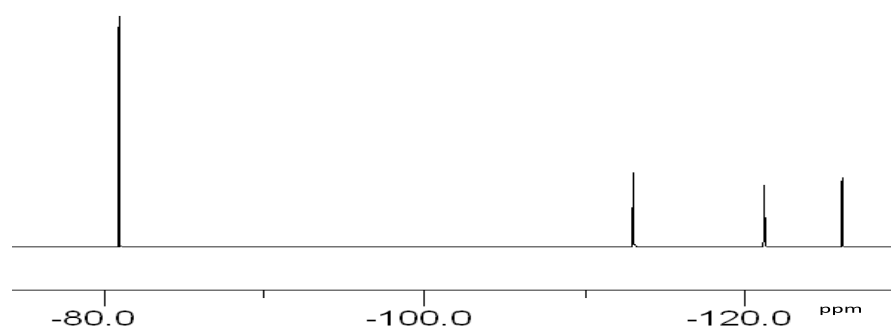
The ^1H NMR and ^{19}F NMR spectra of dimethylbutyltetradecylammonium bisnonafluorobutanesulfonylimide, $\text{N}_{114(14)}\text{NNf}_2$, (spectra 4.10 and 4.11) showed the expected peaks and this was supported by its elemental analysis as shown in table 4.15.

Table 4.15. Elemental analysis for $\text{N}_{114(14)}\text{NNf}_2$.

Sample identity	Physical state	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$\text{N}_{114(14)}\text{NNf}_2$	liquid	38.26	5.05	3.19	38.62	5.29	3.25



Spectrum 4.10. 1H NMR spectrum of dimethylbutyltetradecylammoniumbis(nonafluorobutanesulfonyl)imide, $N_{114(14)}NNf_2$. (** = acetone, * = water impurities)



Spectrum 4.11. ^{19}F NMR spectrum of dimethylbutyltetradecylammoniumbis(nonafluorobutanesulfonyl)imide, $N_{114(14)}NNf_2$.

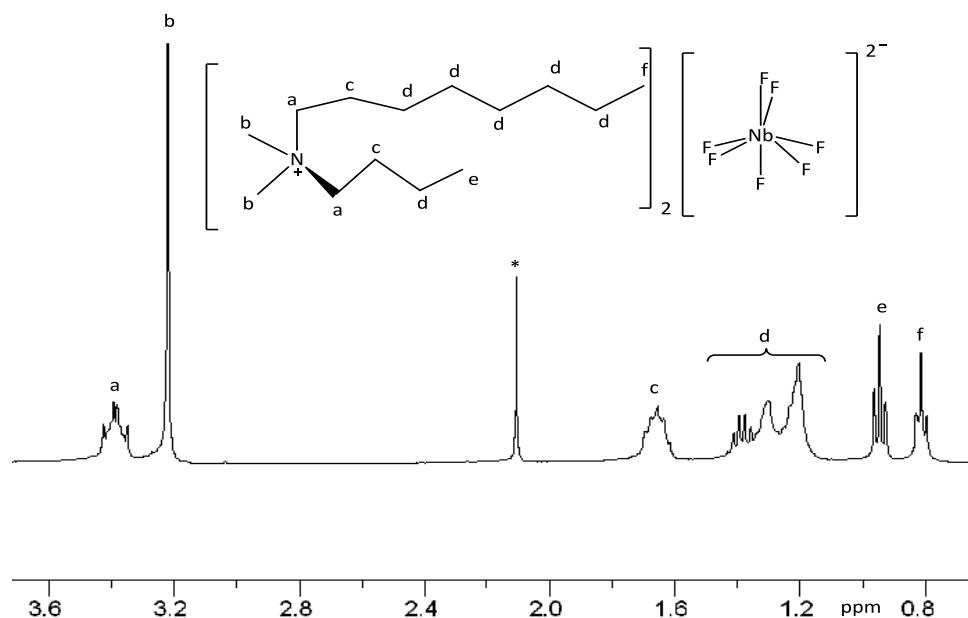
From the collected data it is clear that the product is of relatively high purity. Whereas on exchanging the dimethylhexyloctylammonium iodide (liquid) with KTFSI a room temperature ionic liquid was obtained in contrast to the potassium bis(nonafluorobutanesulfonyl)imide, $KNNf_2$, solid product which was isolated.

We can therefore say that the longer chain bis-substituted sulfonylimide (bisnonafluorobutanesulfonylimide) anion is not a promising candidate in the development of RTILs since it resulted in a solid ionic material at room temperature, whilst our aim is to get the lowest melting point salts.

4.5. Ion-exchange of asymmetric quaternary ammonium halides with potassium heptafluoroniobate(V).

Using a similar ion-exchange process a new class of ionic liquids were synthesized, based on a dianion to give an ionic liquids with 2:1 ratio of cation and anion respectively. The ion-exchange reaction between dimethylbutyloctylammonium iodide and potassium heptafluoroniobate (V) resulted in a liquid of relatively high viscosity (see later) compared with its bistrifluoromethylsulfonylimide analogue. Table 4.16 shows the physical state and elemental analysis of this and other asymmetric quaternary ammonium heptafluoroniobates.

The ^1H NMR spectrum (spectrum 4.12) of the product shows a number of peaks. The resonance at $\delta = 3.38$ ppm (a) shows a second order multiplet resulting from the complex overlapping of the signals due to the CH_2 of the butyl and octyl chains adjacent to the positively charged nitrogen atom.

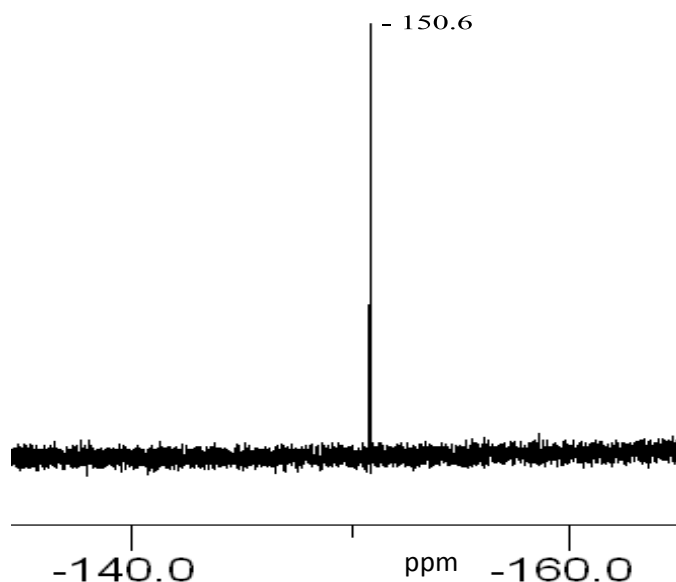


Spectrum 4.12. ^1H NMR spectrum of dimethylbutyloctylammoniumheptafluoronioate(V), $[\text{N}_{1148}]_2\text{NbF}_7$. (* = acetone)

The resonance at $\delta = 3.2$ ppm of relative intensity six (b) is a singlet and corresponds to the two methyl groups of the ammonium cation, the chemical shifts for these methyl groups is significantly higher than that of the corresponding CH_3 group on the octyl ($\delta = 0.81$ ppm) and butyl chain ($\delta = 0.94$ ppm) due to being adjacent to the formally positively charged quaternary nitrogen centre.

The beta CH_2 groups on both the octyl and butyl chains tend to overlap and resonate at $\delta = 1.65$ ppm (c). The remainder of the CH_2 signals appear as a set of multiplets in the shift range of $\delta = 1.2$ - 1.38 ppm (d). These multiplets arise from the overlapping of six CH_2 groups, five from the octyl fragments and one from the butyl chain, each of which are in slightly different chemical environments.

The CH₃ group on the end of the butyl chain resonates at $\delta = 0.94$ ppm (e) appearing as a triplet signal due to the coupling to the adjacent CH₂ protons, this CH₃ group resonates at a slightly higher δ value than that of the CH₃ group of the octyl chain $\delta = 0.81$ ppm possibly due to the relative proximity of the CH₃ group to the ammonium centre. Again this signal is a triplet, and arises due to coupling to the adjacent CH₂ protons. The ¹H NMR spectra of all the exchanged products showed the expected peaks with a slight change in chemical shift values of the CH₃ groups (NCH₃) and the α -CH₂ groups (NCH₂) of the ammonium centre compared to that of the parent halide as expected. The ¹⁹F NMR spectra of all the salts show a single peak, at *ca.* -150.6 ppm, as that observed for [N₁₁₄₈]₂NbF₇ in spectrum 4.13.



Spectrum 4.13. ¹⁹F NMR spectrum of dimethylbutyloctylammoniumheptafluoroniobate, [N₁₁₄₈]₂NbF₇.

Table 4.16. Elemental analysis of asymmetric quaternary ammonium heptafluoronibates.

Sample identity	Elemental analysis					
	Theoretical %			Found %		
	C	H	N	C	H	N
$[\text{N}_{1148}]_2\text{NbF}_7 \cdot 2\text{H}_2\text{O}$	48.67	9.93	4.06	48.55	10.02	4.05
$[\text{N}_{114(10)}]_2\text{NbF}_7 \cdot 2\text{H}_2\text{O}$	51.44	10.26	3.75	51.60	11.27	3.80
$[\text{N}_{114(14)}]_2\text{NbF}_7 \cdot 2\text{H}_2\text{O}$	55.90	10.80	3.26	55.71	11.09	3.24
$[\text{N}_{1138}]_2\text{NbF}_7 \cdot \text{H}_2\text{O}$	48.42	9.70	4.35	48.09	9.50	4.29
$[\text{N}_{113(10)}]_2\text{NbF}_7 \cdot \text{H}_2\text{O}$	51.40	10.07	4.00	51.13	10.04	3.88
$[\text{N}_{1128}]_2\text{NbF}_7 \cdot 4\text{H}_2\text{O}$	42.96	9.62	4.18	43.26	8.87	4.01
$[\text{N}_{112(10)}]_2\text{NbF}_7 \cdot 4\text{H}_2\text{O}$	46.25	9.99	3.86	46.31	9.61	3.62
$[\text{N}_{1168}]_2\text{NbF}_7 \cdot 2\text{H}_2\text{O}$	51.44	10.26	3.75	51.47	10.82	3.72

From the data presented in table 4.16 it is clear that all of the niobates tend to pick up water; where the C4 and C6 series of ammonium salts have 2 molecules of water, the C3 series, one water molecule and the C2 series, 4 water molecules. Once again the isopropyl niobates are solids compared to the rest of the series which are liquids apart from $[\text{N}_{114(14)}]_2\text{NbF}_7$. This may be explained due to the efficiency of the packing of the molecules similar to the trend observed with the asymmetric quaternary ammonium halide salts reported in chapter 2. Fig 4.7 shows the DSC trace for $[\text{N}_{114(10)}]_2\text{NbF}_7 \cdot 2\text{H}_2\text{O}$, showing a melting point of 31 and crystallization temperature of - 26 °C.

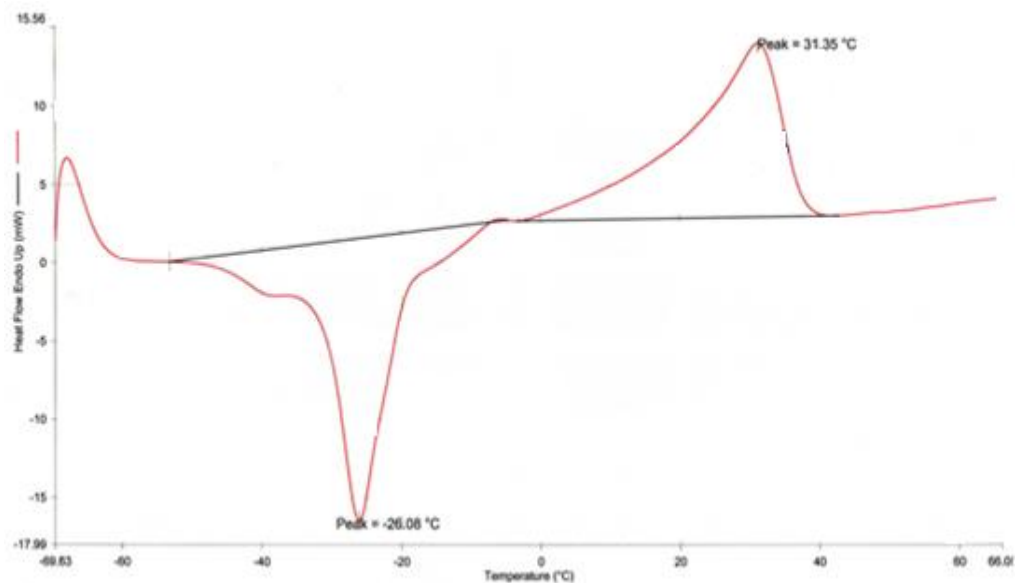


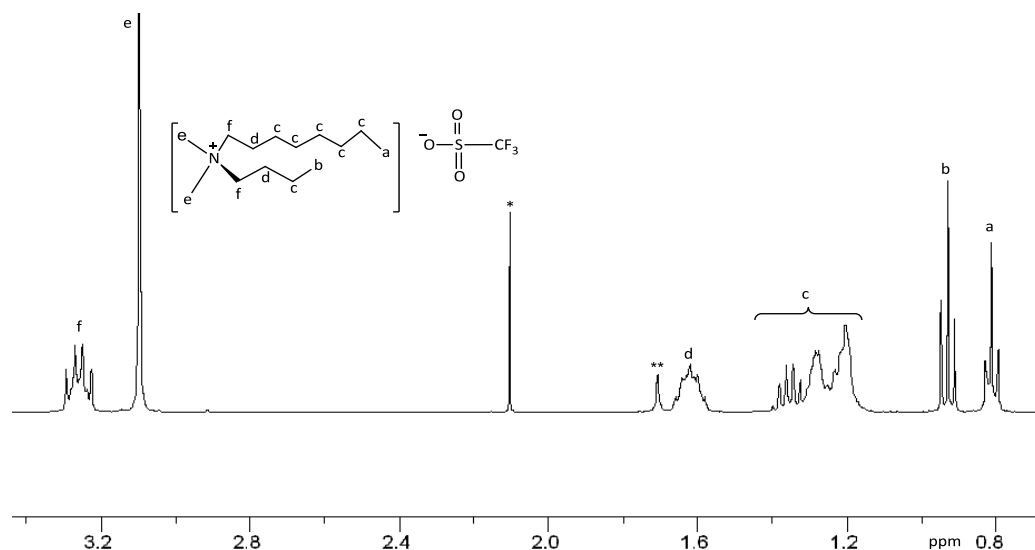
Figure 4.7. DSC trace for $[N_{114(10)}]_2NbF_7 \cdot 2H_2O$.

In all cases the TFSI salts possessed lower melting points for the same cation and therefore work on NbF_7^{2-} systems was not taken further.

4.6. Ion-exchange of asymmetric quaternary ammonium halides with potassium trifluoromethane sulfonate.

Further exchanges were carried out using potassium trifluoromethanesulfonate on almost all of the series, focusing in particular on the cations that gave RTILs with the TFSI anion.

The reaction of dimethylbutyloctylammoniumiodide with potassium trifluoromethanesulfonate resulted in a liquid, formulated as $N_{1148}SO_3CF_3$ on the basis of microanalytical data.



Spectrum 4.14 ^1H NMR spectrum of dimethylbutyloctylammoniumtrifluoromethanesulfonate, $\text{N}_{1148}\text{SO}_3\text{CF}_3$. (* = acetone, ** = water.)

The ^1H NMR spectrum of dimethylbutyloctylammoniumtrifluoromethanesulfonate showed all the anticipated peaks (spectrum 4.14).

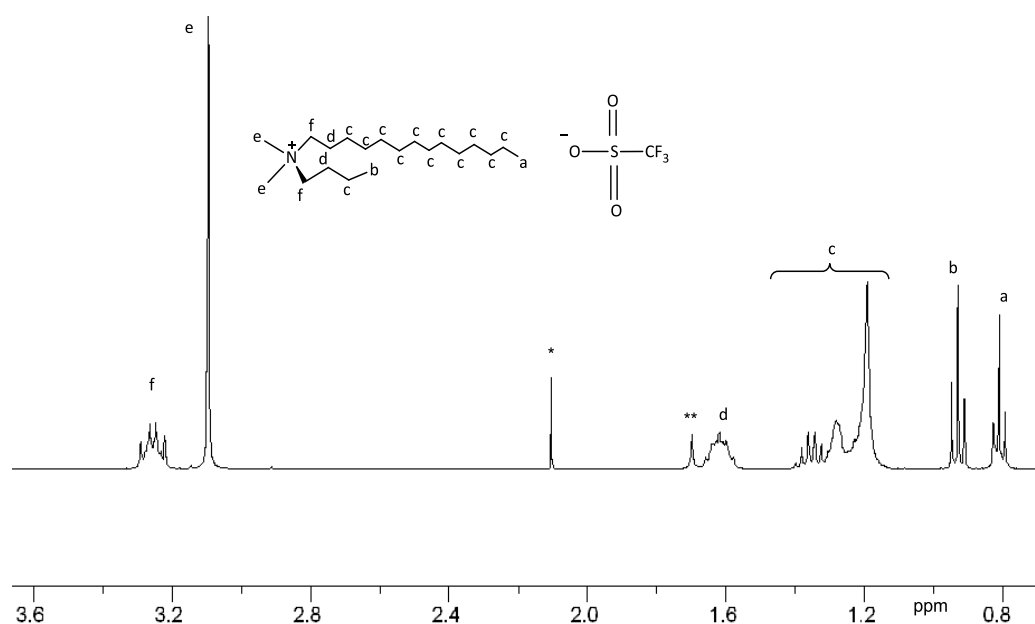
The multiplet at $\delta = 3.25$ ppm (f) which integrates as four hydrogens is due to the overlapping of the $\alpha\text{-CH}_2$ groups on the butyl and octyl groups due to their similar chemical environments. The methyl groups on the nitrogen centre are observed as a singlet at $\delta = 3.09$ ppm. The $\beta\text{-CH}_2$ groups of the butyl and octyl chains appear as a broad multiplet at $\delta = 1.62$ ppm, arising from the overlapping of the two signals due to them being in a similar chemical environment. The rest of the CH_2 groups appear as broad multiplets over the shift range $\delta = 1.2\text{--}1.35$ ppm. This corresponds to the overlapping of 6 CH_2 peaks (five of the octyl chain and one of the butyl chain) in similar chemical environments.

The terminal CH_3 group on the butyl chain appears as a triplet at $\delta = 0.93$ ppm due to coupling to adjacent CH_2 protons. This CH_3 group resonates at a higher chemical shift value than that of the terminal CH_3 of the octyl chain, $\delta = 0.81$ ppm, again presumably due to its relative proximity to the ammonium centre.

The ^{19}F NMR spectrum showed a singlet at $\delta = -78.48$ ppm confirming the presence of the CF_3 group.

The exchange of dimethylbutyldecylammonium iodide with potassium trifluoromethanesulfonate also resulted in a RTIL, whereas exchange with dimethylbutyltetradecylammonium bromide gave a solid product (mp 53 °C).

The ^1H NMR spectra of dimethylbutyltetradecylammonium trifluoromethanesulfonate shows that the product is pure (spectrum 4.15) and this is confirmed by the elemental analysis (as shown in table 4.17). All peaks appeared where they were expected for the products.



Spectrum 4.15. ^1H NMR spectrum of dimethylbutyltetradecylammonium trifluoromethanesulfonate, $\text{N}_{114(14)}\text{SO}_3\text{CF}_3$. (*= acetone, **= water)

Further exchanges were carried out on members of the C3, C1 and C6 series which also resulted in solids but with melting points as was the previous solids lower than 100 °C, so they are still by definition ionic liquids but not at room

temperature. It is surprising that this is the case for the C6 series, where the precursor halide is a liquid originally. These salts seemed to be hygroscopic when left in open air.

Table 4.17 Physical states and elemental analysis of quaternary ammonium trifluoromethanesulfonates.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N ₁₁₄₈ SO ₃ CF ₃ .H ₂ O	-	47.22	8.99	3.67	48.25	9.49	3.91
N ₁₁₄₍₁₀₎ SO ₃ CF ₃ .H ₂ O	-	49.85	9.36	3.42	50.67	9.66	3.92
N ₁₁₄₍₁₄₎ SO ₃ CF ₃	53	56.34	9.91	3.13	56.47	10.95	3.14
N ₁₁₂₈ SO ₃ CF ₃	46	46.54	8.42	4.18	45.18	9.10	4.10
N ₁₁₂₍₁₀₎ SO ₃ CF ₃	76	49.56	8.88	3.86	48.97	9.35	3.88
N ₁₁₁₍₁₀₎ SO ₃ CF ₃	49	48.11	8.66	4.01	48.05	9.08	3.54
N ₁₁₃₈ SO ₃ CF ₃	97	48.11	8.66	4.01	47.82	9.07	3.96
N ₁₁₃₍₁₀₎ SO ₃ CF ₃	-	50.90	9.08	3.71	50.50	9.93	3.53
N ₁₁₆₍₁₀₎ SO ₃ CF ₃	-	54.38	9.61	3.34	53.8	10.28	3.36
N ₁₁₆₈ SO ₃ CF ₃	-	52.14	9.27	3.58	51.89	10.20	3.60

4.7. Ion-exchange of asymmetric quaternary ammonium halides with hexafluorophosphate and tris(pentafluoroethyl)trifluorophosphate.

Further exchanges were made on the C4 series with two fluorinated phosphate anions, PF₆⁻ and an asymmetric analogue P(C₂F₅)₃PF₃⁻. Using a similar method to that stated in previous sections, the reaction of dimethylbutyloctylammonium iodide with potassium hexafluorophosphate in dichloromethane/water solution, after workup resulted in a yellow solid with

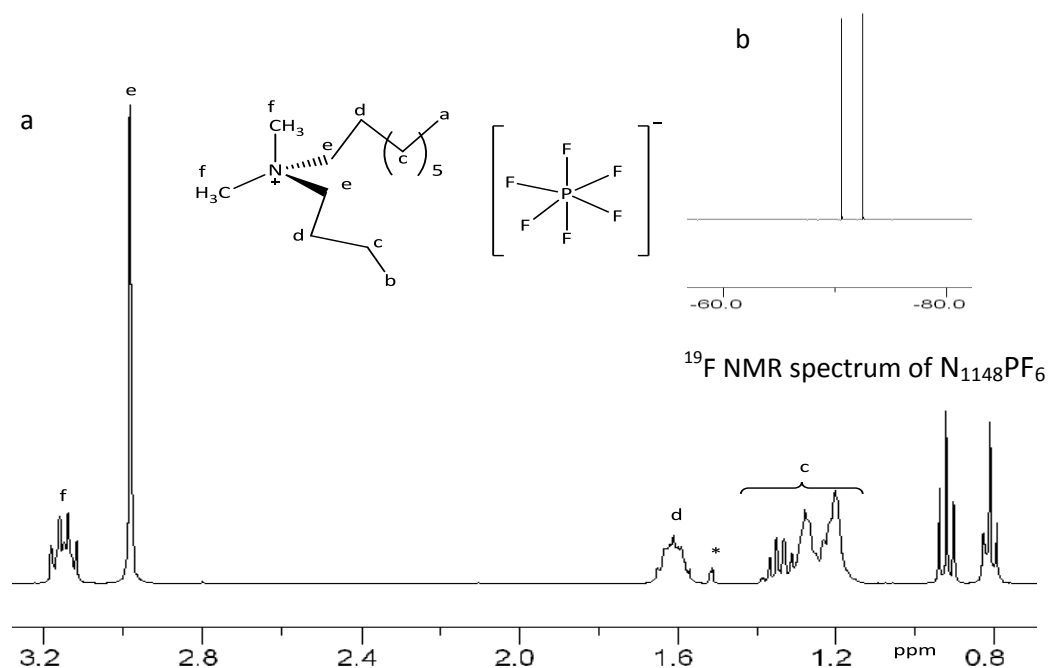
a melting point of 61 °C. The product was characterized by ^1H , ^{19}F and ^{31}P NMR spectroscopy, elemental analysis and TG/ DTA data.

Elemental analysis showed that the purity of the product is high where the obtained values are consistent with those calculated as shown in Table 4.18 and this is supported by its NMR spectroscopy (Spectrum 4.16)

Table 4.18 Elemental analysis and melting points of dimethylbutylalkyl-ammoniumhexafluorophosphate, $\text{N}_{114\text{R}}\text{PF}_6$.

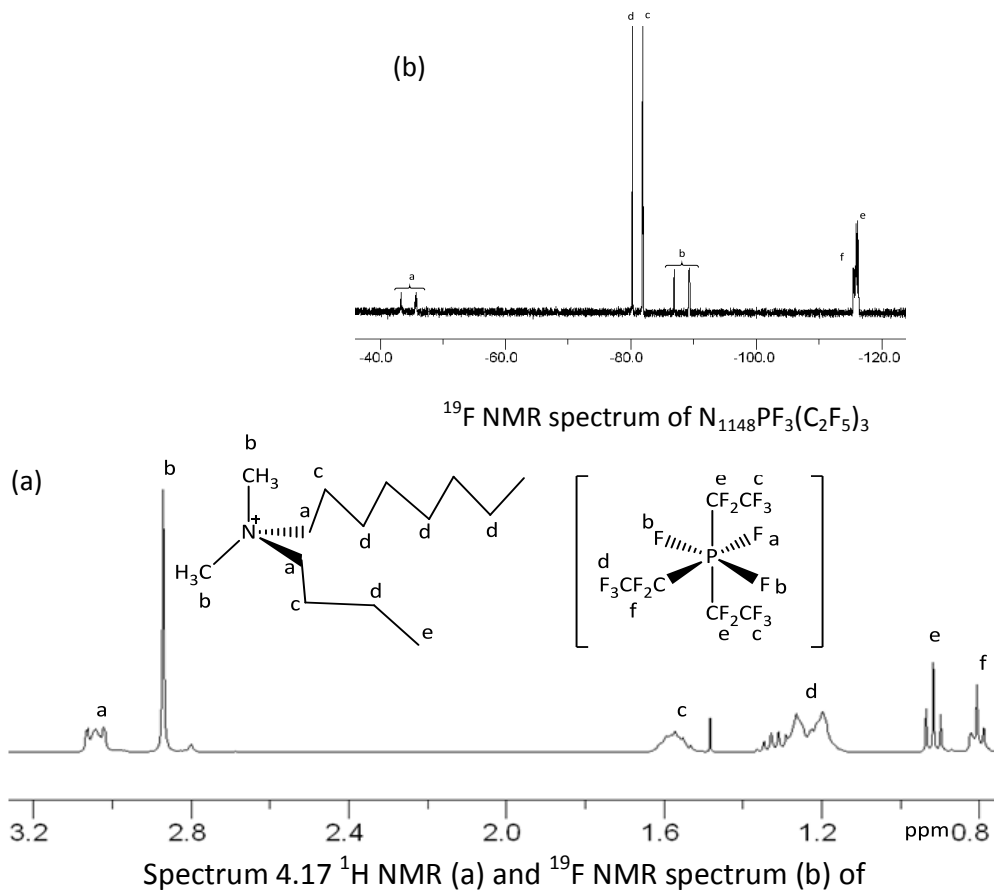
Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
$\text{N}_{1148}\text{PF}_6$	61	46.77	8.98	3.90	46.77	8.81	3.85
$\text{N}_{114(10)}\text{PF}_6$	50	49.58	9.37	3.62	49.86	9.20	3.65
$\text{N}_{114(14)}\text{PF}_6$	60	54.14	10.00	3.16	54.45	9.88	3.09
$\text{N}_{114(18)}\text{PF}_6$	82	57.67	10.49	2.80	57.79	10.33	2.73

In contrast to this, exchanging the C4 series quaternary ammonium halides with the asymmetric anion $[\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3]^-$ (FAP) resulted in room temperature ionic liquids and, surprisingly, even the longest chain C18 substituent, ($\text{N}_{114(18)}\text{FAP}$) resulted in a liquid, which is the only C18 room temperature ionic liquid in the materials studied in this research. With all the other anions studied, the C18-containing systems gave solids.



Spectrum 4.16 ¹H NMR spectrum of N₁₁₄₈PF₆ (a) and ¹⁹F NMR spectrum of N₁₁₄₈PF₆ (b). (* = water)

A typical example is the reaction of dimethylbutyloctylammonium iodide with potassium trispentafluoroethyltrifluorophosphate which, after workup, resulted in a clear liquid formulated as, dimethylbutyloctylammonium trispentafluoroethyltrifluorophosphate on the basis of its elemental analysis and NMR data.



The ^1H NMR (spectrum 4.17 (a)) and the ^{19}F NMR (spectrum 4.17(b)) spectra showed the anticipated peaks. The resonance at $\delta = 3.04$ ppm (a) of relative intensity of four, is a second order multiplet due to the $\alpha\text{-CH}_2$ groups on the butyl and octyl groups adjacent to the nitrogen centre. The resonance at $\delta = 2.87$ ppm (b) of relative intensity six is a singlet due to the methyl groups of the ammonium cation. The $\beta\text{-CH}_2$ groups on the octyl and butyl chains resonate at $\delta = 1.59$ ppm (c) appearing as a broad multiplet, this is due to their coupling to each other since they are in a similar chemical environment. The other CH_2 resonances appear as a broad multiplet in the range of $\delta = 1.19\text{-}1.26$ ppm (d), this is due to the overlapping of five CH_2 groups on the octyl chain and one CH_2 on the butyl chain. The terminal CH_3 group of the butyl resonates at $\delta = 0.91$ ppm (e) at a slightly higher chemical shift value

than that of the octyl chain at $\delta = 0.80$ ppm (f) possible due to the relative proximity of the CH_3 group to the ammonium centre.

The ^{19}F NMR spectrum shows two fluorine (PF) environments and two C_2F_5 environments. The first of these is a large doublet at $\delta = -44.54$ ppm (a) with a coupling constant of 894.7 Hz, this is due to the unique P-F coupling with phosphorus nucleus. The unique CF_3 group resonates at $\delta = -80.21$ ppm (d) appearing as a multiplet. The other 2 CF_3 groups which have similar chemical environments resonate at $\delta = -81.8$ ppm (c) of relative intensity of six, appearing as multiplet. The two equivalent fluorine atoms resonate at $\delta = -88.06$ ppm (b) with a coupling constant of 909.07 Hz, appearing as a multiplet. The CF_2 group appears as a broad multiplet in the range of -115.5 to -115.69 ppm (f), with relative intensity of two. While the two other equivalent, CF_2 groups overlap and resonate in the range of -115.9 to -116.2 ppm (e), appearing as a multiplet with relative intensity of four. The ^1H NMR and ^{19}F NMR spectra both indicate the product has been prepared in high purity, and this is supported by the elemental analysis as shown in table 4.19.

Table 4.19 Elemental analysis and melting points of $\text{N}_{114\text{R}}$ FAP salts.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N_{1148} FAP	-21*	36.41	4.89	2.12	36.44	4.73	2.10
$\text{N}_{114(10)}$ FAP	-21*	38.42	5.28	2.04	39.83	5.63	2.80
$\text{N}_{114(14)}$ FAP	-42	41.98	5.97	1.88	42.43	6.26	1.85
$\text{N}_{114(18)}$ FAP	25	45.04	6.56	1.75	45.30	6.70	1.85

*= T_g (glass transition temperature)

On introduction of the asymmetric analogue of hexafluorophosphate, tris(pentafluoroethyl)trifluorophosphate, a dramatic decrease in melting point is observed, by up to 100 °C in some cases, as shown in Table 4.20.

Table 4.20. Melting points of N_{114R}PF₆ and N_{114R}FAP salts.

Sample identity	Melting point or T _g (°C)
N ₁₁₄₈ FAP	-21 *
N ₁₁₄₈ PF ₆	61
N ₁₁₄₍₁₀₎ PF ₆	50
N ₁₁₄₍₁₀₎ FAP	-21*
N ₁₁₄₍₁₄₎ PF ₆	60
N ₁₁₄₍₁₄₎ FAP	-42
N ₁₁₄₍₁₈₎ PF ₆	82
N ₁₁₄₍₁₈₎ FAP	25

*= T_g (glass transition temperature)

It is reported in literature that the more symmetric tetraalkylammonium-FAP salts are solids with relatively high melting points as for N₂₂₂₂FAP and N₄₄₄₄FAP to be 95 °C and 62 °C respectively. As we have observed the melting point of the asymmetric quaternary ammonium-FAP salts studied in this work all possess melting points below those reported for the symmetric quaternary ammonium-FAP salts.^[8]

From this observation, it again appears that asymmetry plays an important role in depressing the melting point, whether in the cationic or anionic species in the quaternary ammonium salts.

4.8. Ion-exchange of asymmetric non-aliphatic quaternary ammonium halides with lithium bis(trifluoromethanesulfonylimide).

Further exchanges were done using the bis(trifluoromethanesulfonyl)imide anion with the halides of the quaternary ammonium salts of the non-aliphatic substituents. Using a similar method to the one described earlier resulting in ten room temperature ionic liquids with some of them appearing as less viscous liquids than those of the aliphatic quaternary ammonium ionic liquids

discussed earlier, were isolated. Table 4.21 shows the exchanged non-aliphatic quaternary ammonium salts, their elemental analysis and physical state.

Table 4.21. Elemental analysis of non-aliphatic quaternary ammonium bis(trifluoromethanesulfonyl)imides.

Sample identity	Melting point °C	Elemental analysis					
		Theoretical %			Found %		
		C	H	N	C	H	N
N _{11A8} TFSI	-26*	37.65	5.90	5.86	38.18	6.45	6.42
N _{11A10} TFSI	-22*	40.30	6.37	5.53	41.42	7.25	5.65
N _{11A(14)} TFSI	20	44.82	7.17	4.98	45.27	7.60	5.02
N _{11A(18)} TFSI	49	48.52	7.82	4.53	49.30	8.16	4.51
N _{11C8} TFSI	-21*	41.52	6.59	5.38	41.59	7.41	5.45
N _{11C(10)} TFSI	-25*	43.78	6.99	5.11	44.05	7.91	5.60
N _{11C(14)} TFSI	-	47.66	7.67	4.63	48.95	8.86	5.03
N _{11B8} TFSI.H ₂ O	-58	41.75	5.90	5.13	41.90	5.66	5.11
N _{11B(10)} TFSI	-25*	45.31	6.16	5.04	45.51	6.54	5.02
N _{11B(14)} TFSI	-32	49.00	6.91	4.57	49.14	7.73	4.60
N _{11B(18)} TFSI	40	52.07	7.54	4.19	52.26	7.56	4.24

A, C, B stand for allyl, cyclohexyl and benzyl respectively, *= T_g (glass transition temperature).

Whereas, the octadecyl substituents of the non-aliphatic quaternary ammonium salts; N_{11B(18)}TFSI, N_{11C(18)}TFSI, N_{11A(18)}TFSI were all solids but with relatively low melting points, 40, 42 and 49 °C respectively. In addition to this the tetradecyl substituents are all liquids in contrast to their aliphatic

analogues which were all solids except for the C4 series, N₁₁₄₍₁₄₎TFSI. They are classified as ionic liquids since they possess melting points below 100 °C.

The melting point of the longest alkyl substituent, octadecyl chain, of the studied TFSI exchanged series, all of which are solids, with the N₁₁₄₍₁₈₎TFSI possessing the lowest melting point (34 °C) in contrast to its FAP analogue, N₁₁₄₍₁₈₎FAP salt, is the only liquid at room temperature in the octadecyl series with a melting point of 25 °C. Fig 4.8 shows the DSC trace for the N₁₁₄₍₁₈₎FAP salt, showing an endothermic peak at 25 °C and an exothermic peak at -5.69 °C corresponding to its melting point and crystallization temperature respectively.

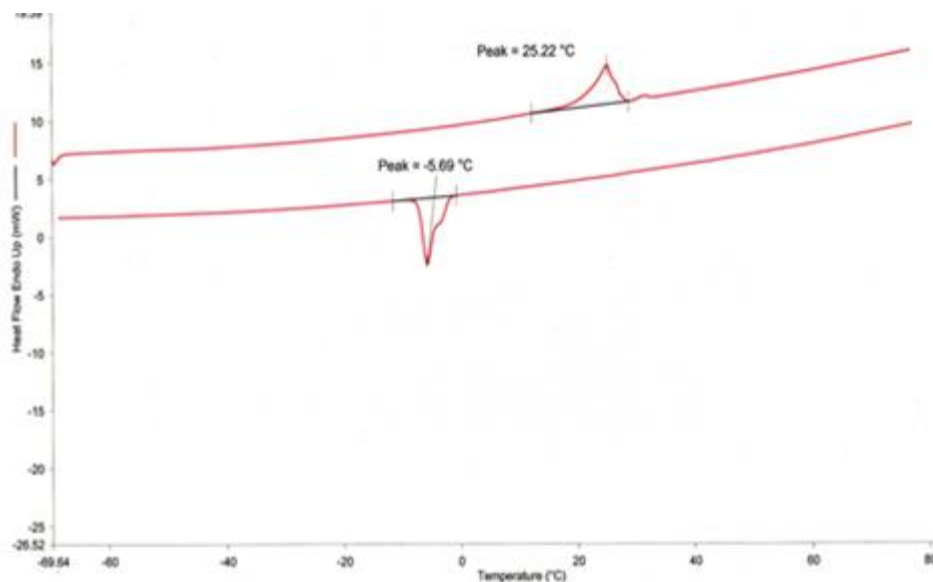


Figure 4.8. DSC trace of N₁₁₄₍₁₈₎FAP under nitrogen and heating /cooling rate of 5 °min⁻¹.

4.9 Conclusion

Overall, the C4 and C6 series seem to be promising cations in terms of lowering the melting points in the aliphatic salts and benzyl and allyl substituents also showed a significant lowering in the melting points compared to the smaller series, C1, C2, C3 and the cyclohexyl series. The lowering in the melting point of the ally and benzyl substituents compared to their aliphatic analogues may be due to the charge delocalization resulting in less interaction between the cationic and anionic species, thus decreasing the lattice energy and thus melting point.

Replacing the halides for a series of fluorinated anions resulted in a dramatic depression in the melting point, by up to 205 °C in the case of TFSI anion which is the most promising anion, combined with the $[N_{113(10)}]^+$ cation. In contrast, when the chain length of the TFSI was extended the melting point increased.

Reducing the symmetry of the anion from PF_6^- to FAP^- resulted in further lowering of the melting points. All of the PF_6^- salts studied are solids but with melting points below 100 °C, whereas the FAP salts are all liquids with relatively very low melting points reaching -42 °C for $N_{114(14)}FAP$ and the $N_{114(18)}FAP$ is exceptionally a room temperature ionic liquid, mp 25 °C.

Whilst the niobates and sulfonates possessed relatively low melting points below 100 °C, they showed a tendency of picking up water.

4.10. References

1. (a) D. R. Lide (ed.) *CRC Handbook of Chemistry and Physics*, 73rd edn. CRC Press, Boca Raton, 1992. (b) A. S. Dworkin, M. A. Bredig, *Journal of Physical Chemistry*, 1960, **64**, 269.
2. V. R. Koch, C. Nanjundiah, R. T. Carlin, *U. S. Patent 1998: 5*, 1998, 602.
3. M. J. Earle, C. M. Gordon, N. V. Plechkova, K. R. Seddon, T. Welton, *Analytical Chemistry*, 2007, **79**, 758.
4. (a) J. Sun, M. Forsyth, D.R. MacFarlane, *J. Phys. Chem. B* 1998, **102**, 8858. (b) S. Katsuta, Y. Shiozawa, K. Imai, Y. Kudo, Y. Takeda, *J. Chem. Eng. Data*, 2010, **55**, 1588. (c) H. Matsumoto, M. Yanagida, K. Tanimoto, M. Nomura, Y. Kitagawa, Y. Miyazaki, *Chem. Lett.*, 2000, 922.
5. K. Sogabe, Y. Hasegawa, Y. Wada, T. Kitamura and S. Yanagida, *Chem. Lett.*, 2000, 944.
6. S. K. Quek, I. M. Lyapkalo, H. V. Huynh, *Tetrahedron*, 2006, **62**, 3137.
7. H. Matsumoto, H. Kageyama and Y. Miyazaki, *Chem. Commun.*, 2002, 1726.
8. N.V. Ignat`ev U. Welz-Biermann, A. Kucheyna, *J Fluorine Chem.*, 2005, **126**, 1150.

5. Physical properties of developed asymmetric quaternary ammonium-based room temperature ionic liquids.

- 5.1** Introduction.
- 5.2** Thermal properties.
- 5.3** Viscosity and conductivity measurements.
- 5.4** Hydrophobicity.
- 5.5** Density.
- 5.6** Electrochemical properties.
- 5.7** Conclusion.
- 5.8** References.

5.1 Introduction

ILs in recent years have received a considerable amount of interest as new media for a number of applications due to their distinctive properties over conventional volatile organic solvents and electrolytes, their particularly attractive properties are their nonvolatility, nonflammability, high thermal stability, and wide liquid ranges.^[1] Ionic liquids are attracting attention in many fields, replacing volatile solvents in organic reactions, electrochemistry, catalysis, physical chemistry and engineering and various other applications. Accordingly, the important physicochemical and electrochemical properties of these asymmetric QA salts, including melting point (T_m), viscosity (η), conductivity (k), density (ρ), hydrophobicity, thermal (T_d) and electrochemical stability (EW) have been investigated. In this chapter an intensive analysis of the physical properties will be presented for the developed RTILs in comparison with some reported RTILs.

5.2. Thermal properties.

One of the most important factors to be considered in the properties of ionic liquids is their melting points (T_m) since our main aim in this research is to study the change in melting point by introducing asymmetry into our cationic species.

Thermal properties measurements were performed using both DSC and TG/DTA techniques. Differential scanning calorimetry, DSC, was carried out on a Perkin-Elmer Diamond instrument using 40 μ l-aluminium sealed pans under an inert atmosphere at two heating and cooling rates 40 and 5°/min from -70 °C to 70 °C to estimate the melting points (T_m) and glass transition temperature (T_g), as shown in the below program and in a few cases -90 °C was used instead of the -70 °C under the same program.

Temperature program for obtaining thermal properties of RTILs:

1. Hold at 30 °C for 2.0 min.
2. Heat from 30 °C to 70 °C at 40 °C/min.
3. Hold at 70 °C for 2.0 min.
4. Cool from 70 °C to -70 °C at 40 °C/min
5. Hold for 2.0 min at -70.0 °C.
6. Heat from -70 °C to 70 °C at 40 °C/min
7. Hold at 70 °C for 2.0 min.
8. Cool from 70 °C to -70 °C at 5 °C/min.
9. Hold for 2.0 min at -70.0 °C.
10. Heat from -70 °C to 70 °C at 5 °C/min.

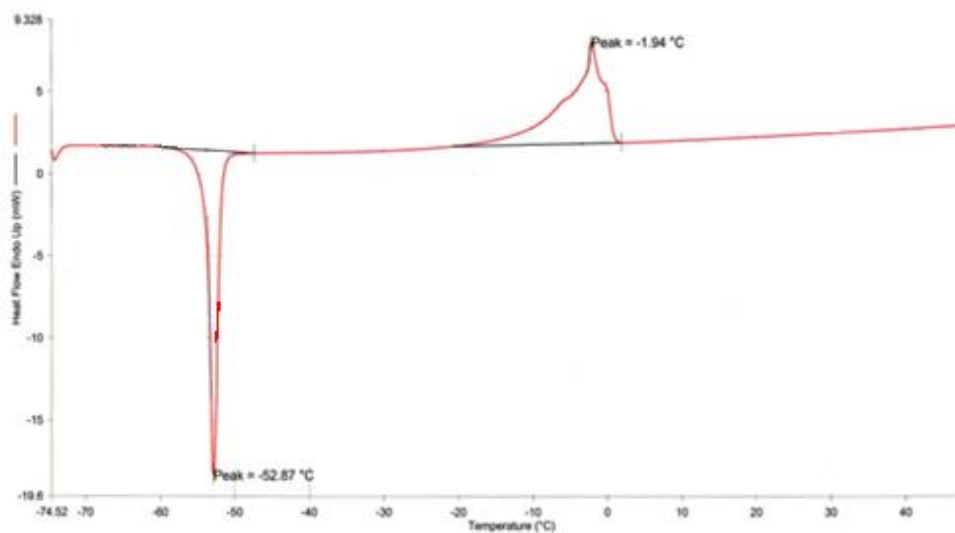


Figure 5.1. DSC trace for N₁₁₃₍₁₀₎TFSI.

The differential scanning calorimetry trace for N₁₁₃₍₁₀₎TFSI shows two transitions, an endotherm at -2 °C which corresponds to its melting point and

an exotherm corresponding to its crystallization temperature (T_c) at $-52\text{ }^{\circ}\text{C}$. Some of our quaternary ammonium ionic liquid samples showed only glass transitions (T_g), reversible transitions of amorphous materials, sometimes called supercooling in viscous liquids as shown in fig 5.2, for the $N_{114(10)}\text{TFSI}$ salt below. This does not uniquely indicate that the compound has no melting point, but just that at these cooling and heating rates crystallization is not observed.

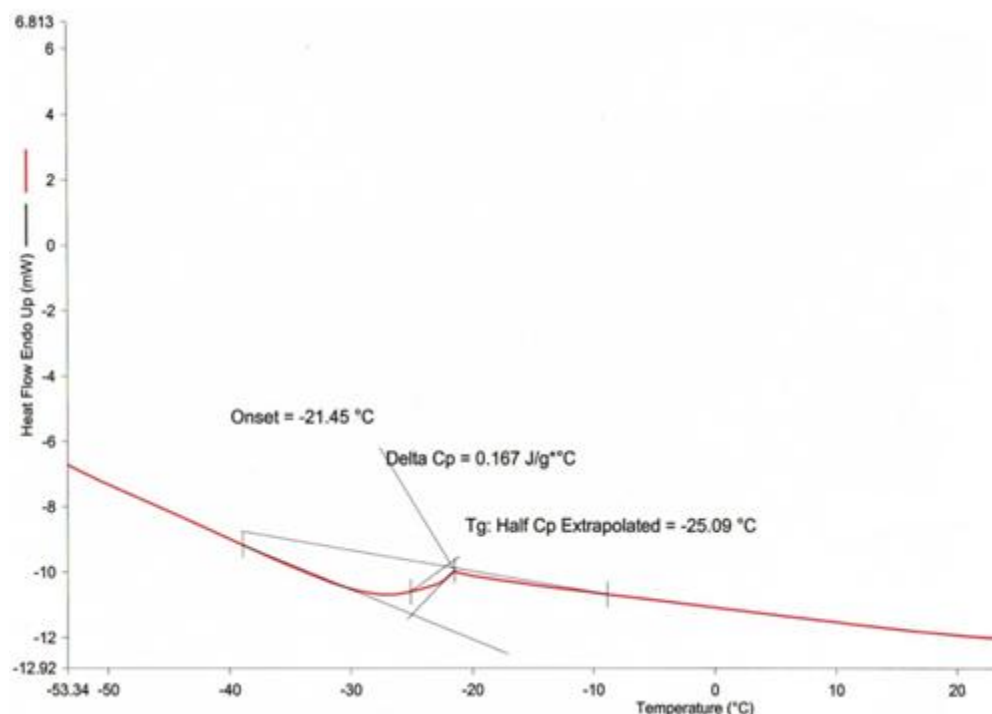


Figure 5.2. DSC trace for $N_{114(10)}\text{TFSI}$.

The melting points of the solid salts were detected using a capillary melting point SMP 10 Stuart Scientific melting point machine.

The melting points of all the non-fluorinated quaternary ammonium halide series is summarized in table 5.1 and fig 5.3, apart from the completely asymmetric salts, $N_{148(14)}\text{I}$ (mp = 11), $N_{143(14)}\text{I}$ (mp = -22), $N_{14\text{allyl}(14)}\text{I} \cdot 2\text{H}_2\text{O}$ (mp = 16.0) and $N_{14(10)(14)}\text{I} \cdot \text{H}_2\text{O}$ (mp = $-21\text{ }^{\circ}\text{C}$).

From the obtained data it seems that the hexyl, benzyl and allyl substituents are the most promising in addition to the completely asymmetric salts, resulting in quaternary ammonium halides that are RTILs. The influence on depressing the melting points of the quaternary ammonium halide salts, for the benzyl and allyl substituents may be explained due to the greater charge delocalization^[2] in the former and planar structure of the latter.^[10b]

Table 5.1 Melting points of non-fluorinated quaternary ammonium salts, N_{11RR'}X (°C).

R/R'	octyl iodide	decyl iodide	tetradecyl bromide	octadecyl bromide
methyl	131	128	109	109
ethyl	111	109	101	110
isopropyl	198	205	206	209
butyl	92	56	52	75
hexyl	liquid@rt	liquid@rt	paste-like	paste-like
allyl	-24*	30	64	86
benzyl	-19*	-21*	48	65
cyclohexyl	144	147	136	137

* = T_g (glass transition)

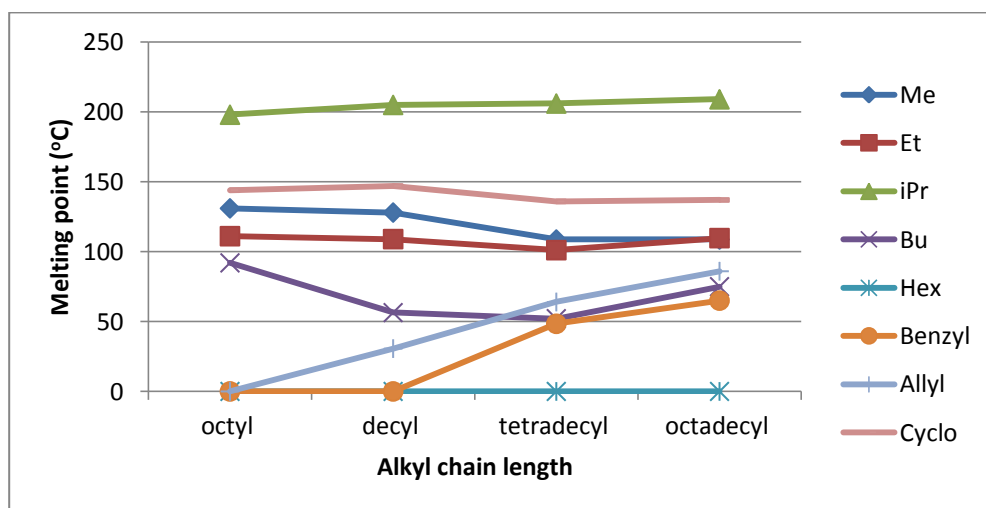


Figure 5.3. Melting points of non-fluorinated quaternary ammonium halide salts.

K. Kim *et al.* have also reported that the presence of benzyl group in the ammonium quaternary salts with smaller alkyl chains played an important role in depressing the melting point due its greater charge delocalization and effectiveness in disrupting symmetry compared to their alkyl substituted analogues.^[2]

A comparison of the melting points of the TFSI-exchanged N_{11R(14)}TFSI series of the asymmetric quaternary ammonium salts is shown in table 5.2. The benzyl substituent and the completely asymmetric salts possessed the lowest melting points compared with the N_{11R(14)}TFSI series.

Whereas, the N₁₁₆₍₁₀₎TFSI showed the lowest melting point of all the developed RTILs, -82.61 °C.

Table 5.2. A comparison of the melting points of some TFSI salts.

Ionic liquids	Melting point °C
N ₁₁₁₁ TFSI	133 ^[3]
N ₁₁₁₍₁₄₎ TFSI	55
N ₁₁₂₍₁₄₎ TFSI	41
N ₁₁₃₍₁₄₎ TFSI	34
N ₁₁₄₍₁₄₎ TFSI	9
N _{11B(14)} TFSI	-32
N _{11A(14)} TFSI	20
N ₁₄₈₍₁₄₎ TFSI	-58

B and A = benzyl and allyl respectively.

Thermogravimetric analysis, was conducted on a TG Mettler-Toledo instrument to measure the decomposition temperature (T_d) of the RTILs, using 70µl aluminium oxide crucibles under a steady flow of inert gas (N₂) at a heating rate of 10 °/min.

The observed thermal stability of the TFSI salts were surprisingly very high, especially that of the fully asymmetric-TFSI ($N_{148(14)}\text{TFSI}$) ionic liquid for which an onset to decomposition was observed at 394 °C as shown in fig 5.4.

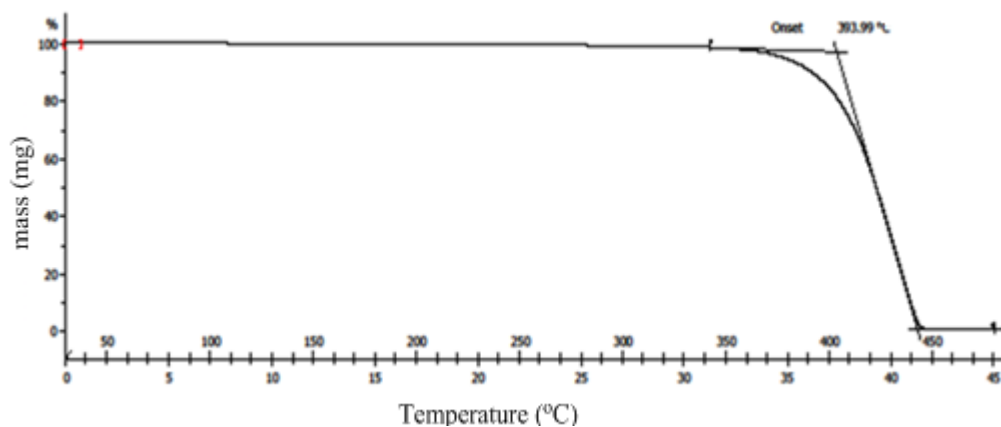


Figure 5.4. TG trace of $N_{148(18)}\text{TFSI}$, under nitrogen and 10 °C/min heating rate.

The thermal stabilities of the TFSI exchanged salts were found to be much higher than their halide analogues, in some cases by more than 200 °C, reaching over 400 °C. Table 5.3 shows a comparison of the decomposition temperatures for the ammonium halides and the TFSI-exchanged analogues. Therefore, exchanging the anion not only reduces the melting point, but increases the thermal stability of the RTIL as well, as shown in fig 5.5.

The thermal stability of the parent halides ranged from 148 to 236 °C whereas the TFSI-exchanged analogues showed higher stability, ranging from 314 to 406 °C.

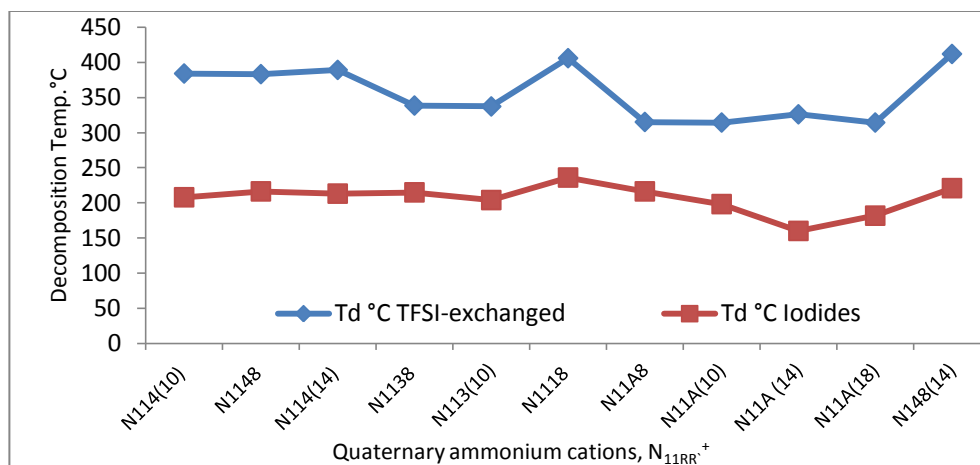


Figure 5.5. Thermal stability of some halides salts and their TFSI-exchanged analogues.

A large number of the developed RTILs showed impressive thermal properties giving them quite large liquid ranges, for example, the completely asymmetric ionic liquid, $N_{148(14)}$ TFSI showed a stable range from -58 to > 390 °C. This property allows it to be used in applications in which wide liquid range and thermal stability are important. Whereas the $N_{116(10)}$ TFSI showed a broader liquid range -82 °C to 395.4 °C.

The most stable RTILs, were the more symmetric quaternary ammonium-TFSI ionic liquids, N_{1118} TFSI and $N_{111(10)}$ TFSI with T_d = 406 and 403.5 °C respectively. Whereas the TFSI-ammonium salts with allyl substituents showed the lowest thermal stability.

In regard to the other anions used in this research, the trifluoromethanesulfonate analogues are the least thermally stable, in some cases starting to decompose at temperatures as low as 80 °C in addition to this, these compounds seem to be hygroscopic, picking up water on standing under normal conditions. The niobate and hexafluorophosphate analogues showed better thermal stability, ranging from 155 to 237 °C whilst FAP-exchanged salts showed a higher stability than niobates and hexafluorophosphates, reaching more than 351 °C for the $N_{114(14)}$ FAP salt.

Table 5.3. Comparison of thermal stabilities of some novel TFSI-RTILs and their halide analogues.

Salt	T _d °C	Salt	T _d °C
N ₁₁₁₈ I	236.1	N ₁₁₁₈ TFSI	406.0
N ₁₁₁₍₁₀₎ I	198.4	N ₁₁₁₍₁₀₎ TFSI	403.0
N ₁₁₂₈ I	218.8	N ₁₁₂₈ TFSI	381.2
N ₁₁₂₍₁₀₎ I	222.3	N ₁₁₂₍₁₀₎ TFSI	390.0
N ₁₁₃₈ I	215.0	N ₁₁₃₈ TFSI	338.6
N ₁₁₃₍₁₀₎ I	204.0	N ₁₁₃₍₁₀₎ TFSI	337.3
N ₁₁₄₈ I	216.4	N ₁₁₄₈ TFSI	383.3
N ₁₁₄₍₁₀₎ I	208.0	N ₁₁₄₍₁₀₎ TFSI	384.2
N ₁₁₄₍₁₄₎ Br	213.2	N ₁₁₄₍₁₄₎ TFSI	389.3
N ₁₁₆₈ I	216.4	N ₁₁₆₈ TFSI	386.3
N ₁₁₆₍₁₀₎ I	220.0	N ₁₁₆₍₁₀₎ TFSI	395.4
N ₁₄₈₍₁₄₎ I	200.0	N ₁₄₈₍₁₄₎ TFSI	394.0
N _{11A8} I	206.3	N _{11A8} TFSI	315.2
N _{11A(10)} I	198.3	N _{11A(10)} TFSI	314.4
N _{11A (14)} Br	160.1	N _{11A (14)} TFSI	314.4
N _{11A(18)} Br	181.8	N _{11A(18)} TFSI	326.1
N _{11C8} I	185.4	N _{11C8} TFSI	279.4
N _{11C(10)} I	184.4	N _{11C(10)} TFSI	307.1

By keeping the cationic species constant for example [N₁₁₄₈]⁺ and changing the anionic species resulted in products with different physical states. Some were solids with relatively high melting points and others were liquids at room temperature as shown in table 5.4. The decomposition temperature varied with the type of anion and followed a trend of I⁻ < NbF₇²⁻ < PF₆⁻ < FAP⁻

< TFSI⁻ with the halide being the lowest as shown in fig 5.6. A similar trend in the thermal stability has been reported by Z. Zhou *et al.*^[1] with the smaller ammonium-based ionic liquids, where the TFSI containing salts showed the highest thermal stability, compared to BF₄ and RBF₃ (R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉) anions. The authors reported that the low stability of the RBF₃ anions is due to their pyrolysis, corresponding to the elimination of CF₂ moiety at low temperatures (~ 200 °C).

This trend is also similar to what has been reported for the imidazolium-based salts where the decomposition temperature varies with the type of anion and follows the stability order Cl⁻ < BF₄⁻ < PF₆⁻ < TFSI⁻.^[4]

Table 5.4. Physical properties of dimethylbutyloctyl ammonium-based ionic liquids, N₁₁₄₈X, with different anions.

Sample type	T _m (°C)	T _d (°C)	Elemental analysis (%)		
			Carbon	Hydrogen	Nitrogen
N ₁₁₄₈ I	92	216.4	49.24(48.79)	9.45(9.51)	4.10(4.06)
N ₁₁₄₈ TFSI	-24*	383.3	38.85(38.73)	6.53(6.69)	5.67(6.17)
[N ₁₁₄₈] ₂ NbF ₇ .2H ₂ O	-	198.7	48.67(48.55)	9.93(10.02)	4.06(4.05)
N ₁₁₄₈ CF ₃ SO ₃	-	-	49.56(48.25)	8.88(9.49)	3.86(3.91)
N ₁₁₄₈ FAP	-21*	378.2	36.41(36.44)	4.89(4.73)	2.12(2.13)
N ₁₁₄₈ PF ₆	61	309	46.77(46.77)	8.98(8.81)	3.90(3.85)

* = T_g (glass transition)

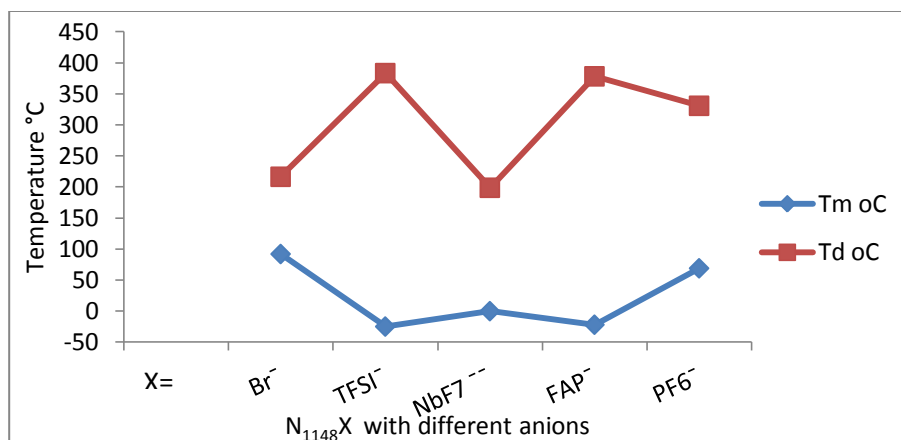


Figure 5.6. Melting point and decomposition temperatures of dimethylbutyloctyl ammonium exchanged salts $N_{1148}X$ as a function of X.

The most promising candidate in terms of melting point and thermal stability in this series as illustrated in fig 5.6 is the $N_{1148}TFSI$ ionic liquid which possessed the lowest glass transition temperature and at the same time it had the highest decomposition temperature, which in turn gives it a wide liquid range and potential applicability. Fig 5.7 shows the change in melting points and decomposition temperatures for $N_{11R(14)}Br$ and $N_{11R(14)}TFSI$ salts as a function of R, it is observed that salts with the lower melting point possess a higher thermal stability.

The onset decomposition temperatures and the liquid ranges for some of the developed TFSI-RTILs are shown in table 5.5.

The liquid range of ionic liquids is generally larger than organic solvents, since they possess very low vapour pressures and high thermal stabilities. For example it has been reported that emimTFSI has a liquid range of 470 °C which is considerably larger than that of water (100 °C) and other common conventional solvents such as diethylether (161 °C) and ethanol (192 °C).

Table 5.5. Liquid range and onset decomposition temperature of selected TFSI-RTILs.

Formula	T _d (°C)	T _m (°C)	Liquid range(°C)
N ₁₁₄ (10)TFSI	384.2	-25*	>359
N ₁₁₄₈ TFSI	383.3	-24*	>358
N ₁₁₄ (14)TFSI	389.3	9.0	380
N ₁₁₃₈ TFSI	338.6	-30*	>313
N ₁₁₃ (10)TFSI	337.3	-2	339
N ₁₁₂₈ TFSI	381.2	-25*	>356
N ₁₁₂ (10)TFSI	390.0	-22*	>365
N ₁₁₆₈ TFSI	386.3	-23*	>361
N ₁₁₆ (10)TFSI	395.4	-82	477
N ₁₁₁₈ TFSI	406.0	3	403
N ₁₁₁ (10)TFSI	403.0	14	389
N ₁₄₈ (14)TFSI	394.0	-58	452
N _{11A8} TFSI	315.2	-26*	>290
N _{11A} (10)TFSI	314.4	-22*	>289
N _{11A} (14)TFSI	314.4	20	293
N _{11C8} TFSI	279.4	-21*	>254
N _{11C} (10)TFSI	307.1	-25*	>282
N _{11B8} TFSI.H ₂ O	382.4	-58	441
N _{11B} (14)TFSI	395.3	-32	427

*= T_g (glass transition), liquid range estimated by taking maximum melting point as 25 °C.

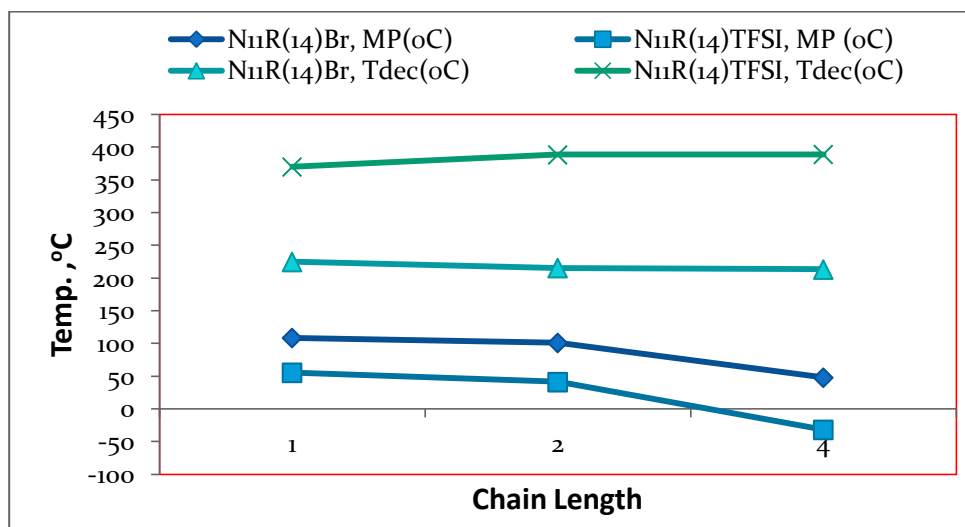
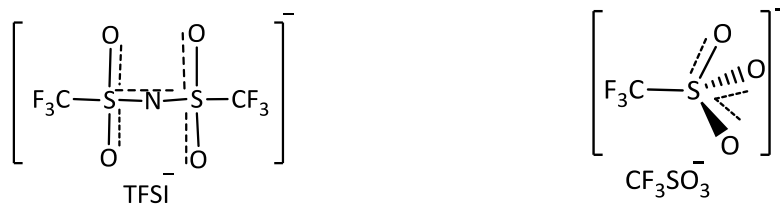


Figure 5.7 Correlation between melting points and decomposition temperatures of N_{11R}(14)Br and TFSI salts.

These developed ionic liquids have a relatively wide liquidus range ($> 255\text{ }^{\circ}\text{C}$) and reached $452\text{ }^{\circ}\text{C}$ and $477\text{ }^{\circ}\text{C}$ in the case of the completely asymmetric quaternary ammonium RTIL, $\text{N}_{148(14)}\text{TFSI}$ and $\text{N}_{116(10)}\text{TFSI}$ respectively followed by $\text{N}_{1188}\text{TFSI}\cdot\text{H}_2\text{O}$ $441\text{ }^{\circ}\text{C}$. This is determined by the range between their melting points and decomposition temperatures, while those having glass transitions their liquid range is estimated by taking $25\text{ }^{\circ}\text{C}$ as the melting point as a maximum. The melting point values are important, as low melting points help to differentiate these ionic liquids from the area of molten salts, which are usually high melting and often highly corrosive when compared with the more benign ILs.

Regarding the physical state obtained for our quaternary ammonium salts, most of the TFSI-exchanged salts are liquids compared to the other anions used in this work. This could be explained due to the flexibility of this anion and the charge dispersion and delocalization throughout the anion, because of the presence of many electronegative elements (scheme 5.1).^[5a,5b] This in turn makes the TFSI anion weakly coordinating and so decreasing the cation and anion interactions, thus lowering the melting point. This may be illustrated by comparing the chemical shifts of the CH_2 groups and dimethyl groups on the ammonium centre in the quaternary cations in the ^1H NMR spectra. For example N_{1148}I and $\text{N}_{1148}\text{TFSI}$ as shown in fig 5.8 where the N_{1148}I chemical shifts ($\delta = 3.48\text{ ppm}$ & 3.32 ppm respectively) are higher than those of the $\text{N}_{1148}\text{TFSI}$ ($\delta = 3.25\text{ ppm}$ & 3.07 ppm respectively) due to the greater availability of the negative charge in the former case. In the case of the iodide, which is more coordinating than TFSI, an increase in inter-ionic interactions is expected, resulting in a higher melting point being expected in N_{1148}I (which is a solid, $T_m = 92\text{ }^{\circ}\text{C}$) than in $\text{N}_{1148}\text{TFSI}$, which is a liquid. In a similar way, the NMR shifts observed for the analogous CF_3SO_3 anion system ($\delta = 3.26$ and 3.09 ppm respectively) are similar to those of the TFSI analogue,

which suggests charge delocalization and hence a room temperature ionic liquid in the case of $N_{1148}CF_3SO_3$.



Scheme 5.1 Delocalization of negative charge on TFSI⁻ and CF₃SO₃⁻ anions.

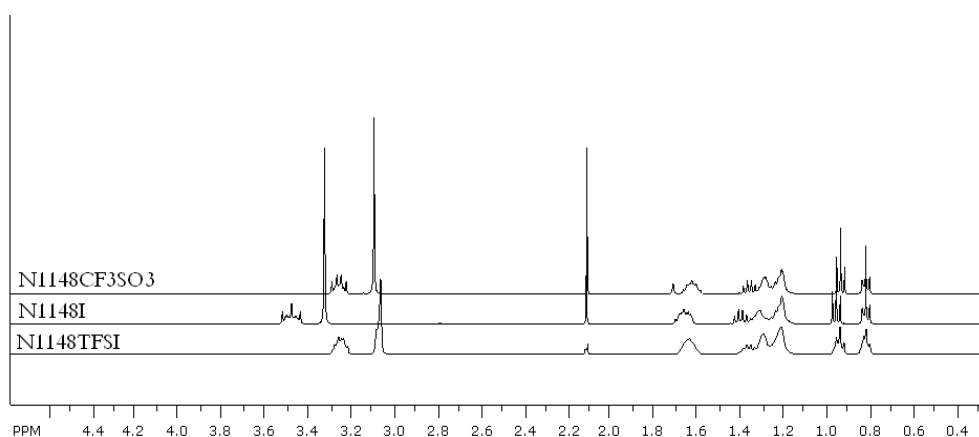


Figure 5.8 Comparison of ¹H NMR spectra of $N_{1148}I$, $N_{1148}TFSI$ and $N_{1148}CF_3SO_3$.

A similar trend has been reported by Chiappe *et al.* on comparing the imidazolium-based IL with triflate and TFSI anions, where the latter possessed lower melting points than the former due to the charge delocalization and the absence of hydrogen bonding between the anion and the H on the cation, especially that at C-2.^[6] The authors also mentioned that the increase in branching in the carbon chain in the cation increases the melting point.

Investigations on the study of the basicity of the anions in different ionic liquids was reported by Bartosik *et al.* based on the determination of the optical basicity scale using UV-Vis absorption spectroscopy and the indicator complex, $[Ni(tmen)(acac)][B(Ph)_4]$, where (tmen = tetramethyl

ethylenediamine, acac = acetylacetonate).^[7] From the authors evaluations, the Lewis basicity of ionic liquid increased in the following order $\text{PF}_6^- < \text{BF}_4^- < \text{TFSI}^- < \text{CF}_3\text{SO}_3^- \ll \text{Cl}^-$. This supports our observations regarding the ^1H NMR spectroscopy chemical shifts of the methyl and CH_2 groups adjacent to the nitrogen centre with respect to the counter ions as shown in fig 5.9 and 5.10.

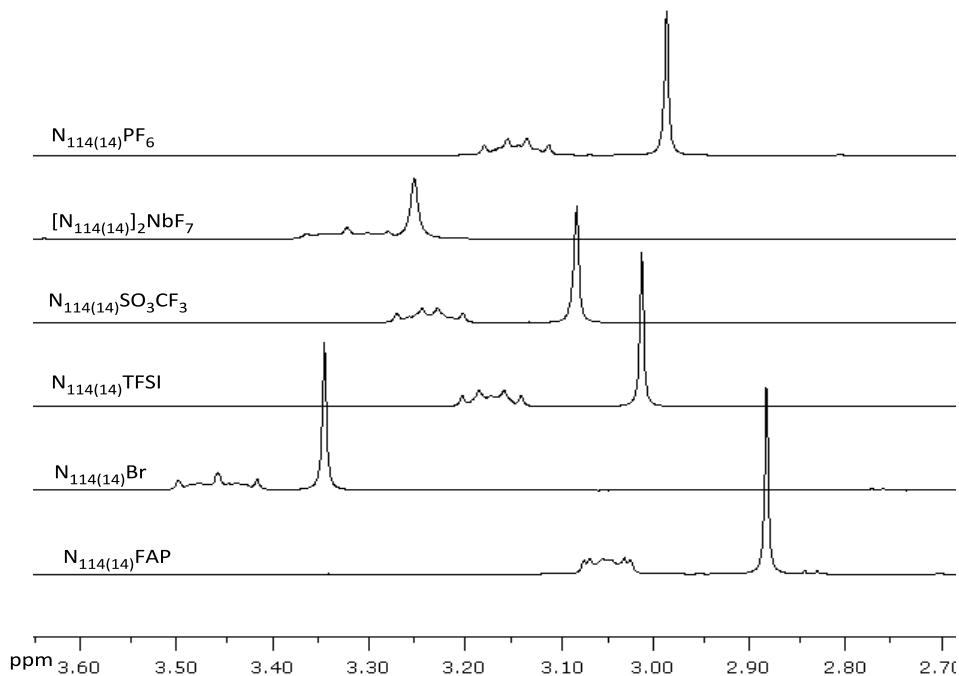


Figure 5.9. Part of ^1H NMR spectra showing different chemical shifts for different anions combined with $[\text{N}_{114(14)}]^+$.

The $\text{N}_{114(14)}\text{FAP}$ possessed the lowest melting point, $-41.9\text{ }^\circ\text{C}$ which showed the lowest chemical shift of the $\alpha\text{-CH}_2$ and methyl groups on the nitrogen centre.

Pringle *et al.* reported the synthesis and X-ray data for a range of ionic liquids with TFSI anion and their non-fluorinated anion analogue, bis(methanesulfonyl)imide $(\text{CH}_3\text{SO}_2)_2\text{N}^-$ combined with pyrrolidinium and imidazolium-based cations.^[5b] The non-fluorinated anion gave hydrophilic ionic liquids with melting points lower than their fluorinated-TFSI analogues

(due to its smaller size) but had higher viscosity and were less stable thermally and electrically.

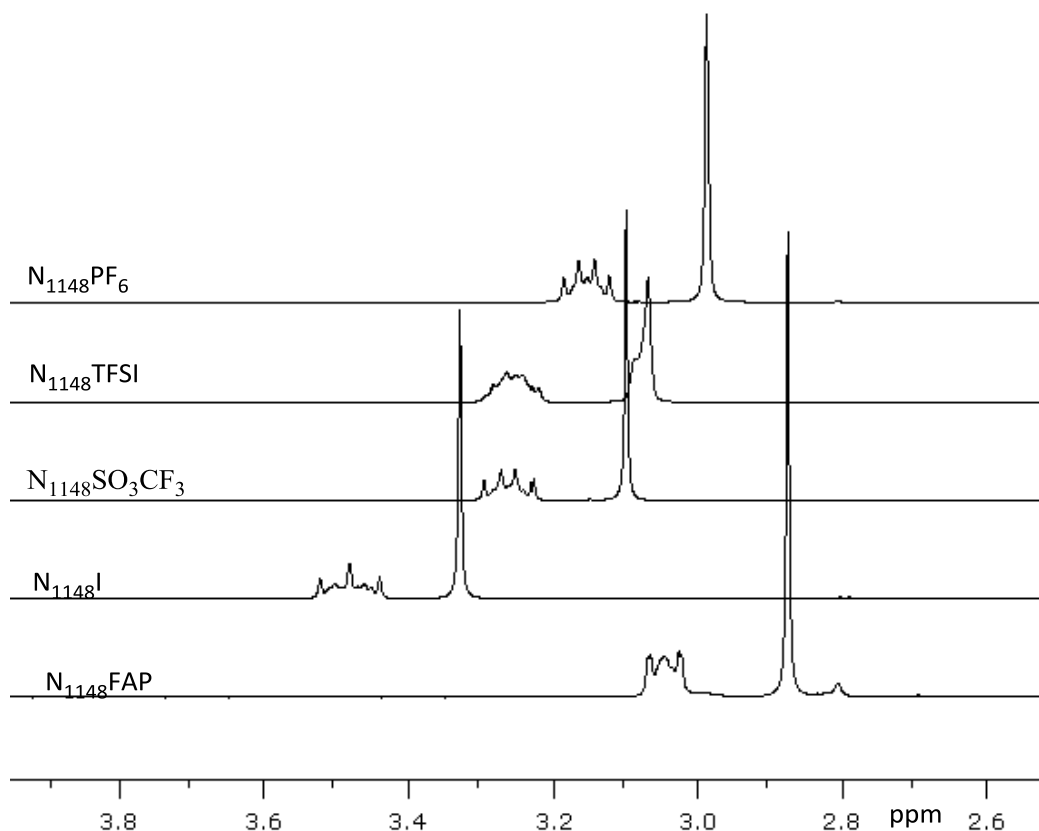


Figure 5.10. Part of ^1H NMR spectra showing different chemical shifts for different anions combined with $[\text{N}_{1148}]^+$.

The non-fluorinated anion showed a considerable increase in hydrogen bonding. From these observations, the authors described the TFSI anion as a weakly coordinating due to the charge dispersion and non-spherical shape and thus decreasing the cation and anion interactions, thus lowering the melting point. The authors also reported that the TFSI exchanged ionic liquids had lower melting points compared to their more localized anions, such as the halides.

Since introducing asymmetry onto the cation was successful in depressing the melting point, asymmetry of the anion has also been investigated. An

example is the comparison of the ammonium salts of the symmetric hexafluorophosphate anion (PF_6^-) and its asymmetric analogue tris(pentafluoroethyl)trifluorophosphate (FAP^-). Table 5.6 shows the physical properties of the PF_6 and FAP-exchanged salts where the PF_6 salts are all solids whereas the FAP salts are all liquids with melting points up to 100 °C lower than the PF_6 analogue.

Table 5.6. Liquid range and physical properties of PF_6 and FAP-exchanged salts.

Formula	T_d (°C)	T_m (°C)	Liquid range (°C)
$\text{N}_{1148}\text{PF}_6$	308	61	246
$\text{N}_{114(10)}\text{PF}_6$	356	50	305
$\text{N}_{114(14)}\text{PF}_6$	311	60	250
$\text{N}_{114(18)}\text{PF}_6$	329	82	246
$\text{N}_{1148}\text{FAP}$	348	-21*	> 323
$\text{N}_{114(10)}\text{FAP}$	292	-21*	> 267
$\text{N}_{114(14)}\text{FAP}$	351	-41	393
$\text{N}_{114(18)}\text{FAP}$	348	25	323

* = T_g (glass transition), liquid range estimated by taking maximum melting point as 25 °C.

For example, the $\text{N}_{114(14)}\text{FAP}$ salt has a melting point of -41 °C compared to 60 °C for $\text{N}_{114(14)}\text{PF}_6$. A similar trend was observed by Zhou *et al.* with the BF_4 and the CF_3BF_3 anions when combined with the same imidazolium-based cation, for example, the melting point of mmim BF_4 is 103 °C whereas that of mmim[CF_3BF_3] is only 15 °C, the authors interpretation related this decrease in melting point was due to the asymmetry of the fluoroanion.^[5c]

Generally the FAP-containing ionic liquids possess a larger liquid range than their PF_6^- analogues. However, both the hexafluorophosphate and the FAP^- exchanged salts possessed a lower liquid range than their TFSI analogues, as shown in Table 5.6. Moreover both $\text{N}_{1148}\text{PF}_6$ and $\text{N}_{114(10)}\text{PF}_6$ showed a two step

decomposition behaviour, while the rest showed only one step. A similar thermal behaviour has been reported by Yang *et al.* regarding the $S_{112}PF_6$ and $S_{114}PF_6$ sulfonium-based ionic liquids compared to the $S_{116}PF_6$ salts and their TFSI analogues.^[8]

5.3 Viscosity and conductivity measurements

Viscosity

As described in the experimental section, the viscosities of the RTILs were measured on an AMVn Automated Micro Viscometer. Ionic liquids in general are quite viscous, for example they have a much higher viscosity than water ($\eta(H_2O) = 0.89$ mPa.s at 25 °C), by comparison typically ionic liquid viscosities lie in the range of 30-50 mPa.s, but are sometimes much higher, reaching several hundreds of mPa.s.

In comparison the viscosities of the more symmetric $N_{R'RRR}$ TFSI salts ($R' = 6-8$, $R = 1, 2, 4$) ranged between 75.5 and 606 mPa.s).^[3] The viscosity values recorded for these asymmetric ammonium-based ionic liquids ranged from 79.15 to 237.08 mPa.s at 25 °C (table 5.7), which are relatively low compared to those QA salts of the formula $[N_{112R}]^+$ where R is a keto-group ROR with nonfluorinated anions > 1300 (mPa.s) at 25 °C but more viscous than traditional organic solvents, e.g. acetone (0.306 mPa.s). The N_{1138} TFSI ionic liquid showed the lowest viscosity, a similar trend has been reported by Chiappe *et al.* in the imidazolium-based ionic liquids, where the branching in the 1-alkyl-3-methyl imidazolium salts always reduced the viscosity.^[6]

In this work, not all the developed RTILs have been tested due to problems encountered with the viscometer, which developed a fault and for the other viscometers larger volumes were required (~15ml) than were available, although the allyl substituent ionic liquids, N_{11A8} TFSI and $N_{11A(10)}$ TFSI were runny liquids and seem to be less viscous than their saturated analogues.

High viscosity is not always a drawback for the applications of ionic liquids, since viscous RTILs have been shown to be useful in certain applications such as stationary phases in the field of gas-liquid chromatography as demonstrated by the Armstrong group.^[10a] The behaviour of two common ionic liquids, bmimPF₆ and bmimCl (bmim = 1-butyl-3-methylimidazolium) were examined as coatings on the stationary phase in gas chromatography and found to be ideal due to their wetting ability and high viscosity.

Imidazolium and ammonium-based ionic liquids with allyl substituents were synthesised and characterized by Oh *et al.* with the TFSI as the counter ion. The authors reported that the ionic liquid with an additional allyl substituent of the formula N_{11AA}TFSI (A = allyl group) showed the lower viscosity value (66 mPa.S) compared to the analogous, N_{113A}TFSI (79 mPa.S) due to probability of the planar structure of the allyl group.^[10b]

Conductivity

Conductivity is of vital importance for solvents to be used in electrochemical processes. Ionic liquids have many unique properties, one of which is their conductivity which is intrinsic, so supporting electrolytes are not needed, as in the case of traditional organic solvents.^[12]

Conductivities of our newly developed ionic liquids were measured on an Ecoscan con5 conductivity meter. All measurements were performed at 19 °C. Generally speaking, ion size, ion association and viscosity influence the conductivity of a pure ionic liquid.^[13] The conductivity values ranged from 67 to 770 μS.cm⁻¹. Although these salts are purely ionic their conductivity values are expected to be reduced as ion mobility will be limited by the liquid's viscosity, as shown in Table 5.7 and fig 5.11. The lowest viscosity recorded was that of the N₁₁₃₈TFSI ionic liquid (79 mPa.s) which in turn showed the highest conductivity value measured (770 μS.cm⁻¹).

Table 5.7. Viscosities and conductivities of developed RTILs.

RTILs	Viscosity (mPa.s) at 25 °C	Conductivity($\mu\text{S.cm}^{-1}$) at 19 °C
N ₁₁₄₈ TFSI	220	124
N ₁₁₄₍₁₀₎ TFSI	169	171
N ₁₁₄₍₁₄₎ TFSI	255	67
N ₁₁₃₈ TFSI	79	770
N ₁₁₃₍₁₀₎ TFSI	160	213
N ₁₁₂₈ TFSI	127	359
N ₁₁₂₍₁₀₎ TFSI	87	603
N ₁₁₆₈ TFSI	163	155
N ₁₁₆₍₁₀₎ TFSI	237	184
N ₁₁₁₈ TFSI	118	456
N ₁₁₁₍₁₀₎ TFSI	114	582

Similarly, the ionic liquid with the lowest conductivity, N₁₁₄₍₁₄₎TFSI (67 $\mu\text{S.cm}^{-1}$), possessed the highest viscosity (255 mPa.s).

These values are comparable to those of the more symmetric ammonium-based salts of the type N_{R'RRR}TFSI ($R' = 6-8$, $R = 1, 2, 4$) which are in the range 130 - 670 $\mu\text{S.cm}^{-1}$.^[3]

From Table 5.7 it appears that there is no specific trend down a series but it is clear that the relationship between viscosity and conductivity is an inverse relationship (fig. 5.11). This shows a linear relationship as shown in fig 5.12 on plotting 1/viscosity versus conductivity.

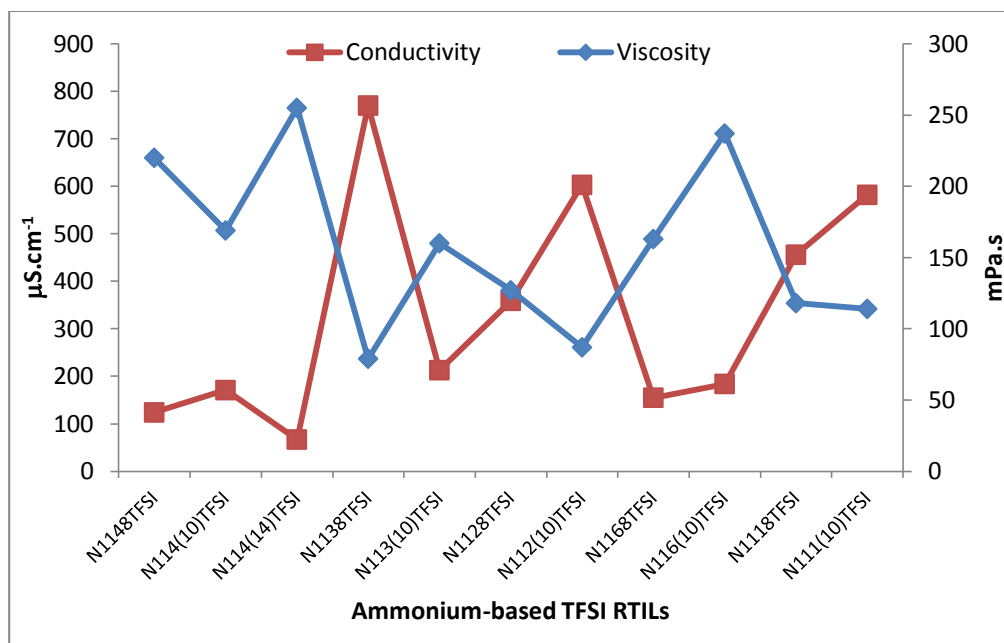


Figure 5.11. Viscosity vs conductivity for asymmetric QA-TFSI RTILs.

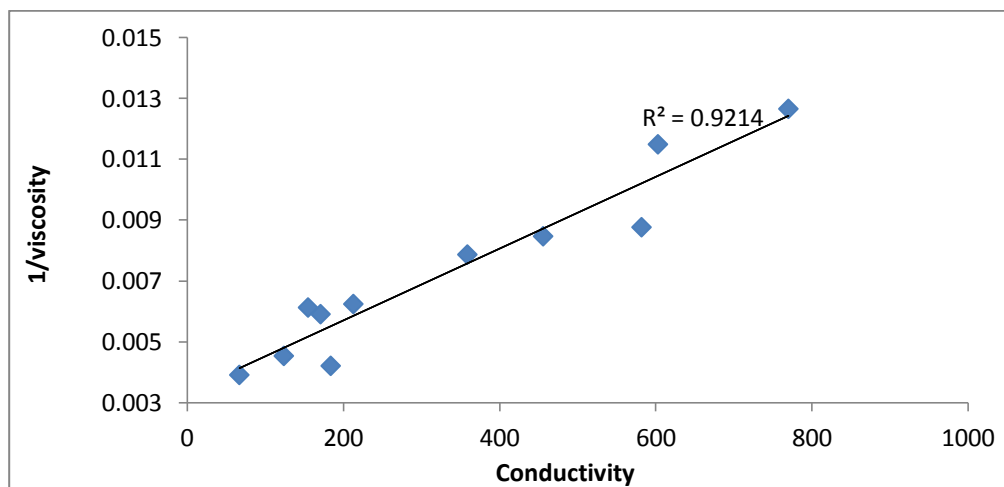


Figure 5.12 Conductivity vs 1/viscosity asymmetric for QA-TFSI RTILs at r.t.

The insertion of double bonds into the phosphonium cations was found to enhance the conductivity properties in ionic liquids. Recently, in 2011 Tsunashima *et al.* reported that quaternary phosphonium cations with groups containing double bonds such as allyltributylphosphonium-TFSI, possessed a lower melting point and higher conductivity than their saturated analogues.^[11]

5.4. Hydrophobicity

All of the developed RTILs were immiscible with water although some of them absorbed water, and are soluble in most polar organic solvents such as dichloromethane, acetone, chloroform, ethanol, methanol and diethylether. Fig 5.13 illustrates this, with a triphasic solution showing the immiscibility of one of the ionic liquid, $N_{111(10)}$ TFSI, with both water and hexane.

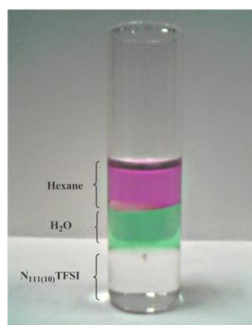


Fig 5.13 A triphasic system of hexane/water/ $N_{111(14)}$ TFSI.

To assess the hydrophobic nature of the asymmetric quaternary ammonium-TFSI RTILs, the solubility of each RTIL in water was investigated using ^{19}F NMR spectroscopy. A small volume of the ionic liquid was shaken with water for 24 hours at room temperature. A 0.5 ml sample of the aqueous layer was added to 0.5ml of a D_2O solution of 1,1,1-trifluoroethanol (0.1M) as an internal calibrant, and the ^{19}F NMR spectra of the aqueous solutions were recorded. Since the concentration of the trifluoroethanol solution is known, and the number of fluorine atoms corresponding to that resonance is also known, comparison of the integrals of the signals due to the trifluoroethanol and our IL will allow us to calculate the solubility of these room temperature ionic liquids in water.

Fig 5.14 shows part of the ^{19}F NMR spectra of (a) 0.1 M trifluoroethanol in D_2O , and spectra after stirring with N_{1138} TFSI (b) and N_{1148} TFSI (c) (an example of a miscible and immiscible ionic liquid respectively). Two of the

investigated RTILs showed solubility in D₂O, the one with the highest solubility was the N₁₁₃₈TFSI and the other is N₁₁₁₈TFSI.

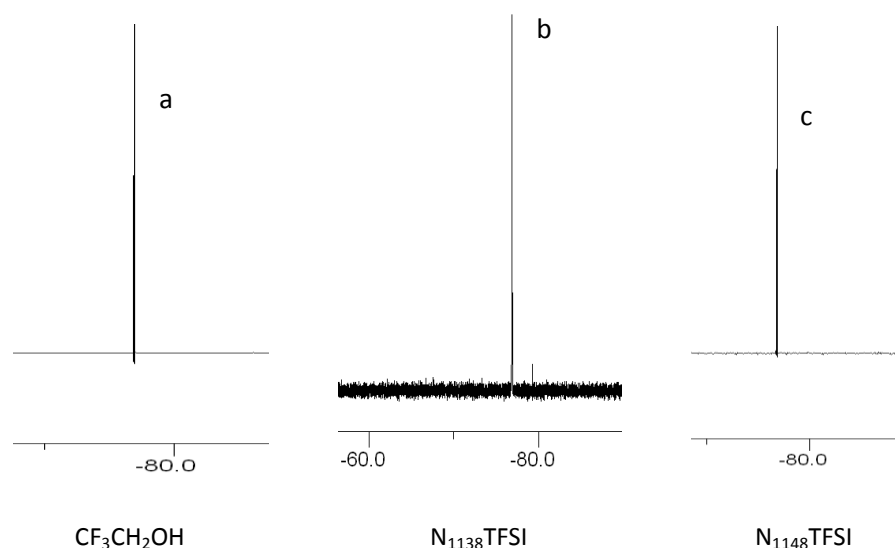


Figure 5.14 ¹⁹F NMR spectra of CF₃CH₂OH in D₂O and of the solubility tests of some RTILs in a D₂O solution containing trifluoroethanol.

Spectrum (a) in fig 5.14 is part of the ¹⁹F NMR for the pure trifluoroethanol showing a signal at $\delta = -76.92$ ppm while spectrum (b) from N₁₁₃₈TFSI showed a peak due to the trifluoroethanol and a peak at $\delta = -79.28$ ppm due to the CF₃ of the TFSI. From the integrals of these signals the solubility of N₁₁₃₈TFSI in D₂O was calculated to be 1.7 mmol/L. The ionic liquid N₁₁₁₈TFSI also showed a limited solubility of 0.2 mmol/L, Whereas spectrum (c) is for N₁₁₄₈TFSI (which is immiscible in water) only shows a peak due to CF₃CH₂OH.

Based on an estimate for the smallest peak that could be observed above the noise level an estimate for the lowest limit of detection in this procedure is 0.2 mmol/L. None of the other RTILs showed peaks due to their fluorinated anions and therefore none exhibit solubility greater than 0.2 mmol/L.

5.5. Density

Density is an important factor for solvents generally and for ionic liquids in particular especially for development of specific types of batteries where weight issues are a concern. The densities of the new aliphatic asymmetric hydrophobic RTILs were measured by placing 2ml of the ionic liquid into a 2ml volumetric flask and the difference in weight was recorded resulting in densities in the range 1.11 – 1.37 gml^{-1} as shown in fig 5.15.

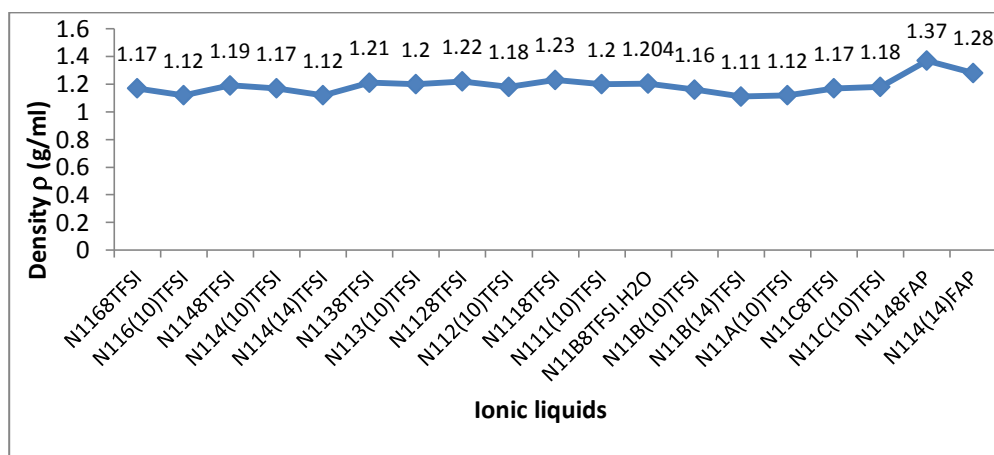


Figure 5.15. The densities of selected RTILS at r.t.

The resulting figures showed that the density generally decreases with increasing alkyl chain length within a series i.e. the ionic liquid with the highest molecular weight $\text{N}_{114(14)}\text{TFSI}$ (578.26 g/mol) showed the lowest density 1.12 gml^{-1} (table 5.8). This trend has been reported by Jacquenim *et al.*^[14] and Huddelston *et al.* for imidazolium-based ionic liquids where the density decreases with increasing length of alkyl chains substituents.^[15]

Table 5.8. Densities at 19 °C of asymmetric quaternaryalkylammonium RTILS and derived molar volumes.

Salt	Molecular weight(g/mol)	d _{obs.} ρ (gml ⁻¹)	Estimated Molar volumes (mol ⁻¹)	d _{calc.} ρ (gml ⁻¹)
N ₁₁₄₈ TFSI	494.17	1.19	415.26	1.22
N ₁₁₄₍₁₀₎ TFSI	522.2	1.17	446.325	1.19
N ₁₁₄₍₁₄₎ TFSI	578.26	1.12	516.30	1.15
N ₁₁₃₈ TFSI	480.15	1.21	396.81	1.23
N ₁₁₃₍₁₀₎ TFSI	508.19	1.20	423.49	1.20
N ₁₁₂₈ TFSI	466.14	1.22	382.08	1.24
N ₁₁₂₍₁₀₎ TFSI	494.17	1.18	418.79	1.21
N ₁₁₆₈ TFSI	522.2	1.17	446.325	1.19
N ₁₁₆₈ I	369.19	1.15	322.44	
N ₁₁₆₍₁₀₎ TFSI	550.23	1.12	491.2	1.17
N ₁₁₆₍₁₀₎ I	397.22	1.14	348.4	
N ₁₁₁₈ TFSI	452.12	1.23	367.57	1.26
N ₁₁₁₍₁₀₎ TFSI	480.15	1.20	400.125	1.23
N ₁₁₄₈ FAP	659.2	1.37	481.16	
N ₁₁₄₍₁₄₎ FAP	743.29	1.28	580.69	

d_{calc.} using the molinspiration website to calculate volumes of the quaternary ions.

From table 5.8 the highest densities were those of the tris(perfluoroethyl)trifluorophosphate (FAP) salts. For example, the density of N₁₁₄₈TFSI, is 1.19 gml⁻¹, exchanging the anion (TFSI, 279.92 g/mol) with a larger mass anion (FAP, 444.95 g/mol), to give N₁₁₄₈FAP led to a higher density, ρ = 1.37 gml⁻¹, this is consistent with that reported in the literature that increasing the anion mass corresponds to a higher density of the ionic liquid.^[12]

N. V. Ignat`ev *et al.* have also reported the density of the imidazolium-based ionic liquids with the anions iodides, PF₆⁻ and FAP⁻, and have reported that the density increased in that order.^[13] A typical example is 1-hexyl-3-methylimidazolium where the density values are 1.05, 1.29 and 1.620 gml⁻¹ with the anions iodide, PF₆⁻ and FAP⁻ respectively.

Figure 5.16 illustrates the relationship between the observed density and calculated density using the Molinspiration website. Where the ionic liquid with the larger alkyl chain substituent $N_{114(14)}\text{TFSI}$ (578.26 g/mol) showed the lowest density 1.12 gml^{-1} and therefore the larger molecular volume ($516 \text{ \AA}^3$). It has been reported in literature that $N_{4448}\text{TFSI}$ with a similar molecular weight had a density of 1.12 gml^{-1} , exactly the same as that recorded in this work where both salts have the same molecular weight.^[4]

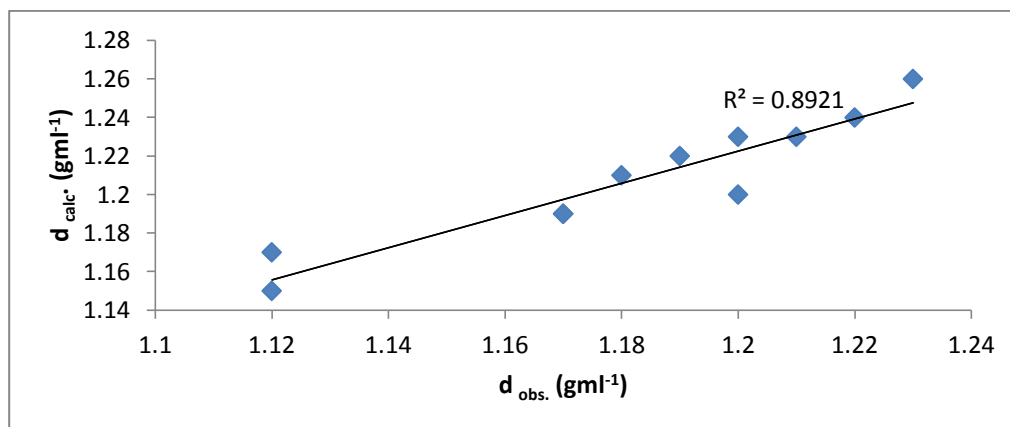


Figure 5.16. Observed density vs calculated density (gml^{-1}) for $N_{11\text{RR}}\text{TFSI}$ ILs

The same trend is observed for the TFSI RTILs of non-aliphatic asymmetric ammonium salts (table 5.9), for example $N_{11\text{B}(14)}\text{TFSI}$ which possesses the highest molecular weight (612.25 gml^{-1}) in the series recorded the lowest density (1.11 gml^{-1}) and therefore the highest molecular volume.

Table 5.9 Densities at 19°C of non-aliphatic quaternaryalkylammonium RTILs.

Salt	Molecular weight (g/mol)	ρ (gml^{-1})	Estimated molar volumes (mol^{-1})
$N_{11\text{B}8}\text{TFSI.H}_2\text{O}$	546.17	1.20	453.63
$N_{11\text{B}(10)}\text{TFSI}$	556.19	1.16	479.47
$N_{11\text{B}(10)}\text{I}$	403.17	1.16	348.76
$N_{11\text{B}(14)}\text{TFSI}$	612.25	1.11	551.58
$N_{11\text{A}(10)}\text{TFSI}$	506.17	1.12	451.93
$N_{11\text{A}8}\text{I}$	325.13	1.12	290.8
$N_{11\text{C}8}\text{TFSI}$	520.19	1.17	444.61
$N_{11\text{C}(10)}\text{TFSI}$	604.28	1.18	512.10

For comparison, by selecting the $N_{11R(10)}$ TFSI ionic liquid series where R = methyl, ethyl, isopropyl, butyl, hexyl, allyl, benzyl and cyclohexyl as shown in table 5.10, illustrates that the smallest estimated molar volume is that of the $N_{111(10)}$ TFSI and the largest volume is that of the $N_{116(10)}$ TFSI ionic liquid, this is an expected trend since the methyl groups are small in size and the cyclohexyl group is a bulky group.

The estimated molecular volumes are calculated from equation 1.^[14a]

$$\text{Molar Volume (V}_m\text{)} = \text{Molecular mass/ density} \quad (1)$$

Table 5.10. Densities, estimated molar volumes and viscosities of $N_{11R(10)}$ TFSI series.

salt	Density ρ (gml ⁻¹)	Viscosity (mPa.s) at 25 °C	Molecular volume (nm ³ mol ⁻¹)
$N_{111(10)}$ TFSI	1.2	114	400.125
$N_{112(10)}$ TFSI	1.18	87	418.79
$N_{113(10)}$ TFSI	1.2	160	423.49
$N_{114(10)}$ TFSI	1.17	169	446.325
$N_{116(10)}$ TFSI	1.12	237	491.2

One can conclude that the molar volume increases with the increase in the alkyl chain length and decrease in the density of the ionic liquid. The lower the density the higher is the viscosity and the greater is the molar volume.

It has been reported in literature by a number of groups, that the molecular volume (V_m) of the ions in ionic liquids has an influence on their properties. The molecular volume (V_m) for some of these ionic liquids was determined, some of which could be directly determined from the X-ray data and compared to that calculated using MOPAC and semi-empirical PM3 Hamiltonian.^[14b] For example the compound $N_{111(14)}$ TFSI the calculated volume is 0.641 nm³ whilst that derived directly from X-ray data is 0.65 nm³.

The densities were then calculated based on Shreeve's work from the below equations: ^[14c]

$$d(\text{solid}) = M_r / (0.6022V_m) \quad (2)$$

$$d(\text{liq}) = 0.948 d(\text{solid}) - 0.11 \quad (3)$$

And the values obtained were found to agree well with the measured values. Furthermore, it was noticed that the observed density of the quaternary ammonium-TFSI ionic liquids may be determined fairly precisely based on the number of CH₂ units in the cation *m* (equation 3) as shown in table 5.11.

$$d(\text{gml}^{-1}) = 1.3232 - 0.0113m \quad (4)$$

Table 5.11 Comparison of observed density with that calculated using two different methods.

Salt	$d_{\text{calc}}^a (\text{gml}^{-1})$	$d_{\text{calc}}^b (\text{gml}^{-1})$	$D_{\text{obs}}^c (\text{gml}^{-1})$
N ₁₁₁₈ TFSI	1.25	1.24	1.23
N ₁₁₁₍₁₀₎ TFSI	1.22	1.22	1.20
N ₁₁₂₈ TFSI	1.24	1.22	1.22
N ₁₁₂₍₁₀₎ TFSI	1.21	1.21	1.18
N ₁₁₃₈ TFSI	1.22	1.21	1.21
N ₁₁₃₍₁₀₎ TFSI	1.19	1.20	1.20
N ₁₁₄₈ TFSI	1.21	1.21	1.19
N ₁₁₄₍₁₀₎ TFSI	1.18	1.18	1.17
N ₁₁₄₍₁₄₎ TFSI	1.13	1.14	1.12
N ₁₁₆₈ TFSI	1.18	1.19	1.17
N ₁₁₆₍₁₀₎ TFSI	1.16	1.16	1.12

^a using equations (2) and (3); ^b using equation (4).

5.6. Electrochemical properties.

The electrochemical window (electrochemical stability) of a solvent is the potential range between which no oxidation and reduction processes are seen. A wide electrochemical window is one of the many advantages ionic liquids display as electrochemical solvents. Accordingly, ionic liquids have been shown to have useful applications in electrodeposition,^[16] electrosynthesis,^[17] lithium batteries,^[18] solar cells,^[19] fuel cells^[20] and electrochemical gas sensors.^[21] Matsumoto *et al.* reported that saturated quaternary ammoniums are more stable electrochemically than the 1,3-dialkylimidazoliums when combined with the TFSI anion.^[1]

The wider the electrochemical window (EW) the more applications that can be implemented. Having established the relatively low viscosity, reasonable conductivity and low solubility in water, preliminary electrochemical studies of these hydrophobic room temperature ionic liquids have been undertaken which are commonly determined by cyclic voltammetry (fig 5.17).

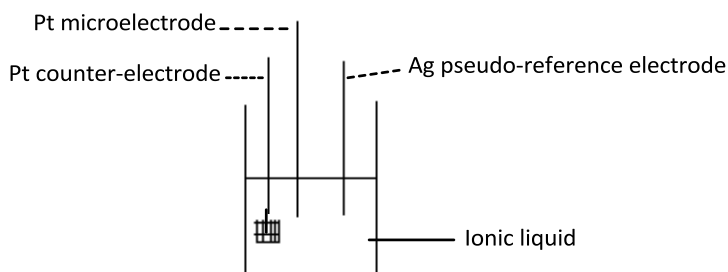


Figure 5.17. Experimental setup for electrochemical cell.

CVs of the RTILs were recorded using an in-house built cell (fig. 5.17), using a 10 μ m platinum microelectrode as the working electrode, silver wire as a pseudo-reference electrode and a platinum counter electrode.

Table 5.12 shows a summary of the electrochemical data of some of our novel asymmetric hydrophobic room temperature ionic liquids. Figures 5.18, 5.19 & 5.21 show typical examples of the electrochemical windows of N₁₁₄₈TFSI and N₁₁₆₈TFSI and N₁₁₄₍₁₄₎TFSI respectively at a Pt microelectrode of 10 µm diameter, Pt counter electrode with a scan rate of 100 mV s⁻¹ referenced to Ag.

All ionic liquids showed good electrochemical stability with a minimum electrochemical window of 4 V, according to Lewandowski *et al.* these ionic liquids may be used as conducting electrolytes in Li-batteries since a minimum of 4V is required for electrolytes in practical applications.^[22]

Table 5.12. Electrochemical windows of selected TFSI-RTILs.

Ionic liquid	EWs (V)	Ionic liquid	EWs (V)
N ₁₁₄₍₁₀₎ TFSI	4.3	N ₁₁₆₈ TFSI	4.5
N ₁₁₄₈ TFSI	4.7	N ₁₁₆₍₁₀₎ TFSI	4.8
N ₁₁₄₍₁₄₎ TFSI	5.5	N ₁₁₁₈ TFSI	4.2
N ₁₁₃₈ TFSI	4.0	N ₁₁₁₍₁₀₎ TFSI	4.4
N ₁₁₃₍₁₀₎ TFSI	4.5	N _{11A(14)} TFSI	4.5
N ₁₁₂₈ TFSI	4.2	N _{11B(14)} TFSI	4.0
N ₁₁₂₍₁₀₎ TFSI	4.7	N ₁₄₈₍₁₄₎ TFSI	6.2
N ₁₁₄₈ FAP	6.5		

Interestingly from the data obtained the electrochemical window of the completely asymmetric salt showed the highest electrochemical window of the TFSI salts. Whilst the FAP-ionic liquid, N₁₁₄₈FAP, possessed an even wider electrochemical window than its TFSI analogue. It has been reported in the literature that FAP-ionic liquids possess broad electrochemical windows, for example the symmetric quaternary ammonium salt, N₄₄₄₄FAP (mp 62 °C) shows a very wide electrochemical window, close to 7 V, which is probably the highest electrochemical window observed for such systems.^[13]

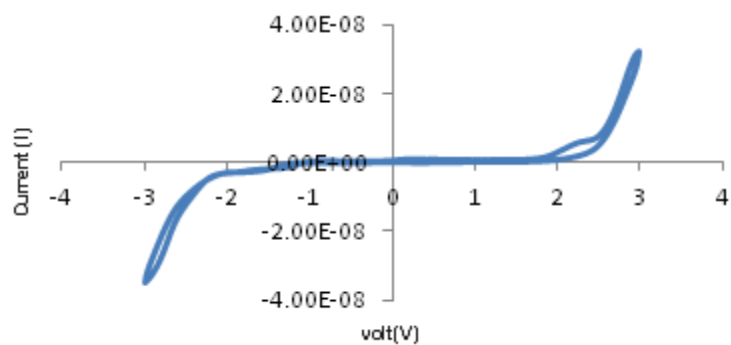


Figure 5.18. Cyclic voltamogram for N_{1148} TFSI at 100 mVs^{-1} , at a $10 \mu\text{m}$ diameter Pt microelectrode referenced to Ag pseudo reference electrode.

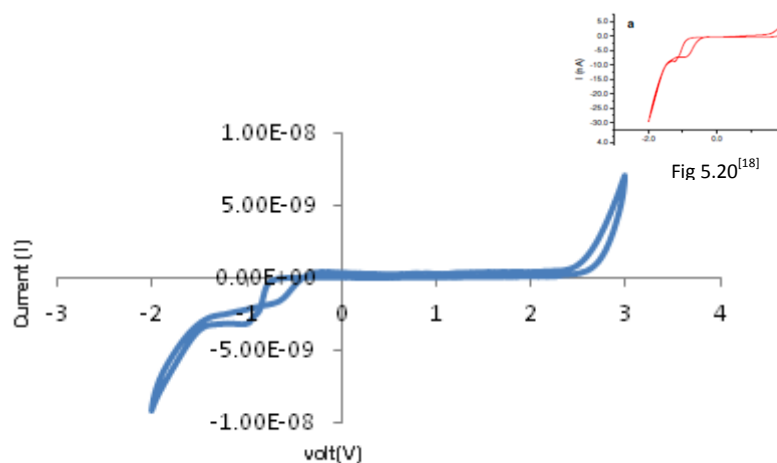


Figure 5.19. Cyclic voltamogram for N_{1168} TFSI at 100 mVs^{-1} , at a $10 \mu\text{m}$ diameter Pt microelectrode referenced to Ag pseudo reference electrode.

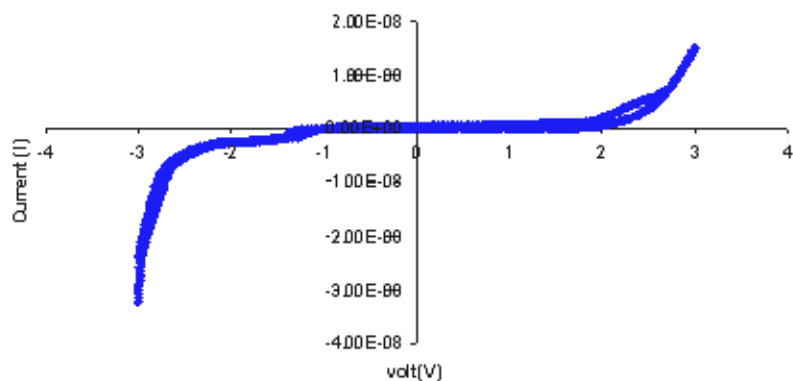


Figure 5.21 Cyclic voltamogram for $N_{114(14)}$ TFSI at 100 mVs^{-1} , at a $10 \mu\text{m}$ diameter Pt microelectrode referenced to Ag pseudo reference electrode.

In some cases, such as that shown for N₁₁₆₈TFSI in fig. 5.19, a feature is observed at the negative end of the CV over the potential interval of -0.5 V to -1.5 V due to the presence of oxygen from air in the sample. This arose because this data was recorded for a sample that was 3-months old and ionic liquids are known to be good solvents for gases. A similar behaviour (fig 5.20) has been reported by Oliveri *et al.* when studying trihexyltetradecylphosphoniumdecanoate, ([TETDP]decanoate) in the presence of oxygen using platinum electrode.^[23] This reduction process was ascertained by performing CVs in the RTILs after purging with nitrogen, where this feature was reduced gradually but not completely.

5.7. Conclusion

In this chapter a wide range of properties are reported. Our main aim in this research is to lower the melting point of our quaternary ammonium salts as much as possible. We found that both the cation symmetry and choice of a specific anion can influence the depression of melting point. For example, introducing asymmetry into the cation such as going from N₁₁₁₍₁₀₎TFSI to N₁₁₃₍₁₀₎TFSI to N₁₁₆₍₁₀₎TFSI the melting point decreases from 14 to -2 to -82 °C respectively. Some RTILs showed neither a melting point nor a glass transition lying within the usual limit of the working range down to -70 °C this may be due to their melting points being below the working range. The most promising anion used in this work is TFSI, resulting in a significant decrease in melting point by more than 150 °C in some cases, compared to the CF₃SO₃⁻, NbF₇²⁻, NNf₂⁻, PF₆⁻ and FAP⁻ counter parts.

The TFSI-exchanged ionic liquids showed the highest thermal stability of more than 400 °C for N₁₁₁₈TFSI, N₁₁₁₍₁₀₎TFSI and 394 °C for the completely asymmetric RTIL N₁₄₈₍₁₄₎TFSI.

The viscosity range for the measured TFSI-RTILs was 79 – 255 mPa.s (at 25 °C) which is lower than that reported by Ballantyne in our lab previously for

the more symmetric quaternary ammonium salts, $N_{RRRR}^+TFSI^-$, where the lowest viscosity was 280 mPa.s recorded for $N_{666(10)}TFSI$. The conductivity values showed an inverse relationship to the viscosity, ranging from 67-770 $\mu S.cm^{-1}$. The RTIL with the lowest viscosity which showed the highest conductivity was $N_{1138}TFSI$. These conductivities showed higher values compared to those previously reported for $N_{666(10)}TFSI$ and $N_{666(14)}TFSI$, which were 125 and 113 $\mu S.cm^{-1}$ respectively. Most of the developed RTILs were immiscible in water and saturated alkanes such as hexane and are soluble in a wide range of polar solvents such as DCM, acetone, $CHCl_3$. Based on NMR integration experiments against a known amount of an internal calibrant the solubility of most of the RTILs were less than 0.2 mmol. The developed TFSI-RTILS possessed wide electrochemical windows, the smallest window recorded is 4.0 V for $N_{1138}TFSI$ and the widest for a TFSI salt is 6.2 V for $N_{148(14)}TFSI$, whereas the RTIL $N_{1148}FAP$ showed the widest electrochemical window, 6.5 V.

5.8. References

1. Z. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.*, 2005, **11**, 752 .
2. K. Kim, C. M. Lang and P. A. Kohl., *J. Electrochem. Soc.*, 2005, **152**, E56.
3. J. Sun, M. Forsyth, and D.R. Macfarlene, *J. Phys. Chem. B* 1998, **102**, 8858.
4. T. Welton, P. Wasserscheid, *Ionic liquids in Synthesis*, 2nd edition Wiley-VCH, Weinheim New York, 2002.
5. (a)V. Kumar, C. Pei, C. E. Olsen, S. J. C. Shaffer, V. S. Parmar, S. V. Malhotra, *Tetrahedron*, 2008, **19**, 664. (b) J. M. Pringle, J. Golding, K. Baranyai, C. M. Forsyth, G. B. Deacon, J. L. Scott and D R. MacFarlene, *New J. Chem.*, 2003, **27**, 1504. (c) Z. Zhou, H. Matsumoto, K. Tatsumi, *Chem. Eur. J.*, 2004, **10**, 6581.
6. C. Chiappe and D. Pieraccini, *J. Phys. Org. Chem.* 2005, **18**, 275.
7. J. Bartosik and A.-V. Mudring, *Phys. Chem. Chem. Phys.*, 2010, **12**, 4005.
8. L. Yang, Z. Zhang, X. Gao, H. Zhang, K. Mashita, *J. power sources*, 2006, **162**, 614.
9. W. Xu, L. M. Wang, R. A. Nieman, C. A. Angell, *J. Phys. Chem. B*, 2003, **107**, 11749.
10. (a) J. L. Anderson, R. Ding, A. Ellern, D. W. Armstrong, *J. Am. Chem. Soc.*, 2005, **127**, 593. (b) T. Yim, C. Y. Choi, J. Mun, S. M. Oh and Y. G. Kim, *Molecules*, 2009, **14**, 1840.
11. K. Tsunashima, Y. Ono, M. Sugiya, *Electrochimica Acta*, 2011, **56**, 4351.

12. M. O'Mahony, D. S. Silvester, L. Aldous, C. Hardacre, R. G. Compton, *J. Chem. Eng. Data*, 2008, **53**, 2884.
13. N. V. Ignat'ev, U. Welz-Biermann, A. Kucheryna, G. Bissky, H. Willner, *J. Fluorine Chem.*, 2005, **126**, 1150.
14. (a) J. Jacquemin, P. Husson, A. H. Padua, V. Majer, *Green Chem.* 2006, **8**, 172, (b) James J. P. Stewart, Stewart Computational Chemistry, Colorado Springs, CO, USA, [HTTP://OpenMOPAC.net](http://OpenMOPAC.net) (2012), (c) C. Ye, J. M. Shreeve, *J. Phys. Chem. A*, 2007, **111**, 1456.
15. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker, R. D. Rogers, *Green Chem.*, 2001, **3**, 156.
16. A. P. Abbott, K. J. McKenzie, *Phys. Chem. Chem. Phys.*, 2006, **8**, 4265.
17. K. P. Ho, K. Y. Wong, T. H. Chan, *Tetrahedron*, 2006, **62**, 6650.
18. H. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley & Sons, New Jersey, 2005.
19. N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhote, H. Pettersson, A. Azam, M. Gratzel, *J. Electrochemical Society*, 1996, **143**, 3099.
20. H. Nakamoto, M. Watanabe, *Chem. Commun.*, 2007, 2539.
21. M. C. Buzzeo, C. Hardacre, R. G. Compton, *Analytical Chemistry*, 2004, **76**, 4583.
22. A. Lewandowski, A. S'widerska-Mocek, *Journal Power Sources* 2009, **194**, 601.
23. P. Oliveri, M. A. Baldo, S. Daniele, M. Forina, *Anal. Bioanal. Chem.* 2009, **395**, 1135.

6. Experimental

- 6.1 General details.
- 6.2 Synthesis of asymmetric aliphatic quaternary ammonium halide salts.
- 6.3 Synthesis of asymmetric quaternary ammonium halide salts with cyclohexyl, benzyl and allyl groups.
- 6.4 Synthesis of completely asymmetric aliphatic quaternary ammonium halide salts.
- 6.5 Synthesis of fluorinated asymmetric quaternary ammonium halide salts.
- 6.6 Synthesis of completely asymmetric fluorinated quaternary ammonium salts.
- 6.7 Synthesis of asymmetric quaternary ammonium salts of bis(trifluoromethanesulfonylimide) anion.
- 6.8 Synthesis of potassium bis(perfluoroalkylsulfonyl)imide ($\text{C}_8\text{F}_{18}\text{KNO}_4\text{S}_2$) and potassium perfluoroalkylsulfonates.
- 6.9 Synthesis of asymmetric quaternary ammonium salts containing the heptafluoroniobate(V) anion.
- 6.10 Synthesis of asymmetric quaternary ammonium salts of trifluoromethane sulfonate anion.
- 6.11 Synthesis of asymmetric quaternary ammonium salts of hexafluorophosphate and (trispentafluoro)trifluorophosphate anions.

6.1. General details

6.1.1 Spectroscopic and physical analyses.

^1H NMR spectra were recorded on either Bruker DPX 300 or Bruker Avance (III) spectrometers operating at 300.13 and 399.99 MHz respectively, and referenced to SiMe_4 .

^{19}F NMR spectra were recorded on a Bruker Avance (III) spectrometer at 376.49 MHz and referenced to CFCl_3 . Deuterated solvents were obtained from Aldrich. Elemental analyses were performed by the microanalysis lab, sulfur: using a Carlo Erba Instrument EA1108 elemental analyser and C,H,N: using a Thermo Scientific Flass 2000 organic elemental analyser. X-ray crystallographic data for the compounds for which single crystals could be grown was recorded on a Nonius k-CCD 4-circle diffractometer using graphite monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structural data was solved by direct methods using Shelxs 97.^[1]

The melting point for most samples was measured on an SMP 10 Stuart Scientific melting point machine or on a Perkin-Elmer Diamond differential scanning calorimeter (DSC). Thermal decompositions of the RTILs was carried out on a Seiko TG/DTA 220 instrument.

Viscosity was measured on an AMVn (Anton Paar) falling ball viscometer at 25 °C. The viscosity of the liquid is determined by observing the rolling time of a solid-sphere through liquids under the influence of gravity in an inclined cylindrical tube with a repeatability and reproducibility of better than 0.1 % and 0.5 % respectively in a closed system (no sample/air contact). The time taken by the ball to travel the fixed distances is measured with two sensors. For each single measured rolling time, the result is expressed as a dynamic viscosity (mPa.s).

Densities were measured using a 2 ml volumetric flask and an OHAUS model E11140 microbalance. Conductivity was measured on an Ecoscan con5 conductivity meter. All measurements were performed at 19 °C.

Cyclic voltamograms using GPES 4.9 (AUTOLAB) of the RTILs were performed in an in-house built cell, using a 10 μm platinum microelectrode as the working electrode, Ag wire as a pseudo-reference electrode and a platinum counter electrode at 100 mVs^{-1} scan rate.

The hydrophobic nature of the asymmetric quaternary ammonium RTILs was investigated using ^{19}F NMR spectroscopy. The ionic liquid was stirred for 24 hours with water, then 0.5 ml of the aqueous solution was doped with a known quantity of 1,1,1-trifluoroethanol, (0.1M) in D_2O . From the obtained ^{19}F NMR spectra of the water layer the integrals of the ionic liquid were compared with the integral of the known amount of trifluoroethanol, from which the concentration of ionic liquid was calculated.

6. 1.2 Solvents and Reagents

All reagents were obtained from standard chemical suppliers and were used as supplied. **Acros**: 1-bromooctadecane, 1-bromotetradecane, **Aldrich**: 1-iodopropane, 1-iododecane, allyliodide, 1-iodooctane, butylmethylamine, trimethylamine, tributylamine, lithium bistrifluoromethane sulfonylimide, perfluorooctanesulfonylfluoride, trifluoroacetamide, pyridine, *N,N*-dimethylhexylamine, *N,N*-dimethylisopropyl amine, *N,N*-dimethylbutylamine, *N,N*-dimethylethyl amine, trifluoroacetamide, potassium hexafluoro-niobate(V), *1H,1H,2H,2H,3H,3H*-perfluoroundecyl iodide, *1H,1H,2H,2H,3H,3H*-perfluoroheptyl iodide, **Fluka**: ethyldimethylamine, **Fisher Scientific**: potassium carbonate, magnesium sulfate, sodium hydroxide, activated carbon, **Apollo**: nonafluorobutylsulfonylfluoride, *1H,1H,2H,2H*-perfluorooctyl iodide, *1H,1H,2H,2H*-perfluorodecyl iodide, 3-iodo1,1,1-trifluorobutane, **Fluorochem**; potassium trifluoromethane sulfonate, **Merck**; potassium (trispentafluoro)trifluorophosphate (KFAP).

The solvents diethylether and hexane were obtained from Fisher Scientific and dried over sodium wire. Dichloromethane, acetonitrile and acetone were used as supplied.

6.2 Synthesis of asymmetric aliphatic quaternary ammonium halide salts.

In general, quaternary ammonium halide salts were prepared by mixing equimolar quantities of the asymmetric amine with an alkyl halide in a Schlenk tube and heating for 48 – 72 h at 90 °C. The products were washed with hexane to remove any unreacted amine or alkylhalide and dried.

6.2.1. Trimethyloctylammonium iodide ($N_{1118}I$).

Trimethylamine (3.4 ml, 2.12 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a white solid (yield 7.6 g, 71 %) mp 131 °C. 1H NMR ($CDCl_3$) δ 3.54 (m, 2H, NCH_2), 3.4 (s, 9H, $N(CH_3)_3$), 1.7 (bm, 2H, NCH_2CH_2), 1.2-1.3 (bm, 10H, $(CH_2)_5$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{11}H_{26}NI$ (299.11 g mol^{-1}) **C** 44.13, **H** 8.76, **N** 4.68 Found **C** 44.19, **H** 9.00, **N** 4.57 %.

6.2.2. Trimethyldecylammonium iodide ($N_{111(10)}I$).

Trimethylamine (3.4 ml, 2.12 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a white solid (yield 4.7 g, 40 %), mp 128 °C. 1H NMR ($CDCl_3$) δ 3.52 (m, 2H, NCH_2), 3.39 (s, 9H, $N(CH_3)_3$), 1.69 (bm, 2H, NCH_2CH_2), 1.19-1.3 (bm, 14H, $(CH_2)_7$), 0.83 (t, 3H, CH_3). Elemental analysis calc. for $C_{13}H_{30}NI$ (327.15 g mol^{-1}) **C** 47.69, **H** 9.24, **N** 4.28 Found **C** 47.90, **H** 9.48, **N** 4.25 %.

6.2.3. Trimethyltetradecylammonium bromide ($N_{111(14)}Br$).

Trimethylamine (3.4 ml, 2.12 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.98 g, 36 mmol) gave a white solid (yield 4.9 g, 40 %), mp 109 °C. 1H NMR ($CDCl_3$) δ 3.5 (m, 2H, NCH_2), 3.39 (s, 9H, $N(CH_3)_3$), 1.69 (bm, 2H, NCH_2CH_2), 1.18 – 1.3 (bm, 20H, $(CH_2)_{10}$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{17}H_{38}NBr$ (336.20 g mol^{-1}) **C** 60.68, **H** 11.39, **N** 4.16 Found **C** 60.78, **H** 11.71, **N** 4.15 %.

6.2.4. Trimethyloctadecylammonium bromide ($N_{111(18)}Br$).

Trimethylamine (3.4 ml, 2.12 g, 36 mmol) and 1-bromooctadecane (12.0 g, 36 mmol) gave a white solid (yield 1.9 g, 14 %), mp 109 °C. 1H NMR ($CDCl_3$) δ 3.5 (m, 2H, NCH_2), 3.4 (s, 9H, $N(CH_3)_3$), 1.68 (bm, 2H, NCH_2CH_2), 1.18 (bm, 30H, $(CH_2)_{15}$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{21}H_{46}NBr$ (392.27 $gmol^{-1}$) **C** 64.24, **H** 11.82, **N** 3.57 Found **C** 64.07, **H** 12.17, **N** 3.53 %.

6.2.5. Dimethylethylammonium iodide ($N_{1128}I$).

N,N-Dimethylethylamine (3.9 ml, 2.63 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a white hygroscopic solid (yield 6.5 g, 58 %), mp 111.1 °C. 1H NMR ($CDCl_3$) δ 3.63 (q, 2H, NCH_2CH_3), 3.44 (m, 2H, NCH_2), 3.31 (s, 6H, $N(CH_3)_2$), 1.66 (bm, 2H, CH_2CH_2N), 1.2–1.35 (bm, 13H, CH_3 and $(CH_2)_5$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{12}H_{28}NI$ (313.13 $gmol^{-1}$) **C** 45.99, **H** 9.01, **N** 4.47 Found **C** 45.23, **H** 9.12, **N** 4.30 %.

6.2.6. Dimethylethyldecylammonium iodide ($N_{112(10)}I$).

N,N-Dimethylethylamine (4.3 ml, 2.925 g, 40 mmol) and 1-iododecane (8.5 ml, 10.727 g, 40 mmol) gave a white hygroscopic solid (yield 10 g, 73 %), mp 109.7 °C. 1H NMR ($CDCl_3$) δ 3.63 (q, 2H, NCH_2CH_3), 3.44 (m, 2H, NCH_2), 3.31 (s, 6H, $N(CH_3)_2$), 1.65 (bm, 2H, CH_2CH_2N), 1.19–1.35 (bm, 17H, CH_3 and $(CH_2)_7$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{14}H_{32}NI$ (341.16 $gmol^{-1}$) **C** 49.24, **H** 9.45, **N** 4.10 Found **C** 49.38, **H** 9.91, **N** 4.01 %.

6.2.7. Dimethylethyltetradecylammonium bromide ($N_{112(14)}Br$).

N,N-Dimethylethylamine (4.3 ml, 2.925 g, 40 mmol) and 1-bromotetradecane (11.9 ml, 11.09 g, 40 mmol) gave a white solid (yield 10 g, 63 %), mp 101 °C. 1H NMR ($CDCl_3$) δ 3.71 (q, 2H, NCH_2CH_3), 3.49 (m, 2H, NCH_2), 3.38 (s, 6H, $N(CH_3)_2$), 1.69 (bm, 2H, CH_2CH_2N), 1.2–1.39 (bm, 25H, CH_3 and $(CH_2)_{11}$), 0.86

(t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{18}\text{H}_{40}\text{NBr}$ ($397.22 \text{ g mol}^{-1}$) **C** 61.68, **H** 11.51, **N** 4.00 Found **C** 61.83, **H** 12.16, **N** 3.93 %.

6.2.8. Dimethylethyl octadecyl ammonium bromide ($\text{N}_{112(18)}\text{Br}$).

N,N-Dimethylethylamine (4.3 ml, 2.925 g, 40 mmol) and 1-bromooctadecane (13.33 g, 40 mmol) gave a white solid (yield 10.39 g, 64 %), mp 110°C . ^1H NMR (CDCl_3) δ 3.52 (q, 2H, NCH_2CH_3), 3.29 (m, 2H, NCH_2), 3.19 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.508 (bm, 2H, $\text{CH}_2\text{CH}_2\text{N}$), 1.04–1.19 (bm, 33H, CH_3 and $(\text{CH}_2)_{15}$), 0.67 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{22}\text{H}_{48}\text{NBr}$ ($406.28 \text{ g mol}^{-1}$) **C** 64.98, **H** 11.91, **N** 3.45 Found **C** 65.08, **H** 12.89, **N** 3.32 %.

6.2.9. Dimethylisopropyl octyl ammonium iodide (N_{1138}I).

N,N-Dimethylisopropylamine (4.4 ml, 3.129 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a white solid product (yield 9.67 g, 42 %) mp 198°C . ^1H NMR (CDCl_3) δ 3.9 (sep ($J = 6.6\text{Hz}$), 1H, NCH), 3.4 (t, 2H, NCH_2), 3.22 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.4 (d ($J = 6.6\text{Hz}$), 6H, $(\text{CH}_3)_2\text{CHN}$), 1.7 (bs, 2H, CH_2), 1.2 (bm, 10H, $(\text{CH}_2)_5$), 0.82 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{13}\text{H}_{30}\text{NI}$ ($327.14 \text{ g mol}^{-1}$) **C** 47.69, **H** 9.24, **N** 4.28 Found **C** 47.63, **H** 10.02, **N** 4.27 %.

6.2.10. Dimethylisopropyl decyl ammonium iodide ($\text{N}_{113(10)}\text{I}$).

N,N-Dimethylisopropylamine (4.4 ml, 3.129 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a white solid product (yield 9.6 g, 75 %) mp 205°C . ^1H NMR (CDCl_3) δ 3.9 (sep ($J = 6.6\text{Hz}$), 1H, $\text{NCH}(\text{CH}_3)_2$), 3.46 (t, 2H, NCH_2CH_2), 3.22 (s, 6H, $(\text{CH}_3)_2\text{N}$), 1.4 (d ($J = 6.6\text{Hz}$), 6H, $(\text{NCH}(\text{CH}_3)_2)$), 1.5 (bs, 2H, CH_2), 1.18 (bm, 14H, $(\text{CH}_2)_7$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{15}\text{H}_{34}\text{NI}$ ($355.17 \text{ g mol}^{-1}$) **C** 50.68, **H** 9.65, **N** 3.94 Found **C** 50.71, **H** 10.05, **N** 3.83 %.

6.2.11. Dimethylisopropyltetradecylammonium bromide ($N_{113(14)}\text{Br}$).

N,N-Dimethylisopropylamine (4.4 ml, 3.129 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.98 g, 36 mmol) gave a white solid product (yield 4.23 g, 32 %) mp 206 °C. ^1H NMR (CDCl_3) δ 3.65 (sep ($J=6.6\text{Hz}$), 1H, $\text{NCH}(\text{CH}_3)_2$), 3.22 (m, 2H, NCH_2CH_2), 2.94 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.67 (bm, 2H, NCH_2CH_2), 1.19 (bs, 22H, $(\text{CH}_2)_{11}$), 1.29 (d ($J=6.6\text{Hz}$), 6H, $\text{CH}(\text{CH}_3)_2$), 0.78 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{19}\text{H}_{42}\text{NBr}$ (364.23 g mol^{-1}) **C** 62.60, **H** 11.62, **N** 3.84 Found **C** 61.79, **H** 11.93, **N** 3.17 %.

6. 2.12 Dimethylisopropyloctadecylammonium bromide ($N_{113(18)}\text{Br}$).

N,N-Dimethylisopropylamine (2.4 ml, 1.743 g, 20 mmol) and 1-bromooctadecane (6.66 g, 20 mmol) gave a white solid product (yield 3.12 g, 37 %) mp 209 °C. ^1H NMR (CDCl_3) δ 3.97 (sep ($J = 6.6\text{Hz}$), 1H, $\text{NCH}(\text{CH}_3)_2$), 3.48 (m, 2H, NCH_2CH_2), 3.25 (s, 6H, $(\text{CH}_3)_2\text{N}$), 1.67 (b, 2H, NCH_2CH_2), 1.38 (d($J=6.6\text{Hz}$), 6H, $(\text{CH}_3)_2\text{CH}$), 1.13 (bm, 30H, $(\text{CH}_2)_{15}$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{23}\text{H}_{50}\text{NBr}$ (420.30 g mol^{-1}) **C** 65.67, **H** 11.99, **N** 3.33 Found **C** 64.93, **H** 12.32, **N** 2.86 %.

6.2.13. Dimethylbutyloctylammonium iodide ($N_{1148}\text{I}$).

N,N-Dimethylbutylamine (10.0 ml, 7.19 g, 71.15 mmol) and 1-iodooctane (12.8 ml, 17.08 g, 71.15 mmol) gave a yellow solid product (yield 18.3 g, 76%) mp 92 °C. ^1H NMR (CDCl_3) δ 3.48 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 3.32 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.65 (bm, 4H, $2\text{CH}_2\text{CH}_2$), 1.39–1.21 (bm, 12H, $(\text{CH}_2)_6$), 0.95 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{14}\text{H}_{32}\text{NI}$ (341.16 g mol^{-1}) **C** 49.24, **H** 9.45, **N** 4.10 Found **C** 48.79, **H** 9.51, **N** 4.06 %.

6.2.14. Dimethylbutyldecylammonium iodide ($N_{114(10)}I$).

N,N-Dimethylbutylamine (10.0 ml, 7.19 g, 71.15 mmol) and 1-iododecane (15.2 ml, 19.08 g, 71.15 mmol) gave a yellow solid product (yield 11.93 g, 45 %) mp 56.4 °C. 1H NMR ($CDCl_3$) δ 3.5 (m, 4H, $2NCH_2$), 3.4 (s, 6H, $N(CH_3)_2$), 1.73 (bm, 4H, $2CH_2$), 1.26–1.37 (bm, 16H, $(CH_2)_8$), 1.02 (t, 3H, CH_3), 0.89 (t, 3H, CH_3). Elemental analysis calc. for $C_{16}H_{36}NI$ (369.19 g mol^{-1}) **C** 52.01, **H** 9.83, **N** 3.79 Found **C** 51.82, **H** 10.01, **N** 3.75 %.

6.2.15. Dimethylbutyltetradecylammonium bromide ($N_{114(14)}Br \cdot H_2O$).

N,N-Dimethylbutylamine (5.0 ml, 3.64 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.98 g, 36 mmol) gave a white solid product (yield 12.8 g, 90 %) mp 52.1 °C. 1H NMR ($CDCl_3$) δ 3.46 (m, 4H, $2NCH_2$), 3.34 (s, 6H, $N(CH_3)_2$), 1.64 (bm, 4H, $2NCH_2CH_2$), 1.18–1.38 (bm, 24H, $(CH_2)_{12}$), 0.94 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{20}H_{46}NBrO$ (396.26 g mol^{-1}) **C** 60.57, **H** 11.70, **N** 3.53 Found **C** 60.45, **H** 11.77, **N** 3.52 %.

6.2.16. Dimethylbutyloctadecylammonium bromide ($N_{114(18)}Br \cdot H_2O$).

N,N-Dimethylbutylamine (2.8 ml, 2.02 g, 20 mmol) and 1-bromooctadecane (6.66 g, 20 mmol) gave a white solid product (yield 6.93 g, 76 %) mp 75 °C. 1H NMR ($CDCl_3$) δ 3.45 (m, 4H, NCH_2), 3.33 (s, 6H, $N(CH_3)_2$), 1.63 (bm, 4H, NCH_2CH_2), 1.18–1.38 (bm, 32H, $(CH_2)_{16}$), 0.93 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{24}H_{54}BrNO$ (452.32 g mol^{-1}) **C** 63.67, **H** 12.03, **N** 3.10 Found **C** 63.87, **H** 12.25, **N** 3.06 %.

6.2.17. Dimethylhexyloctylammonium iodide ($N_{1168}I$).

N,N-Dimethylhexylamine (6.3 ml, 4.64 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a viscous honey coloured product (yield 12.2 g, 92 %). 1H NMR ($CDCl_3$) δ 3.46 (m, 4H, $2NCH_2$), 3.32 (s, 6H, $N(CH_3)_2$), 1.64 (bm, 4H,

2NCH₂CH₂), 1.2–1.3 (bm, 16H, (CH₂)₈), 0.81 (t, 6H, 2CH₃). Elemental analysis calc. for C₁₆H₃₆NI (369.19 g mol⁻¹) **C** 52.01, **H** 9.83, **N** 3.79 Found **C** 51.67, **H** 10.09, **N** 3.79%.

6.2.18. Dimethylhexyldecylammonium iodide (N₁₁₆₍₁₀₎I).

N,N-Dimethylhexylamine (6.3 ml, 4.64 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a viscous dark brown transparent product (yield 11.3 g, 79 %). ¹H NMR (CDCl₃) δ 3.47 (m, 4H, 2NCH₂), 3.32 (s, 6H, N(CH₃)₂), 1.66 (bm, 4H, 2 NCH₂CH₂), 1.19–1.29 (bm, 20H, (CH₂)₁₀), 0.812 (m, 6H, 2CH₃). Elemental analysis calc. for C₁₈H₄₀NI (397.22 g mol⁻¹) **C** 54.38, **H** 10.15, **N** 3.53 Found **C** 54.33, **H** 10.82, **N** 3.59 %.

6.3. Synthesis of asymmetric tetraalkylammonium halide salts with cyclohexyl, benzyl and allyl groups.

6.3.1 Dimethylbenzyldecylammonium iodide (N_{11B8}I).

N,N-Dimethylbenzylamine (5.4 ml, 4.9 g, 35.9 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a viscous light yellow product (yield 12.5 g, 92 %). ¹H NMR (CDCl₃) δ 7.61 (m, 2H, C₆H₅), 7.39 (m, 3H, C₆H₅), 4.99 (s, 2H, CH₂C₆H₅), 3.51 (m, 2H, NCH₂), 3.22 (s, 6H, N(CH₃)₂), 1.75 (bm, 2H, NCH₂CH₂), 1.17–1.26 (bm, 10H, (CH₂)₅), 0.79 (t, 3H, CH₃). Elemental analysis calc. for C₁₇H₃₀IN (375.14 g mol⁻¹) **C** 54.38, **H** 8.06, **N** 3.73, **I** 33.83 found **C** 54.46, **H** 8.60, **N** 3.79, **I** 33.25%.

6.3.2 Dimethylbenzyldecylammonium iodide (N_{11B(10)}I).

N,N-Dimethylbenzylamine (5.4 ml, 4.86 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a viscous light yellow product (yield 10.6 g, 73 %). ¹H NMR (CDCl₃) δ 7.62 (m, 2H, C₆H₅), 7.38 (m, 3H, C₆H₅), 4.98 (s, 2H, CH₂C₆H₅),

3.52 (m, 2H, NCH_2), 3.22 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.74 (bm, 2H, NCH_2CH_2), 1.16–1.26 (bm, 14H, $(\text{CH}_2)_7$), 0.80 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{19}\text{H}_{34}\text{IN}$ ($403.17 \text{ g mol}^{-1}$) **C** 56.55, **H** 8.50, **N** 3.47 found **C** 57.00, **H** 8.56, **N** 3.63 %.

6.3.3. Dimethylbenzyltetradecylammonium bromide ($\text{N}_{11\text{B}(14)}\text{Br}\cdot\text{H}_2\text{O}$).

N,N-Dimethylbenzylamine (5.4 ml, 4.86 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.98 g, 36 mmol) gave a beige solid product (yield 10.5 g, 68 %), mp 48.4 °C. ^1H NMR (CDCl_3) δ 7.68 (m, 2H, Ar), 7.46 (m, 3H, Ar), 5.10 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_5$), 3.54 (m, 2H, NCH_2), 3.32 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.80 (bm, 2H, NCH_2CH_2), 1.26–1.33 (bm, 22H, $(\text{CH}_2)_{11}$), 0.89 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{23}\text{H}_{44}\text{BrNO}$ ($430.25 \text{ g mol}^{-1}$) **C** 64.15, **H** 10.31, **N** 3.25 found **C** 64.09, **H** 10.18, **N** 3.24 %.

6.3.4. Dimethylbenzyloctadecylammonium bromide ($\text{N}_{11\text{B}(18)}\text{Br}\cdot\text{H}_2\text{O}$).

N,N-Dimethylbenzylamine (5.4 ml, 4.86 g, 36 mmol) and 1-bromooctadecane (12.0 g, 36 mmol) gave an off-white solid product (yield 15.34 g, 88 %), mp 65 °C. ^1H NMR (CDCl_3) δ 7.68 (m, 2H, Ar), 7.40 (m, 3H, Ar), 4.99 (s, 2H, $\text{CH}_2\text{C}_6\text{H}_5$), 3.45 (m, 2H, NCH_2), 3.21 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.73 (bm, 2H, NCH_2CH_2), 1.18–1.27 (bm, 30H, $(\text{CH}_2)_{15}$), 0.80 (t, 3H, CH_3). Elemental analysis calc. for $\text{C}_{27}\text{H}_{52}\text{BrNO}$ ($486.31 \text{ g mol}^{-1}$) **C** 66.62, **H** 10.78, **N** 2.88 found **C** 67.75, **H** 10.48, **N** 2.93 %.

6.3.5. Dimethylallyloctylammonium iodide ($\text{N}_{11\text{A}8\text{I}}$).

N,N-Dimethylallylamine (4.25 ml, 3.056 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.64 g, 36 mmol) gave a honey-like product (yield 11.5 g, 99 %). ^1H NMR (CDCl_3) δ 5.96 (m, 1H, NCH_2CH), 5.86 (m, 1H, $=\text{CHH}$), 5.71 (m, 1H, $=\text{CHH}$), 4.29 (d, 2H, $\text{NCH}_2\text{CH}=\text{CH}_2$), 3.47 (m, 2H, NCH_2), 3.28 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.71 (bm, 2H, NCH_2CH_2), 1.19–1.29 (bm, 10H, $(\text{CH}_2)_5$), 0.8 (t, 3H, CH_3). Elemental analysis

calc. for $C_{13}H_{28}IN$ ($325.13 \text{ g mol}^{-1}$) **C** 47.98, **H** 8.68, **N** 4.31 found **C** 47.52, **H** 8.55, **N** 4.25 %.

6.3.6. Dimethylallyldecylammonium iodide ($N_{11A(10)}I$).

N,N-Dimethylallylamine (4.25 ml, 3.056 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a honey-like product (yield 12.0 g, 95 %). 1H NMR ($CDCl_3$) δ 5.96 (m, 1H, NCH_2CH), 5.85 (m, 1H, $=CHH$), 5.71 (m, 1H, $=CHH$), 4.29 (d, 2H, $NCH_2CH=CH_2$), 3.45 (m, 2H, NCH_2), 3.28 (s, 6H, $N(CH_3)_2$), 1.7 (bm, 2H, NCH_2CH_2), 1.19–1.29 (bm, 14H, $(CH_2)_7$), 0.8 (t, 3H, CH_3). Elemental analysis calc. for $C_{15}H_{32}IN$ ($353.16 \text{ g mol}^{-1}$) **C** 50.97, **H** 9.13, **N** 3.97 found **C** 50.67, **H** 9.11, **N** 3.82 %.

6.3.7. Dimethylallyltetradecylammonium bromide ($N_{11A(14)}Br$).

N,N-Dimethylallylamine (4.25 ml, 3.056 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.982 g, 36 mmol) gave a light yellow solid (yield 12.79 g, 98 %), mp $64^\circ C$. 1H NMR ($CDCl_3$) δ 5.97 (m, 1H, NCH_2CH), 5.9 (m, 1H, $=CHH$), 5.77 (m, 1H, $=CHH$), 4.39 (d, 2H, $NCH_2CH=CH_2$), 3.50 (m, 2H, NCH_2), 3.4 (s, 6H, $N(CH_3)_2$), 1.75 (bm, 2H, NCH_2CH_2), 1.26–1.36 (bm, 22H, $(CH_2)_{11}$), 0.8 (t, 3H, CH_3). Elemental analysis calc. for $C_{19}H_{40}BrN$ ($362.22 \text{ g mol}^{-1}$) **C** 62.95, **H** 11.13, **N** 3.87 found **C** 62.25, **H** 11.14, **N** 3.92 %.

6.3.8. Dimethylallyloctadecylammonium bromide ($N_{11A(18)}Br$).

N,N-Dimethylallylamine (4.25 ml, 3.056 g, 36 mmol) and 1-bromooctadecane (12.0 g, 36 mmol) gave a white solid (yield 14.11 g, 94 %), mp $86^\circ C$. 1H NMR ($CDCl_3$) δ 5.97 (m, 1H, NCH_2CH), 5.86 (m, 1H, $=CHH$), 5.77 (m, 1H, $=CHH$), 4.39 (d, 2H, $NCH_2CH=CH_2$), 3.50 (m, 2H, NCH_2), 3.4 (s, 6H, $N(CH_3)_2$), 1.75 (bm, 2H, NCH_2CH_2), 1.26–1.36 (bm, 30H, $(CH_2)_{15}$), 0.89 (t, 3H, CH_3). Elemental analysis

calc. for $C_{23}H_{48}BrN$ ($418.28 \text{ g mol}^{-1}$) **C** 65.98, **H** 11.57, **N** 3.35 found **C** 65.69, **H** 11.68, **N** 3.41 %.

6.3.9. Dimethylcyclohexyloctylammonium iodide ($N_{11C8}I$).

N,N-Dimethylcyclohexylamine (5.4 ml, 4.567 g, 36 mmol) and 1-iodooctane (6.5 ml, 8.6 g, 36 mmol) gave a white solid (yield 12.72 g, 97 %), mp 144 °C. 1H NMR ($CDCl_3$) δ 3.44–3.48 (m, 3H, $NCH_2 + Cy$), 3.23 (s, 6H, $N(CH_3)_2$), 2.13 (bm, 2H, Cy), 1.95 (bm, 2H, Cy), 1.66 (bm, 3H, $NCH_2CH_2 + Cy$), 1.20–1.43 (bm, 15H, $(CH_2)_5 + Cy$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{16}H_{34}IN$ ($367.17 \text{ g mol}^{-1}$) **C** 52.29, **H** 9.33, **N** 3.81 found **C** 51.55, **H** 9.77, **N** 3.75 %.

6.3.10. Dimethylcyclohexyldecylammonium iodide ($N_{11C(10)}I$).

N,N-Dimethylcyclohexylamine (5.4 ml, 4.567 g, 36 mmol) and 1-iododecane (7.7 ml, 9.65 g, 36 mmol) gave a white solid (yield 14.1 g, 99 %), mp 147 °C. 1H NMR ($CDCl_3$) δ 3.42–3.48 (m, 3H, $NCH_2 + NCy$), 3.23 (s, 6H, $N(CH_3)_2$), 2.14 (bm, 2H, Cy), 1.95 (bm, 2H, Cy), 1.65 (bm, 3H, $CH_2 + Cy$), 1.19–1.44 (bm, 19H, $(CH_2)_7 + Cy$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{18}H_{38}IN$ ($395.20 \text{ g mol}^{-1}$) **C** 54.66, **H** 9.69, **N** 3.54 found **C** 54.73, **H** 9.47, **N** 3.62 %.

6.3.11. Dimethylcyclohexyltetradecylammonium bromide ($N_{11C(14)}Br$).

N,N-Dimethylcyclohexylamine (5.4 ml, 4.567 g, 36 mmol) and 1-bromotetradecane (10.7 ml, 9.98 g, 36 mmol) gave an off-white solid (yield 8.3 g, 57 %), mp 136 °C. 1H NMR ($CDCl_3$) δ 3.52 (m, 2H, NCH_2), 3.41 (bm, 1H, NCy), 3.26 (s, 6H, $N(CH_3)_2$), 2.12 (bm, 2H, Cy), 1.95 (bm, 2H, Cy), 1.63 (bm, 3H, $CH_2 + Cy$), 1.18–1.41 (bm, 27H, $N(CH_2)_{11} + Cy$), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{22}H_{46}BrN$ ($404.27 \text{ g mol}^{-1}$) **C** 65.30, **H** 11.47, **N** 3.46 found **C** 65.13, **H** 11.65, **N** 3.22 %.

6.3.12. Dimethylcyclohexyloctadecylammonium bromide ($N_{11C(18)}Br$).

N,N-Dimethylcyclohexylamine (5.4 ml, 4.567 g, 36 mmol) and 1-bromooctadecane (12.0 g, 36 mmol) gave a white solid (yield 7.3 g, 44 %), mp 137 °C. 1H NMR ($CDCl_3$) δ 3.61 (m, 2H, NCH_2), 3.5 (bm, 1H, NCy), 3.34 (s, 6H, $N(CH_3)_2$), 2.2 (bm, 2H, Cy), 2.05 (bm, 2H, Cy), 1.73 (bm, 3H, $CH_2 + Cy$), 1.27–1.5 (bm, 35H, $N(CH_2)_{15} + Cy$), 0.89 (t, 3H, CH_3). Elemental analysis calc. for $C_{26}H_{54}BrN$ (460.33 $g\ mol^{-1}$) **C** 67.78, **H** 11.82, **N** 3.04 found **C** 67.27, **H** 11.83, **N** 2.71 %.

6.4. Synthesis of completely asymmetric aliphatic quaternary ammonium halide salts. ^[2]

6.4.1. Synthesis of the asymmetric amine, methylbutyltetradecylamine ($N_{14(14)}$).

Methylbutylamine (10.9 ml, 92.2 mmol) was added dropwise to a mixture of 1-bromotetradecane (6.09 ml, 20.5 mmol) and pyridine (20 ml). The mixture was stirred for 4 h. at 80 °C, resulting in two layers, of which the lower was collected. The liquid was washed with 10 % NaOH aqueous solution (20 ml) and dried with $MgSO_4$, resulting in a yellow oily liquid (yield 1.92 g, 33 %). 1H NMR ($CDCl_3$) δ 2.22 (m, 4H, $2NCH_2$), 2.13 (s, 3H, NCH_3), 1.37 (bm, 4H, $2NCH_2CH_2$), 1.18–1.24 (bm, 24H, $(CH_2)_{12}$), 0.83 (t, 6H, $2CH_3$). Elemental analysis calc. for $C_{19}H_{41}N$ (283.32 $g\ mol^{-1}$) **C** 80.47, **H** 14.58, **N** 4.94 found **C** 79.99, **H** 14.64, **N** 5.31 %.

6.4.2. Synthesis of methylbutyloctyltetradecylammonium iodide ($N_{148(14)}I$).

Methylbutyltetradecylamine (1.9 g, 6.75 mmol) and 1-iodooctane (1.2 ml, 1.62 g, 6.75 mmol) gave a brown viscous liquid (yield 2.1 g, 60 %), mp 11 °C. 1H NMR ($CDCl_3$) δ 3.38 (m, 6H, $3NCH_2$), 3.25 (s, 3H, CH_3), 1.63 (bm, 6H, $3NCH_2CH_2$), 1.18–1.4 (bm, 34H, $(CH_2)_{17}$), 0.94 (t, 3H, CH_3), 0.82 (t, 6H, $2CH_3$).

Elemental analysis calc. for $C_{27}H_{58}IN$ ($523.36 \text{ g mol}^{-1}$) **C** 61.91, **H** 11.17, **N** 2.68
found **C** 62.28, **H** 10.97, **N** 2.96 %.

6. 4.2 Synthesis of methylpropylbutyltetradecylammonium iodide ($N_{134(14)}I$).

Methylbutyltetradecylamine (1.9 g, 6.75 mmol) and 1-iodopropane (1.14 g, 6.75 mmol) gave a brown viscous liquid (yield 1.8 g, 59 %). 1H NMR ($CDCl_3$) δ 3.37 (m, 6H, $3NCH_2$), 3.25 (s, 3H, CH_3), 1.62 (bm, 6H, $3NCH_2CH_2$), 1.18-1.39 (bm, 24H, $(CH_2)_{12}$), 0.95 (t, 3H, CH_3), 0.81 (t, 6H, $2CH_3$). Elemental analysis calc. for $C_{22}H_{48}IN$ ($453.28 \text{ g mol}^{-1}$) **C** 58.24, **H** 10.67, **N** 3.09 found **C** 59.77, **H** 10.43, **N** 2.71 %.

6. 4.4 Synthesis of methylbutyldecyltetradecylammonium iodide ($N_{14(10)(14)}I \cdot H_2O$).

Methylbutyltetradecylamine (1.9 g, 6.75 mmol) and 1-iododecane (1.81 g, 6.75 mmol) gave a brown viscous liquid (yield 2.0 g, 52 %). 1H NMR ($CDCl_3$) δ 3.38 (m, 6H, $3NCH_2$), 3.24 (s, 3H, CH_3), 1.64 (bm, 6H, $3NCH_2CH_2$), 1.19-1.39 (bm, 36H, $(CH_2)_{18}$), 0.94 (t, 3H, CH_3), 0.81 (t, 6H, $2CH_3$). Elemental analysis calc. for $C_{29}H_{64}INO$ ($569.40 \text{ g mol}^{-1}$) **C** 61.12, **H** 11.33, **N** 2.46 found **C** 60.70, **H** 10.41, **N** 2.77 %.

6. 4.5 Synthesis of methylbutylallyltetradecylammonium iodide ($N_{14A(14)}I \cdot 2H_2O$).

Methylbutyltetradecylamine (1.9 g, 6.75 mmol) and allyliodide (1.134 g, 6.75 mmol) gave a brown liquid (yield 2.3 g, 70 %). 1H NMR ($CDCl_3$) δ 5.8 (m, 3H, $CH_2=CH$), 4.21 (d, ($J = 6.69 \text{ Hz}$), 2H, $NCH_2CH=CH_2$), 3.34 (m, 4H, $2NCH_2$), 3.2 (s, 3H, CH_3), 1.66 (bm, 4H, $2NCH_2CH_2$), 1.19-1.39 (bm, 24H, $(CH_2)_{12}$), 0.94 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). Elemental analysis calc. for $C_{22}H_{50}INO_2$ ($487.29 \text{ g mol}^{-1}$) **C** 54.18, **H** 10.34, **N** 2.87 found **C** 54.13, **H** 9.46, **N** 3.35 %.

6.5. Synthesis of fluorinated asymmetric quaternary ammonium halide salts.

6.5.1. Synthesis of dimethylisopropyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoro- undecyl iodide.

Dimethylisopropylheptadecafluoroundecyl ammonium iodide was prepared by mixing approximately equimolar quantities of dimethylisopropylamine (0.286 g, 3.3 mmol), 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl iodide (1.80 g, 3 mmol) in a sealed Schlenk tube charged with 30ml acetonitrile. The reaction mixture was stirred at 150 °C for 24 h. The solvent was removed under vacuum and the crude material washed with hexane affording 1.5 g of dimethylisopropylheptadecafluoroundecyl ammonium iodide as a beige solid (68 %). ¹⁹F NMR (CDCl₃) δ -80.75 (t, 3F, *J* = 10 Hz), -113.5 to -113.9 (br, 2F), -121.79 (bs, 6F), -123.09 (bs, 4F), -126.13 (bs, 2F). ¹H NMR (CDCl₃) δ 1.43 (d, 6H), 2.1 (bm, 2H), 2.33 (bm, 2H), 3.28 (s, 6H), 3.83 (m, 2H), 3.9 (m, 1H). Elemental analysis calc. for C₁₆H₁₉F₁₇IN (675.03 g mol⁻¹) **C** 28.44, **H** 2.84, **N** 2.07 Found **C** 28.75, **H** 3.12, **N** 2.50 %.

6.5.2. Synthesis of dimethylbutyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl iodide.

Following procedure 2.1.6.1 dimethylbutyl amine (0.33 g, 3.3 mmol), 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl iodide (1.80 g, 3 mmol) resulted in a white solid 1.8 g of dimethylbutylheptadecafluoroundecylammonium iodide (80 %). ¹⁹F NMR (CDCl₃) δ -80.77 (t, 3F, *J* = 9.9 Hz), -113.68 (m, 2F), -121.8 (bs, 2F), -121.9 (bs, 4F), -122.76 (bs, 2F), -123.16 (bs, 2F), -126.16 (bs, 2F). ¹H NMR (CDCl₃) δ 1.04 (t, 3H), 1.48 (sep, 2H), 1.78 (m, 2H), 2.15 (m, 2H), 2.36 (m, 2H), 3.44 (s, 6H), 3.6 (m, 2H), 3.89 (m, 2H). Elemental analysis calc. for C₁₇H₂₁F₁₇IN (689.04 g mol⁻¹) **C** 29.61, **H** 3.07, **N** 2.03 Found **C** 30.13, **H** 2.88, **N** 2.08 %.

6.5.3. Synthesis of dimethylisopropyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl ammonium iodide.

Following procedure 2.1.6.1 dimethylisopropylamine (0.286 g, 3.3 mmol), 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl iodide (0.64 ml, 3 mmol) in acetonitrile (30ml) was stirred at 150 °C for 24 h in a sealed Schlenk tube resulted in a yellow solid (1.18 g, 76 %). ¹⁹F NMR (CDCl₃) δ -80.97 (t, 3F), -113.7 (m, 2F), -124.1 (m, 2F), -125.96 (t, 2F). ¹H NMR (CDCl₃) δ 1.43 (d (*J* = 6.6Hz), 6H), 2.11 (bm, 2H), 2.33 (bm, 2H), 3.27 (s, 6H), 3.81 (m, 2H), 3.9 (sep (*J* = 6.6Hz), 1H). Elemental analysis calc. for C₁₂H₁₉F₉IN (475.04 g mol⁻¹) **C** 30.31, **H** 4.03, **N** 2.95 Found **C** 30.54, **H** 3.87, **N** 3.29 %.

6.5.4. Synthesis of dimethylbutyl-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl ammonium iodide.

Following procedure 2.1.6.1 dimethylbutylamine (0.33 g, 3.3 mmol) 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroheptyl iodide (0.64 ml, 3 mmol) in acetonitrile (30ml) was stirred at 150 °C for 24 h in a sealed Schlenk tube resulted in a yellow solid (1.23 g, 77 %). ¹⁹F NMR (CDCl₃) δ -80.9 (t, 3F), -113.8 (m, 2F), -124.15 (m, 2F), -125.94 (t, 2F). ¹H NMR (CDCl₃) δ 0.96 (t, 3H), 1.41 (sextet, 2H), 1.69 (m, 2H), 2.07 (m, 2H), 2.28 (m, 2H), 3.38 (s, 6H), 3.5 (m, 2H), 3.82 (m, 2H). Elemental analysis calc. for C₁₃H₂₁F₉IN (489.06 g mol⁻¹) **C** 31.90, **H** 4.33, **N** 2.86 Found **C** 32.31, **H** 4.38, **N** 3.13 %.

6.5.5. Attempted preparation of dimethylbutyl-1*H*,1*H*,2*H*,2*H*-perfluorooctyl ammonium iodide.

Equimolar quantities of *N,N*-dimethylbutylamine (2.023 g, 20 mmol), 1*H*,1*H*,2*H*,2*H*-perfluorooctyl iodide (9.48 g, 20 mmol) were mixed neat in a sealed Schlenk tube and stirred at 90 °C for 24h to give a brownish-white solid, N₁₁₄HI (yield 3.694 g, 80 %), mp 120.7 °C. ¹H NMR (CDCl₃) δ 0.91 (t, 3H,

CH_3), 1.37 (sextet, 2H, CH_2CH_3), 1.8 (m, 2H, NCH_2CH_2), 2.8 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.07 (m, 2H, NCH_2). Elemental analysis calc for $\text{C}_{14}\text{H}_{19}\text{F}_{13}\text{IN}$ ($575.03 \text{ g mol}^{-1}$) **C** 29.22 **H** 3.33, **N** 2.44, actual product $\text{C}_6\text{H}_{16}\text{IN}$ ($229.03 \text{ g mol}^{-1}$) **C** 31.44 **H** 7.04, **N** 6.11, Found **C** 31.95, **H** 6.10, **N** 5.01 %.

6.5.6. Attempted preparation of dimethylbutyl-1*H*,1*H*,2*H*,2*H*-perfluoro decylammonium iodide.

Same as above procedure *N,N*-dimethylbutylamine (2.023 g, 20 mmol) and 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide (11.47 g, 20 mmol) were mixed neat in a Schlenk tube which was sealed and stirred at 90 °C for 24 h resulting in a beige solid, N_{114}HI (yield 0.55 g, 12 %). ^1H NMR (CDCl_3) δ 1.0 (t, 3H, CH_3), 1.46 (sextet, 2H, CH_2CH_3), 1.89 (m, 2H, NCH_2CH_2), 2.81 (s, 6H, $\text{N}(\text{CH}_3)_2$), 3.06 (m, 2H, NCH_2). Elemental analysis calc for $\text{C}_{16}\text{H}_{19}\text{F}_{17}\text{IN}$ ($675.03 \text{ g mol}^{-1}$) **C** 28.44, **H** 2.84, **N** 2.07 % actual product $\text{C}_6\text{H}_{16}\text{IN}$ ($229.03 \text{ g mol}^{-1}$) **C** 31.44, **H** 7.04, **N** 6.11 Found **C** 30.63, **H** 5.16, **N** 4.31 %.

6.5.7. Attempted preparation of tributyl-1*H*,1*H*,2*H*,2*H*-perfluorodecyl ammonium iodide.

Tri-*n*-butylamine (0.79 ml, 3.3 mmol) was added to 1*H*,1*H*,2*H*,2*H*-perfluorodecyl iodide (1.89 g, 3.3 mmol) in 30ml acetonitrile and heated at 150 °C for 24 h in a sealed Schlenk tube. The solvent was removed under vacuum resulting in a beige solid, N_{444}HI (0.9 g, 87 %). ^1H NMR (CDCl_3) δ 0.92(t, 9H, 3 CH_3), 1.34 (m, 6H, 3 CH_2CH_3), 1.77 (m, 6H, 3 NCH_2CH_2), 2.97 (m, 6H, $\text{N}(\text{CH}_3)_2$). Elemental analysis calc. for $\text{C}_{22}\text{H}_{31}\text{F}_{17}\text{IN}$ ($759.12 \text{ g mol}^{-1}$) **C** 34.78, **H** 4.12, **N** 1.84, actual product $\text{C}_{12}\text{H}_{28}\text{IN}$ ($313.13 \text{ g mol}^{-1}$) **C** 45.99, **H** 9.01, **N** 4.47 Found **C** 46.0, **H** 9.3, **N** 4.44 %.

6.5.8. Attempted preparation of dimethylbutyl-1,1,1-trifluoro-3-butane ammonium iodide.

A neat reaction was performed using equimolar quantities of *N,N*-dimethylbutylamine (1.019 g, 10 mmol), 3-iodo-1,1,1-trifluoro butane (2.379 g, 10 mmol) in a sealed Schlenk tube at 90 °C for 24 h, a white solid, N₁₁₄H₁I (1.88 g, 82 %), was isolated and washed with hexane. ¹H NMR (CDCl₃) δ 0.91 (t, 3H, CH₃), 1.37 (m, 2H, CH₂CH₃), 1.81 (m, 2H, CH₂), 2.78 (s, 6H, N(CH₃)₂), 3.06 (m, 2H, NCH₂). Elemental analysis calc for C₁₀H₂₁F₃NI (339.07 g mol⁻¹) C 35.39, H 6.24, N 4.13, actual product C 31.44, H 7.04, N 6.11 Found C 31.86, H 7.14, N 6.02 %.

6.6. Synthesis of completely asymmetric fluorinated quaternary ammonium salt.

6.6.1. Preparation of asymmetric amine with fluorinated chain, N₁₄C₁₁H₆F₁₇.

MeBuNH (3.63 ml, 30.73 mmol) was added dropwise to a mixture of C₁₁H₆F₁₇I (4.015 g, 6.83 mmol) and pyridine (6.6 ml) the reaction mixture was stirred at 80 °C for 4h. After working up with ~ 10 ml NaOH (10 %) solution and drying with MgSO₄ a clear yellow oily liquid was isolated (1.71 g, 10 % yield). ¹H NMR (CDCl₃) δ 0.84 (t, 3H, CH₃), 1.25 (m, 2H, CH₂), 1.36 (m, 2H, CH₂), 1.68 (m, 2H, CH₂), 2.03 (bm, 2H, CH₂), 2.12 (s, 3H, CH₃), 2.24 (t, 2H, NCH₂), 2.31 (t, 2H, NCH₂). ¹⁹F NMR (CDCl₃) δ - 80.75 (t, 3F, CF₃), -114.14 (bm, 2F, CF₂), -121.7 (bm, 2F, CF₂), -121.92 (bm, 4F, 2CF₂), -122.7 (bm, 2F, CF₂), -123.4 (bm, 2F, CF₂), -126.1 (bm, 2F, CF₂). Elemental analysis calc. for C₁₆H₁₈F₁₇N (547.12 g mol⁻¹) C 35.09, H 3.32, N 2.56 Found C 35.71, H 3.08, N 2.98 %.

6.6.2. Quaternisation of N₁₄C₁₁H₆F₁₇ with 1-iodooctane.

A neat reaction was performed using equimolar quantities of N₁₄C₁₁H₆F₁₇ (1.64 g, 3 mmol) and 1-iodooctane (0.54 ml, 3 mmol) in a sealed Schlenk tube at 90 °C for 24 h. A yellow solid was isolated and washed with hexane (0.5g, 20 %).

^1H NMR (CDCl_3) δ 0.81 (t, 3H, CH_3), 0.96 (t, 3H, CH_3), 1.2-1.4 (bs, 12H, $(\text{CH}_2)_6$), 1.64 (bm, 4H, NCH_2), 2.05 (bm, 2H, Rf-CH_2), 2.30 (bm, 2H, RfCH_2CH_2), 3.31 (s, 3H, CH_3), 3.38 (bm, 4H, NCH_2), 3.76 (m, 2H, NCH_2). ^{19}F NMR (CDCl_3) δ -80.74 (t, 3F, CF_3), -113.48 (bm, 2F, CF_2), -121.6 (bm, 2F, CF_2), -121.94 (bm, 4F, 2CF_2), -122.7 (bm, 2F, CF_2), -123.09 (bm, 2F, CF_2), -126.14 (bm, 2F, CF_2). Elemental analysis calc for $\text{C}_{24}\text{H}_{35}\text{F}_{17}\text{IN}$ (787.15 g mol^{-1}) **C** 36.59, **H** 4.48, **N** 1.78 Found **C** 38.13, **H** 4.70, **N** 1.86 %.

6.7. Synthesis of asymmetric quaternary ammonium salts of bis(trifluoromethanesulfonyl)imide anion.

6.7.1. Dimethylethylloctylammoniumbis(trifluoromethanesulfonyl)imide ($\text{N}_{1128}\text{TFSI}$).

In a 100ml conical flask was placed dimethylethylloctylammonium iodide (6.25 g, 19.95 mmol), lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) (5.727 g, 19.95 mmol) in DCM (25 ml) and deionised water (25 ml); these were stirred at room temperature overnight. The DCM layer was separated from the aqueous layer and washed with deionised water (5x10 ml). The DCM layer was passed through a column of (from top to bottom): activated carbon (15 cm), silica (2cm) and celite (2 cm) and washed through with DCM (200 ml). The resulting solution was dried over MgSO_4 , filtered and the solvent removed *in vacuo* to produce a clear yellow oil (yield 5.25 g, 56 %). ^1H NMR (CDCl_3) δ 3.3 (q ($J = 7.36$ Hz), 2H, NCH_2CH_3), 3.14 (m, 2H, NCH_2), 2.96 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.61 (bm, 2H, NCH_2CH_2), 1.30–1.19 (bm, 13H, $(\text{CH}_2)_5$ and CH_3), 0.81 (t, 3H, CH_3), ^{19}F NMR (CDCl_3) δ -78.91 (s, CF_3). Elemental analysis calc. for $\text{C}_{14}\text{H}_{28}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ (466.14 g mol^{-1}) **C** 36.04, **H** 6.05, **N** 6.01 Found **C** 36.04, **H** 6.34, **N** 6.15 %.

6.7.2. Dimethylethyldecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₂₍₁₀₎TFSI).

Procedure as for 6.7.1

The reaction of dimethylethyldecylammoniumiodide (10.40 g, 30.48 mmol), lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) (8.75 g, 30.48 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a yellow oil (yield 13.3 g, 88 %). ¹H NMR (CDCl₃) δ 3.31 (q (*J* = 7.36 Hz), 2H, NCH₂CH₃), 3.14 (m, 2H, NCH₂), 2.97 (s, 6H, N(CH₃)₂), 1.62 (bm, 2H, NCH₂CH₂), 1.32–1.19 (bm, 17H, (CH₂)₇ and CH₃), 0.81 (t, 3H, CH₃), ¹⁹F NMR (CDCl₃) δ -78.99 (s, CF₃). Elemental analysis calc. for C₁₆H₃₂F₆N₂O₄S₂ (494.17 g mol⁻¹) **C** 38.85, **H** 6.53, **N** 5.67 Found **C** 38.90, **H** 6.94, **N** 5.53 %.

6.7.3. Dimethylethyltetradecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₂₍₁₄₎TFSI).

Procedure as for 6.7.1

The reaction of dimethylethyltetradecylammonium bromide (10 g, 25.17 mmol), lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) (7.22 g, 25 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a white solid (yield 6.8 g, 49 %), mp 41.2 °C. ¹H NMR (CDCl₃) δ 3.31 (q (*J* = 7.36 Hz), 2H, NCH₂CH₃), 3.13 (m, 2H, NCH₂), 2.96 (s, 6H, N(CH₃)₂), 1.6 (bm, 2H, NCH₂CH₂), 1.18–1.3 (bm, 25H, (CH₂)₁₁ + CH₃), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.9 (s, CF₃). Elemental analysis calc. for C₂₀H₄₀F₆N₂O₄S₂ (550.23 g mol⁻¹) **C** 43.62, **H** 7.33, **N** 5.09 Found **C** 43.67, **H** 7.75, **N** 4.98 %.

6.7.4. Dimethylethyl octadecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₂₍₁₈₎TFSI).

Procedure as for 6.7.1

The reaction of dimethylethyloctadecylammonium bromide (10 g, 24.6 mmol), lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) (7.06 g, 24.6 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a white solid (yield 5.0 g, 33 %), mp 65.0 °C. ^1H NMR (CDCl_3) δ 3.32 (q ($J=7.36$ Hz), 2H, NCH_2CH_3), 3.14 (m, 2H, NCH_2), 2.98 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (bm, 2H, NCH_2CH_2), 1.31–1.18 (bm, 33H, $(\text{CH}_2)_{15} + \text{CH}_3$), 0.80 (t, 3H, CH_3), ^{19}F NMR (CDCl_3) δ -78.99 (s, CF_3). Elemental analysis calc. for $\text{C}_{24}\text{H}_{48}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ (606.30 g mol^{-1}) **C** 47.50, **H** 7.98, **N** 4.62 Found **C** 48.04, **H** 8.46, **N** 4.43 %.

6.7.5. Dimethylisopropyloctylammonium bis(trifluoromethanesulfonyl)imide ($\text{N}_{1138}\text{TFSI}$).

Procedure as for 6.7.1

The reaction of dimethylisopropyloctylammonium iodide (9.67 g, 29.55 mmol), lithiumbis(trifluoromethanesulfonyl)imide (LiTFSI) (8.483 g, 29.55 mmol) in DCM (25 ml) and deionised water (25 ml); resulted in a clear oil (yield 10.06 g, 71 %). ^1H NMR (CDCl_3) δ 3.65 (sep ($J = 6.6\text{Hz}$), 1H, $\text{NCH}(\text{CH}_3)_2$), 3.14 (m, 2H, NCH_2CH_2), 2.91 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.65 (bm, 2H, NCH_2CH_2), 1.33 (d ($J = 6.6\text{Hz}$), 6H, $\text{CH}(\text{CH}_3)_2$), 1.27 (bm, 4H, 2CH_2), 1.2 (bs, 6H, $(\text{CH}_2)_3$), 0.81 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.91 (s, CF_3). Elemental analysis calc. for $\text{C}_{15}\text{H}_{30}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ (480.15 g mol^{-1}) **C** 37.49, **H** 6.30, **N** 5.83 Found **C** 37.54, **H** 6.22, **N** 5.85 %.

6.7.6. Dimethylisopropyldecylammonium bistrifluoromethanesulfonyl imide ($\text{N}_{113(10)}\text{TFSI}$).

Procedure as for 6.7.1.

The reaction of dimethylisopropyldecylammonium iodide (10.0 g, 28.1 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (8.06 g, 28.1 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear oil (yield 3.95 g, 28 %). ^1H

NMR (CDCl₃) δ 3.66 (sep (J = 6.6Hz), 1H, NCH(CH₃)₂), 3.15 (m, 2H, NCH₂CH₂), 2.92 (s, 6H, N(CH₃)₂), 1.65 (bm, 2H, CH₂), 1.34 (d (J = 6.6Hz), 6H, CH(CH₃)₂), 1.28 (bs, 4H, 2CH₂), 1.19 (bm, 10H, (CH₂)₅), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.88 (s, CF₃). Elemental analysis calc. for C₁₇H₃₄F₆N₂O₄S₂ (508.19 g mol⁻¹) **C** 40.14, **H** 6.74, **N** 5.51 Found **C** 39.80, **H** 6.87, **N** 5.24 %.

6.7.7. Dimethylisopropyltetradecylammonium bis(trifluoromethanesulfonyl)imide (N₁₁₃₍₁₄₎TFSI).

Procedure as for 6.7.1.

The reaction of dimethylisopropyltetradecylammonium bromide (2.0 g, 5.5 mmol), lithiumbis(trifluoromethanesulfonyl)imide (1.579 g, 5.5 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear liquid which solidified on cooling (yield 1.1 g, 36 %), mp 35 °C. ¹H NMR (CDCl₃) δ 3.65 (sep (J = 6.6Hz), 1H, NCH(CH₃)₂), 3.15 (m, 2H, NCH₂CH₂), 2.9 (s, 6H, N(CH₃)₂), 1.65 (m, 2H, NCH₂CH₂), 1.18 – 1.27 (bm, 22H, (CH₂)₁₁), 1.34 (d (J = 6.6Hz), 6H, CH(CH₃)₂), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.88 (s, CF₃). Elemental analysis calc. for C₂₁H₄₂F₆N₂O₄S₂ (564.25 g mol⁻¹) **C** 44.66, **H** 7.50, **N** 4.96 Found **C** 46.21, **H** 8.00, **N** 4.13 %.

6.7.8. Dimethylisopropyloctadecylammonium bis(trifluoromethanesulfonyl)imide (N₁₁₃₍₁₈₎TFSI).

Procedure as for 6.7.1.

The reaction of dimethylisopropyloctadecylammonium bromide (1.99 g, 4.75 mmol) and lithium bis(trifluoromethanesulfonyl)imide (1.36 g, 4.75 mmol) in DCM (25 ml) and deionised water (25ml) resulted in a white solid (yield 1.12 g, 38 %) mp 57 °C. ¹H NMR (CDCl₃) δ 3.61 (sep (J = 6.6Hz), 1H, NCH(CH₃)₂), 3.15 (m, 2H, NCH₂CH₂), 2.9 (s, 6H, N(CH₃)₂), 1.65 (bs, 2H, NCH₂CH₂), 1.35 (d (J = 6.6Hz), 6H, CH(CH₃)₂), 1.18 – 1.28 (bm, 30H, (CH₂)₁₅), 0.81 (t, 3H, CH₃). ¹⁹F

NMR (CDCl₃) δ -78.88 (s, CF₃). Elemental analysis calc. for C₂₅H₅₀F₆N₂O₄S₂ (620.31 g mol⁻¹) **C** 48.36, **H** 8.12, **N** 4.52 Found **C** 51.11, **H** 8.84, **N** 3.77 %.

6.7.9. Dimethylbutyloctylammoniumbis(trifluoromethanesulfonyl)imide (N₁₁₄₈TFSI).

Procedure as for 6.7.1.

The reaction of dimethylbutyloctylammonium iodide (6.49 g, 19.05 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (5.46 g, 19.05 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear liquid (yield 4.3 g, 46 %). ¹H NMR (CDCl₃) δ 3.24 (bm, 4H, 2NCH₂), 3.06 (bs, 6H, N(CH₃)₂), 1.63 (b, 4H, 2NCH₂CH₂), 1.2 – 1.35 (bm, 12H, (CH₂)₆), 0.93 (t, 3H, CH₃), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.9 (s, CF₃). Elemental analysis calc. for C₁₆H₃₂F₆N₂O₄S₂ (494.17 g mol⁻¹) **C** 38.85, **H** 6.53, **N** 5.67 Found **C** 38.73, **H** 6.69, **N** 6.17 %.

6.7.10. Dimethylbutyldecylammoniumbis(trifluoromethanesulfonyl)imide (N₁₁₄₍₁₀₎TFSI).

Procedure as for 6.7.1.

The reaction of dimethylbutyldecylammonium iodide (10.44 g, 28.27 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (8.115 g, 28.27 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear liquid (yield 6.17 g, 42 %). ¹H NMR (CDCl₃) δ 3.34 (m, 4H, 2CH₂N), 3.1 (s, 6H, N(CH₃)₂), 1.65 (m, 4H, 2NCH₂CH₂), 1.19 – 1.37 (bm, 16H, (CH₂)₈), 0.94 (t, 3H, CH₃), 0.81(t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.97 (s, CF₃). Elemental analysis calc. for C₁₈H₃₆F₆N₂O₄S₂ (522.20 g mol⁻¹) **C** 41.36, **H** 6.95, **N** 5.36 Found **C** 41.19, **H** 7.38, **N** 5.23 %.

6.7.11. Dimethylbutyltetradecylammonium bis(trifluoroethylsulfonyl)imide (N₁₁₄₍₁₄₎TFSI).

Procedure as for 6.7.1.

The reaction of dimethylbutyltetradecylammonium bromide (4.77 g, 12.04 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (3.456 g, 12.04 mmol) in DCM (25ml) and deionised water (25 ml) resulted in a clear liquid (yield 2.3 g, 33 %). ^1H NMR (CDCl_3) δ 3.1 (m, 4H, $2\text{CH}_2\text{N}$), 3.0 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 1.18–1.3 (bm, 24H, $(\text{CH}_2)_{12}$), 0.93 (t, 3H, CH_3), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.89 (s, CF_3). Elemental analysis calc. for $\text{C}_{22}\text{H}_{44}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ ($578.26 \text{ g mol}^{-1}$) **C** 45.65, **H** 7.67, **N** 4.84 Found **C** 45.71, **H** 8.00, **N** 4.76 %.

6.7.12.

Dimethylbutyloctadecylammoniumbis(trifluoromethanesulfonyl)imide ($\text{N}_{114(18)}\text{TFSI}$).

Procedure as for 6.7.1.

The reaction of dimethylbutyloctadecylammonium bromide (2.08 g, 4.6 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.32 g, 4.6 mmol) in DCM (25 ml) and deionised water (25 ml); resulted in a clear liquid which crystallised on standing (yield 0.5 g, 17 %). ^1H NMR (CDCl_3) δ 3.16 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 3.0 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.61 (m, 4H, NCH_2CH_2), 1.18 – 1.34 (bm, 32H, $(\text{CH}_2)_{16}$), 0.93 (t, 3H, CH_3), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.9 (s, CF_3). Elemental analysis calc. for $\text{C}_{26}\text{H}_{52}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ ($634.33 \text{ g mol}^{-1}$) **C** 49.19, **H** 8.26, **N** 4.42 Found **C** 48.21, **H** 8.29, **N** 4.18 %.

6.7.13. Dimethylhexyloctylammoniumbis(trifluoromethanesulfonyl)imide

($\text{N}_{1168}\text{TFSI}$).

Procedure as for 6.7.1.

The reaction of dimethylhexyloctylammonium iodide (11.99 g, 32.5 mmol) with lithiumbis(trifluoromethanesulfonyl)imide (9.3 g, 32.5 mmol) in DCM (25ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 10.5 g, 62 %). ^1H NMR (CDCl_3) δ 3.15 (m, 4H, 2NCH_2), 2.98 (s, 6H, $\text{N}(\text{CH}_3)_2$),

1.61 (bm, 4H, 2NCH₂CH₂), 1.2 – 1.26 (bm, 16H, (CH₂)₈), 0.82 (m, 6H, 2CH₃). ¹⁹F NMR (CDCl₃) δ -78.9 (s, CF₃). Elemental analysis calc. for C₁₈H₃₆F₆N₂O₄S₂ (522.20 g mol⁻¹) **C** 41.36, **H** 6.95, **N** 5.36 Found **C** 41.25, **H** 7.18, **N** 5.39 %.

6.7.14. Dimethylhexyldecylammoniumbis(trifluoromethanesulfonyl)imide (N₁₁₆₍₁₀₎TFSI).

Procedure as for 6.7.1.

The exchange reaction between dimethylhexyldecylammonium iodide (7.11 g, 17.9 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (5.13 g, 17.9 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 5.75 g, 58 %). ¹H NMR (CDCl₃) δ 3.17 (m, 4H, 2 NCH₂), 3.0 (s, 6H, N(CH₃)₂), 1.61 (bm, 4H, 2NCH₂CH₂), 1.19–1.26 (bm, 20H, (CH₂)₁₀), 0.80 (q, 6H, 2CH₃). ¹⁹F NMR (CDCl₃) δ -78.94 (s, CF₃). Elemental analysis calc. for C₂₀H₄₀F₆N₂O₄S₂ (550.23 g mol⁻¹) **C** 43.62, **H** 7.33, **N** 5.09 Found **C** 43.62, **H** 7.49, **N** 5.27 %.

6.7.15. Trimethyloctylammoniumbis(trifluoromethanesulfonyl)imide.

(N₁₁₈TFSI).

Procedure as for 6.7.1 .

The reaction of trimethyloctylammonium iodide (7.151 g, 23.91 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (6.864 g, 23.91 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 5.18 g, 48 %). ¹H NMR (CDCl₃) δ 3.2 (m, 2H, NCH₂), 3.04 (s, 9H, N(CH₃)₃), 1.65 (m, 2H, NCH₂CH₂), 1.2 (bm, 10H, (CH₂)₅), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.9 (s, CF₃). Elemental analysis calc. for C₁₃H₂₆F₆N₂O₄S₂ (452.12 g mol⁻¹) **C** 34.5, **H** 5.80, **N** 6.19 Found **C** 34.78, **H** 5.72, **N** 6.34 %.

6.7.16. Trimethyldecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₁₍₁₀₎TFSI).

Procedure as for 6.7.1.

The reaction of trimethyldecylammonium iodide (7.239 g, 22.13 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (6.352 g, 22.13 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 5.56 g, 52 %). ¹H NMR (CDCl₃) δ 3.2 (m, 2H, NCH₂), 3.06 (s, 9H, N(CH₃)₃), 1.66 (m, 2H, NCH₂), 1.19 (bm, 14H, (CH₂)₇), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -79.08 (s, CF₃). Elemental analysis calc for C₁₅H₃₀F₆N₂O₄S₂ (480.15 g mol⁻¹) **C** 37.49, **H** 6.30, **N** 5.83 Found **C** 37.73, **H** 6.31, **N** 6.06 %.

6.7.17. Trimethyltetradecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₁₍₁₄₎TFSI).

Procedure as for 6.7.1

The reaction of trimethyltetradecylammonium bromide (1.98 g, 5.9 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.69 g, 5.9 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid which solidified on cooling (yield 0.34 g, 11 %), mp 55.5 °C. ¹H NMR (CDCl₃) δ 3.21 (m, 2H, NCH₂), 3.07 (s, 9H, N(CH₃)₃), 1.67 (m, 2H, NCH₂), 1.18 (bm, 22H (CH₂)₁₁), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.9 (s, CF₃). Elemental analysis calc. for C₁₉H₃₈F₆N₂O₄S₂ (536.22 g mol⁻¹) **C** 42.52, **H** 7.14, **N** 5.22 Found **C** 42.83, **H** 7.27, **N** 5.12 %.

6.7.18. Trimethyloctadecylammoniumbis(trifluoromethanesulfonyl)imide
(N₁₁₁₍₁₈₎TFSI).

Procedure as for 6.7.1.

The reaction of trimethyloctadecyl ammonium bromide (1.765 g, 4.5 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.29 g, 4.5 mmol) in DCM (25

ml) and deionised water (25 ml); resulted in a clear non-viscous liquid which solidified on cooling (yield 0.016 g, 0.6 %), mp 58.3 °C. ^1H NMR (CDCl_3) δ 3.2 (m, 2H, NCH_2), 3.11 (s, 9H, $\text{N}(\text{CH}_3)_3$), 1.68 (m, 2H, NCH_2CH_2), 1.18–1.27 (bm, 30H, $(\text{CH}_2)_{15}$), 0.81 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.9 (s, CF_3). Elemental analysis calc. for $\text{C}_{23}\text{H}_{46}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ (592.28 g mol^{-1}) **C** 46.60, **H** 7.83, **N** 4.73 Found **C** 49.68, **H** 8.39, **N** 3.93%.

6.7.19. Methylbutyloctyltetradecylammoniumbistrifluoromethane

sulfonylimide ($\text{N}_{148(14)}\text{TFSI}$).

Procedure as for 6.7.1.

The reaction of methylbutyloctyltetradecylammonium iodide (1.99 g, 3.82 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.096 g, 3.82 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear liquid (yield 1.15g, 45 %). ^1H NMR (CDCl_3) δ 3.1 (m, 6H, 3NCH_2), 2.92 (s, 3H, NCH_3), 1.57 (bm, 6H, $3\text{NCH}_2\text{CH}_2$), 1.18–1.27 (bm, 34H, $(\text{CH}_2)_{14}$), 0.92 (t, 3H, CH_3), 0.80 (t, 6H, 2CH_3). ^{19}F NMR -78.9 (s, CF_3). Elemental analysis calc. for $\text{C}_{29}\text{H}_{58}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ (676.37 g mol^{-1}) **C** 51.45, **H** 8.64, **N** 4.14 Found **C** 51.12, **H** 8.60, **N** 4.68 %.

6.7.20. Dimethylbenzyloctylammoniumbis(trifluoromethanesulfonyl)imide ($\text{N}_{11\text{B}8}\text{TFSI} \cdot \text{H}_2\text{O}$).

Procedure as for 6.7.1 .

The reaction of dimethylbenzyloctylammonium iodide (3.75 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 2.88 g, 53 %). ^1H NMR (CDCl_3) δ 7.38 - 7.43 (bm, 5H, Ar), 4.35 (s, 2H, NCH_2Ar) 3.17 (m, 2H, NCH_2), 2.9 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.7 (bm, 2H, CH_2), 1.23 (bm, 10H, $(\text{CH}_2)_5$), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.87 (s, CF_3). Elemental analysis calc. for

$C_{19}H_{32}F_6N_2O_5S_2$ (546.17 $gmol^{-1}$) **C** 41.75, **H** 5.90, **N** 5.13 Found **C** 41.90, **H** 5.66, **N** 5.11 %.

6.7.21. Dimethylbenzyldecylammoniumbis(trifluoromethanesulfonyl)imide ($N_{11B(10)}$ TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylbenzyldecylammonium iodide (4.03 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 2.32 g, 42%). 1H NMR ($CDCl_3$) δ 7.38–7.42 (bm, 5H, Ar), 4.34 (s, 2H, NCH_2Ar) 3.17 (m, 2H, NCH_2), 2.9 (s, 6H, $N(CH_3)_2$), 1.7 (bm, 2H, CH_2), 1.18–1.26 (bm, 14H, $(CH_2)_7$), 0.80 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -78.8 (s, CF_3). Elemental analysis calc. for $C_{21}H_{34}F_6N_2O_4S_2$ (556.19 $gmol^{-1}$) **C** 45.31, **H** 6.16, **N** 5.04 Found **C** 45.51, **H** 6.54, **N** 5.02 %.

6.7.22. Dimethylbenzyltetradecylammoniumbis(trifluoromethanesulfonyl)imide ($N_{11B(14)}$ TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylbenzyltetradecylammonium bromide (4.30 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear non-viscous liquid (yield 2.342 g, 38 %). 1H NMR ($CDCl_3$) δ 7.38-7.43 (bm, 5H, Ar), 4.34 (s, 2H, NCH_2Ar) 3.17 (m, 2H, NCH_2), 2.92 (s, 6H, $N(CH_3)_2$), 1.72 (bm, 2H, CH_2), 1.18–1.26 (bm, 22H, $(CH_2)_{11}$), 0.80 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -78.86 (s, CF_3). Elemental analysis calc. for $C_{25}H_{42}F_6N_2O_4S_2$ (612.25 $gmol^{-1}$) **C** 49.00, **H** 6.91, **N** 4.57 Found **C** 49.14, **H** 7.73, **N** 4.60 %.

6.7.23. Dimethylbenzyloctadecylammoniumbis(trifluoromethanesulfonyl)imide (N_{11B(18)}TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylbenzyloctadecylammonium bromide (4.86 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a white solid (yield 4.523 g, 68 %). ¹H NMR (CDCl₃) δ 7.38 (m, 5H, Ar), 4.35 (s, 2H, NCH₂Ar), 3.16 (m, 2H, NCH₂), 2.92 (s, 6H, N(CH₃)₂), 1.71 (bm, 2H, NCH₂CH₂), 1.18-1.26 (bm, 30H, (CH₂)₁₅), 0.78 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.86 (s, CF₃). Elemental analysis calc. for C₂₉H₅₀F₆N₂O₄S₂ (668.31 g mol⁻¹) **C** 52.07, **H** 7.54, **N** 4.19 Found **C** 52.26, **H** 7.56, **N** 4.24 %.

6.7.24. Dimethylallyloctylammoniumbis(trifluoromethanesulfonyl)imide (N_{11A8}TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylallyloctylammonium iodide (1.95 g, 6 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.722 g, 6 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in non-viscous liquid (yield 1.2 g, 42 %). ¹H NMR (CDCl₃) δ 5.84 (m, 1H, CH=CH₂), 5.64-5.69 (m, 2H, CH=CH₂), 3.8 (d, 2H, NCH₂CH), 3.14 (m, 2H, NCH₂CH₂), 2.95 (s, 6H, N(CH₃)₂), 1.65 (m, 2H, NCH₂CH₂), 1.19-1.2 (bm, 10H, (CH₂)₅), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.99 (s, CF₃). Elemental analysis calc. for C₁₅H₂₈F₆N₂O₄S₂ (478.14 g mol⁻¹) **C** 37.65, **H** 5.90, **N** 5.86 % Found **C** 38.18, **H** 6.45, **N** 6.42 %.

6.7.25. Dimethylallyldecylammoniumbis(trifluoromethanesulfonyl)imide (N_{11A(10)}TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylallyldecylammonium iodide (2.330 g, 6.6 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.894 g, 6.6 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in non-viscous liquid (yield 1.35 g, 40%). ^1H NMR (CDCl_3) δ 5.84 (m, 1H, $\text{CH}=\text{CH}_2$), 5.65-5.68 (m, 2H, $\text{CH}=\text{CH}_2$), 3.82 (d, 2H, NCH_2CH), 3.14 (m, 2H, NCH_2CH_2), 2.96 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.65 (m, 2H, NCH_2CH_2), 1.19-1.26 (bm, 14H, $(\text{CH}_2)_7$), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.96 (s, CF_3). Elemental analysis calc. for $\text{C}_{17}\text{H}_{32}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ ($506.17 \text{ g mol}^{-1}$) **C** 40.30, **H** 6.37, **N** 5.53 Found **C** 41.42, **H** 7.25, **N** 5.65 %.

6.7.26.

Dimethylallyltetradecylammoniumbis(trifluoromethanesulfonyl)imide ($\text{N}_{11\text{A}(14)}\text{TFSI}$).

Procedure as for 6.7.1 .

The reaction of dimethylallyltetradecylammonium bromide (2.173 g, 6 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.722 g, 6 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a non-viscous liquid (yield 1.3 g, 39 %). ^1H NMR (CDCl_3) δ 5.84 (m, 1H, $\text{CH}=\text{CH}_2$), 5.69 (m, 2H, $\text{CH}=\text{CH}_2$), 3.81 (d, 2H, NCH_2CH), 3.14 (m, 2H, NCH_2CH_2), 2.96 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.65 (m, 2H, NCH_2CH_2), 1.18–1.26 (bm, 22H, $(\text{CH}_2)_{11}$), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.96 (s, CF_3). Elemental analysis calc. for $\text{C}_{21}\text{H}_{40}\text{F}_6\text{N}_2\text{O}_4\text{S}_2$ ($562.23 \text{ g mol}^{-1}$) **C** 44.82, **H** 7.17, **N** 4.98 Found **C** 45.27, **H** 7.60, **N** 5.02 %.

6.7.27. Dimethylallyloctadecylammoniumbis(trifluoromethanesulfonyl)imide ($\text{N}_{11\text{A}(18)}\text{TFSI}$).

Procedure as for 6.7.1 .

The reaction of dimethylallyloctadecylammonium bromide (2.509 g, 6 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (1.722 g, 6 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a white solid (yield 1.4 g, 39 %). ^1H

NMR (CDCl₃) δ 5.84 (m, 1H, CH=CH₂), 5.69 (m, 2H, CH=CH₂) 3.83 (d (J = 7.3Hz), 2H, NCH₂CH=CH₂), 3.15 (m, 2H, NCH₂), 2.99 (s, 6H, N(CH₃)₂), 1.66 (m, 2H, NCH₂CH₂), 1.18–1.28 (bm, 30H, (CH₂)₁₅), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.87 (s, CF₃). Elemental analysis calc. for C₂₅H₄₈F₆N₂O₄S₂ (618.30 g mol⁻¹) **C** 48.52, **H** 7.82, **N** 4.53 Found **C** 49.30, **H** 8.16, **N** 4.51 %.

6.7.28. Dimethylcyclohexyloctylammoniumbistri(fluoromethanesulfonyl)imide (N_{11C8}TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylcyclohexyloctylammonium iodide (3.672g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a liquid (yield 2.512 g, 48 %). ¹H NMR (CDCl₃) δ 3.17 (m, 3H, NCH₂+ Cy), 2.93 (s, 6H, N(CH₃)₂), 2.07 (bm, 2H, Cy), 1.94 (bm, 2H, Cy), 1.64 (bm, 3H, NCH₂CH₂+ Cy), 1.11–1.39 (bm, 15H, (CH₂)₅+ Cy), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.85 (s, CF₃). Elemental analysis calc. for C₁₈H₃₄F₆N₂O₄S₂ (520.19 g mol⁻¹) **C** 41.52, **H** 6.59, **N** 5.38 Found **C** 41.59, **H** 7.41, **N** 5.45 %.

6.7.29.

Dimethylcyclohexyldecylammoniumbis(trifluoromethanesulfonyl)imide (N_{11C(10)}TFSI).

Procedure as for 6.7.1 .

The reaction of dimethylcyclohexyldecylammonium iodide (3.952 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a liquid (yield 3.22 g, 59 %). ¹H NMR (CDCl₃) δ 3.17 (m, 3H, NCH₂+ Cy), 2.93 (s, 6H, N(CH₃)₂), 2.07 (bm, 2H, Cy), 1.94 (bm, 2H, Cy), 1.64 (bm, 3H, NCH₂CH₂+ Cy), 1.11-1.39 (bm, 19H, (CH₂)₇+ Cy), 0.80 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.85 (s, CF₃). Elemental analysis

calc. for $C_{20}H_{38}F_6N_2O_4S_2$ ($548.22 \text{ g mol}^{-1}$) **C** 43.78, **H** 6.99, **N** 5.11 Found **C** 44.05, **H** 7.91, **N** 5.60 %.

6.7.30. Dimethylcyclohexyltetradecylammoniumbis(trifluoromethane sulfonyl)imide ($N_{11C(14)}TFSI$).

Procedure as for 6.7.1 .

The reaction of dimethylcyclohexyltetradecylammonium bromide (4.04 g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a liquid (yield 3.02 g, 50 %). 1H NMR ($CDCl_3$) δ 3.15 (m, 3H, NCH_2+ Cy), 2.91 (s, 6H, $N(CH_3)_2$), 2.06 (bm, 2H, Cy), 1.93 (bm, 2H, Cy), 1.62 (bm, 3H, NCH_2CH_2+ Cy), 1.18–1.38 (bm, 27H, $(CH_2)_{11}+$ Cy), 0.80 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -78.89 (s, CF_3). Elemental analysis calc. for $C_{24}H_{46}F_6N_2O_4S_2$ ($604.28 \text{ g mol}^{-1}$) **C** 43.78, **H** 6.99, **N** 5.11 Found **C** 44.05, **H** 7.91, **N** 5.60 %.

6.7.31. Dimethylcyclohexyloctadecylammoniumbis(trifluoromethanesulfonyl)imide ($N_{11C(18)}TFSI$).

Procedure as for 6.7.1 .

The reaction of dimethylcyclohexyloctadecylammonium bromide (4.60g, 10 mmol) and lithiumbis(trifluoromethanesulfonyl)imide (2.87 g, 10 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a liquid (yield 3.4 g, 52 %). 1H NMR ($CDCl_3$) δ 3.15 (m, 3H, NCH_2+ Cy), 2.91 (s, 6H, $N(CH_3)_2$), 2.06 (bm, 2H, Cy), 1.93 (bm, 2H, Cy), 1.62 (bm, 3H, NCH_2CH_2+ Cy), 1.18–1.38 (bm, 35H, $(CH_2)_{15}+$ Cy), 0.80 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -78.89 (s, CF_3). Elemental analysis calc. for $C_{28}H_{54}F_6N_2O_4S_2$ ($660.34 \text{ g mol}^{-1}$) **C** 50.88, **H** 8.24, **N** 4.24 Found **C** 53.59, **H** 9.08, **N** 3.56 %.

6.8. Synthesis of potassium bisperfluoroalkylsulfonylimide and potassium perfluoroalkyl sulfonate salts.

Preliminary attempts to prepare the bis-substituted potassium salt as the procedure reported by K. Sogabe et al have been made, which resulted in the nonafluorobutanesulfonate instead of the bis(nonafluorobutane) sulfonylimide as described in 6.8.1.^[4]

6.8.1. Attempts to prepare Potassiumbis(nonafluorobutylsulfonyl)imide ($C_8F_{18}KNO_4S_2$) from trifluoroacetamide.

Potassium carbonate (10.22 g, 74 mmol), trifluoroacetamide (3.21 g, 28.4 mmol) and sodium dried THF (50 ml) were placed in a 100 ml flame dried three necked round bottomed flask under dry nitrogen and equipped with a septum and a reflux condenser. The solution was heated to reflux for 15 minutes in an oil bath followed by the dropwise addition of 1 equivalent of nonafluorobutylsulfonyl fluoride (5 ml, 8.58 g, 28.4 mmol) over 30 mins by syringe. The reaction was heated for 2 hours followed by the addition of a further equivalent of nonafluorobutylsulfonyl fluoride (5 ml, 8.58 g, 28.4 mmol) and refluxed overnight. The mixture was evaporated to dryness *in vacuo* then acetone (50 ml) was added to dissolve all products and remaining reactants with the exception of potassium fluoride and potassium carbonate which were insoluble. The solids were removed by vacuum filtration. The acetone was removed *in vacuo* and the residual solid was washed with ether (3×30 ml) to remove any remaining non-ionic organic compounds. The solid was recrystallised from boiling methanol to give the product as a white crystalline solid (3.34 g, 38 %). ^{19}F NMR (DMSO- d_6) δ -80.45 (t, 3F, CF_3), -114.9ppm (t, 2F, CCF_2C), -121.4 (m, 2F, CCF_2C), -125.7 (bt, 2F, CCF_2C). Elemental analysis Calculated for $C_8F_{18}KNO_4S_2$ (619.0 g mol $^{-1}$) C 15.51, H 0.00, N 2.26, S 10.33 Found C 13.97, H 0.00, N Trace, S 9.46%. The actual product

was $\text{C}_4\text{F}_9\text{KO}_3\text{S}$ Anal. Calc. for $\text{C}_4\text{F}_9\text{KO}_3\text{S}$ ($388.04 \text{ g mol}^{-1}$) **C** 14.20, **H** 0.00, **N** 0.00, **S** 9.46.

6.8.2. Attempts to prepare potassium bis(perfluorooctylsulfonylimide) from trifluoroacetamide.

Procedure as for 6.8.1

Potassium carbonate (5g, 36mmol), trifluoroacetamide (1.65 g, 14 mmol) and perfluorooctylsulfonyl fluoride ($2 \times 3.88 \text{ ml}$, $2 \times 7.07 \text{ g}$, 28.4 mmol) produced a white crystalline solid (0.75 g, 10 %) ^{19}F NMR (DMSO-d_6) δ -128.1 (bs, 2F, CF_2), -124.3 (bs, 2F, CF_2), -123.4 (bs, 6F, $(\text{CF}_2)_3$), -121.7 (bs, 2F, CF_2), -109 (bs, 2F, CF_2), -83.3 (t, 3F, CF_3). Anal. Calc for $\text{C}_{16}\text{F}_{36}\text{KNO}_4\text{S}_2$ ($1056.97 \text{ g mol}^{-1}$) **C** 18.17, **H** 0.00, **N** 1.32, **S** 6.05.

The major product was potassiumperfluorooctylsulfonate ($\text{C}_8\text{F}_{17}\text{KO}_3\text{S}$), Anal. Calc for $\text{C}_8\text{F}_{17}\text{KO}_3\text{S}$ ($538.03 \text{ g mol}^{-1}$) **C** 17.84, **H** 0.00, **N** 0.00, **S** 5.94 found **C** 17.88, **H** 0.00, **N** 0.32, **S** 5.75 %.

6.8.3. Synthesis of Potassiumbis(nonafluorobutylsulfonyl)imide, NNf_2 ($\text{C}_8\text{F}_{18}\text{KNO}_4\text{S}_2$) from triethylamine.

Ammonium chloride (1.39 g, 25 mmol) was placed in a 250ml round bottomed flask equipped with an efficient magnetic stirrer bar and dried under high vacuum to remove all traces of moisture before MeCN (12.5 ml) and nonafluorosulfonyl fluoride (10 ml, 55 mmol) were added. The resulting two-phase suspension was cooled to -40°C , and triethylamine (17.5 ml, 12.50 mmol) pre-cooled with liquid nitrogen was quickly added to the reaction mixture with vigorous stirring. After gradual warming to ambient temperature, the resulting mixture was heated to 65°C and stirred at this temperature overnight. After cooling to room temperature the bulk of the MeCN was removed under vacuum. The residue was partitioned between DCM (40ml) and deionised water (20ml). The organic layer was thoroughly

washed with deionised water until it showed a negative chloride test with aqueous AgNO_3 . Volatiles were removed in vacuum to give the intermediate $\text{Et}_3\text{NH}^+\text{NNf}_2^-$ as a tawny coloured residue. ^1H NMR (CDCl_3) δ 1.24 (t, 9H, $3\text{CH}_2\text{CH}_3$), 3.1 (q, 6H, $3\text{CH}_2\text{CH}_3$), 7.19 (bs, 1H, NH^+). ^{13}C NMR (CDCl_3) δ 8.4 (CH_2CH_3), 47.0 (CH_2CH_3). ^{19}F NMR (CDCl_3) δ -126.17(4F, 2CF_2), -121.2 (4F, 2CF_2), -113.0 (4F, 2CF_2), -81.05 (6F, 2CF_3). Without further purification, $\text{Et}_3\text{NH}^+\text{NNf}_2^-$ was dissolved in MeOH (5ml) and added dropwise to a solution of KOH (2.79 g, 59 mmol) in water (30 ml) with vigorous stirring. Instantaneous precipitation of the desired KNNf_2 was observed. The reaction mixture was stirred overnight before filtering the precipitate. The crystalline residue was washed thoroughly with cold deionised water until neutral pH, followed by drying on a sinter funnel and washing additionally with CHCl_3 (3x15 ml) to give the salt KNNf_2 (3.3 g, 20 %) as a white crystalline solid, mp 341.7°C (mp^[3] $340\text{--}341^\circ\text{C}$). ^{19}F NMR δ -125.77 (t, 2F, CF_2), -121.07 (s, 2F, CF_2), -113.36 (t, 2F, CF_2), -80.39 (s, 3F, CF_3). Elemental analysis calc. for $\text{C}_8\text{F}_{18}\text{KNO}_4\text{S}_2$ (619.0 g mol^{-1}) C 15.51, N 2.26 Found C 15.51, N 2.45 %.

6.8.4. Synthesis of asymmetric tetraalkylammonium salts of the bisnonafluoromethanesulfonylimide anion.

6.8.5. Dimethylbutyltetradecylammoniumbis(nonafluoromethylsulfonyl)imide, ($\text{N}_{114(14)}\text{NNf}_2$).

Procedure as for 6.7.1 .

The reaction of dimethylbutyltetradecylammonium bromide (1.196 g, 3.02 mmol) and potassium bisnonafluorobutylsulfonylimide, KNNf_2 (1.869 g, 3.02 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a clear liquid which soon solidified. ^1H NMR (CDCl_3) δ 3.86 (m, 4H, $2\text{CH}_2\text{N}$), 2.97 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.59 (bm, 4H, $2\text{CH}_2\text{CH}_2\text{N}$), 1.17–1.24 (bm, 24H, $(\text{CH}_2)_{12}$), 0.90 (t, 3H, CH_3), 0.80 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -80.92 (t, 3F, CF_3), -113.03 (m, 2F,

CF₂), -121.23 (m, 2F, CF₂), -126.08 (m, 2F, CF₂). Elemental analysis calc. for C₂₈H₄₄F₁₈N₂O₄S₂ (878.24 g mol⁻¹) **C** 38.26, **H** 5.05, **N** 3.19 Found **C** 38.62, **H** 5.29, **N** 3.25 %.

6.8.6. Dimethylhexyloctylammoniumbis(nonafluorobutylsulfonyl)imide (N₁₁₆₈NNf₂).

Procedure as 6.7.1.

The reaction of dimethylhexyloctylammonium iodide (0.738 g, 2.02 mmol) and potassium bisnonafluorobutylsulfonylimide, KNNf₂ (1.238 g, 2.5 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a white solid. ¹H NMR (CDCl₃) δ 3.16 (m, 4H, 2NCH₂), 3.0 (s, 6H, N(CH₃)₂), 1.59 (bm, 4H, CH₂CH₂N), 1.18-1.25 (bm, 16H, (CH₂)₈), 0.81 (m, 6H, 2CH₃). ¹⁹F NMR (CDCl₃) δ -80.83 (t, 3F, CF₃), -113.03 (t, 2F, CF₂), -121.18 (m, 2F, CF₂), -126.08 (m, 2F, CF₂).

6.8.7. Synthesis of asymmetric tetraalkylammonium salts of the nonafluorobutylsulfonates, [C₄F₉SO₃]⁻ anion.

6.8.8. Dimethylbutyltetradecylammoniumnonafluorobutylsulfonate (N₁₁₄₍₁₄₎C₄F₉SO₃).

Procedure as for 6.7.1

The reaction of dimethylbutyltetradecylammonium bromide (1.046 g, 2.64 mmol) and potassium nonafluorobutylsulfonate (1.164 g, 3 mmol) in DCM (25 ml) and deionised water (25 ml) results in a clear liquid which crystallised on cooling (yield 0.6 g, 38 %). ¹H NMR (CDCl₃) δ 3.23 (m, 4H, NCH₂), 3.09 (s, 6H, N(CH₃)₂), 1.60 (m, 4H, NCH₂), 1.35–1.18 (bm, 24H, (CH₂)₆), 0.93 (t, 3H, CH₃), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -80.89 (CF₃), -114.76 (CF₂), -121.64 (CF₂), -126.0 (CF₂). Elemental analysis calc. for C₂₄H₄₄F₉NO₃S (597.29 g mol⁻¹) **C** 48.22, **H** 7.42, **N** 2.34 Found **C** 48.48, **H** 7.61, **N** 2.31 %.

6.8.9. Dimethylhexyloctylammoniumnonafluorobutylsulfonate

(N₁₁₆₈C₄F₉SO₃).

Procedure as for 6.7.1.

The reaction of dimethylhexyloctylammonium iodide (0.99 g, 2.7 mmol) with potassium nonafluorobutylsulfonate (1.164 g, 3.0 mmol) in DCM (25 ml) and deionised water (25 ml) results in a liquid which solidified on cooling (yield 0.33 g, 21 %). ¹H NMR (CDCl₃) δ 3.21 (m, 4H, NCH₂), 3.07 (s, 6H, N(CH₃)₂), 1.60 (bs, 4H, 2CH₂), 1.26–1.19 (bm, 16H, (CH₂)₈), 0.814 (m, 6H, 2CH₃). ¹⁹F NMR δ -126.07 (CF₂), -121.69 (CF₂), -114.8 (CF₂), -80.96 (CF₃). Elemental analysis calc. for C₂₀H₃₆F₉NO₃S (541.23 gmol⁻¹) C 44.34, H 6.70, N 2.59 Found C 44.33, H 6.81, N 2.50 %.

6.9. Synthesis of asymmetric quaternary ammonium salts containing the heptafluoroniobate(V) anion.

6.9.1. Synthesis of dimethylbutyloctylammoniumheptafluoroniobate, ([N₁₁₄₈]₂NbF₇·2H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoroniobate(V), K₂NbF₇, (1.782 g, 5.86 mmol) with *N,N*-dimethylbutyloctylammonium iodide (1.99 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a brown viscous liquid (0.15 g, 8 %). ¹H NMR (CDCl₃) δ 3.38 (m, 4H, 2NCH₂), 3.2 (s, 6H, N(CH₃)₂), 1.65 (bm, 4H, 2NCH₂CH₂), 1.2–1.38 (bm, 12H, (CH₂)₆), 0.94 (t, 3H, CH₃), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -150.59 (NbF₇)²⁻. Elemental analysis calc. for C₂₈H₆₄F₇N₂Nb·2H₂O (688.41 gmol⁻¹) C 48.67, H 9.93, N 4.06 Found C 48.55, H 10.02, N 4.05 %.

6.9.2. Synthesis of dimethylbutyldecylammoniumheptafluoroniobate.

([N₁₁₄₍₁₀₎]₂NbF₇·2H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoronioate(V), K_2NbF_7 , (1.782 g, 5.86 mmol) with *N,N*-dimethylbutyldecylammonium iodide (2.163 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a viscous brown liquid (0.5 g, 22 %). 1H NMR ($CDCl_3$) δ 3.43 (m, 4H, $2NCH_2CH_2$), 3.27 (s, 6H, $N(CH_3)_2$), 1.65 (bm, 4H, $2NCH_2CH_2$), 1.19-1.38 (bm, 16H, $(CH_2)_8$), 0.94 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -150.6 (NbF_7) $^{2-}$. Elemental analysis calc. for $C_{32}H_{72}F_7N_2Nb \cdot 2H_2O$ (746.48 $g\ mol^{-1}$) **C** 51.44, **H** 10.26, **N** 3.75 Found **C** 51.60, **H** 11.27, **N** 3.80 %.

6.9.3. Synthesis of dimethylbutyltetradecylammoniumheptafluoronioate ($[N_{114(14)}]_2 NbF_7 \cdot 2H_2O$).

Procedure as 6.7.1.

The reaction of potassium heptafluoronioate(V), K_2NbF_7 , (1.782 g, 5.86 mmol) with *N,N*-dimethylbutyltetradecylammonium bromide (2.32 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a beige solid (0.51 g, 11 %). 1H NMR ($CDCl_3$) δ 3.32 (m, 4H, $2NCH_2CH_2$), 3.25 (s, 6H, $N(CH_3)_2$), 1.6 (bm, 4H, $2NCH_2CH_2$), 1.17–1.3 (bm, 24H, $(CH_2)_{12}$), 0.92 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR ($CDCl_3$) δ -150.85 (NbF_7) $^{2-}$. Elemental analysis calc. for $C_{38}H_{86}F_7N_2NbO_2$ (828.56 $g\ mol^{-1}$) **C** 55.04, **H** 10.46, **N** 3.38 Found **C** 55.71, **H** 11.09, **N** 3.24 %.

6.9.4. Synthesis of dimethylisopropyloctylammoniumheptafluoronioate ($[N_{1138}]_2 NbF_7 \cdot H_2O$).

Procedure as 6.7.1.

The reaction of potassium heptafluoronioate(V), K_2NbF_7 , (1.782 g, 5.86 mmol) with *N,N*-dimethylisopropyloctylammonium iodide (1.917 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a brownish-orange solid (0.6 g, 16 %). 1H NMR ($CDCl_3$) δ 3.87 (sep (J = 6.6Hz), 1H, NCH),

3.4(m, 2H, NCH₂), 3.17 (s, 6H, N(CH₃)₂), 1.7 (bm, 2H, NCH₂CH₂), 1.39 (d (J=6.6Hz), 6H, CH(CH₃)₂), 1.19–1.3 (bm, 10H, (CH₂)₅), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -151.35 (NbF₇)²⁻. Elemental analysis calc. for C₂₆H₆₂F₇N₂NbO (644.38 g mol⁻¹) **C** 48.42, **H** 9.70, **N** 4.35 Found **C** 48.09, **H** 9.50, **N** 4.29 %.

6.9.5. Synthesis of dimethylisopropyldecylammoniumheptafluoroniobate,
([N₁₁₃₍₁₀₎]₂NbF₇·H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoroniobate(V), K₂NbF₇, (1.782 g, 5.86 mmol) with *N,N*-dimethylisopropyldecylammonium iodide (2.08 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a brownish-orange solid (0.44 g, 11 %). ¹H NMR (CDCl₃) δ 3.84 (sep (J=6.6Hz), 1H, NCH), 3.37 (m, 2H, NCH₂), 3.14 (s, 6H, N(CH₃)₂), 1.7 (bm, 2H, NCH₂CH₂), 1.39 (d (J=6.6Hz), 6H, CH(CH₃)₂), 1.19–1.3 (bm, 14H, (CH₂)₇), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -150.85 (NbF₇)²⁻. Elemental analysis calc. for C₃₀H₇₀F₇N₂NbO (700.44 g mol⁻¹) **C** 48.42, **H** 9.70, **N** 4.35 Found **C** 48.09, **H** 9.50, **N** 4.29 %.

6.9.6. Synthesis of dimethylethylloctylammoniumheptafluoroniobate
([N₁₁₂₈]₂NbF₇·4H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoroniobate(V), K₂NbF₇, (0.891 g, 2.93 mmol) with *N,N*-dimethylethylloctylammonium iodide (1.83 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a brown viscous liquid (0.15 g, 8 %). ¹H NMR (CDCl₃) δ 3.6 (q, 2H, NCH₂CH₃), 3.41 (m, 2H, NCH₂), 3.28 (s, 6H, N(CH₃)₂), 1.66 (bm, 2H, NCH₂CH₂), 1.2-1.35 (bm, 13H, (CH₂)₅ + CH₃), 0.81 (t, 3H, CH₃). ¹⁹F NMR δ -150.85 (NbF₇)²⁻. Elemental analysis calc. for C₂₄H₆₄F₇N₂NbO₄ (670.38 g mol⁻¹) **C** 48.42, **H** 9.70, **N** 4.35 Found **C** 48.09, **H** 9.50, **N** 4.29 %.

6.9.7. Synthesis of dimethylethyldecylammoniumheptafluoroniobate
([N₁₁₂₍₁₀₎]₂NbF₇·4H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoroniobate(V), K₂NbF₇, (0.891 g, 2.93 mmol) with *N,N*-dimethylethyldecylammonium iodide (1.99 g, 5.86 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a brownish-yellow viscous liquid (0.25 g, 6 %). ¹H NMR (CDCl₃) δ 3.6 (q, 2H, NCH₂CH₃), 3.41(m, 2H, NCH₂), 3.27 (s, 6H, N(CH₃)₂), 1.66 (bm, 2H, NCH₂CH₂), 1.19–1.36 (bm, 17H, (CH₂)₇+ CH₃), 0.81 (t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -150.7 (NbF₇)²⁻. Elemental analysis calc. for C₂₈H₇₂F₇N₂NbO₄ (726.44 g mol⁻¹) **C** 46.25, **H** 9.99, **N** 3.86 Found **C** 46.31, **H** 9.61, **N** 3.62 %.

6.9.8. Synthesis of dimethylhexyloctylammoniumheptafluoroniobate
([N₁₁₆₈]₂NbF₇·2H₂O).

Procedure as 6.7.1.

The reaction of potassium heptafluoroniobate(V), K₂NbF₇, (0.912 g, 3.0 mmol) with *N,N*-dimethylhexyloctylammonium iodide (2.215 g, 6.0 mmol) in DCM (25 ml) and deionised water (25 ml) resulted in a dark brownish-yellow liquid (0.75 g, 17 %). ¹H NMR (CDCl₃) δ 3.45 (m, 4H, 2NCH₂), 3.3 (s, 6H, N(CH₃)₂), 1.66 (bm, 4H, 2NCH₂CH₂), 1.2-1.28 (bm, 16H, (CH₂)₈), 0.82(m, 6H, CH₃). ¹⁹F NMR (CDCl₃) δ -150.5 (NbF₇)²⁻. Elemental analysis calc. for C₃₂H₇₆F₇N₂NbO₂ (746.48 g mol⁻¹) **C** 51.44, **H** 10.26, **N** 3.75 Found **C** 51.47, **H** 10.82, **N** 3.72 %.

6.10. Synthesis of asymmetric quaternary ammonium salts of trifluoromethane sulfonate.

6.10.1. Synthesis of dimethylbutyloctylammoniumtrifluoromethane sulfonate (N₁₁₄₈CF₃SO₃·H₂O).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, $\text{CF}_3\text{SO}_3\text{K}$, (1.88 g, 10 mmol), *N,N*-dimethylbutyloctylammonium iodide (10 mmol, 3.411 g), DCM (25 ml) and deionised water (25 ml) were stirred for 24 h and resulted in a brownish-red liquid (0.655 g, 18 %). ^1H NMR (CDCl_3) δ 3.25 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 3.09 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (bm, 4H, $2\text{NCH}_2\text{CH}_2$), 1.2–1.35 (bm, 12H, $(\text{CH}_2)_6$), 0.93 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR δ -78.48 (s, CF_3). Elemental analysis calc. for $\text{C}_{15}\text{H}_{32}\text{F}_3\text{NO}_3\text{S}\cdot\text{H}_2\text{O}$ ($363.20 \text{ g mol}^{-1}$) **C** 47.22, **H** 8.99, **N** 3.67, **S** 8.80 Found **C** 48.25, **H** 9.49, **N** 3.91, **S** 7.74 %.

6.10.2. Synthesis of dimethylbutyldecylammoniumtrifluoromethane sulfonate ($\text{N}_{114(10)}\text{CF}_3\text{SO}_3\cdot\text{H}_2\text{O}$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, $\text{CF}_3\text{SO}_3\text{K}$, (1.88 g, 10 mmol), *N,N*-dimethylbutyldecylammonium iodide (3.692 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) were stirred for 24 h and resulted in a clear liquid (1.3 g, 33 %). ^1H NMR (CDCl_3) δ 3.25 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 3.09 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (bm, 4H, NCH_2CH_2), 1.19–1.35 (bm, 16H, $(\text{CH}_2)_8$), 0.92 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR (CDCl_3) δ -78.53 (s, CF_3). Elemental analysis calc. for $\text{C}_{17}\text{H}_{36}\text{F}_3\text{NO}_3\text{S}$ ($391.24 \text{ g mol}^{-1}$) **C** 49.85, **H** 9.36, **N** 3.42 Found **C** 50.67, **H** 9.66, **N** 3.92 %.

6.10.3. Synthesis of dimethylbutyltetradecylammoniumtrifluoromethane sulfonate, ($\text{N}_{114(14)}\text{CF}_3\text{SO}_3$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, $\text{CF}_3\text{SO}_3\text{K}$, (1.88 g, 10 mmol,) *N,N*-dimethylbutyltetradecylammonium bromide (3.96 g, 10 mmol), DCM (25ml) and deionised water (25 ml) were stirred for 24 h and resulted in waxy white solid, (1.873 g, 42 %), mp 53.7 °C. ^1H NMR (CDCl_3) δ 3.23 (m, 4H, $2\text{NCH}_2\text{CH}_2$), 3.08 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.60 (bm, 4H, NCH_2CH_2), 1.18–1.35 (bm, 24H, $(\text{CH}_2)_{12}$),

0.93 (t, 3H, CH₃), 0.81(t, 3H, CH₃). ¹⁹F NMR δ -78.48 (s, CF₃). Elemental analysis calc. for C₂₁H₄₄F₃NO₃S (447.30 g mol⁻¹) **C** 56.34, **H** 9.91, **N** 3.13 Found **C** 56.47 **H** 10.95, **N** 3.14 %.

6.10.4. Synthesis of dimethylisopropyloctylammoniumtrifluoromethane sulfonate, (N₁₁₃₈CF₃SO₃).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, CF₃SO₃K, (1.88 g, 10 mmol) *N,N*-dimethylisopropyloctylammonium iodide (3.27 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) were stirred for 24 h and resulted in a yellowish-brown fluffy solid (0.70 g, 20 %). ¹H NMR (CDCl₃) δ 3.71 (sep (*J*=6.6Hz), 1H, NCH), 3.24 (m, 2H, N-CH₂), 3.02 (s, 6H, N(CH₃)₂), 1.66 (bm, 2H, NCH₂CH₂), 1.36 (d(*J*=6.6Hz), 6H, (CH(CH₃)₂), 1.2–1.28 (bm, 10H, (CH₂)₅), 0.81 (t, 3H, CH₃). ¹⁹F NMR δ -78.45 (s, CF₃). Elemental analysis calc. for C₁₄H₃₀F₃NO₃S (349.19 g mol⁻¹) **C** 48.11, **H** 8.66, **N** 4.01 Found **C** 47.82, **H** 9.07, **N** 3.96 %.

6.10.5. Synthesis of dimethylisopropyldecylammoniumtrifluoromethane sulfonate, (N₁₁₃₍₁₀₎CF₃SO₃).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, CF₃SO₃K, (1.88 g, 10 mmol), *N,N*-dimethyl isopropyldecylammonium iodide (3.55 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellowish-brown fluffy solid (0.6 g, 16 %). ¹H NMR (CDCl₃) δ 3.72 (sep (*J*=6.6Hz), 1H, NCH(CH₃)₂), 3.24 (m, 2H, N-CH₂), 3.03 (s, 6H, N(CH₃)₂), 1.66 (bm, 2H, NCH₂CH₂), 1.36 (d (*J*=6.6Hz), 6H, CH(CH₃)₂), 1.20–1.29 (bm, 14H, (CH₂)₇), 0.81(t, 3H, CH₃). ¹⁹F NMR (CDCl₃) δ -78.44 (s, CF₃). Elemental analysis calc. for C₁₆H₃₄F₃NO₃S (377.22 g mol⁻¹) **C** 50.90, **H** 9.08, **N** 3.71 Found **C** 50.50, **H** 9.93, **N** 3.53 %.

6.10.6. Synthesis of trimethyloctylammoniumtrifluoromethanesulfonate, ($N_{1118}CF_3SO_3$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, CF_3SO_3K , (3.76 g, 20 mmol), trimethyloctylammonium iodide (5.982 g, 20 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellowish-brown waxy solid (0.8 g, 25 %). 1H NMR ($CDCl_3$) δ 3.3 (m, H, $N-CH_2$), 3.17 (s, 3H, NCH_3), 1.67 (bm, 2H, NCH_2CH_2), 1.29–1.20 (bm, 10H, $(CH_2)_5$), 0.81(t, 3H, CH_3). ^{19}F NMR δ -78.55 (s, CF_3). Elemental analysis calc. for $C_{12}H_{26}F_3NO_3S$ (321.16 g mol^{-1}) **C** 44.84, **H** 8.16, **N** 4.36 Found **C** 38.98, **H** 7.57, **N** 1.90 %.

6.10.7. Synthesis of trimethyldecylammoniumtrifluoromethanesulfonate, ($N_{111(10)}CF_3SO_3$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate CF_3SO_3K (3.76 g, 20 mmol), trimethyldecylammonium iodide (6.5 g, 20 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellowish-orange waxy solid (1.69 g, 24 %). 1H NMR ($CDCl_3$) δ 3.33 (m, 2H, NCH_2), 3.19 (s, 7H, $N(CH_3)_2$), 1.68 (bm, 2H, NCH_2CH_2), 1.28-1.19 (bm, 14H, $(CH_2)_7$), 0.81(t, 3H, CH_3). ^{19}F NMR δ -78.54 (CF_3). Elemental analysis calc. for $C_{14}H_{30}F_3NO_3S$ (349.19 g mol^{-1}) **C** 48.11, **H** 8.66, **N** 4.01 Found **C** 48.05, **H** 9.08, **N** 3.54 %.

6.10.8. Synthesis of dimethylhexyloctylammoniumtrifluoromethanesulfonate, ($N_{1168}CF_3SO_3$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, CF_3SO_3K , (1.88 g, 10 mmol), *N,N*-dimethyl hexyloctylammonium iodide (3.69 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellowish-brown fluffy solid (0.772 g, 20

%). ^1H NMR (CDCl_3) δ 3.28 (m, 4H, 2NCH_2), 3.12 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (bm, 4H, $2\text{NCH}_2\text{CH}_2$), 1.2–1.28 (bm, 16H, $(\text{CH}_2)_8$), 0.82 (m, 6H, 2CH_3). ^{19}F NMR (CDCl_3) δ -78.46 (s, CF_3). Elemental analysis calc. for $\text{C}_{17}\text{H}_{36}\text{F}_3\text{NO}_3\text{S}$ ($391.24 \text{ g mol}^{-1}$) **C** 52.14, **H** 9.27, **N** 3.58 Found **C** 51.89, **H** 10.20, **N** 3.60 %.

6.10.9. Synthesis of dimethylhexyldecylammoniumtrifluoromethane sulfonate ($\text{N}_{116(10)}\text{CF}_3\text{SO}_3$).

Procedure as 6.7.1.

Potassium trifluoromethanesulfonate, $\text{CF}_3\text{SO}_3\text{K}$, (1.88 g, 10 mmol), *N,N*-dimethyl hexyldecylammonium iodide (3.97 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellowish-brown fluffy solid (0.15 g, 4 %). ^1H NMR (CDCl_3) δ 3.27(m, 4H, 2NCH_2), 3.12 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.62 (bm, 4H, $2\text{NCH}_2\text{CH}_2$), 1.19–1.27 (bm, 20H, $(\text{CH}_2)_{10}$), 0.81(q, 6H, 2CH_3). ^{19}F NMR δ -78.47 (CF_3). Elemental analysis calc. for $\text{C}_{19}\text{H}_{40}\text{F}_3\text{NO}_3\text{S}$ ($419.27 \text{ g mol}^{-1}$) **C** 54.38, **H** 9.61, **N** 3.34 Found **C** 53.80, **H** 10.28, **N** 3.36 %.

6.11. Synthesis of asymmetric quaternary ammonium salts of hexafluorophosphate (PF_6) and trispentafluoroethyltrifluorophosphate (FAP) anions.

6.11.1. Synthesis of dimethylbutyloctylammoniumtrispentafluoroethyl trifluorophosphate ($\text{N}_{1148}\text{FAP}$).

Procedure as 6.7.1.

Potassiumtris(pentafluoroethyl)trifluorophosphate, KFAP (4.84g, 10 mmol), *N,N*-dimethyl butyloctylammonium iodide (3.41 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) resulted after workup in a yellowish-brown liquid (4.32 g, 66 %). ^1H NMR (CDCl_3) δ 3.04 (m, 4H, 2NCH_2), 2.87 (s, 6H, $\text{N}(\text{CH}_3)_2$), 1.59 (bm, 4H, $2\text{NCH}_2\text{CH}_2$), 1.19-1.26 (bs, 12H, $(\text{CH}_2)_6$), 0.91(t, 3H, CH_3), 0.80 (t, 3H, CH_3). ^{19}F NMR δ -44.45 (d, ($J = 894.7 \text{ Hz}$), 1F, PF), -80.21 (m,

3F, CF₃), -81.8 (m, 6F, 2CF₃), -88.1(d, (*J* = 909.1 Hz), 2F, 2PF), -115.4–115.69 (bm, 2F, CF₂), -115.94 – -116.2Hz (bm, 4F, 2CF₂), ³¹P NMR (CDCl₃) δ -146.4 (m). Elemental analysis calc. for C₂₀H₃₂F₁₈NP (659.20 g mol⁻¹) **C** 36.41, **H** 4.89, **N** 2.12 Found **C** 36.44, **H** 4.73, **N** 2.10 %.

6.11.2. Synthesis of dimethylbutydecylammoniumtris(pentafluoroethyl)trifluorophosphate (N₁₁₄₍₁₀₎FAP).

Procedure as 6.7.1.

Potassiumtris(pentafluoroethyl)trifluorophosphate, KFAP, (4.84g, 10 mmol), *N,N*-dimethylbutyldecylammonium iodide (3.69 g, 10 mmol) , DCM (25 ml) and deionised water (25 ml) resulted in a yellow liquid (4.556 g, 66 %). ¹H NMR (CDCl₃) δ 3.09 (m, 4H, 2NCH₂), 2.91(s, 6H, N(CH₃)₂), 1.57 (bm, 4H, 2NCH₂CH₂), 1.19-1.26 (bm, 16H, (CH₂)₈), 0.91(t, 3H, CH₃), 0.80 (t, 3H, CH₃). ¹⁹F NMR δ -44.49 (d, (*J* = 896 Hz), 1F, PF), -80.21 (m, 3F, CF₃), -81.8 (m, 6F, 2CF₃), -88.1 (d, (*J* = 905.6 Hz), 2F, 2PF), -115.4 to -115.67 (bm, 2F, CF₂), -115.9 to -116.2 (bm, 4F, 2CF₂), ³¹P NMR (CDCl₃) δ -146.2 (m). Elemental analysis calc. for C₂₂H₃₆F₁₈NP (687.23 g mol⁻¹) **C** 36.41, **H** 4.89, **N** 2.12 Found **C** 36.44, **H** 4.73, **N** 2.10 %.

6.11.3. Synthesis of dimethylbutytetradecylammoniumtris(pentafluoroethyl)trifluorophosphate (N₁₁₄₍₁₄₎FAP).

Procedure as 6.7.1.

Potassiumtris(pentafluoroethyl)trifluorophosphate, KFAP, (4.84 g, 10 mmol), *N,N*-dimethylbutyltetradecylammonium bromide (3.96 g, 10 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellow liquid (4.99 g, 67 %). ¹H NMR (CDCl₃) δ 3.05 (m, 4H, 2NCH₂), 2.88 (s, 6H, N(CH₃)₂), 1.57 (bm, 4H, 2NCH₂CH₂), 1.18-1.32 (bm, 24H, (CH₂)₁₂), 0.92 (t, 3H, CH₃), 0.80 (t, 3H, CH₃). ¹⁹F NMR δ -44.5 (d, (*J* = 895.1 Hz), 1F, PF), -80.19 (m, 3F, CF₃), -81.84 (m, 6F,

2CF₃), -88.1(d, (*J* = 899.1 Hz), 2F, 2PF), -115.4 to -115.7 (bm, 2F, CF₂), -115.93 to -116.18Hz (bm, 4F, 2CF₂). ³¹P NMR (CDCl₃) δ -147.0 (m). Elemental analysis calc. for C₂₆H₄₄F₁₈NP (743.29 g mol⁻¹) **C** 41.98, **H** 5.97, **N** 1.88 Found **C** 42.43, **H** 6.26, **N** 1.85 %.

6.11.4. Synthesis of dimethylbutyloctadecylammoniumtris(pentafluoroethyl)trifluorophosphate (N₁₁₄₍₁₈₎FAP).

Procedure as 6.7.1.

Potassiumtris(pentafluoroethyl)trifluorophosphate, KFAP (4.84 g, 10 mmol), *N,N*-dimethylbutyloctadecylammonium bromide (4.52 g, 10 mmol) , DCM (25 ml) and deionised water (25 ml) resulted in a yellow liquid (4.83 g, 61 %). ¹H NMR (CDCl₃) δ 3.04 (m, 4H, 2NCH₂), 2.86 (s, 6H, N(CH₃)₂), 1.57 (bm, 4H, 2NCH₂CH₂), 1.18-1.31 (bm, 32H, (CH₂)₁₆), 0.92 (t, 3H, CH₃), 0.80 (t, 3H, CH₃). ¹⁹F NMR δ -44.5 (d, (*J* = 894 Hz), 1F, PF), -80.2 (m, 3F, CF₃), -81.8 (m, 6F, 2CF₃), -88.14 (d, (*J* = 904 Hz), 2F, 2PF), -115.4 to -115.7 (bm, 2F, CF₂), -115.9 to -116.19 (bm, 4F, 2CF₂), ³¹P NMR (CDCl₃) δ -147.0 (m). Elemental analysis calc. for C₃₀H₅₂F₁₈NP (799.35 g mol⁻¹) **C** 45.04, **H** 6.56, **N** 1.75 Found **C** 45.30, **H** 6.70, **N** 1.85 %.

6.11.5. Synthesis of dimethylbutyloctylammoniumhexafluorophosphate, (N₁₁₄₈PF₆).

Procedure as 6.7.1.

Potassiumhexafluorophosphate, KPF₆ (1.84 g, 10 mmol), *N,N*-dimethylbutyloctylammonium iodide (3.41 g, 10 mmol) , DCM (25 ml) and deionised water (25 ml) resulted in a yellow solid (1.92 g, 53 %). ¹H NMR (CDCl₃) δ 3.15 (m, 4H, 2NCH₂), 2.98 (s, 6H, N(CH₃)₂), 1.61 (bm, 4H, 2NCH₂CH₂), 1.2–1.35 (bm, 12H, (CH₂)₆), 0.92 (t, 3H, CH₃), 0.80 (t, 3H, CH₃). ¹⁹F NMR δ -71.6 (d, (*J*=713 Hz), PF₆), ³¹P NMR (CDCl₃) δ -146.4 (septet *J*= 712.9 Hz). Elemental analysis

calc. for $C_{14}H_{32}F_6NP$ ($359.22 \text{ g mol}^{-1}$) **C** 45.04, **H** 6.56, **N** 1.75 Found **C** 45.30, **H** 6.70, **N** 1.85 %.

6.11.6. Synthesis of dimethylbutyldecylammoniumhexafluorophosphate, $N_{114(10)}PF_6$.

Procedure as 6.7.1.

Potassiumhexafluorophosphate, KPF_6 , (0.92 g, 5 mmol), *N,N*-dimethylbutyl decylammonium iodide (1.845 g, 5 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellow solid (1.348 g, 70 %). 1H NMR ($CDCl_3$) δ 3.16 (m, 4H, $2NCH_2$), 2.99 (s, 6H, $N(CH_3)_2$), 1.61 (bm, 4H, $2NCH_2CH_2$), 1.19–1.34 (bm, 16H, $(CH_2)_8$), 0.91 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR δ -71.55 (d, ($J = 713 \text{ Hz}$), PF_6), ^{31}P NMR ($CDCl_3$) δ -144.3 (septet, $J = 713 \text{ Hz}$). Elemental analysis calc. for $C_{16}H_{36}F_6NP$ ($387.25 \text{ g mol}^{-1}$) **C** 49.58, **H** 9.37, **N** 3.62 Found **C** 49.86, **H** 9.20, **N** 3.55 %.

6.11.7. Synthesis of dimethylbutyltetradecylammoniumhexafluoro phosphate $N_{114(14)}PF_6$.

Procedure as 6.7.1.

Potassiumhexafluorophosphate, KPF_6 (0.92 g, 5 mmol), *N,N*-dimethylbutyl tetradecylammonium bromide (1.98 g, 5 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a yellow solid (1.133 g, 51 %). 1H NMR ($CDCl_3$) δ 3.14 (m, 4H, $2NCH_2$), 2.98 (s, 6H, $N(CH_3)_2$), 1.60 (bm, 4H, $2NCH_2CH_2$), 1.18–1.34 (bm, 24H, $(CH_2)_{12}$), 0.92(t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR δ -71.55 (d, ($J = 714 \text{ Hz}$), PF_6), ^{31}P NMR ($CDCl_3$) δ -144.19 (septet, $J = 713.8 \text{ Hz}$). Elemental analysis calc. for $C_{20}H_{44}F_6NP$ ($443.31 \text{ g mol}^{-1}$) **C** 54.14, **H** 10.00, **N** 3.16 Found **C** 54.45, **H** 9.88, **N** 3.09 %.

6.11.8. Synthesis of dimethylbutyloctadecylammoniumhexafluorophosphate $N_{114(18)}PF_6$.

Procedure as 6.7.1.

Potassiumhexafluorophosphate KPF_6 (0.92g, 5 mmol), *N,N*-dimethylbutyloctadecylammonium bromide (2.26 g, 5 mmol), DCM (25 ml) and deionised water (25 ml) resulted in a white solid (1.43 g, 57 %). 1H NMR ($CDCl_3$) δ 3.15 (m, 4H, $2NCH_2$), 2.99 (s, 6H, $N(CH_3)_2$), 1.61 (bm, 4H, $2NCH_2CH_2$), 1.18-1.35 (bm, 32H, $(CH_2)_{16}$), 0.93 (t, 3H, CH_3), 0.81 (t, 3H, CH_3). ^{19}F NMR δ -71.7 (d, ($J = 713.47$ Hz), PF_6), ^{31}P NMR ($CDCl_3$) δ -144.7 (septet, $J = 713$ Hz). Elemental analysis calc. for $C_{24}H_{52}F_6NP$ (499.37 $g\ mol^{-1}$) **C** 57.67, **H** 10.49, **N** 2.80 Found **C** 57.79, **H** 10.33, **N** 2.73 %.

6.12. References

1. Shelxs G.M. Sheldrick, 2008, *Acta Cryst.* A64, 112-122.
2. M. Tanaka, A. Rastogi, G. N. Toepperwein, R. A. Riggelman, N. M. Felix, J. J. de Pablo and C. K. Ober., *Chem. Mater.* 2009, **21**, 3125.
3. S. Quek, I. M. Lyapkalo, V. Han, *Tetrahedron*, 2006, **62**, 3137.
4. K. Sogabe, Y. Hasegawa, Y. Wada, T. Kitamura and S. Yanagida, *Chem. Lett.*, 2000, 944.

7. Conclusions and future work

7.1 Conclusions

Introducing asymmetry into quaternary ammonium halides was found to have a considerable influence on their melting points making this a potential route for the development of new RTILs or for tailoring the properties of existing compounds.

Asymmetric quaternary ammonium salts were obtained by reacting the nonsymmetric amines (N_{11R} , $R = \text{Me, Et, iPr, Bu, Hex, allyl, benzyl, cyclohexyl}$) with a range of alkyl halides ($R'X$, $R' = C_8H_{17}, C_{10}H_{21}, C_{14}H_{29}, C_{18}H_{37}$). The completely asymmetric ammonium iodides of the formula ($N_{14R(14)}I$, $R = \text{propyl, octyl, decyl and allyl}$) were prepared by first synthesizing the asymmetric amine $N_{14(14)}$ and reacting it with the alkyl iodides ($R-I$, $R = \text{allyl, propyl, octyl, decyl}$). Fluorinated quaternary ammonium salts of the type $[NR_3(CH_2)_3Rf]I$, ($Rf = (CF_2)_nCF_3$, $n = 7, 3$) were also prepared and were all found to be solids possessing high melting points, making them unsuitable for the development of room temperature ionic liquids. However, attempts to prepare analogues possessing a two-carbon spacer in the Rf resulted in a competitive elimination reaction resulting in formation of $[NR_3H]I$ and a fluoroalkyl-containing alkene.

The most promising series of quaternary ammonium halides for ionic liquid work are the butyl (C_4), hexyl (C_6), benzyl and allyl series which showed low melting points compared to the smaller analogues in addition to the completely asymmetric quaternary ammonium iodides. All the butyl series showed melting points below $100\text{ }^\circ\text{C}$, whereas the hexyl, allyl and benzyl series along with the completely asymmetric quaternary ammonium iodides are liquids at room temperature which is unusual for compounds of this type, and so they may be considered as promising precursor halides for the

development of room temperature ionic liquids. The lowering of the melting point of the ally and benzyl substituents compared to their aliphatic analogues may be due to the charge delocalization resulting in less interaction between the cationic and anionic species, thus decreasing the lattice energy and so the melting point.

In contrast to this, the branched alkyl chains (based on the isopropyl (C3) systems) and the cyclohexyl series of quaternary ammonium halides showed higher melting points.

The halide-containing ionic liquids were used in exchange reactions to replace the halides by a series of fluorinated anions (including TFSI, sulfonate, PF_6^- , $\text{P}(\text{C}_2\text{F}_5)_3\text{F}_3^-$ (FAP) and heptafluoronioate) resulting in the formation of 42 new RTILs.

The TFSI⁻ anion is found to be the most promising candidate for RTIL applications, and it led to a depression in the melting point by up to 205 °C compared with the analogous halide salt, resulting in the development of 21 new stable, hydrophobic room temperature ionic liquids.

Investigation on the properties of these new ionic liquids showed that the TFSI-exchanged ionic liquids showed the highest thermal stability of all the compounds tested, this was more than 400 °C for $\text{N}_{1118}\text{TFSI}$, $\text{N}_{111(10)}\text{TFSI}$ and 394 °C for the completely asymmetric RTIL $\text{N}_{148(14)}\text{TFSI}$. Other properties determined for these compounds include, wide liquid ranges (over 420 °C) and viscosities ranging from 79 – 255 mPa.s (at 25 °C). The conductivity values showed an inverse relationship to the viscosities, ranging from 67-770 $\mu\text{S}\cdot\text{cm}^{-1}$ (at 19 °C). The RTIL with the lowest viscosity and therefore showing the highest conductivity was $\text{N}_{1138}\text{TFSI}$.

Both the cation symmetry and choice of a specific anion was found to influence the depression of the RTIL melting point. For example, introducing

asymmetry into the cation such as going from $N_{111(10)}\text{TFSI}$ to $N_{113(10)}\text{TFSI}$ to $N_{116(10)}\text{TFSI}$ results in the melting point decreasing from 14 to -2 to -82 °C respectively.

In addition to this, introducing asymmetry into the anion resulted in further lowering of the melting points, for example replacing the PF_6^- anion in an ionic liquid with the less symmetric FAP^- ion. All of the PF_6^- salts studied were found to be solids at room temperature, but with melting points below 100 °C, whereas the FAP salts prepared are all liquids with relatively low melting points, reaching -42 °C for $N_{114(14)}\text{FAP}$.

Most of the developed RTILs were found to be immiscible in water and saturated alkanes such as hexane but are soluble in a wide range of polar solvents such as DCM, acetone and CHCl_3 . The developed TFSI-RTILs possessed wide electrochemical windows, the smallest window recorded was 4.0 V for $N_{1138}\text{TFSI}$ and the widest achieved was 6.2 V for $N_{148(14)}\text{TFSI}$. When all ionic liquids are considered, not just those containing the TFSI anion, the widest electrochemical window, of 6.5 V, was observed for $N_{1148}\text{FAP}^-$.

The X-ray crystal structures of $N_{112(18)}\text{Br}$, $N_{114(18)}\text{Br}\cdot\text{H}_2\text{O}$, $N_{114}\text{HI}$, $N_{118(18)}\text{Br}\cdot\text{H}_2\text{O}$, $N_{111(10)}\text{I}$ and $N_{111(14)}\text{TFSI}$ are reported. All of which show extensive hydrogen bonding, classical hydrogen bonds are formed between the $\text{N-H}\cdots\text{I}$ in $N_{114}\text{HI}$ whilst for the hydrated salts, $N_{114(18)}\text{Br}\cdot\text{H}_2\text{O}$ and $N_{118(18)}\text{Br}\cdot\text{H}_2\text{O}$ hydrogen bonds are formed between two water molecules and two bromide anions forming diamond shaped motifs.

7.2 Future work

The main aim of this work was to develop hydrophobic asymmetric ammonium-based room temperature ionic liquids with relatively low melting points. With the generation of hydrophobic RTILs which possess melting points as low as -82 °C, this goal has been achieved. In the available time the number of completely asymmetric systems which could be investigated was

limited, it would therefore be worth extending this study to a larger, systematic range of asymmetric ammonium salts. If increasing the degree of asymmetry results in further reductions in melting point, then it may be possible to use the halides directly, rather than requiring a change in anion, as low-melting point RTILs.

This work has shown that the developed RTILs possess high thermal stabilities, wide electrochemical windows and non-volatility. Whilst the physical properties of these RTILs have been studied, such as density, conductivity, viscosity, there have been no investigations on their solvent properties and potential applications. Since such systems are inherently conducting, and they have wide electrochemical windows (typically > 4 V), their use as electrolyte components in Li-ion batteries might be investigated, as well as the potential these systems have for investigating electrochemical reactions which necessitate greater potentials than are available in more conventional solvents. Such work might deal with reduction of carbon dioxide and electro-deposition.

8. Appendix

- 8.1.** Abstract for poster presentation at Shape of Science Symposium, University of Manchester, July 2010.
- 8.2.** Abstract for poster presentation at 1st international conference on Ionic Liquids in Separation and Purification Technology/Sitges, Spain (4-7/09/2011) and oral presentation at 1st Northern Chemistry Postgraduate Research Conference, New Castle University 31/07/2012.
- 8.3.** X-ray Data.

8.1 Development of asymmetric room temperature ionic liquids

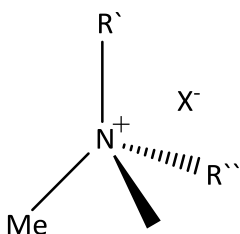
Hana B. Alhanash, Alan K. Brisdon,

School of Chemistry, The University of Manchester, UK.

As a group, ionic liquids have many properties that extend beyond the ranges of normal molecular solvents; typically these include very large liquidus ranges, low volatility, high conductivity, wide electrochemical windows, the ability to solubilise a broad variety of organic, inorganic and organometallic materials as well as gases. One advantage of ionic liquids is that they can be tailored to optimized, by substituting the cations and anions to obtain specific properties solvent, and as such they are sometimes called 'designer solvents'.

One class of ionic liquids are based on quaternary ammonium salts of the type $(NR_4)^+X^-$. We have been investigating the effects of introducing asymmetry into the ammonium cation as a primary step in the development of hydrophobic RTILs^[1].

Table 1: Melting points of asymmetric quaternary ammonium halides.



R'	R''	X	mp °C
Methyl	Methyl	Br	>300 ^[2]
ethyl	tetradecyl	Br	101.1
Methyl	Tetradecyl	Br	109
Isopropyl	Tetradecyl	Br	205(dec)
butyl	Tetradecyl	Br	48
hexyl	tetradecyl	Br	Paste-like material

The introduction of asymmetry into the ammonium cation reduces the melting point significantly compared with the $Me_4N^+Br^-$ (Table1). Replacing the halide of the asymmetric quaternary ammonium salts eg $N_{114(14)}Br$ (mp = 48 °C) with fluorinated anions, such as bis(trifluoromethylsulfonylimide) $TFSI^-$, results in a further reduction in the melting point to give a room temperature ionic liquid $N_{114(14)}TFSI$ with a melting point below 0 °C.

Combining the low melting point asymmetric quaternary ammonium halides with larger fluorinated anions (TFSI) resulted in hydrophobic RTILs such as:- $N_{1148}I$ (mp 93 °C), $N_{1148}TFSI$ is liquid@rt. Combining the high melting point asymmetric quaternary ammonium halides with larger anions led to a significant decrease in the mp such as :- $N_{113(14)}Br$ (mp 205 °C) and $N_{113(14)}TFSI$ (mp 35 °C).

Introduction of asymmetry in the quaternary ammonium halides is a potential route for the development of hydrophobic RTILs

References

- 1.Andrew D. Ballantyne, Alan K. Brisdon, *Chem.Comm.*, 2008, 4980-4982.
- 2.Ionic Liquids in Synthesis, by P.Wasserscheild and Tom Welton.

8.2 Development of asymmetric room temperature ionic liquids

Hana B. Alhanash, Alan K. Brisdon*

School of Chemistry, The University of Manchester, UK.

As a group, ionic liquids have many properties that extend beyond the ranges of normal molecular solvents; typically these include very large liquidus ranges, low volatility, high conductivity, wide electrochemical windows, high solvation ability for a broad variety of organic, inorganic and organometallic materials as well as gases. One advantage of ionic liquids is that they can be tailored to be optimized, by modifying the cations and anions to obtain specific solvent properties, and as such they are sometimes called 'designer solvents'.

Here we report a novel class of asymmetric ammonium-based low melting and hydrophobic ionic liquids have been synthesised and characterised, with the general formula, $[\text{NRR}'\text{R}'']^+\text{X}^-$, where $\text{R} = \text{CH}_3$, $\text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7, \text{C}_4\text{H}_9$ and C_6H_{13} , $\text{CH}_2=\text{CHCH}_2$, PhCH_2 , C_6H_{11} $\text{R}'' = \text{C}_8\text{H}_{17}, \text{C}_{10}\text{H}_{21}, \text{C}_{14}\text{H}_{29}$ and $\text{C}_{18}\text{H}_{37}$ with different counterions such as halides, TFSI and CF_3SO_3^- . The physical properties, such as melting point, glass transition temperature, thermal stability, conductivity, viscosity, density and electrochemical stability have been investigated.

The introduction of asymmetry into the cationic species of the quaternary ammonium (QA) salt has a great influence on the melting point. This decreases dramatically on going from the more symmetric $[\text{NMe}_3\text{R}']^+ (\text{N}_{111\text{R}'})^{[1]}$ containing quaternary ammonium ionic liquids to the more asymmetric $(\text{N}_{11\text{R}'\text{R}''})$ series and finally to the completely asymmetric $(\text{N}_{14\text{R}(14)})$ series ($\text{R} = \text{allyl, propyl, octyl}$). For example, $(\text{N}_{116\text{R}'})$ and $(\text{N}_{14\text{R}(14)})$ - containing quaternary ammonium halides are liquids at room temperature. Exchanging the halides of the QA salts with larger fluorinated anions resulted in a series of hydrophobic room temperature ionic liquids of high thermal stability, with melting points nearly 150 °C less than that of the symmetric ammonium halide analogues, see below.

N₁₁₁₍₁₄₎Br 108.7 (225)	N₁₁₁₍₁₄₎TFSI 55.5 (370)
N₁₁₄₍₁₄₎Br 48.0 (213)	N₁₁₄₍₁₄₎TFSI -32.0 (389)

Observed melting points (and decomposition temperature) (°C)
of some quaternary ammonium-based ionic liquids.

1. Andrew D. Ballantyne, Alan K. Brisdon, *Chem. Commun.*, 2008, 4980.

8.3. X-Ray Data

- 8.3.1** Crystal data and details of the structure determination for $N_{114}Hl$.
- 8.3.2** Crystal data and details of the structure determination for $N_{11(10)}l$.
- 8.3.3** Crystal data and details of the structure determination for $N_{112(18)}Br$.
- 8.3.4** Crystal data and details of the structure determination for $N_{111(14)}TFSI$.
- 8.3.5** Crystal data and details of the structure determination for $N_{11B(18)}Br.H_2O$.
- 8.3.6** Crystal data and details of the structure determination for $N_{114(18)}Br.H_2O$.

8.3.1. Crystal Data and Details of the Structure Determination for $N_{114H}I$

Crystal Data

Formula	C6 H16 I1 N1		
Formula Weight	228.97		
Crystal System	Trigonal		
Space group	R-3	(No.148)	
a, b, c [Angstrom]	36.558(8)	36.558(8)	7.828(8)
alpha, beta, gamma [deg]	90	90	120
V [Ang**3]	9060(12)		
Z	36		
D(calc) [g/cm**3]	1.512		
Mu(MoKa) [/mm]	3.111		
F(000)	4032		
Crystal Size [mm]	0.03 x 0.06 x 0.18		

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	3.1, 25.5		
Dataset	-31: 0 ;	1: 44 ;	-8: 8
Tot., Uniq. Data, R(int)	2323,	2323,	0.000
Observed data [I > 2.0 sigma(I)]	1887		

Refinement

Nref, Npar	2323, 146
R, wR2, S	0.0907, 0.2139, 1.44
$w = 1/[\sigma^2(F_o^2) + (0.0210P)^2 + 188.4633P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Å ³]	-1.07, 1.49

Bond Distances (Angstrom)

N1	-C1	1.51(2)	C5	-H5B	0.9800
N1	-C5	1.50(3)	C6	-H6A	0.9800
N1	-C6	1.51(2)	C6	-H6B	0.9800
N1	-H1	0.9300	C6	-H6C	0.9800
N2	-C7	1.50(2)	C7	-C8	1.48(3)
N2	-C11	1.52(3)	C8	-C9	1.11(6)
N2	-C12	1.52(2)	C9	-C10	1.53(5)
N2	-H2	0.9300	C7	-H7A	0.9900
C1	-C2	1.53(3)	C7	-H7B	0.9900
C2	-C3	1.54(3)	C8	-H8A	0.9900
C3	-C4	1.51(4)	C8	-H8B	0.9900
C1	-H1A	0.9900	C9	-H9A	0.9900
C1	-H1B	0.9900	C9	-H9B	0.9900
C2	-H2A	0.9900	C10	-H10A	0.9800
C2	-H2B	0.9900	C10	-H10B	0.9800
C3	-H3A	0.9900	C10	-H10C	0.9800
C3	-H3B	0.9900	C11	-H11A	0.9800
C4	-H4B	0.9800	C11	-H11B	0.9800
C4	-H4A	0.9800	C11	-H11C	0.9800
C4	-H4C	0.9800	C12	-H12A	0.9800
C5	-H5A	0.9800	C12	-H12B	0.9800
C5	-H5C	0.9800	C12	-H12C	0.9800

Bond Angles (Degrees)

C1	-N1	-C5	111.5(13)	C4	-C3	-H3B	109.00
C1	-N1	-C6	111.7(15)	C2	-C3	-H3A	109.00
C5	-N1	-C6	110.4(14)	C3	-C4	-H4A	109.00
C1	-N1	-H1	108.00	H4B	-C4	-H4C	110.00
C5	-N1	-H1	107.00	C3	-C4	-H4B	110.00
C6	-N1	-H1	108.00	C3	-C4	-H4C	109.00

C7	-N2	-C11	114.0(13)	H4A	-C4	-H4C	109.00
C7	-N2	-C12	112.0(14)	H4A	-C4	-H4B	110.00
C11	-N2	-C12	109.4(13)	N1	-C5	-H5B	110.00
C11	-N2	-H2	107.00	N1	-C5	-H5C	110.00
C12	-N2	-H2	107.00	N1	-C5	-H5A	110.00
C7	-N2	-H2	107.00	H5A	-C5	-H5B	110.00
N1	-C1	-C2	113.0(14)	H5B	-C5	-H5C	109.00
C1	-C2	-C3	111.6(15)	H5A	-C5	-H5C	109.00
C2	-C3	-C4	112.3(17)	N1	-C6	-H6C	109.00
H1A	-C1	-H1B	108.00	H6A	-C6	-H6B	110.00
N1	-C1	-H1A	109.00	N1	-C6	-H6B	110.00
N1	-C1	-H1B	109.00	H6B	-C6	-H6C	110.00
C2	-C1	-H1B	109.00	H6A	-C6	-H6C	109.00
C2	-C1	-H1A	109.00	N1	-C6	-H6A	109.00
C3	-C2	-H2A	109.00	N2	-C7	-C8	114.0(19)
C1	-C2	-H2B	109.00	C7	-C8	-C9	132(4)
C1	-C2	-H2A	109.00	C8	-C9	-C10	135(4)
C3	-C2	-H2B	109.00	N2	-C7	-H7A	109.00
H2A	-C2	-H2B	108.00	N2	-C7	-H7B	109.00
C4	-C3	-H3A	109.00	C8	-C7	-H7A	109.00
H3A	-C3	-H3B	108.00	C8	-C7	-H7B	109.00
C2	-C3	-H3B	109.00	H7A	-C7	-H7B	108.00
C7	-C8	-H8A	104.00	H10A	-C10	-H10C	110.00
C7	-C8	-H8B	105.00	H10B	-C10	-H10C	109.00
C9	-C8	-H8A	104.00	N2	-C11	-H11A	110.00
C9	-C8	-H8B	104.00	N2	-C11	-H11B	109.00
H8A	-C8	-H8B	106.00	N2	-C11	-H11C	109.00
C8	-C9	-H9A	104.00	H11A	-C11	-H11B	109.00
C8	-C9	-H9B	103.00	H11A	-C11	-H11C	110.00
C10	-C9	-H9A	103.00	H11B	-C11	-H11C	109.00

C10	-C9	-H9B	103.00	N2	-C12	-H12A	110.00
H9A	-C9	-H9B	105.00	N2	-C12	-H12B	109.00
C9	-C10	-H10A	109.00	N2	-C12	-H12C	109.00
C9	-C10	-H10B	109.00	H12A	-C12	-H12B	110.00
C9	-C10	-H10C	109.00	H12A	-C12	-H12C	109.00
H10A	-C10	-H10B	110.00	H12B	-C12	-H12C	109.00

Contact Distances(Angstrom)

I1	.N1	3.458(15)	C6	.H2B	2.7700
I2	.C6_o	3.84(2)	C8	.H11A	2.7800
I2	.N2	3.463(15)	C11	.H8A	2.6400
I2	.C12_q	3.71(2)	H1	.H2A	2.4300
I1	.H11A	3.2300	H1	.I1	2.5300
I1	.H1	2.5300	H1A	.H6B	2.5000
I1	.H2A	3.3700	H1A	.H5C	2.5600
I1	.H5A_m	3.3700	H1B	.I2_d	3.2300
I1	.H7B_a	3.1000	H1B	.H5B	2.4300
I1	.H12C_a	3.2800	H1B	.H3A	2.4300
I1	.H8A	3.2700	H2	.I2	2.5500
I1	.H6A_m	3.2000	H2	.H8A	2.3100
I1	.H6B_o	3.3500	H2A	.I1	3.3700
I1	.H5C_o	3.1000	H2A	.H1	2.4300
I2	.H2	2.5500	H2A	.H4B	2.5200
I2	.H7A_p	3.3000	H2B	.H4C	2.5800
I2	.H11B_p	3.3000	H2B	.H6C	2.2000
I2	.H1B_k	3.2300	H2B	.C6	2.7700
I2	.H5B_k	3.2400	H3A	.H1B	2.4300
I2	.H12B_p	3.3300	H4A	.H4C_e	2.3600
I2	.H12B_q	3.3600	H4B	.H10A_a	2.2900
N1	.I1	3.458(15)	H4B	.H10B	2.3800
N2	.I2	3.463(15)	H4B	.H2A	2.5200

C6	.I2_c	3.84(2)	H4C	.H2B	2.5800
C12	.I2_i	3.708(16)	H4C	.H4A_f	2.3600
C2	.H6C	2.6900	H5A	.I1_g	3.3700
C4	.H10A_a	2.8300	H5A	.H6A	2.4200
C5	.H11C_b	3.0000	H5B	.H11C_b	2.4000
H5B	.H1B	2.4300	H9B	.H7B	2.2900
H5B	.I2_d	3.2400	H10A	.C4_k	2.8300
H5C	.H1A	2.5600	H10A	.H4B_k	2.2900
H5C	.H6B	2.5400	H10B	.H8B	2.4700
H5C	.I1_h	3.1000	H10B	.H4B	2.3800
H6A	.I1_g	3.2000	H11A	.I1	3.2300
H6A	.H5A	2.4200	H11A	.C8	2.7800
H6B	.I1_h	3.3500	H11A	.H8A	2.1000
H6B	.H1A	2.5000	H11B	.I2_c	3.3000
H6B	.H5C	2.5400	H11B	.H12C_l	2.5800
H6C	.C2	2.6900	H11B	.H12B	2.5300
H6C	.H2B	2.2000	H11B	.H7A	2.5700
H7A	.I2_c	3.3000	H11C	.H5B_m	2.4000
H7A	.H11B	2.5700	H11C	.C5_m	3.0000
H7B	.H9B	2.2900	H11C	.H12A	2.4300
H7B	.H12C	2.4100	H12A	.H11C	2.4300
H7B	.I1_j	3.1000	H12B	.H11B	2.5300
H8A	.H2	2.3100	H12B	.I2_c	3.3300
H8A	.H11A	2.1000	H12B	.I2_i	3.3600
H8A	.C11	2.6400	H12C	.H11B_n	2.5800
H8A	.I1	3.2700	H12C	.H7B	2.4100
H8B	.H10B	2.4700	H12C	.I1_j	3.2800

Hydrogen Bonds (Angstrom, Deg)

N1	-- H1	.. I1	0.9300	2.5300	3.458(15)	177.00	.
N2	-- H2	.. I2	0.9300	2.5500	3.463(15)	169.00	.

Translation of Symmetry Code to Equiv.Pos

```

a =[ 5555.00] = [ 11_555] =y, -x+y, -z
b =[ 16555.00] = [ 13_555] =2/3-x, 1/3-y, 1/3-z
c =[ 1556.00] = [ 1_556] =x, y, 1+z
d =[ 5555.00] = [ 11_555] =y, -x+y, -z
e =[ 5556.00] = [ 11_556] =y, -x+y, 1-z
f =[ 6556.00] = [ 12_556] =x-y, x, 1-z
g =[ 16555.00] = [ 13_555] =2/3-x, 1/3-y, 1/3-z
h =[ 1556.00] = [ 1_556] =x, y, 1+z
i =[ 9555.00] = [ 9_555] =1/3-x+y, 2/3-x, 2/3+z
j =[ 6555.00] = [ 12_555] =x-y, x, -z
k =[ 6555.00] = [ 12_555] =x-y, x, -z
l =[ 14555.00] = [ 5_555] =2/3-y, 1/3+x-y, 1/3+z
m =[ 16555.00] = [ 13_555] =2/3-x, 1/3-y, 1/3-z
n =[ 9554.00] = [ 9_554] =1/3-x+y, 2/3-x, -1/3+z
o =[ 1554.00] = [ 1_554] =x, y, -1+z
p =[ 1554.00] = [ 1_554] =x, y, -1+z
q =[ 14554.00] = [ 5_554] =2/3-y, 1/3+x-y, -2/3+z

```

8.3.2. Crystal Data and Details of the Structure Determination for

$N_{111(10)}I$

Crystal Data

Formula	C13 H30 I1 N1		
Formula Weight	327.28		
Crystal System	Monoclinic		
Space group	P21	(No. 4)	
a, b, c [Angstrom]	5.7450(15)	7.4401(19)	18.830(6)
alpha, beta, gamma [deg]	90	92.552(13)	90
V [Ang**3]	804.1(4)		
Z	2		
D(calc) [g/cm**3]	1.352		
Mu(MoKa) [/mm]	1.969		
F(000)	336		
Crystal Size [mm]	0.06 x 0.08 x 0.20		

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	2.9, 21.0		
Dataset	-5: 5 ; -7: 7 ; -18: 18		
Tot., Uniq. Data, R(int)	1454,	1454,	0.000
Observed data [I > 2.0 sigma(I)]	1020		

Refinement

Nref, Npar	1454, 433
R, wR2, S	0.0859, 0.2197, 1.08
w = 1/[\s2^(Fo^2)+(0.0003P)^2+33.9296P] where P=(Fo^2+2Fc^2)/	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-1.24, 1.16

Bond Distances (Angstrom)

N1	-C13	1.467(7)	C7	-H7A	0.9900
C1	-C2	1.474(6)	C7	-H7B	0.9900
N1	-C1	1.506(6)	C5	-H5B	0.9900
N1	-C11	1.476(6)	C6	-H6A	0.9900
N1	-C12	1.465(7)	C6	-H6B	0.9900
C2	-C3	1.463(7)	C8	-H8A	0.9900
C3	-C4	1.452(7)	C8	-H8B	0.9900
C4	-C5	1.442(7)	C9	-H9A	0.9900
C5	-C6	1.446(5)	C9	-H9B	0.9900
C6	-C7	1.454(8)	C10	-H10A	0.9800
C7	-C8	1.459(8)	C10	-H10B	0.9800
C8	-C9	1.424(7)	C10	-H10C	0.9800
C9	-C10	1.440(8)	C11	-H11A	0.9800
C1	-H1A	0.9900	C11	-H11B	0.9800
C1	-H1B	0.9900	C11	-H11C	0.9800
C2	-H2A	0.9900	C12	-H12A	0.9800
C2	-H2B	0.9900	C12	-H12B	0.9800
C3	-H3A	0.9900	C12	-H12C	0.9800
C3	-H3B	0.9900	C13	-H13A	0.9800
C4	-H4A	0.9900	C13	-H13B	0.9800
C4	-H4B	0.9900	C13	-H13C	0.9800
C5	-H5A	0.9900			

Bond Angles (Degrees)

C1	-N1	-C11	105.6(4)	C4	-C3	-H3B	105.00
C1	-N1	-C12	114.4(8)	H3A	-C3	-H3B	106.00
C1	-N1	-C13	108.4(9)	C3	-C4	-H4A	106.00
C11	-N1	-C12	114.8(8)	C3	-C4	-H4B	106.00
C11	-N1	-C13	101.4(9)	C5	-C4	-H4A	106.00
C12	-N1	-C13	111.3(4)	C5	-C4	-H4B	106.00

N1	-C1	-C2	117.0(5)	H4A	-C4	-H4B	106.00
C1	-C2	-C3	114.1(5)	C4	-C5	-H5A	105.00
C2	-C3	-C4	128.1(5)	C4	-C5	-H5B	105.00
C3	-C4	-C5	124.7(5)	C6	-C5	-H5A	105.00
C4	-C5	-C6	129.8(4)	C6	-C5	-H5B	105.00
C5	-C6	-C7	126.3(5)	H5A	-C5	-H5B	106.00
C6	-C7	-C8	117.0(6)	C5	-C6	-H6A	106.00
C7	-C8	-C9	130.1(5)	C5	-C6	-H6B	106.00
C8	-C9	-C10	132.1(6)	C7	-C6	-H6A	106.00
N1	-C1	-H1A	108.00	C7	-C6	-H6B	106.00
N1	-C1	-H1B	108.00	H6A	-C6	-H6B	106.00
C2	-C1	-H1A	108.00	C6	-C7	-H7A	108.00
C2	-C1	-H1B	108.00	C6	-C7	-H7B	108.00
H1A	-C1	-H1B	107.00	C8	-C7	-H7A	108.00
C1	-C2	-H2A	109.00	C8	-C7	-H7B	108.00
C1	-C2	-H2B	109.00	H7A	-C7	-H7B	107.00
C3	-C2	-H2A	109.00	C7	-C8	-H8A	105.00
C3	-C2	-H2B	109.00	C7	-C8	-H8B	105.00
H2A	-C2	-H2B	108.00	C9	-C8	-H8A	105.00
C2	-C3	-H3A	105.00	C9	-C8	-H8B	105.00
C2	-C3	-H3B	105.00	H8A	-C8	-H8B	106.00
C4	-C3	-H3A	105.00	C8	-C9	-H9A	104.00
C8	-C9	-H9B	104.00	H11A	-C11	-H11C	109.00
C10	-C9	-H9A	104.00	H11B	-C11	-H11C	109.00
C10	-C9	-H9B	104.00	N1	-C12	-H12A	109.00
H9A	-C9	-H9B	105.00	N1	-C12	-H12B	110.00
C9	-C10	-H10A	109.00	N1	-C12	-H12C	109.00
C9	-C10	-H10B	109.00	H12A	-C12	-H12B	109.00
C9	-C10	-H10C	110.00	H12A	-C12	-H12C	109.00
H10A	-C10	-H10B	109.00	H12B	-C12	-H12C	110.00
H10A	-C10	-H10C	110.00	N1	-C13	-H13A	109.00

H10B	-C10	-H10C	110.00	N1	-C13	-H13B	109.00
N1	-C11	-H11A	110.00	N1	-C13	-H13C	109.00
N1	-C11	-H11B	109.00	H13A	-C13	-H13B	109.00
N1	-C11	-H11C	109.00	H13A	-C13	-H13C	109.00
H11A	-C11	-H11B	110.00	H13B	-C13	-H13C	109.00

Contact Distances(Angstrom)

I1	.C13	3.848(6)	H1B	.I1	3.1800
I1	.C11_o	3.805(5)	H2A	.C10_f	3.0500
I1	.C12_l	3.652(6)	H2A	.C13	2.6600
I1	.C13_m	3.766(6)	H2A	.H13B	2.2500
I1	.H1B	3.1800	H2A	.H10B_f	2.1500
I1	.H12C_n	3.1600	H2B	.H10C_a	2.5700
I1	.H11A	3.3200	H2B	.H12B	2.2300
I1	.H12A_l	3.2300	H2B	.C12	2.7900
I1	.H1A_n	3.0600	H3A	.H1A	2.2200
I1	.H11B_k	3.1100	H3B	.H5A	2.4100
I1	.H13A	2.8800	H4A	.H6B	2.4900
I1	.H13C_m	3.2900	H4A	.H8B_f	2.3100
C11	.I1_b	3.805(5)	H4B	.H8A_a	2.3800
C12	.I1_c	3.652(6)	H5A	.H3B	2.4100
C13	.I1_d	3.766(6)	H5A	.H9B_g	2.1300
C13	.I1	3.848(6)	H5B	.H9A_h	2.5800
C2	.H13B	2.7100	H6A	.H8B	2.1100
C2	.H13A	3.0800	H6A	.H6B_a	2.4300
C2	.H12B	2.8200	H6B	.H6A_f	2.4300
C10	.H2A_a	3.0500	H6B	.H4A	2.4900
C12	.H2B	2.7900	H7B	.H9A	2.5300
C13	.H2A	2.6600	H8A	.H4B_f	2.3800
H1A	.H3A	2.2200	H8B	.H6A	2.1100
H1A	.H11C	2.5000	H8B	.H4A_a	2.3100

H1A	.I1_e	3.0600	H9A	.H5B_g	2.5800
H1A	.H12C	2.5100	H9A	.H7B	2.5300
H1B	.H11A	2.1200	H9B	.H5A_h	2.1300
H1B	.H13A	2.3300	H10B	.H13B_a	2.5400
H10B	.H2A_a	2.1500	H12B	.C2	2.8200
H10C	.H2B_f	2.5700	H12C	.I1_e	3.1600
H11A	.H13A	2.2400	H12C	.H1A	2.5100
H11A	.I1	3.3200	H12C	.H11C	2.5200
H11A	.H1B	2.1200	H13A	.C2	3.0800
H11B	.H12A	2.5400	H13A	.H1B	2.3300
H11B	.H13C	2.1600	H13A	.H11A	2.2400
H11B	.I1_i	3.1100	H13A	.I1	2.8800
H11C	.H13C_j	2.5600	H13B	.C2	2.7100
H11C	.H1A	2.5000	H13B	.H2A	2.2500
H11C	.H12C	2.5200	H13B	.H12B	2.4500
H12A	.H13C	2.4400	H13B	.H10B_f	2.5400
H12A	.H11B	2.5400	H13C	.H12A	2.4400
H12A	.I1_c	3.2300	H13C	.H11C_k	2.5600
H12B	.H2B	2.2300	H13C	.H11B	2.1600
H12B	.H13B	2.4500	H13C	.I1_d	3.2900

Hydrogen Bonds (Angstrom, Deg)

C13 -- H13A .. I1 0.9800 2.8800 3.848(6) 169.00

Translation of Symmetry Code to Equiv.Pos

```

a = [ 2646.00] = [ 2_646] = 1-x, -1/2+y, 1-z
b = [ 2647.00] = [ 2_647] = 1-x, -1/2+y, 2-z
c = [ 1645.00] = [ 1_645] = 1+x, -1+y, z
d = [ 1655.00] = [ 1_655] = 1+x, y, z
e = [ 1545.00] = [ 1_545] = x, -1+y, z
f = [ 2656.00] = [ 2_656] = 1-x, 1/2+y, 1-z
g = [ 2556.00] = [ 2_556] = -x, 1/2+y, 1-z
h = [ 2546.00] = [ 2_546] = -x, -1/2+y, 1-z
i = [ 2747.00] = [ 2_747] = 2-x, -1/2+y, 2-z
j = [ 2747.00] = [ 2_747] = 2-x, -1/2+y, 2-z
k = [ 2757.00] = [ 2_757] = 2-x, 1/2+y, 2-z
l = [ 1465.00] = [ 1_465] = -1+x, 1+y, z
m = [ 1455.00] = [ 1_455] = -1+x, y, z
n = [ 1565.00] = [ 1_565] = x, 1+y, z
o = [ 2657.00] = [ 2_657] = 1-x, 1/2+y, 2-z

```

8.3.3. Crystal Data and Details of the Structure Determination N₁₁₂₍₁₈₎Br

Crystal Data

Formula	C22 H48 Br1 N1		
Formula Weight	406.52		
Crystal System	Triclinic		
Space group	P-1	(No. 2)	
a, b, c [Angstrom]	10.6630(7)	8.4255(7)	26.570(3)
alpha, beta, gamma [deg]	84.726(3)	94.410(3)	88.041(2)
V [Ang**3]	2367.9(4)		
Z	4		
D(calc) [g/cm**3]	1.140		
Mu(MoKa) [/mm]	1.740		
F(000)	888		
Crystal Size [mm]	0.10 x 0.14 x 0.20		

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	3.0, 17.7		
Dataset	-9: 9 ; -7: 7 ; -22: 22		
Tot., Uniq. Data, R(int)	5859,	3009,	0.150
Observed data [I > 2.0 sigma(I)]	1490		

Refinement

Nref, Npar	3009, 433
R, wR2, S	0.0780, 0.2073, 1.11
$w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 10.2921P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang ³]	-0.41, 0.93

Bond Distances (Angstrom)

N1	-C1	1.54(2)	C2	-H2A	0.9900
N1	-C19	1.47(2)	C2	-H2B	0.9900
N1	-C21	1.53(2)	C3	-H3B	0.9900
N1	-C22	1.53(2)	C3	-H3A	0.9900
N2	-C23	1.52(2)	C4	-H4B	0.9900
N2	-C41	1.52(2)	C4	-H4A	0.9900
N2	-C43	1.49(2)	C5	-H5A	0.9900
N2	-C44	1.43(2)	C5	-H5B	0.9900
C1	-C2	1.52(2)	C6	-H6A	0.9900
C2	-C3	1.56(2)	C6	-H6B	0.9900
C3	-C4	1.52(3)	C7	-H7A	0.9900
C4	-C5	1.51(2)	C7	-H7B	0.9900
C5	-C6	1.51(2)	C8	-H8B	0.9900
C6	-C7	1.52(2)	C8	-H8A	0.9900
C7	-C8	1.53(2)	C9	-H9A	0.9900
C8	-C9	1.55(2)	C9	-H9B	0.9900
C9	-C10	1.52(2)	C10	-H10B	0.9900
C10	-C11	1.52(2)	C10	-H10A	0.9900
C11	-C12	1.56(2)	C11	-H11A	0.9900
C12	-C13	1.50(2)	C11	-H11B	0.9900
C13	-C14	1.51(2)	C12	-H12B	0.9900
C14	-C15	1.51(2)	C12	-H12A	0.9900
C15	-C16	1.52(2)	C13	-H13A	0.9900
C16	-C17	1.54(2)	C13	-H13B	0.9900
C17	-C18	1.49(3)	C14	-H14A	0.9900
C19	-C20	1.55(2)	C14	-H14B	0.9900
C1	-H1A	0.9900	C15	-H15A	0.9900
C1	-H1B	0.9900	C15	-H15B	0.9900
C16	-H16B	0.9900	C33	-C34	1.56(2)
C16	-H16A	0.9900	C34	-C35	1.54(2)

C17	-H17A	0.9900	C35	-C36	1.54(2)
C17	-H17B	0.9900	C36	-C37	1.56(2)
C18	-H18C	0.9800	C37	-C38	1.52(3)
C18	-H18A	0.9800	C38	-C39	1.56(2)
C18	-H18B	0.9800	C39	-C40	1.53(3)
C19	-H19B	0.9900	C41	-C42	1.47(2)
C19	-H19A	0.9900	C23	-H23A	0.9900
C20	-H20A	0.9800	C23	-H23B	0.9900
C20	-H20B	0.9800	C24	-H24A	0.9900
C20	-H20C	0.9800	C24	-H24B	0.9900
C21	-H21A	0.9800	C25	-H25A	0.9900
C21	-H21B	0.9800	C25	-H25B	0.9900
C21	-H21C	0.9800	C26	-H26A	0.9900
C22	-H22B	0.9800	C26	-H26B	0.9900
C22	-H22C	0.9800	C27	-H27A	0.9900
C22	-H22A	0.9800	C27	-H27B	0.9900
C23	-C24	1.50(2)	C28	-H28A	0.9900
C24	-C25	1.50(2)	C28	-H28B	0.9900
C25	-C26	1.53(2)	C29	-H29A	0.9900
C26	-C27	1.49(2)	C29	-H29B	0.9900
C27	-C28	1.54(2)	C30	-H30A	0.9900
C28	-C29	1.50(2)	C30	-H30B	0.9900
C29	-C30	1.52(2)	C31	-H31A	0.9900
C30	-C31	1.50(2)	C31	-H31B	0.9900
C31	-C32	1.53(2)	C32	-H32A	0.9900
C32	-C33	1.52(2)	C32	-H32B	0.9900
C33	-H33A	0.9900	C40	-H40A	0.9800
C33	-H33B	0.9900	C40	-H40B	0.9800
C34	-H34A	0.9900	C40	-H40C	0.9800
C34	-H34B	0.9900	C41	-H41A	0.9900
C35	-H35A	0.9900	C41	-H41B	0.9900

C35	-H35B	0.9900	C42	-H42A	0.9800
C36	-H36A	0.9900	C42	-H42B	0.9800
C36	-H36B	0.9900	C42	-H42C	0.9800
C37	-H37A	0.9900	C43	-H43A	0.9800
C37	-H37B	0.9900	C43	-H43B	0.9800
C38	-H38A	0.9900	C43	-H43C	0.9800
C38	-H38B	0.9900	C44	-H44A	0.9800
C39	-H39A	0.9900	C44	-H44B	0.9800
C39	-H39B	0.9900	C44	-H44C	0.9800

Bond Angles		(Degrees)					
C1	-N1	-C19	114.1(13)	C16	-C17	-C18	114.5(14)
C1	-N1	-C21	105.5(12)	N1	-C19	-C20	115.8(13)
C1	-N1	-C22	109.4(13)	H1A	-C1	-H1B	108.00
C19	-N1	-C21	111.8(13)	N1	-C1	-H1A	109.00
C19	-N1	-C22	108.3(13)	N1	-C1	-H1B	109.00
C21	-N1	-C22	107.7(12)	C2	-C1	-H1A	109.00
C23	-N2	-C44	113.6(12)	C2	-C1	-H1B	109.00
C41	-N2	-C43	105.7(12)	C1	-C2	-H2B	110.00
C41	-N2	-C44	111.8(13)	C3	-C2	-H2A	110.00
C43	-N2	-C44	107.7(12)	C1	-C2	-H2A	110.00
C23	-N2	-C41	106.8(12)	H2A	-C2	-H2B	108.00
C23	-N2	-C43	111.0(12)	C3	-C2	-H2B	110.00
N1	-C1	-C2	113.3(13)	C4	-C3	-H3A	108.00
C1	-C2	-C3	108.1(13)	C2	-C3	-H3B	108.00
C2	-C3	-C4	117.3(14)	C2	-C3	-H3A	108.00
C3	-C4	-C5	112.1(14)	C4	-C3	-H3B	108.00
C4	-C5	-C6	116.6(14)	H3A	-C3	-H3B	107.00
C5	-C6	-C7	114.2(14)	H4A	-C4	-H4B	108.00
C6	-C7	-C8	114.8(14)	C3	-C4	-H4A	109.00
C7	-C8	-C9	113.0(14)	C3	-C4	-H4B	109.00

C8	-C9	-C10	115.0(13)	C5	-C4	-H4A	109.00
C9	-C10	-C11	113.7(13)	C5	-C4	-H4B	109.00
C10	-C11	-C12	112.7(13)	H5A	-C5	-H5B	107.00
C11	-C12	-C13	112.8(14)	C4	-C5	-H5B	108.00
C12	-C13	-C14	113.8(14)	C6	-C5	-H5A	108.00
C13	-C14	-C15	113.7(14)	C4	-C5	-H5A	108.00
C14	-C15	-C16	114.0(14)	C6	-C5	-H5B	108.00
C15	-C16	-C17	116.5(14)	C7	-C6	-H6A	109.00
C7	-C6	-H6B	109.00	C12	-C11	-H11B	109.00
C5	-C6	-H6B	109.00	C13	-C12	-H12B	109.00
C5	-C6	-H6A	109.00	H12A	-C12	-H12B	108.00
H6A	-C6	-H6B	108.00	C11	-C12	-H12B	109.00
C6	-C7	-H7B	109.00	C13	-C12	-H12A	109.00
C6	-C7	-H7A	109.00	C11	-C12	-H12A	109.00
H7A	-C7	-H7B	108.00	C12	-C13	-H13A	109.00
C8	-C7	-H7A	109.00	C14	-C13	-H13B	109.00
C8	-C7	-H7B	108.00	C12	-C13	-H13B	109.00
C7	-C8	-H8A	109.00	C14	-C13	-H13A	109.00
C9	-C8	-H8A	109.00	H13A	-C13	-H13B	108.00
C9	-C8	-H8B	109.00	C15	-C14	-H14A	109.00
C7	-C8	-H8B	109.00	C13	-C14	-H14A	109.00
H8A	-C8	-H8B	108.00	C13	-C14	-H14B	109.00
C10	-C9	-H9A	109.00	H14A	-C14	-H14B	108.00
C10	-C9	-H9B	109.00	C15	-C14	-H14B	109.00
C8	-C9	-H9A	108.00	C14	-C15	-H15A	109.00
C8	-C9	-H9B	109.00	H15A	-C15	-H15B	108.00
H9A	-C9	-H9B	108.00	C16	-C15	-H15B	109.00
C9	-C10	-H10B	109.00	C14	-C15	-H15B	109.00
C9	-C10	-H10A	109.00	C16	-C15	-H15A	109.00
H10A	-C10	-H10B	108.00	C15	-C16	-H16A	108.00
C11	-C10	-H10A	109.00	C17	-C16	-H16B	108.00

C11	-C10	-H10B	109.00	C15	-C16	-H16B	108.00
C10	-C11	-H11A	109.00	C17	-C16	-H16A	108.00
H11A	-C11	-H11B	108.00	H16A	-C16	-H16B	107.00
C10	-C11	-H11B	109.00	C18	-C17	-H17A	109.00
C12	-C11	-H11A	109.00	C16	-C17	-H17A	109.00
C16	-C17	-H17B	109.00	N1	-C22	-H22B	110.00
C18	-C17	-H17B	109.00	N1	-C22	-H22C	109.00
H17A	-C17	-H17B	108.00	H22A	-C22	-H22B	109.00
C17	-C18	-H18A	109.00	H22A	-C22	-H22C	109.00
H18A	-C18	-H18C	109.00	N2	-C23	-C24	115.6(14)
H18B	-C18	-H18C	109.00	C23	-C24	-C25	113.4(14)
H18A	-C18	-H18B	109.00	C24	-C25	-C26	115.5(14)
C17	-C18	-H18B	109.00	C25	-C26	-C27	117.2(14)
C17	-C18	-H18C	110.00	C26	-C27	-C28	114.1(14)
N1	-C19	-H19A	108.00	C27	-C28	-C29	115.2(14)
C20	-C19	-H19B	108.00	C28	-C29	-C30	113.0(14)
N1	-C19	-H19B	108.00	C29	-C30	-C31	115.3(14)
C20	-C19	-H19A	108.00	C30	-C31	-C32	114.6(14)
H19A	-C19	-H19B	107.00	C31	-C32	-C33	112.0(13)
C19	-C20	-H20C	109.00	C32	-C33	-C34	112.5(13)
C19	-C20	-H20A	110.00	C33	-C34	-C35	113.0(13)
C19	-C20	-H20B	109.00	C34	-C35	-C36	113.3(13)
H20A	-C20	-H20C	109.00	C35	-C36	-C37	112.6(13)
H20B	-C20	-H20C	109.00	C36	-C37	-C38	112.0(14)
H20A	-C20	-H20B	109.00	C37	-C38	-C39	112.2(14)
H21A	-C21	-H21B	109.00	C38	-C39	-C40	110.4(14)
H21A	-C21	-H21C	110.00	N2	-C41	-C42	116.6(14)
N1	-C21	-H21A	110.00	N2	-C23	-H23A	108.00
N1	-C21	-H21B	109.00	N2	-C23	-H23B	108.00
N1	-C21	-H21C	110.00	C24	-C23	-H23A	108.00

H21B	-C21	-H21C	109.00	C24	-C23	-H23B	108.00
H22B	-C22	-H22C	109.00	H23A	-C23	-H23B	108.00
N1	-C22	-H22A	109.00	C23	-C24	-H24A	109.00
C23	-C24	-H24B	109.00	H29A	-C29	-H29B	108.00
C25	-C24	-H24A	109.00	C29	-C30	-H30A	108.00
C25	-C24	-H24B	109.00	C29	-C30	-H30B	108.00
H24A	-C24	-H24B	108.00	C31	-C30	-H30A	109.00
C24	-C25	-H25A	108.00	C31	-C30	-H30B	108.00
C24	-C25	-H25B	108.00	H30A	-C30	-H30B	107.00
C26	-C25	-H25A	108.00	C30	-C31	-H31A	108.00
C26	-C25	-H25B	108.00	C30	-C31	-H31B	109.00
H25A	-C25	-H25B	107.00	C32	-C31	-H31A	108.00
C25	-C26	-H26A	108.00	C32	-C31	-H31B	109.00
C25	-C26	-H26B	108.00	H31A	-C31	-H31B	108.00
C27	-C26	-H26A	108.00	C31	-C32	-H32A	109.00
C27	-C26	-H26B	108.00	C31	-C32	-H32B	109.00
H26A	-C26	-H26B	107.00	C33	-C32	-H32A	109.00
C26	-C27	-H27A	109.00	C33	-C32	-H32B	109.00
C26	-C27	-H27B	109.00	H32A	-C32	-H32B	108.00
C28	-C27	-H27A	109.00	C32	-C33	-H33A	109.00
C28	-C27	-H27B	109.00	C32	-C33	-H33B	109.00
H27A	-C27	-H27B	108.00	C34	-C33	-H33A	109.00
C27	-C28	-H28A	108.00	C34	-C33	-H33B	109.00
C27	-C28	-H28B	109.00	H33A	-C33	-H33B	108.00
C29	-C28	-H28A	108.00	C33	-C34	-H34A	109.00
C29	-C28	-H28B	109.00	C33	-C34	-H34B	109.00
H28A	-C28	-H28B	108.00	C35	-C34	-H34A	109.00
C28	-C29	-H29A	109.00	C35	-C34	-H34B	109.00
C28	-C29	-H29B	109.00	H34A	-C34	-H34B	108.00
C30	-C29	-H29A	109.00	C34	-C35	-H35A	109.00
C30	-C29	-H29B	109.00	C34	-C35	-H35B	109.00

C36	-C35	-H35A	109.00	H40A	-C40	-H40B	109.00
C36	-C35	-H35B	109.00	H40A	-C40	-H40C	110.00
H35A	-C35	-H35B	108.00	H40B	-C40	-H40C	109.00
C35	-C36	-H36A	109.00	N2	-C41	-H41A	108.00
C35	-C36	-H36B	109.00	N2	-C41	-H41B	108.00
C37	-C36	-H36A	109.00	C42	-C41	-H41A	108.00
C37	-C36	-H36B	109.00	C42	-C41	-H41B	108.00
H36A	-C36	-H36B	108.00	H41A	-C41	-H41B	107.00
C36	-C37	-H37A	109.00	C41	-C42	-H42A	109.00
C36	-C37	-H37B	109.00	C41	-C42	-H42B	110.00
C38	-C37	-H37A	109.00	C41	-C42	-H42C	109.00
C38	-C37	-H37B	109.00	H42A	-C42	-H42B	110.00
H37A	-C37	-H37B	108.00	H42A	-C42	-H42C	109.00
C37	-C38	-H38A	109.00	H42B	-C42	-H42C	110.00
C37	-C38	-H38B	109.00	N2	-C43	-H43A	110.00
C39	-C38	-H38A	109.00	N2	-C43	-H43B	110.00
C39	-C38	-H38B	109.00	N2	-C43	-H43C	109.00
H38A	-C38	-H38B	108.00	H43A	-C43	-H43B	110.00
C38	-C39	-H39A	109.00	H43A	-C43	-H43C	109.00
C38	-C39	-H39B	109.00	H43B	-C43	-H43C	109.00
C40	-C39	-H39A	110.00	N2	-C44	-H44A	109.00
C40	-C39	-H39B	110.00	N2	-C44	-H44B	110.00
H39A	-C39	-H39B	108.00	N2	-C44	-H44C	109.00
C39	-C40	-H40A	109.00	H44A	-C44	-H44B	110.00
C39	-C40	-H40B	109.00	H44A	-C44	-H44C	109.00
C39	-C40	-H40C	110.00	H44B	-C44	-H44C	109.00

Contact Distances(Angstrom)

Br1	.C43_c	3.698(15)	Br2	.H44A	2.8800
Br1	.C44	3.746(16)	C2	.C20	3.60(2)
Br2	.C21_p	3.642(16)	C2	.Br2_a	3.730(16)

Br2	.C44	3.737(17)	C19	.Br2_a	3.729(16)
Br2	.C2_o	3.730(16)	C20	.C2	3.60(2)
Br2	.C19_o	3.729(16)	C21	.Br2_b	3.642(16)
Br2	.C22_o	3.667(16)	C22	.Br2_a	3.667(16)
Br1	.H21A	3.0500	C43	.Br1_k	3.698(15)
Br1	.H22A	2.9400	C44	.Br2	3.737(17)
Br1	.H22C_g	3.0700	C44	.Br1	3.746(16)
Br1	.H41B_c	3.1400	C1	.H4A	2.7800
Br1	.H42B	3.0000	C1	.H20B	2.6800
Br1	.H23B_c	2.9500	C2	.H19B	2.8700
Br1	.H1B	2.9000	C2	.H22B	2.6500
Br1	.H21B_g	2.9200	C2	.H20B	3.0800
Br1	.H43A_c	2.7700	C4	.H1B	2.8200
Br1	.H44B	2.8400	C19	.H2A	2.7300
Br2	.H41A_s	2.9800	C20	.H1A	2.6400
Br2	.H22B_o	2.7800	C20	.H21C	2.8400
Br2	.H43C_s	2.8500	C21	.H20C	2.8800
Br2	.H21C_p	2.6900	C22	.H2B	2.7100
Br2	.H2A_o	3.0800	C22	.H41B_c	2.9600
Br2	.H19B_o	2.7800	C23	.H42C	2.5900
Br2	.H20C_p	3.1200	C24	.H44A	2.8500
Br2	.H42A_q	3.2100	C24	.H43B	2.6200
Br2	.H43B	2.8900	C24	.H43A	3.0900
Br2	.H24B	3.0500	C39	.H42C_i	3.0800
Br2	.H40A_r	3.1600	C42	.H23B	2.9300
C42	.H23A	2.7300	H5A	.H3B	2.4600
C42	.H44B	2.7500	H5B	.H3A	2.4700
C42	.H22B_j	3.0900	H5B	.H7B	2.5400
C43	.H24A	2.6500	H6A	.H8B	2.5800
C43	.H24B	3.0600	H6A	.H4A	2.6000

C44	.H42B	2.8200	H6B	.H8A	2.5800
C44	.H24B	2.8500	H7A	.H5A	2.5100
H1A	.H21C	2.4900	H7A	.H9B	2.5600
H1A	.H3B	2.3400	H7B	.H5B	2.5400
H1A	.H20B	2.1600	H7B	.H9A	2.5400
H1A	.C20	2.6400	H8A	.H6B	2.5800
H1B	.Br1	2.9000	H8B	.H6A	2.5800
H1B	.C4	2.8200	H9A	.H11B	2.5400
H1B	.H22A	2.5000	H9A	.H7B	2.5400
H1B	.H21A	2.2700	H9B	.H11A	2.5500
H1B	.H4A	2.2900	H9B	.H7A	2.5600
H2A	.H19B	2.2700	H10A	.H12A	2.5700
H2A	.Br2_a	3.0800	H10B	.H12B	2.5500
H2A	.C19	2.7300	H11A	.H13A	2.5500
H2B	.H22B	2.2300	H11A	.H9B	2.5500
H2B	.C22	2.7100	H11B	.H13B	2.5400
H3A	.H5B	2.4700	H11B	.H9A	2.5400
H3B	.H5A	2.4600	H12A	.H10A	2.5700
H3B	.H1A	2.3400	H12A	.H14A	2.5100
H4A	.C1	2.7800	H12B	.H14B	2.5400
H4A	.H1B	2.2900	H12B	.H10B	2.5500
H4A	.H6A	2.6000	H13A	.H11A	2.5500
H5A	.H7A	2.5100	H13A	.H15A	2.5400
H13B	.H15B	2.5200	H21A	.H1B	2.2700
H13B	.H11B	2.5400	H21A	.Br1	3.0500
H14A	.H12A	2.5100	H21A	.H22A	2.4600
H14A	.H16B	2.5500	H21B	.H41B_h	2.4700
H14B	.H16A	2.5100	H21B	.H22C	2.4400
H14B	.H12B	2.5400	H21B	.Br1_f	2.9200
H15A	.H13A	2.5400	H21B	.H22A_g	2.5400
H15B	.H13B	2.5200	H21B	.H19A	2.4300

H16A	.H14B	2.5100	H21C	.H20C	2.3000
H16A	.H18B	2.5900	H21C	.C20	2.8400
H16B	.H18C	2.5500	H21C	.Br2_b	2.6900
H16B	.H14A	2.5500	H21C	.H1A	2.4900
H18B	.H16A	2.5900	H22A	.H21A	2.4600
H18C	.H16B	2.5500	H22A	.H41B_c	2.2400
H19A	.H21B	2.4300	H22A	.H1B	2.5000
H19A	.H22C	2.4700	H22A	.Br1	2.9400
H19B	.H22B	2.3200	H22A	.H21B_g	2.5400
H19B	.Br2_a	2.7800	H22B	.C2	2.6500
H19B	.C2	2.8700	H22B	.Br2_a	2.7800
H19B	.H2A	2.2700	H22B	.H42A_c	2.4100
H19B	.H43B_d	2.5800	H22B	.H2B	2.2300
H20B	.H1A	2.1600	H22B	.H19B	2.3200
H20B	.C1	2.6800	H22B	.C42_c	3.0900
H20B	.C2	3.0800	H22C	.H19A	2.4700
H20C	.C21	2.8800	H22C	.Br1_f	3.0700
H20C	.Br2_b	3.1200	H22C	.H21B	2.4400
H20C	.H44A_e	2.5500	H23A	.C42	2.7300
H20C	.H21C	2.3000	H23A	.H25B	2.4300
H23A	.H42C	2.2200	H28A	.H30A	2.4700
H23A	.H44B	2.4400	H28B	.H30B	2.5100
H23B	.H25A	2.5300	H28B	.H26B	2.5100
H23B	.H43A	2.5800	H29A	.H31A	2.5700
H23B	.H41B	2.3100	H29A	.H27A	2.5900
H23B	.H42C	2.4500	H29B	.H31B	2.5500
H23B	.Br1_k	2.9500	H29B	.H27B	2.5900
H23B	.C42	2.9300	H30A	.H28A	2.4700
H24A	.H43B	2.2400	H30A	.H32A	2.5700
H24A	.C43	2.6500	H30B	.H32B	2.5600

H24A	.H26A	2.5500	H30B	.H28B	2.5100
H24B	.Br2	3.0500	H31A	.H33A	2.4900
H24B	.C43	3.0600	H31A	.H29A	2.5700
H24B	.C44	2.8500	H31B	.H33B	2.5300
H24B	.H26B	2.5800	H31B	.H29B	2.5500
H24B	.H43B	2.5600	H32A	.H30A	2.5700
H24B	.H44A	2.2700	H32A	.H34A	2.5500
H25A	.H27A	2.5900	H32B	.H34B	2.5600
H25A	.H23B	2.5300	H32B	.H30B	2.5600
H25B	.H23A	2.4300	H33A	.H31A	2.4900
H26A	.H28A	2.5400	H33A	.H35B	2.6000
H26A	.H24A	2.5500	H33B	.H31B	2.5300
H26B	.H28B	2.5100	H33B	.H35A	2.5700
H26B	.H24B	2.5800	H34A	.H36B	2.5800
H27A	.H29A	2.5900	H34A	.H32A	2.5500
H27A	.H25A	2.5900	H34B	.H32B	2.5600
H27B	.H29B	2.5900	H34B	.H36A	2.5700
H28A	.H26A	2.5400	H35A	.H37A	2.6000
H35A	.H33B	2.5700	H41B	.H22A_j	2.2400
H35B	.H33A	2.6000	H41B	.H23B	2.3100
H35B	.H37B	2.5700	H42A	.Br2_b	3.2100
H36A	.H34B	2.5700	H42A	.H22B_j	2.4100
H36A	.H38A	2.5500	H42B	.Br1	3.0000
H36B	.H38B	2.5500	H42B	.H44B	2.2400
H36B	.H34A	2.5800	H42B	.C44	2.8200
H37A	.H35A	2.6000	H42C	.H39A_i	2.5000
H37A	.H39A	2.5400	H42C	.C39_i	3.0800
H37B	.H35B	2.5700	H42C	.C23	2.5900
H37B	.H39B	2.5900	H42C	.H23A	2.2200
H38A	.H40B	2.5200	H42C	.H23B	2.4500
H38A	.H36A	2.5500	H43A	.C24	3.0900

H38B	.H40C	2.5500	H43A	.H23B	2.5800
H38B	.H36B	2.5500	H43A	.Br1_k	2.7700
H39A	.H37A	2.5400	H43A	.H41B	2.2800
H39A	.H42C_i	2.5000	H43B	.H19B_o	2.5800
H39B	.H37B	2.5900	H43B	.H24A	2.2400
H40A	.Br2_l	3.1600	H43B	.Br2	2.8900
H40B	.H38A	2.5200	H43B	.C24	2.6200
H40C	.H38B	2.5500	H43B	.H44A	2.4000
H41A	.H43C	2.3700	H43B	.H24B	2.5600
H41A	.H44C	2.4200	H43C	.H41A	2.3700
H41A	.Br2_m	2.9800	H43C	.Br2_m	2.8500
H41B	.H43A	2.2800	H43C	.H44C	2.2700
H41B	.C22_j	2.9600	H44A	.C24	2.8500
H41B	.H21B_n	2.4700	H44A	.Br2	2.8800
H41B	.Br1_k	3.1400	H44A	.H24B	2.2700
H44A	.H43B	2.4000	H44B	.Br1	2.8400
H44A	.H20C_p	2.5500	H44B	.C42	2.7500
H44B	.H42B	2.2400	H44C	.H43C	2.2700
H44B	.H23A	2.4400	H44C	.H41A	2.4200

Hydrogen Bonds (Angstrom, Deg)

C1	--	H1B	..	Br1	0.9900	2.9000	3.808(18)	154.00	
C19	--	H19B	..	Br2	0.9900	2.7800	3.729(16)	161.00	1_445
C21	--	H21B	..	Br1	0.9800	2.9200	3.854(16)	161.00	2_556
C21	--	H21C	..	Br2	0.9800	2.6900	3.642(16)	165.00	1_455
C22	--	H22B	..	Br2	0.9800	2.7800	3.667(16)	150.00	1_445
C43	--	H43A	..	Br1	0.9800	2.7700	3.698(15)	158.00	1_565
C43	--	H43B	..	Br2	0.9800	2.8900	3.767(17)	150.00	
C43	--	H43C	..	Br2	0.9800	2.8500	3.792(16)	160.00	2_666
C44	--	H44A	..	Br2	0.9800	2.8800	3.737(17)	146.00	
C44	--	H44B	..	Br1	0.9800	2.8400	3.746(16)	154.00	

Translation of Symmetry Code to Equiv.Pos

```

a =[ 1445.00 ] = -1+x,-1+y,z
b =[ 1455.00 ] = -1+x,y,z
c =[ 1545.00 ] = x,-1+y,z
f =[ 2556.00 ] = -x,-y,1-z
h =[ 2566.00 ] = -x,1-y,1-z
i =[ 2675.00 ] = 1-x,2-y,-z
j =[ 1565.00 ] = x,1+y,z
k =[ 1565.00 ] = x,1+y,z
l =[ 2775.00 ] = 2-x,2-y,-z
m =[ 2666.00 ] = 1-x,1-y,1-z
n =[ 2566.00 ] = -x,1-y,1-z
o =[ 1665.00 ] = 1+x,1+y,z
p =[ 1655.00 ] = 1+x,y,z
q =[ 1655.00 ] = 1+x,y,z
r =[ 2775.00 ] = 2-x,2-y,-z

```

8.3.4. Crystal Data and Details of the Structure Determination N₁₁₁₍₁₄₎TFSI

Crystal Data

Formula	C ₁₉ H ₃₈ F ₆ N ₂ O ₄ S ₂		
Formula Weight	536.63		
Crystal System	Monoclinic		
Space group	P2 ₁ /c	(No. 14)	
a, b, c [Angstrom]	24.0211(6)	8.3769(2)	13.1695(3)
alpha, beta, gamma [deg]	90	96.865(1)	90
V [Ang ³]	2631.00(11)		
Z	4		
D(calc) [g/cm ³]	1.355		
Mu(MoKa) [/mm]	0.271		
F(000)	1136		
Crystal Size [mm]	0.06 x	0.06 x	0.20

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	3.0, 28.3		
Dataset	-31: 31 ; -11: 8 ; -17: 17		
Tot., Uniq. Data, R(int)	11020,	6315,	0.062
Observed data [I > 2.0 sigma(I)]	3389		

Refinement

Nref, Npar	6315, 298
R, wR2, S	0.0768, 0.2307, 1.08
w = 1/[\s^2\^(Fo^2\^)+(0.0800P)^2\^+6.3566P] where P=(Fo^2\^+2Fc^2\^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.73, 0.66

Bond Distances (Angstrom)

S1	-O2	1.434(3)	C11	-C12	1.527(6)
S1	-N2	1.572(3)	C12	-C13	1.517(6)
S1	-O1	1.434(3)	C13	-C14	1.529(7)
S1	-C18	1.838(4)	C1	-H1B	0.9900
S2	-C19	1.845(4)	C1	-H1A	0.9900
S2	-N2	1.583(4)	C2	-H2A	0.9900
S2	-O3	1.435(3)	C2	-H2B	0.9900
S2	-O4	1.427(3)	C3	-H3B	0.9900
F1	-C18	1.328(5)	C3	-H3A	0.9900
F2	-C18	1.322(6)	C4	-H4A	0.9900
F3	-C18	1.329(5)	C4	-H4B	0.9900
F4	-C19	1.333(5)	C5	-H5A	0.9900
F5	-C19	1.327(5)	C5	-H5B	0.9900
F6	-C19	1.329(5)	C6	-H6B	0.9900
N1	-C1	1.518(5)	C6	-H6A	0.9900
N1	-C15	1.507(5)	C7	-H7B	0.9900
N1	-C17	1.489(5)	C7	-H7A	0.9900
N1	-C16	1.488(5)	C8	-H8B	0.9900
C1	-C2	1.523(6)	C8	-H8A	0.9900
C2	-C3	1.532(5)	C9	-H9A	0.9900
C3	-C4	1.528(6)	C9	-H9B	0.9900
C4	-C5	1.522(6)	C10	-H10B	0.9900
C5	-C6	1.529(6)	C10	-H10A	0.9900
C6	-C7	1.521(6)	C11	-H11A	0.9900
C7	-C8	1.529(6)	C11	-H11B	0.9900
C8	-C9	1.525(6)	C12	-H12A	0.9900
C9	-C10	1.532(6)	C12	-H12B	0.9900
C10	-C11	1.522(6)	C13	-H13B	0.9900
C13	-H13A	0.9900	C16	-H16A	0.9800
C14	-H14C	0.9800	C16	-H16B	0.9800

C14	-H14A	0.9800	C16	-H16C	0.9800
C14	-H14B	0.9800	C17	-H17C	0.9800
C15	-H15A	0.9800	C17	-H17A	0.9800
C15	-H15B	0.9800	C17	-H17B	0.9800
C15	-H15C	0.9800			

Bond Angles (Degrees)

O1	-S1	-N2	109.7(2)	C9	-C10	-C11	112.9(3)
O1	-S1	-C18	103.49(18)	C10	-C11	-C12	114.1(3)
O2	-S1	-N2	115.64(18)	C11	-C12	-C13	113.4(3)
O2	-S1	-C18	104.8(2)	C12	-C13	-C14	113.0(4)
N2	-S1	-C18	102.1(2)	N1	-C1	-H1A	109.00
O1	-S1	-O2	118.79(18)	N1	-C1	-H1B	109.00
O3	-S2	-O4	118.97(18)	C2	-C1	-H1A	109.00
O3	-S2	-N2	116.31(18)	C2	-C1	-H1B	109.00
O4	-S2	-N2	108.28(19)	H1A	-C1	-H1B	108.00
O4	-S2	-C19	104.77(19)	C3	-C2	-H2B	110.00
N2	-S2	-C19	101.6(2)	H2A	-C2	-H2B	108.00
O3	-S2	-C19	104.6(2)	C3	-C2	-H2A	110.00
C15	-N1	-C17	108.5(3)	C1	-C2	-H2A	110.00
C16	-N1	-C17	109.8(3)	C1	-C2	-H2B	110.00
C15	-N1	-C16	108.3(3)	C2	-C3	-H3A	109.00
C1	-N1	-C15	108.0(3)	C4	-C3	-H3A	109.00
C1	-N1	-C16	110.9(3)	C4	-C3	-H3B	109.00
C1	-N1	-C17	111.2(3)	C2	-C3	-H3B	109.00
S1	-N2	-S2	124.0(2)	H3A	-C3	-H3B	108.00
N1	-C1	-C2	114.7(3)	C3	-C4	-H4B	109.00
C1	-C2	-C3	110.6(3)	C5	-C4	-H4A	109.00
C2	-C3	-C4	111.8(3)	C3	-C4	-H4A	109.00
C3	-C4	-C5	113.9(3)	H4A	-C4	-H4B	108.00
C4	-C5	-C6	112.0(3)	C5	-C4	-H4B	109.00

C5	-C6	-C7	113.5(3)	C4	-C5	-H5A	109.00
C6	-C7	-C8	113.8(3)	H5A	-C5	-H5B	108.00
C7	-C8	-C9	113.0(3)	C6	-C5	-H5B	109.00
C8	-C9	-C10	113.6(3)	C4	-C5	-H5B	109.00
C6	-C5	-H5A	109.00	C10	-C11	-H11A	109.00
C5	-C6	-H6A	109.00	H11A	-C11	-H11B	108.00
H6A	-C6	-H6B	108.00	C12	-C11	-H11B	109.00
C5	-C6	-H6B	109.00	C13	-C12	-H12A	109.00
C7	-C6	-H6A	109.00	C11	-C12	-H12B	109.00
C7	-C6	-H6B	109.00	C11	-C12	-H12A	109.00
C6	-C7	-H7A	109.00	C13	-C12	-H12B	109.00
C6	-C7	-H7B	109.00	H12A	-C12	-H12B	108.00
C8	-C7	-H7A	109.00	H13A	-C13	-H13B	108.00
C8	-C7	-H7B	109.00	C14	-C13	-H13A	109.00
H7A	-C7	-H7B	108.00	C14	-C13	-H13B	109.00
H8A	-C8	-H8B	108.00	C12	-C13	-H13A	109.00
C7	-C8	-H8A	109.00	C12	-C13	-H13B	109.00
C9	-C8	-H8B	109.00	H14B	-C14	-H14C	109.00
C9	-C8	-H8A	109.00	C13	-C14	-H14B	109.00
C7	-C8	-H8B	109.00	C13	-C14	-H14C	109.00
C10	-C9	-H9A	109.00	C13	-C14	-H14A	110.00
C8	-C9	-H9B	109.00	H14A	-C14	-H14C	109.00
C8	-C9	-H9A	109.00	H14A	-C14	-H14B	109.00
H9A	-C9	-H9B	108.00	N1	-C15	-H15C	109.00
C10	-C9	-H9B	109.00	N1	-C15	-H15B	110.00
H10A	-C10	-H10B	108.00	N1	-C15	-H15A	109.00
C11	-C10	-H10B	109.00	H15A	-C15	-H15C	110.00
C9	-C10	-H10A	109.00	H15B	-C15	-H15C	109.00
C9	-C10	-H10B	109.00	H15A	-C15	-H15B	109.00
C11	-C10	-H10A	109.00	N1	-C16	-H16C	109.00

C10	-C11	-H11B	109.00	H16A	-C16	-H16B	109.00
C12	-C11	-H11A	109.00	N1	-C16	-H16A	109.00
N1	-C16	-H16B	109.00	S1	-C18	-F3	110.9(3)
H16B	-C16	-H16C	109.00	F1	-C18	-F2	108.5(3)
H16A	-C16	-H16C	109.00	F1	-C18	-F3	108.6(4)
H17B	-C17	-H17C	109.00	F2	-C18	-F3	107.7(3)
H17A	-C17	-H17C	109.00	S2	-C19	-F4	110.9(3)
N1	-C17	-H17A	110.00	S2	-C19	-F5	111.0(3)
N1	-C17	-H17B	109.00	S2	-C19	-F6	109.8(3)
N1	-C17	-H17C	110.00	F4	-C19	-F5	108.3(3)
H17A	-C17	-H17B	109.00	F4	-C19	-F6	108.1(4)
S1	-C18	-F1	110.0(3)	F5	-C19	-F6	108.6(4)
S1	-C18	-F2	111.0(3)				

Contact Distances(Angstrom)

S1	.F5	3.421(3)	F1	.H16B_j	2.7100
S2	.F3	3.377(3)	F1	.H15B_k	2.7400
F1	.01	3.018(4)	F2	.H17A_m	2.8500
F1	.02	2.943(4)	F2	.H17B_m	2.7100
F1	.F2_c	2.897(4)	F3	.H16A_e	2.5500
F1	.C16_j	3.331(5)	F3	.H17A_m	2.7400
F2	.F1_l	2.897(4)	F3	.H16C_e	2.7600
F2	.02_l	2.881(4)	F4	.H2B_o	2.6300
F2	.C17_m	3.229(5)	F4	.H3B_o	2.7400
F2	.01	2.890(4)	F4	.H1A_o	2.7900
F2	.N2	3.013(4)	F5	.H2A	2.6100
F3	.S2	3.377(3)	F5	.H3A	2.8600
F3	.03	3.089(4)	F6	.H14A_p	2.8200
F3	.C16_e	3.092(5)	O1	.C16_o	3.239(5)
F3	.01_n	3.083(4)	O1	.F2	2.890(4)
F3	.02	3.013(3)	O1	.F1	3.018(4)
F3	.N2	2.973(4)	O1	.F3_d	3.083(4)

F4	.N2	3.034(4)	O2	.C17	3.245(5)
F4	.C2_o	3.196(5)	O2	.F1	2.943(4)
F4	.O4	2.902(4)	O2	.F3	3.013(3)
F4	.C3_o	3.362(5)	O2	.F2_c	2.881(4)
F5	.C2	3.274(5)	O2	.C15_e	3.211(5)
F5	.N2	2.967(4)	O2	.F5	3.131(4)
F5	.S1	3.421(3)	O2	.O3	2.864(4)
F5	.O2	3.131(4)	O3	.F5	3.029(4)
F5	.O3	3.029(4)	O3	.O2	2.864(4)
F6	.O4	3.062(4)	O3	.F6	2.931(4)
F6	.O3	2.931(4)	O3	.F3	3.089(4)
O4	.F6	3.062(4)	C17	.O2	3.245(5)
O4	.F4	2.902(4)	C17	.F2_d	3.229(5)
O1	.H17B_k	2.7600	C2	.H17C	2.7100
O1	.H16C_k	2.9000	C2	.H16B	2.7300
O2	.H17C	2.4200	C16	.H2B	2.7300
O2	.H15B_e	2.8600	C17	.H2A	2.7000
O2	.H15A_e	2.6800	H1A	.F4_a	2.7900
O2	.H2A	2.8700	H1A	.H3B	2.4900
O3	.H15A_e	2.5900	H1A	.H16A	2.4500
O3	.H4B	2.6800	H1A	.H15A	2.4100
O4	.H4A_o	2.6000	H1B	.H15C	2.4000
O4	.H14A_p	2.8100	H1B	.H17A	2.4800
O4	.H15C_m	2.6500	H1B	.H3A	2.4800
O4	.H1B_m	2.5800	H1B	.O4_d	2.5800
N2	.F2	3.013(4)	H2A	.C17	2.7000
N2	.C16_o	3.441(5)	H2A	.H17C	2.1600
N2	.F5	2.967(4)	H2A	.O2	2.8700
N2	.F3	2.973(4)	H2A	.H4B	2.5300
N2	.F4	3.034(4)	H2A	.F5	2.6100

N2	.H16B_o	2.7400	H2B	.F4_a	2.6300
C2	.F4_a	3.196(5)	H2B	.H15C_e	2.5600
C2	.F5	3.274(5)	H2B	.C16	2.7300
C3	.F4_a	3.362(5)	H2B	.H4A	2.5300
C15	.O2_b	3.211(5)	H2B	.H16B	2.1900
C16	.F1_c	3.331(5)	H3A	.F5	2.8600
C16	.F3_b	3.092(5)	H3A	.H1B	2.4800
C16	.N2_a	3.441(5)	H3B	.H1A	2.4900
C16	.O1_a	3.239(5)	H3B	.H5A	2.5500
H3B	.F4_a	2.7400	H10B	.H12B	2.5600
H4A	.O4_a	2.6000	H11A	.H13A	2.5400
H4A	.H2B	2.5300	H11A	.H9A	2.5300
H4A	.H6A	2.4700	H11B	.H5B_f	2.5800
H4B	.H2A	2.5300	H11B	.H13B	2.5400
H4B	.H6B	2.5600	H11B	.H9B	2.5400
H4B	.O3	2.6800	H12A	.H14C	2.5600
H5A	.H3B	2.5500	H12A	.H10A	2.5700
H5A	.H7A	2.5100	H12B	.H10B	2.5600
H5B	.H11B_f	2.5800	H12B	.H14B	2.5500
H6A	.H4A	2.4700	H13A	.H11A	2.5400
H6A	.H8A	2.5200	H13B	.H11B	2.5400
H6B	.H4B	2.5600	H14A	.F6_g	2.8200
H7A	.H9A	2.5000	H14A	.O4_g	2.8100
H7A	.H5A	2.5100	H14B	.H12B	2.5500
H7B	.H9B	2.5700	H14C	.H12A	2.5600
H7B	.H9B_f	2.6000	H15A	.O3_b	2.5900
H8A	.H10A	2.5400	H15A	.O2_b	2.6800
H8A	.H6A	2.5200	H15A	.H1A	2.4100
H8B	.H10B	2.5900	H15A	.H16A	2.4300
H9A	.H7A	2.5000	H15B	.H16C	2.4000
H9A	.H11A	2.5300	H15B	.H17B	2.4100

H9B	.H7B	2.5700	H15B	.F1_h	2.7400
H9B	.H7B_f	2.6000	H15B	.O2_b	2.8600
H9B	.H11B	2.5400	H15C	.H17A	2.4400
H10A	.H8A	2.5400	H15C	.O4_d	2.6500
H10A	.H12A	2.5700	H15C	.H2B_i	2.5600
H10B	.H8B	2.5900	H15C	.H1B	2.4000
H16A	.H1A	2.4500	H17A	.F2_d	2.8500
H16A	.H15A	2.4300	H17A	.F3_d	2.7400
H16A	.F3_b	2.5500	H17A	.H1B	2.4800
H16B	.H17C	2.4400	H17A	.H15C	2.4400
H16B	.F1_c	2.7100	H17B	.H16C	2.4400
H16B	.H2B	2.1900	H17B	.O1_h	2.7600
H16B	.N2_a	2.7400	H17B	.H15B	2.4100
H16B	.C2	2.7300	H17B	.F2_d	2.7100
H16C	.H15B	2.4000	H17C	.H2A	2.1600
H16C	.O1_h	2.9000	H17C	.H16B	2.4400
H16C	.F3_b	2.7600	H17C	.O2	2.4200
H16C	.H17B	2.4400	H17C	.C2	2.7100

Hydrogen Bonds (Angstrom, Deg)

C1	--	H1B	..	O4	0.9900	2.5800	3.507(5)	156.00	4_544
C15	--	H15A	..	O3	0.9800	2.5900	3.531(6)	161.00	4_554
C17	--	H17C	..	O2	0.9800	2.4200	3.245(5)	142.00	

Translation of Symmetry Code to Equiv.Pos

a	=	[1565.00]	=	x,1+y,z
b	=	[4554.00]	=	x,1/2-y,-1/2+z
c	=	[2556.00]	=	-x,1/2+y,3/2-z
d	=	[4544.00]	=	x,-1/2-y,-1/2+z
e	=	[4555.00]	=	x,1/2-y,1/2+z
f	=	[3657.00]	=	1-x,-y,2-z
g	=	[2657.00]	=	1-x,1/2+y,5/2-z
h	=	[3556.00]	=	-x,-y,1-z
j	=	[2546.00]	=	-x,-1/2+y,3/2-z
k	=	[3556.00]	=	-x,-y,1-z
l	=	[2546.00]	=	-x,-1/2+y,3/2-z
m	=	[4545.00]	=	x,-1/2-y,1/2+z
n	=	[4545.00]	=	x,-1/2-y,1/2+z
o	=	[1545.00]	=	x,-1+y,z
p	=	[2647.00]	=	1-x,-1/2+y,5/2-z

8.3.5. Crystal Data and Details of the Structure Determination for N_{11B(18)}Br.H₂O

Crystal Data

Formula	C ₂₇ H ₅₂ Br ₁ N ₁ O ₁		
Formula Weight	486.61		
Crystal System	Triclinic		
Space group	P-1	(No. 2)	
a, b, c [Angstrom]	8.1882(1)	8.8075(1)	21.7792(5)
alpha, beta, gamma [deg]	89.773(1)	98.888(1)	114.941(1)
V [Ang**3]	1403.80(4)		
Z	2		
D(calc) [g/cm**3]	1.151		
Mu(MoKa) [/mm]	1.481		
F(000)	528		
Crystal Size [mm]	0.08 x 0.12 x 0.20		

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	2.9, 26.0		
Dataset	-10: 10 ; -10: 10 ; -26: 26		
Tot., Uniq. Data, R(int)	9974,	5490,	0.047
Observed data [I > 0.0 sigma(I)]	4807		

Refinement

Nref, Npar	5490, 479
R, wR2, S	0.0347, 0.0862, 1.03
w = 1/[\s^2\^(Fo^2\^)+(0.0364P)^2\^+0.6705P] where P=(Fo^2\^+2Fc^2\^)/3	
Max. and Av. Shift/Error	0.00, 0.00
Min. and Max. Resd. Dens. [e/Ang^3]	-0.61, 0.40

Bond Distances (Angstrom)

O1	-H51	0.73(3)	C25	-C26	1.387(4)
O1	-H52	0.82(3)	C26	-C27	1.389(3)
N1	-C20	1.506(3)	C1	-H1	0.93(2)
N1	-C21	1.537(3)	C1	-H2	0.96(3)
N1	-C1	1.522(3)	C2	-H4	0.99(3)
N1	-C19	1.507(3)	C2	-H3	0.95(3)
C1	-C2	1.519(3)	C3	-H6	0.97(3)
C2	-C3	1.529(3)	C3	-H5	0.99(3)
C3	-C4	1.530(3)	C4	-H8	1.02(3)
C4	-C5	1.526(3)	C4	-H7	0.94(3)
C5	-C6	1.521(3)	C5	-H9	1.01(3)
C6	-C7	1.523(3)	C5	-H10	0.96(3)
C7	-C8	1.525(3)	C6	-H12	0.94(3)
C8	-C9	1.524(3)	C6	-H11	0.96(3)
C9	-C10	1.527(3)	C7	-H14	0.99(3)
C10	-C11	1.526(3)	C7	-H13	0.98(3)
C11	-C12	1.529(4)	C8	-H16	0.99(3)
C12	-C13	1.525(3)	C8	-H15	0.94(2)
C13	-C14	1.522(3)	C9	-H17	0.97(3)
C14	-C15	1.524(3)	C9	-H18	0.99(3)
C15	-C16	1.525(3)	C10	-H19	0.95(3)
C16	-C17	1.523(3)	C10	-H20	0.99(3)
C17	-C18	1.520(4)	C11	-H21	0.99(3)
C21	-C22	1.501(3)	C11	-H22	1.03(3)
C22	-C23	1.400(4)	C12	-H24	0.99(3)
C22	-C27	1.399(3)	C12	-H23	0.99(2)
C23	-C24	1.387(3)	C13	-H25	0.96(3)
C24	-C25	1.390(3)	C13	-H26	1.00(3)
C14	-H28	0.99(3)	C19	-H40	0.92(3)
C14	-H27	0.94(3)	C19	-H38	0.94(3)

C15	-H30	0.99(3)	C20	-H43	0.96(3)
C15	-H29	0.97(3)	C20	-H41	0.97(3)
C16	-H32	0.96(3)	C20	-H42	0.92(2)
C16	-H31	0.98(3)	C21	-H45	0.92(2)
C17	-H33	0.95(3)	C21	-H44	0.95(2)
C17	-H34	0.93(3)	C23	-H46	0.91(2)
C18	-H35	0.99(4)	C24	-H47	0.94(3)
C18	-H37	0.96(3)	C25	-H48	0.93(3)
C18	-H36	0.97(4)	C26	-H49	0.94(3)
C19	-H39	0.97(3)	C27	-H50	0.90(3)

Bond Angles (Degrees)

H51	-O1	-H52	110(3)	C22	-C23	-C24	120.9(2)
C1	-N1	-C19	110.16(17)	C23	-C24	-C25	119.7(2)
C1	-N1	-C21	113.02(16)	C24	-C25	-C26	120.1(2)
C19	-N1	-C20	108.39(17)	C25	-C26	-C27	120.3(2)
C19	-N1	-C21	107.78(17)	C22	-C27	-C26	120.3(2)
C20	-N1	-C21	109.56(18)	N1	-C1	-H1	106.4(16)
C1	-N1	-C20	107.86(17)	N1	-C1	-H2	105.5(14)
N1	-C1	-C2	114.67(18)	C2	-C1	-H2	109.2(15)
C1	-C2	-C3	110.86(19)	H1	-C1	-H2	110(2)
C2	-C3	-C4	111.93(19)	C2	-C1	-H1	111.1(15)
C3	-C4	-C5	113.31(19)	C1	-C2	-H3	110.6(16)
C4	-C5	-C6	113.52(19)	C3	-C2	-H3	108.0(14)
C5	-C6	-C7	113.91(19)	C3	-C2	-H4	111.1(15)
C6	-C7	-C8	113.70(19)	C1	-C2	-H4	108.7(14)
C7	-C8	-C9	113.89(19)	H3	-C2	-H4	108(2)
C8	-C9	-C10	113.68(19)	C2	-C3	-H6	108.3(14)
C9	-C10	-C11	113.62(19)	C4	-C3	-H5	110.6(14)
C10	-C11	-C12	113.48(19)	C4	-C3	-H6	111.2(15)
C11	-C12	-C13	113.36(19)	H5	-C3	-H6	107(2)

C12	-C13	-C14	113.67(19)	C2	-C3	-H5	107.4(15)
C13	-C14	-C15	113.64(19)	C3	-C4	-H7	110.4(16)
C14	-C15	-C16	114.17(19)	C3	-C4	-H8	108.6(14)
C15	-C16	-C17	113.79(19)	C5	-C4	-H8	109.2(14)
C16	-C17	-C18	113.6(2)	H7	-C4	-H8	110(2)
N1	-C21	-C22	114.36(19)	C5	-C4	-H7	105.4(15)
C21	-C22	-C27	120.6(2)	C4	-C5	-H9	110.0(18)
C23	-C22	-C27	118.7(2)	C6	-C5	-H9	107.6(18)
C21	-C22	-C23	120.7(2)	C6	-C5	-H10	112(2)
C4	-C5	-H10	107.8(17)	C10	-C11	-H22	108.0(13)
H9	-C5	-H10	106(3)	C12	-C11	-H22	111.1(14)
C5	-C6	-H12	107.8(15)	H21	-C11	-H22	108(2)
C7	-C6	-H11	108.5(15)	C12	-C11	-H21	108.8(14)
C7	-C6	-H12	111.1(17)	C11	-C12	-H24	107.9(14)
H11	-C6	-H12	106(2)	C13	-C12	-H23	109.7(14)
C5	-C6	-H11	109.3(18)	C13	-C12	-H24	107.9(14)
C6	-C7	-H14	109.7(14)	H23	-C12	-H24	108(2)
C8	-C7	-H13	106.7(14)	C11	-C12	-H23	109.5(15)
C6	-C7	-H13	110.7(15)	C12	-C13	-H25	108.5(17)
H13	-C7	-H14	106(2)	C12	-C13	-H26	110.3(14)
C8	-C7	-H14	110.2(17)	C14	-C13	-H26	108.5(15)
C7	-C8	-H15	107.8(16)	H25	-C13	-H26	110(2)
C7	-C8	-H16	107.8(14)	C14	-C13	-H25	106.0(15)
C9	-C8	-H16	110.3(15)	C13	-C14	-H28	107.5(14)
H15	-C8	-H16	106(2)	C15	-C14	-H27	109.4(16)
C9	-C8	-H15	110.9(15)	C15	-C14	-H28	107.8(14)
C8	-C9	-H18	109.1(16)	H27	-C14	-H28	111(2)
C10	-C9	-H17	106.4(14)	C13	-C14	-H27	107.2(18)
C10	-C9	-H18	108.6(19)	C14	-C15	-H29	109.1(15)
H17	-C9	-H18	110(2)	C14	-C15	-H30	110.6(14)
C8	-C9	-H17	108.8(15)	C16	-C15	-H30	107.7(17)

C9	-C10	-H20	107.7(14)	H29	-C15	-H30	108(2)
C11	-C10	-H19	109.8(15)	C16	-C15	-H29	107.0(15)
C9	-C10	-H19	110.7(18)	C15	-C16	-H31	110.4(18)
H19	-C10	-H20	109(2)	C15	-C16	-H32	108.1(15)
C11	-C10	-H20	106.1(14)	C17	-C16	-H32	107.8(16)
C10	-C11	-H21	107.8(14)	H31	-C16	-H32	110(2)
C17	-C16	-H31	107.2(15)	N1	-C20	-H41	104.3(14)
C16	-C17	-H34	110.7(17)	H41	-C20	-H43	112(2)
C18	-C17	-H33	107.5(15)	H42	-C20	-H43	114(2)
C18	-C17	-H34	109(2)	H41	-C20	-H42	110(2)
H33	-C17	-H34	107(2)	N1	-C21	-H45	104.6(17)
C16	-C17	-H33	108.4(16)	C22	-C21	-H44	109.7(15)
C17	-C18	-H35	111(2)	C22	-C21	-H45	113.2(14)
C17	-C18	-H36	111.8(19)	H44	-C21	-H45	110(2)
H35	-C18	-H36	107(3)	N1	-C21	-H44	104.3(16)
H35	-C18	-H37	108(3)	C24	-C23	-H46	120.3(16)
H36	-C18	-H37	109(3)	C22	-C23	-H46	118.9(16)
C17	-C18	-H37	110(2)	C23	-C24	-H47	119.2(16)
N1	-C19	-H38	108.8(16)	C25	-C24	-H47	121.1(16)
N1	-C19	-H39	108.4(14)	C26	-C25	-H48	119.3(17)
H38	-C19	-H39	110(2)	C24	-C25	-H48	120.6(17)
H38	-C19	-H40	109(2)	C25	-C26	-H49	119.0(16)
N1	-C19	-H40	108.7(16)	C27	-C26	-H49	120.7(16)
H39	-C19	-H40	112(2)	C22	-C27	-H50	117.5(17)
N1	-C20	-H42	109.8(15)	C26	-C27	-H50	122.2(17)
N1	-C20	-H43	106.0(14)				

Contact Distances(Angstrom)

Br1	.01_s	3.354(2)	C15	.H48_c	3.10(3)
Br1	.01	3.332(3)	C17	.H48_c	3.04(3)
Br1	.H51	2.61(3)	C19	.H4	2.73(3)
Br1	.H46_h	3.09(3)	C19	.H4_e	2.98(3)

Br1	.H47_h	3.25(3)	C19	.H3	3.05(2)
Br1	.H43_e	3.10(3)	C20	.H46	2.98(3)
Br1	.H52_s	2.53(3)	C21	.H3	2.81(3)
Br1	.H45_r	2.99(2)	C22	.H42	2.75(3)
Br1	.H40_e	2.94(3)	C22	.H1	2.65(3)
Br1	.H3_r	3.09(3)	C23	.H42	2.73(3)
Br1	.H41_a	2.96(3)	C23	.H11_f	3.09(3)
O1	.Br1	3.332(3)	C24	.H11_f	3.06(3)
O1	.Br1_t	3.354(2)	C27	.H1	2.76(3)
O1	.C19_u	3.295(4)	H1	.C22	2.65(3)
O1	.H38_r	2.62(3)	H1	.C27	2.76(3)
O1	.H39_u	2.34(3)	H1	.H42	2.43(3)
O1	.H46_e	2.90(2)	H1	.H5	2.45(3)
C1	.C27	3.335(4)	H2	.H39	2.43(3)
C19	.O1_d	3.295(4)	H2	.H41	2.23(3)
C20	.C23	3.238(4)	H3	.C19	3.05(2)
C23	.C20	3.238(4)	H3	.Br1_g	3.09(3)
C27	.C1	3.335(4)	H3	.H38	2.57(3)
C2	.H45	2.86(3)	H3	.C21	2.81(3)
C2	.H39	3.09(2)	H3	.H7	2.52(3)
C2	.H38	2.66(3)	H3	.H50	2.58(4)
C6	.H42_a	3.10(2)	H3	.H45	2.28(4)
C10	.H35_b	3.09(4)	H4	.H38	2.35(4)
C11	.H35_b	3.09(4)	H4	.C19	2.73(3)
H4	.C19_e	2.98(3)	H20	.H16	2.58(4)
H4	.H39_e	2.51(4)	H20	.H30_i	2.56(4)
H5	.H1	2.45(3)	H20	.H24	2.54(3)
H5	.H9	2.55(4)	H20	.H48_h	2.59(4)
H7	.H11	2.49(4)	H21	.H17	2.52(3)
H7	.H3	2.52(3)	H21	.H25	2.58(4)
H8	.H12	2.55(4)	H21	.H35_b	2.49(5)

H9	.H13	2.54(4)	H22	.H18	2.53(4)
H9	.H5	2.55(4)	H22	.H30_i	2.53(4)
H11	.C23_a	3.09(3)	H22	.H28_i	2.60(4)
H11	.H15	2.51(4)	H23	.H27	2.54(4)
H11	.C24_a	3.06(3)	H23	.H31_b	2.53(4)
H11	.H7	2.49(4)	H23	.H19	2.55(4)
H11	.H42_a	2.53(3)	H23	.H33_b	2.59(4)
H12	.H16	2.57(4)	H24	.H20	2.54(3)
H12	.H8	2.55(4)	H24	.H28	2.55(3)
H13	.H17	2.55(3)	H24	.H36_j	2.57(4)
H13	.H9	2.54(4)	H24	.H26_i	2.58(4)
H14	.H18	2.57(4)	H25	.H21	2.58(4)
H15	.H11	2.51(4)	H25	.H29	2.54(4)
H16	.H12	2.57(4)	H25	.H31_b	2.53(4)
H16	.H20	2.58(4)	H26	.H30	2.56(4)
H17	.H13	2.55(3)	H26	.H24_i	2.58(4)
H17	.H21	2.52(3)	H26	.H26_i	2.56(4)
H18	.H22	2.53(4)	H27	.H23	2.54(4)
H18	.H14	2.57(4)	H27	.H27_b	2.54(4)
H19	.H23	2.55(4)	H28	.H32	2.58(3)
H19	.H35_b	2.54(5)	H28	.H22_i	2.60(4)
H28	.H24	2.55(3)	H38	.H3	2.57(3)
H28	.H32_j	2.59(4)	H38	.C2	2.66(3)
H29	.H33	2.53(3)	H39	.H2	2.43(3)
H29	.H25	2.54(4)	H39	.H41	2.39(3)
H30	.H20_i	2.56(4)	H39	.H4_e	2.51(4)
H30	.H22_i	2.53(4)	H39	.H52_d	2.60(5)
H30	.H48_c	2.48(4)	H39	.O1_d	2.34(3)
H30	.H34	2.54(4)	H39	.C2	3.09(2)
H30	.H26	2.56(4)	H40	.Br1_m	2.94(3)
H31	.H23_b	2.53(4)	H40	.H43	2.33(3)

H31	.H35	2.53(4)	H40	.H44	2.39(4)
H31	.H25_b	2.53(4)	H41	.Br1_n	2.96(3)
H32	.H28	2.58(3)	H41	.H2	2.23(3)
H32	.H28_j	2.59(4)	H41	.H39	2.39(3)
H33	.H29	2.53(3)	H42	.C6_f	3.10(2)
H33	.H23_b	2.59(4)	H42	.C23	2.73(3)
H34	.H30	2.54(4)	H42	.H1	2.43(3)
H34	.H48_c	2.45(4)	H42	.H11_f	2.53(3)
H35	.H31	2.53(4)	H42	.H46	2.58(4)
H35	.C10_b	3.09(4)	H42	.C22	2.75(3)
H35	.C11_b	3.09(4)	H43	.H44	2.32(4)
H35	.H19_b	2.54(5)	H43	.Br1_m	3.10(3)
H35	.H21_b	2.49(5)	H43	.H40	2.33(3)
H36	.H24_j	2.57(4)	H44	.H43	2.32(4)
H37	.H49_k	2.43(4)	H44	.H46	2.43(3)
H38	.O1_l	2.62(3)	H44	.H40	2.39(4)
H38	.H4	2.35(4)	H45	.Br1_g	2.99(2)
H38	.H45	2.30(4)	H45	.H3	2.28(4)
H45	.H38	2.30(4)	H48	.H30_c	2.48(4)
H45	.C2	2.86(3)	H48	.H34_c	2.45(4)
H45	.H50	2.45(3)	H48	.C15_c	3.10(3)
H46	.H42	2.58(4)	H48	.C17_c	3.04(3)
H46	.H44	2.43(3)	H49	.H37_k	2.43(4)
H46	.O1_p	2.90(2)	H50	.H45	2.45(3)
H46	.H52_p	2.55(4)	H50	.H3	2.58(4)
H46	.Br1_o	3.09(3)	H51	.Br1	2.61(3)
H46	.C20	2.98(3)	H52	.Br1_t	2.53(3)
H47	.Br1_o	3.25(3)	H52	.H39_u	2.60(5)
H48	.H20_q	2.59(4)	H52	.H46_e	2.55(4)

Hydrogen Bonds (Angstrom, Deg)

O1	--	H51	..	Br1	0.73(3)	2.61(3)	3.332(3)	173(3)	
O1	--	H52	..	Br1	0.82(3)	2.53(3)	3.354(2)	177(3)	2_755
C19	--	H39	..	O1	0.97(3)	2.34(3)	3.295(4)	169(2)	2_765

Translation of Symmetry Code to Equiv.Pos

```

a =[ 1545.00] = [ 1_545] =x,-1+y,z
b =[ 2636.00] = [ 2_636] =1-x,-2-y,1-z
c =[ 2656.00] = [ 2_656] =1-x,-y,1-z
d =[ 2765.00] = [ 2_765] =2-x,1-y,-z
e =[ 2665.00] = [ 2_665] =1-x,1-y,-z
f =[ 1565.00] = [ 1_565] =x,1+y,z
g =[ 1455.00] = [ 1_455] =-1+x,y,z
h =[ 1645.00] = [ 1_645] =1+x,-1+y,z
i =[ 2746.00] = [ 2_746] =2-x,-1-y,1-z
j =[ 2736.00] = [ 2_736] =2-x,-2-y,1-z
k =[ 2646.00] = [ 2_646] =1-x,-1-y,1-z
l =[ 1455.00] = [ 1_455] =-1+x,y,z
m =[ 2665.00] = [ 2_665] =1-x,1-y,-z
n =[ 1565.00] = [ 1_565] =x,1+y,z
o =[ 1465.00] = [ 1_465] =-1+x,1+y,z
p =[ 2665.00] = [ 2_665] =1-x,1-y,-z
q =[ 1465.00] = [ 1_465] =-1+x,1+y,z
r =[ 1655.00] = [ 1_655] =1+x,y,z
s =[ 2755.00] = [ 2_755] =2-x,-y,-z
t =[ 2755.00] = [ 2_755] =2-x,-y,-z

```

8.3.6. Crystal Data and Details of the Structure Determination for N₁₁₄₍₁₈₎Br.H₂O

Crystal Data

Formula	C ₂₄ H ₅₄ Br ₁ N ₁ O ₁		
Formula Weight	452.59		
Crystal System	Triclinic		
Space group	P-1	(No. 2)	
a, b, c [Angstrom]	8.1021(8)	8.5773(9)	20.4765(18)
alpha, beta, gamma [deg]	95.096(8)	90.729(8)	110.255(10)
V [Ang**3]	1328.3(2)		
Z	2		
D(calc) [g/cm**3]	1.132		
Mu(MoKa) [/mm]	1.543		
F(000)	496		
Crystal Size [mm]	0.03 x 0.06 x 0.15		

Data Collection

Temperature (K)	100		
Radiation [Angstrom]	MoKa	0.71073	
Theta Min-Max [Deg]	3.1, 26.0		
Dataset	-9: 6 ; -7: 10 ; -25: 23		
Tot., Uniq. Data, R(int)	8400,	5187,	0.055
Observed data [I > 0.0 sigma(I)]	3132		

Refinement

Nref, Npar	5187, 252
R, wR2, S	0.0533, 0.0966, 1.01
$w = 1/[\sigma^2(F_o^2)+(0.0225P)^2]$	where $P=(F_o^2+2F_c^2)/3$
Max. and Av. Shift/Error	0.02, 0.00
Min. and Max. Resd. Dens. [e/Ång ³]	-0.76, 0.97

Bond Distances (Angstrom)

O1	-H1WB	0.82(7)	C2	-H2A	0.9900
O1	-H1WA	0.78(4)	C2	-H2B	0.9900
N1	-C19	1.515(5)	C3	-H3B	0.9900
N1	-C23	1.507(5)	C3	-H3A	0.9900
N1	-C1	1.513(5)	C4	-H4B	0.9900
N1	-C24	1.506(5)	C4	-H4A	0.9900
C1	-C2	1.514(5)	C5	-H5B	0.9900
C2	-C3	1.515(6)	C5	-H5A	0.9900
C3	-C4	1.534(6)	C6	-H6A	0.9900
C4	-C5	1.507(6)	C6	-H6B	0.9900
C5	-C6	1.521(6)	C7	-H7B	0.9900
C6	-C7	1.517(5)	C7	-H7A	0.9900
C7	-C8	1.526(6)	C8	-H8B	0.9900
C8	-C9	1.522(6)	C8	-H8A	0.9900
C9	-C10	1.519(6)	C9	-H9B	0.9900
C10	-C11	1.528(6)	C9	-H9A	0.9900
C11	-C12	1.523(6)	C10	-H10A	0.9900
C12	-C13	1.521(6)	C10	-H10B	0.9900
C13	-C14	1.519(6)	C11	-H11A	0.9900
C14	-C15	1.513(6)	C11	-H11B	0.9900
C15	-C16	1.521(6)	C12	-H12A	0.9900
C16	-C17	1.513(6)	C12	-H12B	0.9900
C17	-C18	1.515(6)	C13	-H13B	0.9900
C19	-C20	1.516(6)	C13	-H13A	0.9900
C20	-C21	1.522(5)	C14	-H14A	0.9900
C21	-C22	1.530(6)	C14	-H14B	0.9900
C1	-H1B	0.9900	C15	-H15B	0.9900
C1	-H1A	0.9900	C15	-H15A	0.9900
C16	-H16B	0.9900	C21	-H21A	0.9900
C16	-H16A	0.9900	C21	-H21B	0.9900

C17	-H17B	0.9900	C22	-H22B	0.9800
C17	-H17A	0.9900	C22	-H22A	0.9800
C18	-H18C	0.9800	C22	-H22C	0.9800
C18	-H18A	0.9800	C23	-H23B	0.9800
C18	-H18B	0.9800	C23	-H23C	0.9800
C19	-H19B	0.9900	C23	-H23A	0.9800
C19	-H19A	0.9900	C24	-H24C	0.9800
C20	-H20B	0.9900	C24	-H24A	0.9800
C20	-H20A	0.9900	C24	-H24B	0.9800

Bond Angles (Degrees)

H1WA	-O1	-H1WB	96(6)	C2	-C1	-H1A	108.00
C1	-N1	-C19	113.1(3)	C2	-C1	-H1B	108.00
C1	-N1	-C24	108.2(3)	H1A	-C1	-H1B	107.00
C19	-N1	-C23	106.9(3)	N1	-C1	-H1A	108.00
C19	-N1	-C24	110.4(3)	C1	-C2	-H2B	109.00
C23	-N1	-C24	107.9(3)	C3	-C2	-H2A	109.00
C1	-N1	-C23	110.4(3)	C1	-C2	-H2A	109.00
N1	-C1	-C2	116.0(3)	H2A	-C2	-H2B	108.00
C1	-C2	-C3	111.6(3)	C3	-C2	-H2B	109.00
C2	-C3	-C4	113.4(3)	C2	-C3	-H3A	109.00
C3	-C4	-C5	114.5(3)	C2	-C3	-H3B	109.00
C4	-C5	-C6	114.8(3)	C4	-C3	-H3B	109.00
C5	-C6	-C7	114.4(3)	H3A	-C3	-H3B	108.00
C6	-C7	-C8	114.3(3)	C4	-C3	-H3A	109.00
C7	-C8	-C9	113.9(3)	C3	-C4	-H4B	109.00
C8	-C9	-C10	113.9(3)	C5	-C4	-H4A	109.00
C9	-C10	-C11	113.9(3)	C5	-C4	-H4B	109.00
C10	-C11	-C12	114.0(3)	H4A	-C4	-H4B	108.00
C11	-C12	-C13	114.1(3)	C3	-C4	-H4A	109.00
C12	-C13	-C14	114.7(3)	C4	-C5	-H5B	109.00

C13	-C14	-C15	114.1(3)	C6	-C5	-H5A	109.00
C14	-C15	-C16	115.4(3)	C4	-C5	-H5A	109.00
C15	-C16	-C17	114.0(3)	H5A	-C5	-H5B	108.00
C16	-C17	-C18	113.8(3)	C6	-C5	-H5B	109.00
N1	-C19	-C20	115.8(3)	C5	-C6	-H6A	109.00
C19	-C20	-C21	109.2(3)	C5	-C6	-H6B	109.00
C20	-C21	-C22	113.4(3)	C7	-C6	-H6B	109.00
N1	-C1	-H1B	108.00	H6A	-C6	-H6B	108.00
C7	-C6	-H6A	109.00	C11	-C12	-H12A	109.00
C6	-C7	-H7B	109.00	H12A	-C12	-H12B	108.00
C8	C7	-H7A	109.00	C13	-C12	-H12B	109.00
C8	-C7	-H7B	109.00	C12	-C13	-H13A	109.00
H7A	-C7	-H7B	108.00	C14	-C13	-H13A	109.00
C6	-C7	-H7A	109.00	C14	-C13	-H13B	109.00
C7	-C8	-H8A	109.00	H13A	-C13	-H13B	108.00
C9	-C8	-H8A	109.00	C12	-C13	-H13B	109.00
C9	-C8	-H8B	109.00	C13	-C14	-H14B	109.00
C7	-C8	-H8B	109.00	C15	-C14	-H14A	109.00
H8A	-C8	-H8B	108.00	C13	-C14	-H14A	109.00
C8	-C9	-H9B	109.00	H14A	-C14	-H14B	108.00
C10	-C9	-H9A	109.00	C15	-C14	-H14B	109.00
C8	-C9	-H9A	109.00	C14	-C15	-H15A	108.00
H9A	-C9	-H9B	108.00	C16	-C15	-H15A	108.00
C10	-C9	-H9B	109.00	C16	-C15	-H15B	108.00
C9	-C10	-H10A	109.00	H15A	-C15	-H15B	107.00
C11	-C10	-H10A	109.00	C14	-C15	-H15B	108.00
C11	-C10	-H10B	109.00	C15	-C16	-H16B	109.00
H10A	-C10	-H10B	108.00	C17	-C16	-H16A	109.00
C9	-C10	-H10B	109.00	C15	-C16	-H16A	109.00
C10	-C11	-H11A	109.00	H16A	-C16	-H16B	108.00

C12	-C11	-H11A	109.00	C17	-C16	-H16B	109.00
C12	-C11	-H11B	109.00	C16	-C17	-H17B	109.00
C10	-C11	-H11B	109.00	C18	-C17	-H17A	109.00
H11A	-C11	-H11B	108.00	C16	-C17	-H17A	109.00
C11	-C12	-H12B	109.00	H17A	-C17	-H17B	108.00
C13	-C12	-H12A	109.00	C18	-C17	-H17B	109.00
C17	-C18	-H18A	109.00	C20	-C21	-H21B	109.00
C17	-C18	-H18C	109.00	C21	-C22	-H22B	109.00
H18A	-C18	-H18B	109.00	C21	-C22	-H22C	109.00
H18A	-C18	-H18C	109.00	C21	-C22	-H22A	109.00
H18B	-C18	-H18C	110.00	H22A	-C22	-H22C	110.00
C17	-C18	-H18B	109.00	H22B	-C22	-H22C	109.00
N1	-C19	-H19A	108.00	H22A	-C22	-H22B	109.00
N1	-C19	-H19B	108.00	N1	-C23	-H23A	109.00
C20	-C19	-H19B	108.00	N1	-C23	-H23B	109.00
H19A	-C19	-H19B	107.00	H23A	-C23	-H23B	109.00
C20	-C19	-H19A	108.00	H23A	-C23	-H23C	109.00
C19	-C20	-H20B	110.00	N1	-C23	-H23C	110.00
C21	-C20	-H20A	110.00	H23B	-C23	-H23C	109.00
C19	-C20	-H20A	110.00	N1	-C24	-H24B	110.00
H20A	-C20	-H20B	108.00	N1	-C24	-H24C	109.00
C21	-C20	-H20B	110.00	N1	-C24	-H24A	109.00
C20	-C21	-H21A	109.00	H24A	-C24	-H24C	109.00
C22	-C21	-H21A	109.00	H24B	-C24	-H24C	110.00
C22	-C21	-H21B	109.00	H24A	-C24	-H24B	109.00
H21A	-C21	-H21B	108.00				

Contact Distances(Angstrom)

Br1	.O1	3.358(4)	H1WA	.H21B_m	2.5700
Br1	.H23B_n	2.8800	H1A	.H24C	2.3700
Br1	.H24C_n	2.8600	H1A	.H3B	2.3900

Br1	.H1WB	2.70(7)	H1A	.H23B	2.4800
Br1	.H2B_g	2.9900	H1B	.H3A	2.6000
Br1	.H19A_g	2.9300	H1B	.C20	2.7600
Br1	.H22B_l	3.1200	H1B	.H24A	2.4300
Br1	.H23C_m	3.0300	H1B	.H6B_d	2.5700
Br1	.H24B_m	3.0400	H1B	.H20B	2.2300
Br1	.H19B_m	3.0300	H1WB	.Br1	2.70(7)
O1	.Br1	3.358(4)	H2A	.O1_e	2.5200
O1	.C24_l	3.379(6)	H2A	.C23	2.7100
O1	.H21B_m	2.9000	H2A	.H4B	2.4400
O1	.H24B_l	2.7200	H2A	.H22A_a	2.4800
O1	.H23A_g	2.6300	H2A	.H23A	2.1700
O1	.H2A_g	2.5200	H2B	.C19	2.7800
C24	.O1_c	3.379(6)	H2B	.Br1_f	2.9900
C1	.H20B	2.7700	H2B	.H19A	2.2400
C2	.H19A	2.7800	H3A	.H1B	2.6000
C2	.H23A	2.7000	H3B	.H5B	2.5000
C2	.H22A_a	3.0400	H3B	.H1A	2.3900
C3	.H22A_a	3.0300	H3B	.C22_a	3.0200
C19	.H2B	2.7800	H3B	.H22A_a	2.5800
C20	.H1B	2.7600	H4A	.H6A	2.5900
C20	.H24A	2.7300	H4B	.H2A	2.4400
C22	.H3B_b	3.0200	H4B	.H6B	2.5200
C23	.H2A	2.7100	H4B	.H24A_g	2.6000
C24	.H20A	2.7400	H5A	.H7A	2.5500
H5B	.H3B	2.5000	H12A	.H14A	2.5600
H5B	.H7B	2.5500	H12B	.H14B	2.5700
H6A	.H4A	2.5900	H12B	.H10A	2.5600
H6A	.H8A	2.5700	H13A	.H11B	2.5500
H6B	.H8B	2.5500	H13A	.H15A	2.5300
H6B	.H4B	2.5200	H13B	.H11A	2.5600

H6B	.H1B_g	2.5700	H13B	.H15B	2.5400
H7A	.H9B	2.5500	H14A	.H16A	2.5900
H7A	.H5A	2.5500	H14A	.H12A	2.5600
H7B	.H5B	2.5500	H14B	.H16B	2.5700
H7B	.H9A	2.5600	H14B	.H12B	2.5700
H8A	.H6A	2.5700	H15A	.H13A	2.5300
H8A	.H10B	2.5500	H15A	.H17A	2.5500
H8B	.H10A	2.5500	H15B	.H13B	2.5400
H8B	.H6B	2.5500	H15B	.H17B	2.5400
H9A	.H7B	2.5600	H16A	.H18C	2.5500
H9A	.H11A	2.5500	H16A	.H14A	2.5900
H9B	.H11B	2.5600	H16B	.H14B	2.5700
H9B	.H7A	2.5500	H16B	.H18B	2.5700
H10A	.H12B	2.5600	H17A	.H15A	2.5500
H10A	.H8B	2.5500	H17B	.H15B	2.5400
H10B	.H8A	2.5500	H18B	.H16B	2.5700
H10B	.H12A	2.5600	H18C	.H16A	2.5500
H11A	.H13B	2.5600	H19A	.H21A	2.4100
H11A	.H9A	2.5500	H19A	.H23A	2.3900
H11B	.H9B	2.5600	H19A	.C2	2.7800
H11B	.H13A	2.5500	H19A	.H2B	2.2400
H12A	.H10B	2.5600	H19A	.Br1_f	2.9300
H19B	.H21B	2.4300	H23A	.C2	2.7000
H19B	.H23C	2.3400	H23A	.O1_e	2.6300
H19B	.H24B	2.4500	H23A	.H2A	2.1700
H19B	.Br1_h	3.0300	H23A	.H19A	2.3900
H20A	.H24A	2.2100	H23B	.Br1_k	2.8800
H20A	.C24	2.7400	H23B	.H24C	2.4200
H20A	.H22B	2.6000	H23B	.H1A	2.4800
H20B	.C1	2.7700	H23C	.Br1_h	3.0300

H20B	.H1B	2.2300	H23C	.H19B	2.3400
H20B	.H22C	2.5900	H23C	.H24B	2.4200
H21A	.H19A	2.4100	H24A	.C20	2.7300
H21B	.H1WA_i	2.5700	H24A	.H1B	2.4300
H21B	.O1_i	2.9000	H24A	.H4B_d	2.6000
H21B	.H19B	2.4300	H24A	.H20A	2.2100
H22A	.C3_b	3.0300	H24B	.Br1_h	3.0400
H22A	.C2_b	3.0400	H24B	.O1_c	2.7200
H22A	.H2A_b	2.4800	H24B	.H19B	2.4500
H22A	.H3B_b	2.5800	H24B	.H23C	2.4200
H22B	.Br1_j	3.1200	H24C	.Br1_k	2.8600
H22B	.H20A	2.6000	H24C	.H1A	2.3700
H22C	.H20B	2.5900	H24C	.H23B	2.4200

Hydrogen Bonds (Angstrom, Deg)

O1 -- H1WB .. Br1	0.82(7)	2.70(7)	3.358(4)	138(6)	
C2 -- H2A .. O1	0.9900	2.5200	3.429(6)	153.00	1_545
C23 -- H23B .. Br1	0.9800	2.8800	3.788(4)	155.00	1_645
C24 -- H24C .. Br1	0.9800	2.8600	3.771(4)	155.00	1_645

Translation of Symmetry Code to Equiv.Pos

a	= [1665.00]	= 1+x, 1+y, z
b	= [1445.00]	= -1+x, -1+y, z
c	= [1535.00]	= x, -2+y, z
d	= [1545.00]	= x, -1+y, z
e	= [1545.00]	= x, -1+y, z
g	= [1565.00]	= x, 1+y, z
h	= [2797.00]	= 2-x, 4-y, 2-z
i	= [2797.00]	= 2-x, 4-y, 2-z
j	= [1535.00]	= x, -2+y, z
k	= [1645.00]	= 1+x, -1+y, z
l	= [1575.00]	= x, 2+y, z
m	= [2797.00]	= 2-x, 4-y, 2-z
n	= [1465.00]	= -1+x, 1+y, z