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SYNTHESIS AND CHARACTERIZATION OF NEW TYPES OF
IONIC LIQUIDS - LIPs AND PILS

BY

SHARON I. LALL-RAMNARINE

A dissertation submitted to the Graduate Faculty in Chemistry in partial
fulfillment of the requirements for the degree of Doctor of Philosophy,

City University of New York

2003

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8/13/03

Date

Robert Engel

Chair of Examining Committee

9/4/2003

Date

Gerold Koeppe

Executive Officer

Dr. Robert R. Engel

Robert Engel

Dr. David C. Locke

David C. Locke

Dr. Steve Greenbaum

Steve Greenbaum

Dr. Lynn Francesconi

Lynn C. Francesconi

Supervisory Committee

City University of New York

Abstract

SYNTHESIS AND CHARACTERIZATION OF NEW TYPES OF IONIC LIQUIDS - LIPs AND PILS

By

Sharon I. Lall-Ramnarine

Adviser: Professor Robert Engel

Recent awareness and concern for the release of toxic waste into the environment have placed demands on the chemical industry for cleaner processes that generate less toxic waste. Ionic liquids are solvent alternatives to the volatile organic compounds currently being used. They are virtually non-volatile, non-flammable, recyclable materials that are liquids at or near room temperature and dissolve a wide range of organic and inorganic compounds, making them ideal as alternative reaction solvents. In addition, they have been proposed as new types of electrolytes for batteries owing to their high electrical conductivity. They have also been investigated for a

myriad of other applications including separations, liquid/liquid extraction, industrial cleaning, fuel cells, heat transfer fluids² and lubricants.^{3,4}

The present work describes the preparation and properties of two new types of ionic liquids based on polyammonium cations with different anions.

Liquid Ionic Phosphates (LIPs) contain the simple phosphate (PO_4^{3-}) anion, whereas Polyammonium Ionic Liquid Sulfonamides (PILS) bear the bis(trifluoromethanesulfonyl)imide $[(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ anion. LIPs are hydrophilic whereas PILS are hydrophobic illustrating the “designer solvent” description of ionic liquids.

Wherever possible it has been attempted to employ “greener” synthetic methods, such as solvent free reactions, for the preparation of these new species.

Volumetric Karl Fischer Titration was used to measure residual water content. Samples containing less than 1.0 % water were characterized further. Specific conductivity was measured using a YSI conductivity bridge with a dip-type probe. Conductivities on the order of 10^{-1} - 10^1 mS/cm were obtained for LIPs and PILS. Self diffusion coefficients were determined

using Pulse gradient spin echo NMR and were found to be on the order of 10^{-8} - 10^{-7} cm²/s for both anions and cations. Electrochemical windows were determined using cyclic voltammetry and ranged from 2.1-4.4 V. Densities ranged from 0.99 g/mL-2.0 g/mL. LIPs were found to be miscible with solvents such as methanol and water and PILS with ethylacetate, acetone and acetonitrile. Pulse radiolysis studies indicated that the solvated electron in hydroxyl substituted PILS behave similar to that in ethanol.

These results suggest that LIPs and PILS may have applications in batteries and as other types of electrochemical media. LIPs are particularly cost effective.

Dedicated to my parents:

Lynette Etwaria Lall

and

Bansi Gopal Lall.

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Chapter 1

INTRODUCTION

For many decades the chemical industry has been plagued with the bad reputation of being a major contributor to the pollution of our environment. To the general population the word chemistry is not associated with the myriad of products that add comfort to our every day life, such as fabrics and pharmaceuticals, but instead with toxic waste and pollution of our environment. Over the past four decades there has been an increased awareness and concern about the amount of toxic waste released into the environment. The U.S. Pollution Prevention Act in 1990 refocused national environmental policy on preventing the formation of waste at the source. These legislative efforts¹ resulted in the evolution of “Green Chemistry,” which focuses on making whole chemical processes less damaging to the environment. These laws and a global incentive for a cleaner environment have placed demands on the chemical industry for cleaner processes, which produce less toxic waste. New approaches include solvent free reactions,

recyclable solvents and alternative solvents to the volatile organic compounds currently being used. Ionic liquids are in the category of solvent alternatives.

What are ionic liquids?

Ionic liquids are compounds that are composed entirely of ions in a non-aqueous liquid state. Room temperature ionic liquids are salts that are liquid at or slightly above room temperature. This definition has generally been extended to include salts with melting points below 100°C.

In terms of associated ions, these compounds resemble classical molten salts. For example, sodium chloride heated above 800°C produces a molten salt that is liquid ionic material. Sodium chloride at ordinary temperatures dissolves in water to generate an ionic solution.

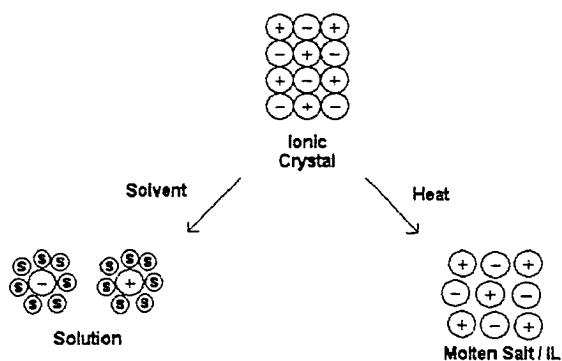


Figure 1: Schematic representation of an ionic liquid versus an ionic solution

However, unlike classical molten salts, ionic liquids exhibit lower viscosity, are not corrosive and are liquid below 100°C . In the early literature (prior to 1979) the terms “ionic liquid” and “molten salt” were commonly used interchangeably. Currently, the term ionic liquid is used almost exclusively to refer to room temperature ionic liquids and the term molten salt denotes salts with melting points above 100°C . According to Wasserscheid and Keim⁵ this arbitrary line drawn between molten salts and ionic liquids at a melt temperature of 100°C can be justified by the abrupt improvement in the range of applications for liquid salts below this temperature.

This fluidity of ionic liquids near room temperature defies traditional expectations for ionic compounds. It is a fascinating property of ionic liquids that has led to their application in numerous processes. The reason for the liquid nature or low melting points of these salts has been somewhat of a mystery. However, recent reports by Holbrey and Rogers⁶ and others have discussed contributing factors. The charge, size, distribution of charge on the respective ions and asymmetry of the cation are believed to be major factors influencing melting point. In general, larger ions result in a decrease in melting point by having more charge delocalization, less charge density and hence reduced Coulombic attractions between the ions. The inability of the ions to fit into a crystal lattice owing to the sizes of the ions involved, described as “packing inefficiency”⁷ has been proposed as an important factor in rationalizing the low melting points of some ionic liquids. Large anions with many degrees of freedom inhibit crystallization until lower melting temperatures are obtained.⁸

Room temperature ionic liquids are generally composed of relatively large organic cations and small inorganic polyatomic anions. The difference

between low melting ionic liquids and their crystalline solid relatives is the presence of an organic cation. The most commonly reported cations include *N, N'*-dialkylimidazolium, *N*-alkylpyridinium, tetraalkylammonium, trialkylsulfonium, tetraalkylphosphonium or *N*-alkylpyrrolodinium monocationic species as shown in Figure 2.

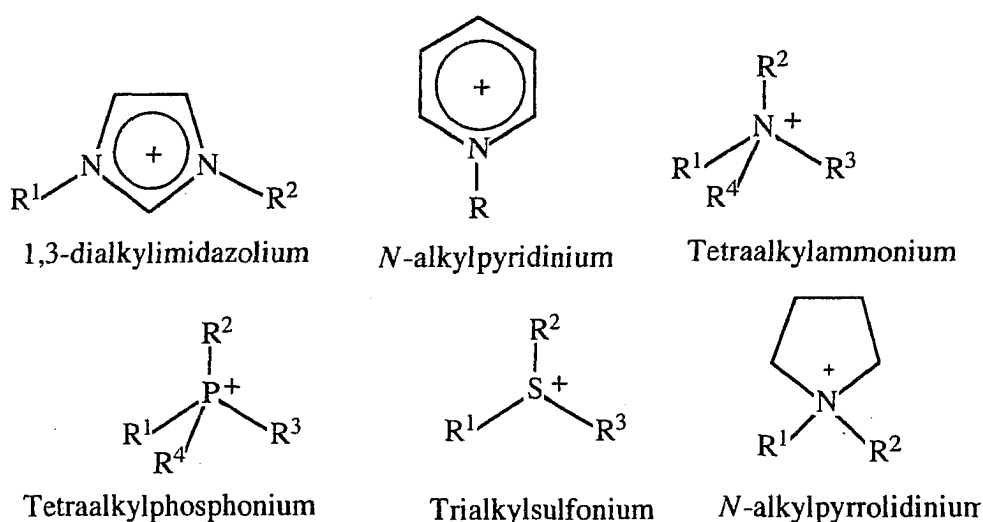


Figure 2: Commonly reported cations of ionic liquids

The associated inorganic anions (Table 1) are relatively small compared to these cations (Figure 2). The presumption is that such a disparity in the sizes for the associated ions inhibits their formation of crystalline lattices.

Table 1: Anions commonly found in ionic liquids

Anion	Reference	Anion	Reference
AlCl_4^-	9, 10, 11, 12	NO_2^-	14, 15
Al_2Cl_7^-	10, 11, 12	HexBET_3	21
PF_6^-	13	OTS^-	18
BF_4^-	14, 15	AuCl_4^-	22
NO_3^-	14, 15	Carborane	23
CF_3SO_3^-	16	Cl^-	10, 24, 11
$(\text{CF}_3\text{SO}_2)_2\text{N}^-$	16	$\text{Al}_3\text{Cl}_{10}^-$	10
SbF_6^-	17	AlEtCl_3^-	20
ArSO_3^-	18	BCl_4^-	24
CF_3CO_2^-	16	AlBr_3^-	25
CH_3CO_2^-	14, 15, 19	PO_4^{3-}	26, 27
HSO_4^-	20	$\text{C}_{10}\text{H}_{21}\text{COO}^-$	28

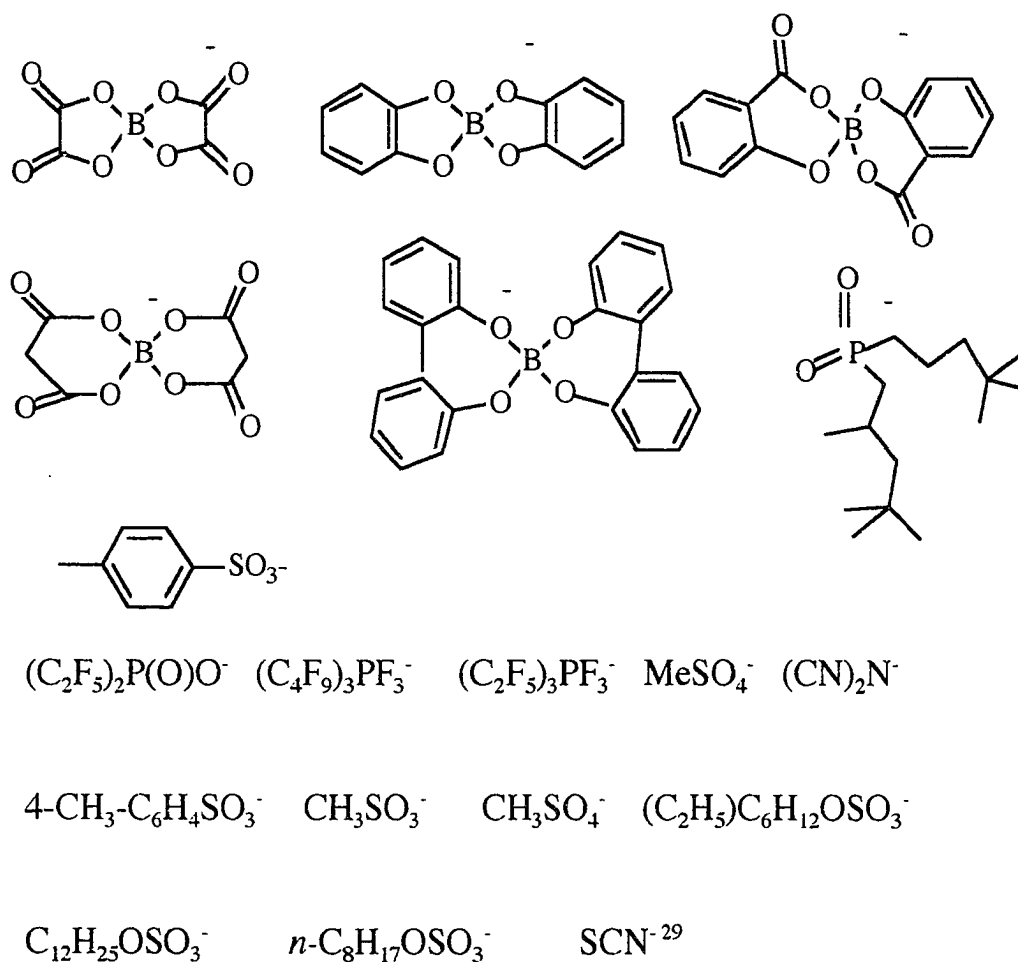


Figure 3: Anions less commonly found in ionic liquids^{28, 18}

The above list is not comprehensive and continues to grow. This array of anions and cations makes it feasible to synthesize a large number of new ionic liquids.

History

Room temperature ionic liquids have been around for quite some time. The synthesis of ethylammonium nitrate, which is a liquid at room temperature, was reported in 1914,³¹ thus being the first low temperature ionic liquid described. This salt has a melting point around 12°C but usually contains 200-600 ppm water.

Even though this first synthesis was described at such an early date, it is only within the last five years that ionic liquids have become very popular and well known. This delay is ostensibly because the field of low temperature ionic liquids was dominated for many years by the chloroaluminate containing ionic liquids, which are air sensitive and were initially high melting. The first ionic liquids with chloroaluminate ions (*N*-alkylpyridinium chloroaluminates) were developed in 1948 by Hurley and Weir at the Rice Institute in Texas as electrolytes for electroplating aluminum.³² However it was not until the mid to late 1970's that again there were reports on the chloroaluminate systems. Researchers at the U.S Air Force Academy began the first major research in the ionic liquid field at that

time. The groups of Wilkes³³ and Osteryoung³⁴ reported then on their discovery of the first *room temperature* chloroaluminate ionic liquids. These were *N*-alkylpyridinium halide mixtures with aluminum chloride. At this time the focus was mainly on the use of these liquids as media for electrochemical applications.^{30, 35-42} According to Wilkes,⁶ “It all started with a battery that was too hot to handle,” referring to the thermal batteries with operating temperatures of 375-550 °C, which caused material problems inside the battery and incompatibilities with nearby materials.⁸ In an effort to find a replacement for the LiCl/KCl molten salt electrolyte used in thermal batteries, the researchers at the Air Force Academy initiated a project in this field that has been continuous ever since. The principal investigators have been Wilkes, King and Carlin. Other important members of this research team have included Hussey, Fuller, Zaworotko, DeLong and Trulove.

In 1979 Hussey and co-workers⁴³ reported on some of the physical properties of alkylpyridinium chloroaluminate liquids. The problem with these liquids was that they were very susceptible to both chemical and electrochemical reduction easily.

In the mid 1960's and early 1970's the synthesis^{4, 21, 44} and applications^{21, 45, 46} of monocationic quaternary ammonium ($R_4N^+ X^-$) salts with melting points below 100°C were also reported. The anions involved were I^- , Br^- , SCN^- , ClO_4^- , NO_3^- , picrate and tetraalkylboride.²¹ The properties of these liquids were examined and they were proposed as new types of solvent systems.⁴⁷ However, these liquids were not studied as extensively as the chloroaluminates.

From 1980 to the early 1990's the chloroaluminate systems were the primary focus of ionic liquid investigations. Much of the focus continued to be on the use of these liquids as media for electrochemical reactions and investigations.^{12, 48-63} This work was performed primarily by Osteryoung and coworkers. The chloroaluminates were characterized by aluminium-27 NMR⁶⁴ and studied by IR⁶⁵ along with other spectroscopic^{55, 66-68} and thermodynamic investigations.^{10, 69}

In 1982 Wilkes *et al.*⁷⁰ reported on the preparation and physical properties of a dialkylimidazolium chloride chloroaluminate room temperature ionic liquid (Figure 2). This was the first dialkylimidazolium

type ionic liquid reported. The ethylmethylimidazolium chloroaluminate liquid was attractive because of its low melting point, stability to reduction, physical, as well as its chemical and electrochemical properties. Wilkes and co-workers at the Air Force Academy continued to study these systems, characterizing them for phase transitions, densities, electrical conductivities and viscosities,⁹ and proposed them as new low temperature electrolytes for battery applications. They showed that these systems could be used in Friedel-Crafts reactions as both the catalyst and solvent⁷¹ and studied the anion-cation interactions in the liquids by NMR.⁷²

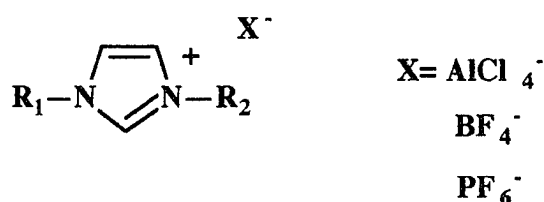


Figure 4: Examples of dialkylimidazolium ionic liquids

In 1986 Hussey²⁵ reported on the preparation and properties of the aluminum bromide-1-methyl-3-ethylimidazolium bromide ionic liquids and later reported⁷³ on their use as media for transition metal solution chemistry. These systems were further investigated by Osteryoung as media for

electrochemical and spectroscopic studies.⁷⁴ Osteryoung *et al.* also reported on the NMR investigation of the *N*-butylpyridinium-aluminum chloride system.⁷⁵ Unlike the alkylpyridinium chloroaluminates which had been around since the late 1940's the ethylmethylimidazolium chloroaluminate compounds exhibited a wider liquid range and an electrochemical window (that is the electrochemical potential range over which the liquid is not reduced or oxidized at an electrode) of greater than 3.0V and resulted in an increase of research activity in this area.¹⁵

However, despite all of the early work on the chloroaluminate systems and the promising results, their widespread use was prevented because of their reactivity toward water. In a later report by Wilkes *et al.*¹⁵ it was noted that a considerable drawback of the ambient chloroaluminate ionic liquids was the need to protect them rigorously from moisture and other oxide impurities, and the tendency of many substrates to react with halometallates.

In 1992 a major breakthrough in the development of ionic liquids occurred with the discovery by Wilkes and Zaworotko of the first tetrafluoroborate (BF_4^-) dialkylimidazolium room temperature ionic liquid.¹⁵

This was ten years after Wilkes and co-workers reported on their discovery of the first dialkylimidazolium chloroaluminate ionic liquid. Shortly after this the 1-ethyl-3-methylimidazolium hexafluorophosphate ionic liquid with a melting point of 58-60°C was reported¹³ and proposed as a model for room temperature ionic liquids. This was the beginning of a new era for ionic liquids. These new types of room temperature ionic liquids exhibited significantly greater air and moisture stability and had the advantage of being relatively stable toward hydrolysis. Their discovery resulted in a dramatic increase in the number of applications investigated for ionic liquids. They became the rave of the field for another ten years and as a result, received widespread publicity. Researchers from government to industry and academia became interested in ionic liquids. The most extensively studied systems were those based on the ethylmethylimidazolium [Emim]⁺, butylmethylimidazolium [Bmim]⁺ and butylpyridinium [BPy]⁺ cations. Subsequently, ionic liquids were synthesized using these imidazolium and pyridinium cations with a range of different anions, including chlorate (ClO₄⁻), nitrate (NO₃⁻),

triflate (CF_3SO_3^-),⁷⁶ hexafluoroantimonate (SbF_6^-),¹⁷ (CF_3CO_2^-) and many others. Extensive research continued on melts of $[\text{Emim}]\text{Cl}$ with AlCl_3 .⁷⁷⁻⁸⁷

The choice of anion allows researchers to synthesize liquids with varying properties. For example, hydrophobic or hydrophilic properties may be provided, and hence ionic liquids can be “custom” synthesized to fit a particular application. They have been described as designer solvents.⁸⁸⁻⁹⁰ This variability allows for virtually limitless possibilities in terms of applications. According to Dr. Wilkes, “the applications will be limited only by our imagination.”⁶

Properties and Applications

Ionic liquids display a number of unique and intriguing properties that promise significant applications for them in many areas. The most promising application arises from a combination of properties that indicate ionic liquids to be environmentally safer solvents than the volatile organic solvents commonly in use. The properties are discussed below.

1. Vapor Pressure

One of the unique properties of ionic liquids is that they have no measurable vapor pressure as typical of ionic materials. This makes them virtually non-volatile and odorless and has led many researchers to describe them as *environmentally benign* and as *green solvents*.⁹¹ Since the liquids do not evaporate, containment problems are eliminated. Another advantage is the separation of products by distillation from a reaction mixture without the formation of azeotropes. Ionic liquids have been proposed and are being investigated as green solvent⁹¹ alternatives to the volatile organic compounds (VOC's) currently in use.

2. Recyclable

Ionic liquids have also been proposed as recyclable solvents because of their ease of separation from many reaction mixtures. This is an added advantage, as it reduces waste management costs. However, the disposal of spent ionic liquids that cannot be cleaned up cost effectively has not been given much attention as yet.

Brennecke's group of the University of Notre Dame developed a method to extract low-volatility organic solvents from ionic liquids using supercritical CO₂ (ScCO₂). Carbon dioxide is in its supercritical state near room temperature (40°C), but is highly pressurized so that it has a liquid-like consistency. Yet, like a gas, it expands to fill the container. The successful separation of naphthalene from [Bmim]PF₆ has been accomplished. When droplets of ScCO₂ were forced through the ionic liquid/naphthalene solution, the naphthalene was quantitatively extracted into the ScCO₂ phase and recovered from the ionic liquid without contamination.⁹² After depressurizing the mixture, pure solid naphthalene and gaseous CO₂ were obtained. The ionic liquid remaining contained a lot of dissolved CO₂ but the CO₂ contained no measurable ionic liquid dissolved in it. The success of this two phase system is based on the pressure controlled solubility of ScCO₂ in the ionic liquid, but insolubility of the ionic liquid in ScCO₂. This ionic liquid/ScCO₂ system has also been successfully applied to biocatalytic transesterification reactions.⁹³ Along similar lines, Brennecke's group⁹⁴ has also shown that both hydrophobic and hydrophilic ionic liquids can be

separated from aqueous solutions with relatively low-pressure gaseous carbon dioxide. The solution of water and ionic liquid separated into three phases in the presence of CO₂. One liquid phase is rich in ionic liquid, one is rich in water and the vapor phase is mostly CO₂ with a small amount of water. It was found that hydrophobic ionic liquids were easier to separate by this method than hydrophilic ionic liquids. This method could be important for the removal of small amounts of ionic liquids from aqueous waste streams before they enter the environment.

Rogers' group has shown that hydrophilic ionic liquids can be recycled or concentrated using K₃PO₄.⁹⁵ Concentrated solutions of K₃PO₄ were used to induce the formation of aqueous biphasic systems consisting of an upper ionic liquid rich phase and a lower K₃PO₄ rich phase.

Lu *et al.*⁹⁶ used spectroscopic techniques to investigate the effect of dissolved CO₂ on the microscopic solvent properties of [Bmim]PF₆ at different temperatures and pressures. They found that the polarity was independent of the amount of dissolved CO₂. The polarity of [Bmim]PF₆ both with and without CO₂ was lower than those of DMSO

(dimethylsulfoxide) and water but higher than those of acetonitrile, acetone and methanol. However the microviscosity of [Bmim]PF₆/CO₂ in the immediate vicinity of the probe molecule was greatly reduced.

3. Melting Points

The melting point of ionic liquids can be considered their most important characteristic as it defines these unique compounds. Melting points below room temperature are desirable for many applications, even though the higher melting compounds also find applications in many areas.

The ability to predict whether a particular cation and anion combination will result in the formation of an ionic liquid has been described as a hit and miss affair.⁹⁷ However, as more investigations are performed on ionic liquids and more information becomes available, it will be easier to predict whether a compound will be relatively low melting or not, based on its structure. It is now known that the structure of both the anion and cation contribute to the melting point. The imidazolium cations were found to have relatively low melting points with most anions.

The [Emim] chloroaluminate ionic liquids reported by Wilkes *et al.*⁷⁰ had melting points of 8°C for the 50 mol% mixtures and -98°C for the 67 mol% mixtures. However, it was noted that the latter temperature may represent a glass transition rather than a melting point. While these low melting point compounds were favorable for some applications, the instability of the chloroaluminate compounds to air and moisture limited their potential use.

Wilkes and Zaworotko's report in 1992¹⁵ on two air- and moisture-stable, ambient temperature non-chloroaluminate liquids, [Emim]BF₄ with a melting point of 15°C and [Emim]MeCO₂ which melts around -45°C was the impetus for the dramatic increase in research in this area. This group also reported on salts of the [Emim] cation with other anions which were higher melting, [Emim]NO₃, [Emim]NO₂, and [Emim]SO₂.H₂O were reported with melting points of 38°C, 55°C and 70°C respectively. The [Emim]PF₆ (ethylmethyylimidazolium hexafluorophosphate) compound was reported by Fuller *et. al.*¹³ with a melting point of 58-60°C.

A series of imidazolium based ionic liquids with differing alkyl groups (including methyl, ethyl, butyl, methoxyethyl and trifluoroethyl) in the 1-, 2-, and 3- positions of the imidazole ring and various anions (including CF_3SO_3^- , CF_3COO^- , $\text{C}_4\text{F}_9\text{SO}_3^-$, CH_3COO^- and $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ were reported by Bonhote *et. al.*¹⁶ Melting points ranged from -3°C for the bis(trifl)amide compound ($[\text{Emim}](\text{CF}_3\text{SO}_3)_2\text{N}$) to 113°C for the 1-ethyl-2-ethyl-3-methyl triflate (CF_3SO_3^-). Most of the salts reported melted close to room temperature and quite a few were glass-forming. It was noted that melting points were difficult to correlate with the chemical composition of the salts. However, symmetrical cations resulted in higher melting points and the $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ anion resulted in a lowering of melting points for these imidazolium salts.

The review by Hagiwara and Yto⁹⁸ of room temperature ionic liquids based on alkylimidazolium cations with fluoroanions presents about 35 such compounds, all of which melt below room temperature. Noda *et. al.*⁹⁹ reported melting points for imidazolium and pyridinium compounds also. The $[\text{Emim}]$ tetrafluoroborate (BF_4^-) was reported as having a melting point

of 15°C, which is the same as that reported earlier by Wilkes.¹⁵ However the [Emim] bis(trifl)amide had a melting point of -16°C which was different from the -3°C reported by Bonhote *et. al.*¹⁶ The butylpyridinium tetrafluoroborate and bis(trifl)amide ionic liquids melted at -1°C and 26°C respectively.

Imidazolium-based tetrachloroaurate liquids have also been reported by Hasan, *et al.*²² [Emim]AuCl₄ and [Bmim]AuCl₄ were reported with melting points of 58°C and 60°C respectively.

Aside from the imidazolium based ionic liquids, quaternary ammonium triflate (CF₃SO₃⁻) and bis(trifl)amide ionic liquids have been investigated by Sun, *et al.*¹⁰⁰ It was found that the simple symmetrical quaternary ammonium imide salts melt well above room temperature but lower symmetry ammonium cations resulted in melting points around room temperature. In most cases the low symmetry of the cation was achieved by keeping three of the alkyl groups the same and small (methyl, ethyl, propyl or butyl) and making the fourth different and longer (C₆ to C₈). Many of the

compounds did not show a melting point but exhibited a glass transition between -55°C and -82°C .

MacFarlane, *et al.*¹⁰¹ also studied new families of salts. His group reported on quaternary ammonium, *N*-alkyl-*N*-methylpyrrolidinium and 1-alkyl-3-methylimidazolium dicyanamides ($\text{N}(\text{CN})_2$). All of the compounds investigated displayed melting points in the range of -10°C to -55°C , except *N*, *N*-dimethylpyrrolidinium dicyanamide, which melted at 115°C . Many of the compounds were also glass forming with glass transition temperatures between -82°C and -106°C . The dicyanamide anion, like the bis(trifl)amide anion seems to produce a depression in melting point when compared to other anions. The pyrrolidinium cations also seem to result in lower melting point liquids. The melting points for several reported ionic liquids are summarized in Table 2. The abbreviations used to describe the structural types in Table 2 are defined on page 13.

Table 2: Summary of melting points of ionic liquids – structures

Ionic Liquid	Melting point ($^{\circ}\text{C}$)	Reference
[Emim]BF ₄	15	15, 99
[Emim]MeCO ₂	-45	15
[Emim]NO ₃	38	15
[Emim]NO ₂	58	15
[Emim]SO ₂ .H ₂ O	70	15
[Emim]PF ₆	58-60	13
[Emim](CF ₃ SO ₂) ₂ N	-3	16
[Bpy](CF ₃ SO ₂) ₂ N	26	99
[Bpy]BF ₄	-1	99
[Emim]AuCl ₄	58	22
[Bmim]AuCl ₄	60	22
[(C ₄ H ₉) ₃ C ₆ H ₁₃ N](NCN) ₂	-43	101
[Emim]N(CN) ₂	-21	101
(Hex)(Et) ₃ N(CF ₃ SO ₂) ₂ N	20	100

4. Thermal stability/ Liquid range

An attractive feature of ionic liquids is their high thermal stability.

[Emim]BF₄ has been reported to be stable up to 300°C and

[Emim](CF₃SO₂)₂N up to 400°C.¹⁶ Many ionic liquids are therefore stable up to 300°C which is an advantage for high temperature applications.

The liquid nature of ionic liquids near room temperature together with their non-volatile property has facilitated the most widely studied application, namely alternative reaction media. The liquidus region is defined as the range of temperatures between the normal freezing point and boiling point. Hence the liquid range of water is 100°C. [Emim] (CF₃SO₂)₂N⁻, that melts at -3°C and is stable up to 400°C, has a liquid range of 403°C.

This very wide liquid range exhibited by some ionic liquids is a very desirable characteristic for many applications. A particularly interesting application recently reported² is the use of ionic liquids such as [C₈mim]PF₆ and [C₄mim]Tf₂N as liquid thermal storage media and as heat transfer fluids in solar thermal power plants/systems.

5. Conductivity

Ionic liquids display a characteristic high ionic conductivity. This is one of the properties that make them promising as electrolytes in batteries. Wilkes has been quoted⁸⁹ as saying that, “the nature of the electrolyte has a huge impact on both the energy the device can store and the power it can deliver” and, “ionic liquids have some properties that make them attractive as electrolytes in batteries.” Some of his work focused on the study of ionic liquids for the development of new low temperature electrolytes, for battery applications. In 1982 Wilkes, *et al.* reported⁷⁰ conductivities for dialkylimidazolium chloroaluminate room temperature ionic liquids in the range of 11.7 mS/cm to 22.7 mS/cm around 30°C, for varying mole percent aluminum chloride in the melt. Wilkes’ group later reported⁹ a conductivity value of 80 mS/cm for methylmethylimidazolium chloride chloroaluminate at 100°C. These values are high, considering that a 0.02M KCl solution, which is a common conductivity reference solution, has a conductivity of 2.7 mS/cm at 25°C.

Carpio and coworkers⁴³ had reported earlier on the conductivity of mixtures of *N*-alkylpyridinium halides with AlCl_3 . Results were on the order of 10 mS/cm at 20°C. This group, (also associated with the United States Air Force Academy), investigated these ionic liquids as potential electrolytes in batteries, and found them to be promising candidates.

There have been continued studies and reports on conductivity as new types of liquids are synthesized. Petrovic, *et al.* reported¹⁰² in 1982 on the conductivity of $\text{AlCl}_3/\text{SbCl}_3$ melts at varying temperatures. The conductivity at 25°C was around 10 mS/cm.

Bonhote, *et al.*¹⁶ investigated a number of ionic liquids for use as potential solvents in dye-sensitized nanocrystalline photoelectrochemical cells. The negligible vapor pressure, good conductivity and resistance to oxidation of ionic liquids made them attractive as stable solvents for these cells. The conductivity of several liquids based on the imidazolium cation with varying alkyl substituents and differing anions were studied. The anions studied included trifluoromethanesulfonate (triflate, TfO^-), nonafluorobutanesulfonate (NfO^-), bis(trifluoromethylsulfonyl)imide

(bistriflate, Tf_2N^-), trifluoroacetate (TA^-), heptafluorobutanoate (HB^-) and acetate (AcO^-). Conductivity results observed at 20°C ranged from 0.45 to 9.6 mS/cm.

Polymer electrolytes consisting of polypyridinium, pyridinium and aluminum chloride have been reported as exhibiting conductivities of 1 mS/cm at room temperature.¹⁷

Ionic liquids have also been incorporated into polymer gels in order to form solid state electrolytes for batteries.¹⁰³ Hydrophilic [Emim] BF_4 and [Emim](triflate) and hydrophobic [Bmim] PF_6 ionic liquids were incorporated into a poly(vinylidene fluoride)-hexafluoropropylene copolymer (PVdF(HFP)) matrix to form ionic liquid-polymer gels. These gel electrolytes exhibited conductivities greater than 1 mS/cm at room temperature.¹⁰³

According to Fuller, *et al.*¹⁰³ the cation and anion of neat ionic liquid electrolytes can be reductively and oxidatively intercalated, respectively, into a graphite electrode. Therefore, simple and inexpensive electrochemical cells can be constructed using only two graphite electrodes as the anode and

cathode and having operating voltages of 3-3.5 V. These systems have been called dual intercalating molten electrolyte (DIME) cells.¹⁰³

The ionic liquid-polymer gel was investigated for use in the DIME cells because solid state electrolytes are reportedly more desirable for battery design and construction. The [Bmim]PF₆-PVdF(HFP) gel was incorporated into DIME cells, employing graphite intercalation electrodes for both the anode and cathode, to construct single and bipolar cells displaying open-circuit voltages of 3.77 and 7.86 V, respectively.¹⁰³

Noda, *et al.*¹⁰⁴ has also reported on highly conductive polymer electrolytes prepared by *in situ* polymerization in [Emim]BF₄ and 1-butylpyridinium tetrafluoroborate (BPyBF₄) ionic liquids. Radical polymerization was attempted of several common vinyl monomers in these liquids. 2-Hydroxyethyl methacrylate (HEMA) network polymers in BPyBF₄ were found to be the most compatible. The ionic conductivity of 6/4 [BPyBF₄]/[Monomer] electrolyte was 1 mS/cm at 30°C and the polymer electrolyte film obtained was optically compatible, transparent and

mechanically strong.¹⁰⁴ These conductivity results are similar to those obtained by Fuller, *et al.*¹⁰³ for ionic liquid polymer-gel electrolyte.

Wilkes and coworkers at the U.S. Air Force Academy have also investigated the use of ionic liquids in the DIME battery.⁸⁹ They have shown that ionic liquids containing cations such as 1-ethyl-3-methylimidazolium or 1-ethyl-3-methyl-2-propylimidazolium and anions such as PF_6^- , BF_4^- , AlCl_4^- and $\text{CF}_3\text{SO}_2\text{O}^-$ (trifluoromethanesulfonate or triflate) work in the DIME battery. Freemantle, in his article on “Eyes on Ionic Liquids” in *Chemical and Engineering News*, May 15, 2000⁸⁹ quoted Wilkes as he outlined the advantages of the DIME battery, “Graphite is cheap and easy to work with, only a single ionic liquid is necessary, no organic solvents or volatiles of any kind are used, the battery can be assembled in the discharged state, and the battery materials probably have low toxicity.” He went on to say that, “The performance of the DIME cells is not yet optimized, but clearly this is a promising system.”

In addition to conductivity reports on the imidazolium-based ionic liquids, there have also been reports on monocationic quaternary ammonium

based ionic liquids. MacFarlane, *et al.*¹⁰⁰ reported on the conductivity of a number of symmetrical and unsymmetrical quaternary ammonium ionic liquids with the bis(trifluoromethylsulfonyl)imide and triflate anion. The highest conductivity observed at 25°C was 0.7 mS/cm.

In general, the conductivity values of ionic liquids appear to range from 10^{-1} to 10^1 mS/cm. Liquids based on tetrafluoroborate (BF_4^-) seem to have higher conductivities than those based on the trifluoromethylsulfonylimide $[(\text{CF}_3\text{SO}_2)_2\text{N}^-]$ anion.⁹⁹ However, Hagiwara, Ito, and coworkers^{98, 105} of Kyoto University in Japan, have recently reported conductivities on the order of 10^2 mS/cm at room temperature, for $[\text{Emim}]\text{F}(\text{HF})_{2,3}$. These values are an order of magnitude greater than those reported by others. It should be noted that no mention of the determination of water content was made in these references. This author feels that water content in ionic liquids is of significance, whether the liquids are hydrophobic or hydrophilic, especially where the measurement of physical properties is concerned.

Table 3: Summary of reported conductivities

Ionic Liquid	Conductivity (mS/cm)	Temperature (°C)	Reference
[Emim]Cl	80	100	9
Rpy ⁺ Cl ⁻	~ 10	20	43
AlCl ₃ /SbCl ₃	~ 10	25	102
R ₄ N ⁺ (CF ₃ SO ₂) ₂ N ⁻	~0.7	25	100
[Bmim]BF ₄	173	25	98
[Bmim]PF ₆	146	25	98

5. Self-Diffusion Coefficients

The self-diffusion coefficient of the ions that comprise the ionic liquids is an indication of the rate at which each species moves. There have been relatively few publications on this property to date. This property has been measured either by electrochemical or by NMR methods. While the methods are slightly different, they give similar results. In the

electrochemical methods the diffusion coefficient of an ion is measured in the presence of a concentration gradient. The NMR methods measure diffusion coefficients in the absence of any concentration gradient⁶ or applied potential. The technique usually used is Pulse Gradient Spin Echo (PGSE) NMR. In this technique a spin-echo pulse sequence is applied to a nucleus in the ion of interest and at the same time a pulsed magnetic field gradient is applied to the nucleus. The spin echo of the nucleus is then measured and its attenuation due to diffusion of the nucleus in the magnetic field gradient is used to determine its diffusion coefficient.⁶

In a basic NMR pulse sequence experiment (shown in Figure 5), there are two radio frequency (RF) pulses and two delays of equal magnitude, so spins are refocused to their original positions.

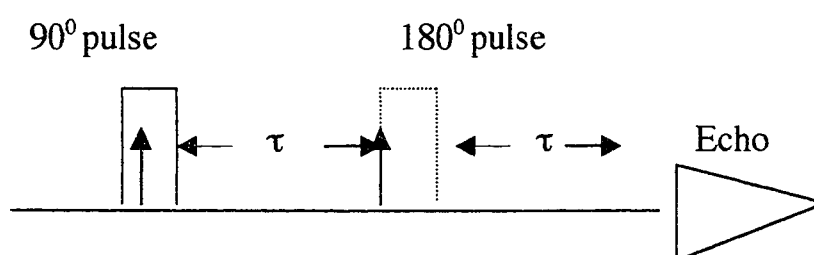


Figure 5: Spin echo pulse sequence

In this basic pulse sequence the position of the spins in the sample are irrelevant (all spins experience the same magnetic field and pulse strength) and there is a complete refocusing of spins (or spin echo). When a gradient pulse is applied (along the length of the tube) this complete refocusing will occur only if spins remain in the same position during and between gradient pulses. The further spins diffuse from the position of the initial gradient pulse, less refocusing occurs and the signal intensity of the refocused spin decreases (as shown in Figure 6).

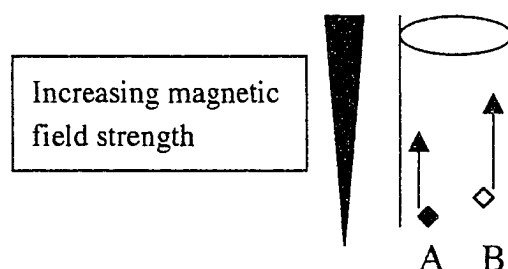


Figure 6: Two molecules A and B diffusing along the length of the tube with increasing field strength.

The observed signal intensity, I , for the PGSE experiment is given by:

$$I = I_0 \exp [(-2\tau/T_2) - (\gamma\delta G)^2 D (\Delta - \delta/3)]$$

Where I_0 denotes the signal intensity at zero gradient strength, G is the gradient strength, D is the diffusion coefficient, Δ is the delay time between

gradient pulses and δ is the pulse width. Plotting $\ln(I/I_0)$ vs. G^2 yields a linear plot whose slope is proportional to D and since the constants γ , δ and Δ are known, the diffusion coefficient can be calculated.¹⁰⁶

The NMR experiments used for the calculations depend on the chemical make up of the anion and cation present in the ionic liquid. It is necessary for the sample components to contain NMR-sensitive nuclei. NMR experiments are chosen such that either the anion or cation lacks the nucleus being investigated. For example, ^1H NMR experiments are used to determine self diffusion coefficients of cations in samples where the anions do not contain protons. ^{19}F NMR has been used to study fluorine-containing anions.⁹⁹ There have been relatively few reports on the measurement of self-diffusion coefficient by this method. Noda, *et al.*⁹⁹ reported self-diffusion coefficients on the order of $10^{-8}\text{cm}^2/\text{s}$ for imidazolium based cations with tetrafluoroborate or bis(trifl)amide anions. Trulove and Mantz reported⁶ a summary of diffusion coefficients from several authors obtained by the same and different methods for [Emim] liquids with various anions, all on the order of $10^{-11}\text{m}^2\text{s}^{-1}$ ($10^{-7}\text{cm}^2\text{s}^{-1}$).

7. Electrochemical Window

The electrochemical window is defined as the electrochemical potential range over which the electrolyte is not reduced or oxidized at an electrode. In other words, it is the potential range over which the electrolyte is stable. The electrochemical stability of electrolytes is of vital importance in many of the electrochemical roles in which they find applications.¹⁰⁰

Molten salts and ionic liquids have shown a characteristic wide electrochemical window ranging from 2-5V. This property has made them attractive for applications in electrochemistry and as electrolytes in batteries. The electrochemical window displayed by ionic liquids is usually much greater than for aqueous electrolytes.⁸⁹

Koch, *et al.*³⁶ reported since the mid 1970's on the 1:2 ethylpyridiniumbromide/ AlCl_3 mixture having an electrochemical window of -0.2-1.8V (2V). Wilkes and coworkers⁷⁰ showed that the 40 mole % ethylmethyylimidazoliumchloride/ AlCl_3 melt had an electrochemical window value of about 3.5V, which was wider than that of the alkylpyridinium melts.

The electrochemical windows of [Emim] bis(trifluoromethanesulfonyl)imide and [Emim] trifluoromethanesulfonate were reported¹⁶ as being around 4V. It was also reported¹⁰⁰ that the quaternary ammonium bis(trifluoromethanesulfonyl)imide ionic liquids exhibit electrochemical windows of at least 4.5-5V, which is wider than that obtained for similar liquids based on the imidazolium cation. It was suggested that the alkylammonium cation has greater electrochemical stability than a comparable imidazolium cation. The same group (McFarlane and coworkers) reported at a later date similar electrochemical window values for differing structural types of quaternary ammonium imides.¹⁰⁷

In a recent report by Mukhopandhay and Freyland¹⁰⁸ it was noted that the large electrochemical window exhibited by ionic liquids, in contrast to aqueous solutions, allows for the electrodeposition of a large number of light and refractory materials such as titanium and their alloys, and even semiconductors. The group performed the electrodeposition of titanium nanowires on highly oriented pyrolytic graphite from 0.24M TiCl₄ in

[Bmim][NTf₂]. The growth mechanism was monitored by electrochemical scanning tunneling microscopy.

Endres¹⁰⁹ discusses the use of ionic liquids for the electrodeposition of metals and semiconductors.

Table 4: Summary of electrochemical window data

Ionic Liquid	Electrochemical Window (V)	Reference
Epy ⁺ Br ⁻ /AlCl ₃ (1:2)	2.0	36
[Emim]/AlCl ₃ (40 mol%)	3.5	70
[Emim] (CF ₃ SO ₂) ₂ N ⁻	~4.0	16
R ₄ N ⁺ (CF ₃ SO ₂) ₂ N ⁻	4.5-5	100
[Bmim]BF ₄	4-6.1	98
Pyrrolidinium SCN ⁻	3.5	29
[Bmim]PF ₆	5-6.4	98

8. Viscosity

High viscosity is a characteristic of most ionic liquids. Many of them exhibit a physical consistency similar to that of maple syrup. The viscosity of water at room temperature is about 0.86 cP (centiPoise = $\text{gm}^{-1}\text{s}^{-1}$). In comparison, viscosity values of more than one to two orders of magnitude greater than that of water at room temperature⁹⁸ have been reported for ionic liquids. This high viscosity makes it very difficult to work with certain ionic liquids and results in an easy loss of sample during sample transfer and characterization. However the high thermal stability exhibited by ionic liquids allows for work at higher temperatures where the viscosity is reduced.

Viscosity is a standard characteristic measured when characterizing new ionic liquids. There have been several reports in the literature on the viscosity of various ionic liquids. Koch, *et al.*³⁶ reported very early on 1:1 and 1:2 ethylpyridiniumbromide/ AlCl_3 melts having viscosities of 4.9 cP and 24.8 cP respectively at 25°C. Bonhote and co-workers¹⁶ reported on the viscosities of alkylated imidazolium salts with various anions and concluded

that viscosity of the ionic liquids appear to be governed by van der Waals interactions and hydrogen bonding.

[Emim] bis(trifluoromethylsulfonyl)imide was found to have a viscosity of 34 cP at 20°C, whereas [Emim]⁺Acetate showed a viscosity of 162 cP at the same temperature. The structure of the cation was also found to influence the viscosity. Alkyl chain lengthening or fluorination makes the salts more viscous due to increased van der Waals interactions.¹⁶ The 1-butyl-3-methylimidazolium [Bmim]⁺ nonafluorobutanesulfonate exhibited a viscosity of 373 cP and the 1-CF₃CH₂-3-methylimidazolium cation with the bis(trifluoromethylsulfonyl)imide anion exhibited a viscosity of 248 cP. All of the liquids reported of various combinations of imidazolium cations and differing anions exhibited viscosities in the range of 34 cP to 373 cP at 20°C.

Hagiwara and Ito reviewed the viscosities of several imidazolium based ionic liquids with fluoroanions.⁹⁸ The [Emim]⁺ F(HF)_n⁻ salts had the lowest viscosity of 4.9 cP. The [Emim]⁺BF₄⁻ compound had a viscosity of 37.7 cP, which is similar to that observed for the other Emim compounds.

Quaternary ammonium salts based on triflamides and bis(trifl)amides (bistrifluoromethylsulfonylimides) were reported as exhibiting viscosities in the range of 75.5 cP to 2.03×10^3 cP at 25 °C.¹⁰⁰ These values are much higher than those exhibited by the imidazolium type salts. Even though in general the triflamide and bis(trifl)amide anions have been observed to lower the viscosity.^{16, 110}

MacFarlane, *et al.*¹¹⁰ reported on quaternary ammonium, *N*-alkyl-*N*-methylpyrrolidinium and 1-alkyl-3-methylimidazolium ionic liquids based on the dicyanamide $[\text{N}(\text{CN})_2]^-$ anion. These liquids were synthesized with the goal of producing lower viscosity liquids that would be more applicable as reaction media. The Emim dicyanamide salt exhibited a viscosity of 21 cP, while the quaternary ammonium and pyrrolidinium types exhibited viscosities of 45 cP and 50 cP respectively. These values were comparatively lower than those reported for liquids based on other anions with the same cations.

Table 5: Summary of viscosity data

Ionic Liquid	Viscosity (cP)	Reference
[Bmim]PF ₆	312, 330	98
R ₄ N ⁺ (CF ₃ SO ₂) ₂ N ⁻	75.5-2.03 x 10 ³	100
[Emim], [Bmim]Tf ₂ N	34, 52	16
[Emim]CH ₃ COO	162	16
[Emim]BF ₄	37.7	98
[Bmim]BF ₄	152	111
[Emim], [Bmim]TfO	45, 90	111

9. Density

The densities of ionic liquids have been reported to lie in the range of 1.3 g/cm³ to 1.6 g/cm³. The 1:2 ethylpyridinium bromide/AlCl₃ mixture was reported³⁶ as having a density of 1.51 g/cm³ at 25 °C. Williams, *et al.* reported²⁴ densities of 1.28 g/cm³ and 1.29 g/cm³ for the 1:1 butylpyridinium chloride/BCl₃ mixture and the 1:1 Emim/BCl₃ mixture respectively. Similar

results (1.27 g/cm^3) were obtained for the quaternary ammonium bis(trifl)amides at 20°C .

The imidazolium cations investigated by Bonhote, *et al.*¹⁶ with several anions yielded densities which ranged from 1.21 g/cm^3 for the [Bmim] trifluoroacetate to 1.66 g/cm^3 for the [Bmim] bis(trifl)amide at 22°C .

Hagiwara and Ito's review⁹⁸ of imidazolium salts based on fluoroanions revealed densities in the same range (1.1 g/cm^3 to 1.6 g/cm^3).

Butylpyridinium salts of bis(trifl)amide and BF_4^- display densities in this range also at room temperature.⁹⁹ However the dicyanamide salts of quaternary ammonium, *N*-alkyl-*N*-methylpyrrolidinium and 1-alkyl-3-methylimidazolium cations reported by MacFarlane, *et al.*¹¹⁰ exhibit lower densities, in the range of 0.92 g/cm^3 - 1.06 g/cm^3 , than those reported for ionic liquids based on other types of anions.

Table 6: Summary of density data

Ionic Liquid	Density (g/cm ³)	Temperature (°C)	Reference
Epy ⁺ Br ⁻ /AlCl ₃ (1:2)	1.51	25	36
BpyCl/BCl ₃ (1:1)	1.28	20	24
[R ₄ N ⁺]Tf ₂ N ⁻	1.27	20	24
[Emim], [Bmim] Tf ₂ N ⁻	1.52, 1.43	20, 22	111, 16
[Bmim] CF ₃ COO, PF ₆	1.21, 1.37	22, 30	16, 98
[Emim], [Bmim]TfO	1.39, 1.29	22	16

10. Dissolution properties/Polarity Characteristics¹¹²⁻¹¹⁴

Ionic liquids do not follow the rule of thumb “like dissolves like.”

When used as a stationary phase for gas-liquid chromatography¹¹⁵ they were found to exhibit dual polarity characteristics, interacting strongly with both polar and non-polar compounds. They are considered to be similar to short-chain alcohols and polar aprotic solvents (such as DMSO and DMF) in their

solvent characteristics.⁶ However, the polarity and solubility characteristics of ionic liquids are influenced and can be tuned by the choice of anion and cation. [Bmim] Br is water-soluble for example, whereas [Bmim] PF₆ is water-insoluble. Ionic liquids are able to dissolve a wide range of organic, inorganic and organometallic compounds and hence find numerous applications as reaction media. (They have been described as being able to dissolve almost anything including coal, plastics, metals and even rock, not to mention glassware if you choose to work with the PF₆⁻ containing liquids!) The substituents on the cation can also alter the solubility of ionic liquids. They become more lipophilic with increasing alkyl substitution, resulting in increasing solubility of hydrocarbons and non-polar organics.⁶

The solubility of gases such as H₂, CO and O₂ in ionic liquids is generally good which makes them attractive solvents for catalytic hydrogenations, carbonylations, hydroformylations and aerobic oxidations.¹¹⁴ Hydrophilic ionic liquids are immiscible with some organic solvents, *e.g.* alkanes, and hence can be used in bi-phasic systems. Similarly hydrophobic ionic liquids can be used in aqueous bi-phasic systems.¹¹⁴ This

hydrophilic or hydrophobic character depending on the anion constituent of the ionic liquid, allows for applications in separations, extractions and bi-phasic catalysis.⁴

Several researchers have attempted to investigate the polarity characteristics of ionic liquids using solvent polarity probes. These probe molecules display solvatochromism, where their absorption or emission spectral shifts vary depending on their chemical (solvent) environment, and they have been used to develop empirical scales of solvent polarities. One of the most popular solvatochromic probes used is Reichardt's betaine-30 absorbance dye, 2,6-diphenyl-4-(2,4,6-triphenyl-*N*-pyridino)phenolate (historically the dye numbered 30 in the first publication by Dimroth, Reichardt, *et al.*).¹¹⁵ This is a zwitterionic compound that exhibits one of the largest observed solvatochromic shifts in its charge transfer absorption band in going from a polar solvent ($\lambda_{\text{max}} = 453$ nm in water) to a non polar solvent ($\lambda_{\text{max}} = 925$ nm in hexane)¹¹³ and is the basis for the $E_{\text{T}}(30)$ solvent polarity scale. $E_{\text{T}}(30)$ [the molar transition energy for charge transfer absorption],

values are calculated from the absorbance maximum, λ_{max} , of the charge transfer band of Reichardt's dye 30:¹¹⁵

$$E_T(30) \text{ (kcal mol}^{-1}\text{)} = 28591/\lambda_{\text{max}} \text{ (nm)}$$

These values are often normalized to give a parameter $E_{T(N)}$ where $E_{T(N)} = 0.0$ for tetramethylsilane and 1.0 for water.¹¹² The position of the charge transfer absorption of the dye has been reported as being strongly influenced by the hydrogen bond-donating ability of the solvent to the phenoxide oxygen atom.^{115, 112} In addition to Reichardt's dye there are several fluorescence solvatochromic probe molecules. Pyrene (consisting of four fused benzene rings) is a popular neutral fluorescent probe. It is preferred when the large size and charge on Reichardt's dye pose a problem.¹¹³ Other fluorescent probes used to study ionic liquids include, dansylamide, Nile Red, and 1-pyrenecarbaldehyde.¹¹²

Gordon, *et al.*¹¹² concluded that the imidazolium-based ionic liquids display hydrogen bond donor abilities similar to those of alcohols and their polarity appears to be cation-controlled, while their nucleophilicities are much lower and anion-dependent. This makes them unique materials since

most solvents of such low nucleophilicity are generally nonpolar. These results are similar to those observed by others.^{115, 116} The general conclusion is that several solvatochromic probes should be used in conjunction before a conclusive result is obtained, since each probe usually reflects only one major type of interaction with the solvent. Anderson, *et al.*¹¹⁶ characterized ionic liquids using 36 probe molecules at three different temperatures. They concluded that the ionic liquids exhibited multiple behaviors and suggested that this accounted for why they acted as polar solvents in organic reactions containing polar molecules but as less polar solvents in the presence of less polar molecules.

11. Pulse Radiolysis

Pulse radiolysis is a technique where samples are irradiated with a laser-generated beam of high energy electrons and the species (electrons, radicals, cations etc.) produced are studied through their absorption spectra. This technique is useful for studying reaction rates, particularly for very fast reactions such as redox reactions and reactions that contain very short-lived

species. Neta and co-workers^{117, 118} have investigated reaction rate constants in ionic liquids compared to traditional solvents, in an effort to determine the suitability of ionic liquids as alternative reaction solvents for specific reactions. They studied reaction kinetics in [Bmim] salts and in methyltributylammonium Bis(trifluoromethylsulfonyl)imide (R_4NNTf_2). More recently Neta and Wishart have reported on the spectrum and reactivity of the solvated electron in the ionic liquid R_4NNTf_2 .¹¹⁹ This study was intended to characterize the initial products of ionic liquid radiolysis and to study their reactivity.

Ionic liquids have also been proposed as suitable alternatives for the cleanup and handling of nuclear waste. However, knowledge of the stability of these ionic liquids to high levels of radiation will first be necessary. Pulse radiolysis, particularly on the pico- and nanosecond time scale can be used to investigate the primary radiolytic species and the dependence of their yields and reactivities on the composition of the ionic liquid.¹¹⁹

12. Ionic Liquids as alternative media

The properties discussed above make ionic liquids excellent candidates as alternative reaction media for certain chemical reactions. In recent years there has been a considerable drive to investigate their use as replacements for the volatile organic solvents currently in use, in order to produce *greener* chemical processes.

Media applications were discussed among the very first reports on ionic liquids. The *N*-alkylpyridinium chloroaluminates reported in the late 1940's were investigated as electrolytes for electroplating aluminium.¹¹⁴

Quaternary ammonium and phosphonium salts reported in the early 1970's were described as phase transfer catalysis agents. Here reaction is brought about by the use of small quantities of an agent, which transfers one reactant across the interface into the other phase so that reaction can proceed.⁴⁶ The media applications can be separated into the following categories for simplicity.

(a) Electrochemistry and Spectroscopy

Research on ionic liquids during the 1970's and early 1980's focused primarily on their use as media for electrochemistry and spectroscopy. The ethylpyridinium bromide chloroaluminates (EPB/ AlCl_3 mixtures) and butylpyridinium chloride chloroaluminates (BPC/ AlCl_3 mixtures) were the major species investigated. These species were used as media to study the electrochemistry^{30, 33-35, 37, 42, 50-53, 55, 56, 58-60, 63, 69, 84, 120} and spectroscopy^{34, 55, 63, 66, 67, 69} of transition metal halide complexes. They were also used to investigate the electrochemical oxidation of aromatic amines³⁹ and in electrochemical synthesis.⁴¹ These ionic liquids have been shown to stabilize a variety of species that usually demonstrate only transient existence in most molecular solvents, and a number of species have been observed in solution for the first time.⁹⁷ For example, Billard, *et al.*¹²¹ recently published spectroscopic studies on the stability of divalent europium in $[\text{Bmim}]\text{PF}_6$. It was noted that previous studies indicated that Eu(II) polymers remain stable for about twenty four hours and that methanol had to be carefully degassed to prevent the oxidation of Eu(II) to Eu(III).

However, a sample of Eu(II)/[Bmim]PF_6 left in a container without special conditions was stable for months.

The ethylmethylimidazolium chloroaluminates (Emim/AlCl_3) reported by Wilkes⁷⁰ in 1982, were also investigated as media for electrochemistry,^{78-82, 122} spectroscopy^{79, 85, 122} and synthesis. These species exhibited a larger liquid range, which includes room temperature and a larger electrochemical window than the BPC/AlCl_3 systems.⁸³ The reviews by Welton⁹⁷ and Wasserscheid and Keim⁴ surveyed the applications of halogenoaluminate(III) and alkylhalogenoaluminate(III) ionic liquids in several reactions.

The potential applications of ionic liquids as electrolytes in batteries were proposed and investigated from a very early date.^{38, 70, 103}

Reports of EmimBF_4 ,¹⁵ EmimPF_6 ,^{13, 17} and BmimPF_6 , BF_4 , and SbF_6 ¹⁷ in the 1990's extended the range of low melting ionic liquids with non chloroaluminate anions, which were air and moisture stable. These species made working with ionic liquids a lot easier and greatly increased their applications in virtually all areas of chemistry.

b) Organic Reaction Media

Recently the use of ionic liquids has become widespread in organic reactions. In some reactions the ionic liquids act as a regular solvent, while in others they facilitate the easy recycling of catalysts and in many cases the ionic liquid is employed as both the solvent and the catalyst. The review by Zhao and Malhotra²⁰ is an excellent overview of ionic liquids in organic synthesis. In many cases it has been reported that reactions involving ionic liquids proceed at the same or enhanced rates and result in comparable or greater yields as those observed in traditional solvents.

(i) Friedel-Crafts^{36, 71, 86, 87}

The Friedel-Crafts alkylation of benzene with long chain α -olefins is used industrially for the manufacture of more than two million tons of linear alkylbenzenes worldwide. The products are the precursors of the corresponding alkylbenzene sulfonates, which are widely used as surfactants. Traditionally the reaction is performed using liquid HF or AlCl_3 as the catalyst.¹¹⁴ These reactions have been reported in ionic liquids.

Friedel-Crafts reactions were among the very first reactions performed in ionic liquids. Koch, *et al.* reported in 1976 on the use of 33/67 mol % ethylpyridinium bromide/aluminum chloride melt for electroinitiated Friedel-Crafts transalkylations.³⁶

In the late 1980's Wilkes and co-workers utilized [Emim]Cl/AlCl₃ ionic liquids as solvent and catalyst for Friedel-Crafts reactions of simple benzene derivatives.⁷¹ The wide range of Lewis acidity exhibited by these liquids made them the ionic liquid of choice. Seddon and co-workers⁸⁷ also used this medium to investigate the Friedel-Crafts reactions of simple aromatic compounds. The reactions were found to proceed with excellent yields and selectivities and in the case of anthracene was found to be reversible. The regioselectivities and rates observed in these reactions are comparable to the best known values for traditional acylations.

The Friedel-Crafts acylation of ferrocene was reported in [Emim]I/AlCl₃.⁸⁶ The facility with which the reactions took place were attributed to the high solubility of organometallic reactants and other organic

compounds, a built-in Lewis catalyst, and the potential to recycle the solvent.

(ii) Diels-Alder¹²³⁻¹²⁷

In Diels-Alder reactions, two neutral species, a diene and a dienophile combine to form a cycloadduct. These reactions are very useful carbon-carbon bond-forming reactions in organic chemistry. Among the earliest reports of ionic liquids employed in Diels-Alder reactions, moisture-stable imidazolium bromides and trifluoroacetates were investigated as heterogenous and homogenous Lewis acid catalysts for the addition of cyclopentadiene to crotonaldehyde or methacrolein in dichloromethane.¹²³ The authors reported high endo:exo selectivities relative to non-catalyzed reactions. Others reported on reaction of cyclopentadiene and methyl acrylate in the pure ionic liquids [Bmim][BF₄], [Bmim][ClO₄], [Emim][CF₃SO₃], [Emim][NO₃] and [Emim][PF₆].¹²⁴ The ionic liquids were reported as showing selectivities characteristic of hydrogen-bonded, polar organic solvents. Substantial endo-selectivity enhancements were reported in

the ionic liquids when compared to non-polar solvents. The authors proposed that the ionic liquids were potentially useful solvents for Diels-Alder cycloadditions and related reactions, particularly those involving moisture and oxygen sensitive reagents. Also, the biphasic nature of the reactions allowed for easily isolation of the products.¹²⁴

The same reaction was also studied in the [Emim]Cl/[AlCl₃] system.¹²⁵ The rate of the reaction in the acidic melt was reported as being 10 times faster than in water and 175 times faster than in ethylammonium nitrate. Enhanced endo/exo-selectivity was also reported.

The ionic liquids [Bmim][PF₆], [Bmim]SbF₆, and [Bmim]OTf were investigated by Song, *et al.* as media (or additives) in scandium triflate catalyzed Diels-Alder reactions for catalyst recycling and improving reaction rate and selectivity.¹²⁶ The ionic liquid [Bmim][OTf] containing the catalyst was reused eleven times without any loss of activity.

In the microwave-promoted hetero-Diels-Alder reactions of 2(1H)-pyrazinones, it has been shown that small amounts of [Bmim][PF₆] (0.150 mmol) added to dichloroethane, was able to change the dielectric properties

of this less polar solvent sufficiently such that rapid heating to higher reaction temperatures became possible.¹²⁷

(iii) Catalysis¹²⁸⁻¹³⁶

Homogenous catalytic processes are appealing because of the mild reaction conditions and the high reaction yields and selectivities obtained compared to heterogenous processes. However, the separation of the products from the reaction mixture, the recovery of the catalysts and the need for organic solvents are major disadvantages that have prevented the use of these processes on an industrial scale.¹³¹ Product removal from the reaction mixture often involves distillation or chromatography. These techniques can be expensive and can degrade the product, catalyst or both, because the products often have boiling points that are higher than the decomposition temperatures of the metal complexes used as catalysts. Thus, heterogenous catalysis is usually chosen to minimize reaction steps and cost. One of the solutions applied to this problem is liquid-liquid biphasic catalysis. Here, the molecular catalyst is soluble in only one phase and the

substrates/products remain in the other phase. The reaction can take place in one or both of the phases or at the interface. In many cases the catalyst phase is recyclable and the products are removed from the reaction mixture by decantation.¹³¹ Dupont¹³¹ proposes that these “biphasic systems might combine the advantages of both homogenous (greater catalyst efficiency and mild reaction conditions) and heterogenous (ease of catalyst recycling and separation of products) catalysis.”

Ionic liquids have proven to be ideal for use in these biphasic systems. Apart from the previously discussed reactions, ionic liquids have been widely employed in catalysis. There are several excellent reviews^{97, 4, 114, 131} on the subject. The [Bmim][PF₆] and [BF₄] salts and the [Emim][PF₆] salts are most commonly utilized. These are weakly coordinating anions, which potentially form highly polar yet non-coordinating solvents. They can be expected to have strong rate enhancing effects on reactions involving cationic intermediates.¹¹⁴ Quaternary ammonium type liquids containing these weakly coordinating anions have been described as excellent immobilizing agents for various transition-metal catalyst precursors in

reactions ranging from the Ziegler-Natta type to the hydroformylation of olefins.¹³¹

Chauvin, *et al.*¹⁷ studied several [Bmim] salts as solvents for two-phase homogenous catalysis. [Bmim][PF₆], [BF₄], [SbF₆] were used for hydrogenation, isomerization and hydroformylation of alkenes catalyzed by rhodium complexes. Reaction rates for hydrogenation in [Bmim][SbF₆] nearly five times higher than in acetone were observed. The catalyst solution in the ionic liquid was recyclable.

There have been several reports where biphasic systems using ionic liquids and supercritical carbon dioxide allow homogenous catalysts to be recycled continuously.¹³⁷ A mobile CO₂ phase containing the reactants and products was combined with a stationary ionic liquid phase containing a catalyst. The hydroformylation of 1-octene was carried out in ScCO₂ with [Bmim][PF₆] containing a dissolved catalyst, in a continuous flow reactor. The activity of the catalyst remained stable over the 72 hour period that the reaction was performed. This has been described as a green process, which

is essentially solvent-free and requires only a small amount of the ionic liquid.¹³⁷

Similarly the hydrovinylation of styrene was performed.¹³⁸ The authors reported being able to activate, tune and immobilize the nickel catalyst in this unusual biphasic system of ionic liquid/ ScCO_2 .

The use of ScCO_2 and ionic liquids have also been reported for other reactions, including the synthesis of propylene carbonate using $[\text{C}_8\text{mim}]\text{BF}_4$,¹³⁹ and the hydrogenation of alkenes and carbon dioxide using $[\text{Bmim}]\text{PF}_6$.¹⁴⁰ These systems have also been utilized in several enzyme-catalyzed reactions.^{141, 142}

Dupont, and co-workers^{143, 131} and Chauvin, and co-workers¹⁷ have reported on the use of $[\text{Bmim}]$ ionic liquids as an alternative to water for the two-phase catalytic oligomerization,^{4, 144} hydroformylation¹⁴⁵ and hydrogenation of olefins by transition metal complexes. They also reported on the use of $[\text{Bmim}][\text{BF}_4]$ with immobilized palladium (II) compounds for the selective hydrodimerization of 1,3-butadiene.¹⁴³ Reactions were facilitated by the temperature dependent miscibility of the $[\text{Bmim}][\text{BF}_4]/\text{H}_2\text{O}$

system. The reaction was performed under homogenous conditions at 70°C, while the formation of a two-phase system at 5°C allowed for the easy removal of products by decantation. The ionic liquid catalyst solution was reused several times.

Imidazolium and pyrrolidinium ionic liquids containing several different types of anions were also investigated for the biphasic rhodium-catalyzed hydroformylation of 1-hexene. It was found that the reaction rate and regioselectivity and the retention of the rhodium could be optimized depending on the constituent anions and cations of the ionic liquid.¹⁴⁵

Methylbutylpyridinium chlorostannate ionic liquids have been demonstrated as solvents for the regioselective, platinum catalyzed hydroformylation of functionalized and non-functionalized olefins. The platinum catalyst showed enhanced stability and selectivity compared to reaction in conventional organic solvents.¹⁴⁶

(iv) Biocatalysis

It has been demonstrated that enzyme catalyzed reactions and other types of biotransformations can be successfully carried out in ionic liquids. Erbeltinger, *et al.* reported on the synthesis of *Z*-aspartame, a precursor to the artificial sweetener aspartame, in the ionic liquid [Bmim]PF₆. The reaction was catalyzed by thermolysin, a proteolytic enzyme. The enzyme which would normally require immobilization, exhibited excellent stability in the ionic liquid. Competitive reaction rates and comparable yields (95% yield) were obtained in comparison to the reaction carried out in an organic solvent.^{7,90} Sheldon's group has shown that lipases are also stable in ionic liquids and "perform well in the total absence of water". Lipases are enzymes that are used to catalyze important industrial reactions such as esterifications and transesterifications. They are used in the synthesis of pharmaceutical and agrochemical intermediates, in the petrochemical industry, and in the manufacture of flavors, fragrances and healthcare products.⁹⁰ Sheldon and co-workers used [Bmim]PF₆ and [Bmim]BF₄ to carry out a lipase (*C. antarctica*)-catalyzed transesterification. The reaction

proceeded with the same yields when anhydrous liquids were used but in the presence of water (10% by volume) the hydrophobic PF_6^- liquid gave higher yields. Sheldon has been quoted as saying that, “these enzyme-catalyzed reactions go at least as well in ionic liquids as in the optimum organic solvents and in some cases even better...”⁹⁰ Several other groups^{141, 142, 147, 148} have performed lipase-catalyzed reactions in ionic liquids. $[\text{Bmim}]\text{PF}_6$ and NTf_2 were the most commonly used, but $[\text{Emim}]\text{PF}_6$ and $[\text{Bmim}]\text{CH}_3\text{COO}^-$, NO_3^- , CH_3SO_3^- , CF_3COO^- and CF_3SO_3^- were also investigated. It was found that there was no detectable activity in the hydrophilic ionic liquids. In $[\text{Bmim}]\text{PF}_6$ enantioselectivity in acetylation reactions was up to six times greater than in organic solvents,¹⁴⁸ and the rate of transesterification was 1.5 times faster.¹⁴⁷ Other types of biotransformations have also been performed in ionic liquids, particularly in $[\text{Bmim}]\text{PF}_6$.⁹⁰ In addition several other types of organic reactions have been carried out using ionic liquids such as those shown in Table 7.

Table 7: Summary of ionic liquids used as alternative organic reaction**media**

Reaction	Ionic liquid used	Reference(s)
Friedel Crafts	[EmimCl]AlCl ₃	71, 87, 86
Diels Alder	[Emim] Br, CF ₃ COO ⁻	123
	[Emim] CF ₃ SO ₃ , NO ₃ ⁻ , PF ₆ ⁻	124
	[Bmim] BF ₄ , ClO ₄ ⁻ , PF ₆ ⁻ , SbF ₆ ⁻	124, 127
	, CF ₃ SO ₃ ⁻ (Otf)	126
	BpyCl/AlCl ₃ , [Emim][AlCl ₃]	125
Transesterification	[Bmim]PF ₆	90
Balzsciemann	[Emim]/[Bmim] PF ₆ , BF ₄	90
Catalysis	[Bmim]BF ₄ , PF ₆ ⁻ , SbF ₆	131, 111, 150
		134, 133, 129
	[1-butyl-4-methyl Py ⁺] AlCl ₄ ⁻	129
	[Emim], [Bmim]CN ₂ N ⁻	132, 151

Table 7 continued: Summary of ionic liquids used as alternative organic reaction media

Hydrogenation	[Bmim]PF ₆ , SbF ₆ ⁻	17, 152, 111
	[Bmim]BF ₄ , PF ₆ ⁻	153, 154, 155
	[MBPy]BF ₄ , [Emim]NTf ₂	156, 157
Catalytic Oxidation	[Bmim]PF ₆	20
Hydroformylation	[Bmim]PF ₆	17, 145
	[Mpy]SnCl ₃ , SnCl ₅ ⁻	146
	[Bmim]BF ₄ ⁻ , CF ₃ CO ₂ ⁻ , Otf ⁻	145
Polymerization	[Bmim]PF ₆	158, 159, 161
Alkene Metathesis	[Bmim]PF ₆ , BF ₄ ⁻ , Otf ⁻	162-164
Electrophilic Nitration	[Emim]Otf, CF ₃ COO ⁻ , NO ₃ ⁻	165
Hydrodimerization	[Bmim]BF ₄ , PF ₆ , Otf ⁻	143
Heck	[Bmim]BF ₄ , PF ₆ , Br ⁻	166, 167
	(C ₄ H ₉) ₄ N ⁺ Br	168, 169

Table 7 continued: Summary of ionic liquids used as alternative organic reaction media

Suzuki cross-coupling	[Bmim]BF ₄	20
	C ₁₄ H ₂₉ (C ₆ H ₁₃) ₃ P ⁺ Cl ⁻	170
Esterification	[BPyCl]AlCl ₃ , [EtPy]CF ₃ CO ₂	20
Beckmann rearrangement	[BPy]BF ₄	171
	[Bmim]PF ₆ , BF ₄ ⁻	172, 173
Biocatalysis	[Bmim]PF ₆ , BF ₄ ⁻	7, 111
Fluorination	[Bmim]BF ₄	174
Cyclopropanation	[Emim]BF ₄ , (CF ₃ SO ₂) ₂ N ⁻ (Ntf ₂ ⁻), [Oct ₃ Nme][Ntf ₂]	175
Alkylation	[Emim], [Bmim]AlCl ₄ ⁻ , PF ₆ ⁻	176, 130
Biginelli	[Bmim]BF ₄ , PF ₆ ⁻	177
Coupling of Aryl Halides	[Bmim]PF ₆	166

Table 7 continued: Summary of ionic liquids used as alternative organic reaction media

Reaction	Ionic liquid used	References
Cyclodimerization	[Bmim]BF ₄ , PF ₆ ⁻	178
Oligomerization	[C _n mim]PF ₆ , SbF ₆ ⁻	144
Trost-Tsuji coupling	[Bmim]Cl	128
Wittig	[Bmim]BF ₄	90
Benzoin Condensation	3-butyl-4/5-methyl thiazolium BF ₄ ⁻	179

(c)Extractions^{14, 181-186/ Partitioning^{187, 188}}

Ionic liquids are being increasingly investigated for applications in liquid-liquid extractions and separations. One such application already discussed is the easy “extraction” or “separation” of products or catalysts in ionic liquids, when they are employed in biphasic catalysis. The Rogers group^{181, 14} has

shown that the partitioning of common organic solutes (including aniline, benzoic acid and salicylic acid) between [Bmim]PF₆ and water was similar (although an order of magnitude less) to that observed in an octan-1-ol/water biphasic system for the same solutes. The group believes that the distribution values obtained are good enough for practical applications.

Researchers at the University of Nebraska, Fadeev and Meagher^{182, 183} have shown that the ionic liquid 1-octyl-3-methylimidazolium hexafluorophosphate ([C₈mim]PF₆) can be used to recover butanol (“an important chemical feedstock and potential biofuel”)¹⁸³ from fermentation broth. Butanol can be produced from the microbial fermentation of carbohydrates to acetone, butanol and ethanol, called ABE fermentation. However the recovery of the butanol by common techniques such as distillation is not economical. The ionic liquid was used to extract the butanol from an aqueous solution and then the butanol was separated from the ionic liquid by pervaporation (a technique using permeation and evaporation). However the results suggested that distillation might be more economical for the recovery of the butanol from the ionic liquid. Also the

group acknowledged the need for toxicity studies of ionic liquids, particularly towards microorganisms.

Others have investigated the effect of structural variation of the imidazolium ionic liquids on the extraction (selectivity and efficiency) of alkali metal salts by a crown ether.¹⁸⁵ Solutions of alkali metal chlorides with solutions of dicyclohexano-18-crown-6 (DC18C6) in 1-alkyl-3-methylimidazolium hexafluorophosphates (where the alkyl group was varied from butyl to nonyl) were studied. It was found that the extraction efficiency decreased but the selectivity increased as the length of the alkyl group increased. The selectivity order coincided with the relative binding affinities of the crown ether for the alkali metal ions. The same study was performed using common organic solvents such as chloroform, nitrobenzene and 1-octanol instead of an ionic liquid and negligible extraction was observed. In the ionic liquid alone with the absence of the crown ether, the extraction efficiency is less and the selectivity changes. The extraction selectivity correlated with the relative hydrophobicities of the alkali metal cations. It was also noted that unlike similar extractions where conventional solvents

are the diluents of the crown ether, varying the anion of the alkali metal salt (from chloride to nitrate to sulfate) does not affect the extraction when ionic liquids are used as the diluents.

Dietz and Dzielawa¹⁸⁴ have also investigated the extraction of strontium ions from acidic nitrate media by DC18C6 (the same crown ether used in the previous study) dissolved in a series of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquids (alkyl = ethyl, butyl, hexyl, pentyl or octyl). In contrast to conventional solvents where there is anion (nitrate) coextraction to maintain electro-neutrality, this is not observed in the ionic liquids and another mechanism is proposed for the extraction. It was concluded that the ionic liquids “offer advantages in terms of enhanced extraction efficiency and reduced volatility (but) these advantages may be diminished by aqueous phase solubility losses when they are employed as diluents in certain metal ion extraction applications.”

In similar work¹⁸⁶ the Rogers group at the University of Alabama have derivatized the imidazolium hexafluorophosphate ionic liquids to include “task specific” functional groups such as thioether, thiourea and urea for the

extraction of heavy metal ions such as Hg^{2+} and Cd^{2+} . The group noted that the problem with metal ion extraction into ionic liquids in liquid/liquid systems is the need for an extractant molecule which complexes directly with the metal ion. Here they have designed compounds to be both the ionic liquids and the extractants. These liquids were proposed for use as the bulk solvent or as extractants doped into less expensive ionic liquids. Lower distribution ratios were observed for Cd^{2+} than for Hg^{2+} in the liquids investigated. It was not determined whether the metal ion could be stripped from the ionic liquid after extraction.

Bates, *et al.*¹⁸⁹ has also reported task specific ionic liquids for the uptake of carbon dioxide. The cation of these liquids consisted of an imidazole unit to which a primary amine group was covalently attached. This salt reversibly sequestered CO_2 .

The Rogers research group has also reported previously¹⁸⁸ on solvent extraction utilizing pH dependent partitioning in ionic liquids. They demonstrated that reversible pH dependent partitioning could be achieved in ionic liquids. They used 1-alkyl-3-methylimidazolium PF_6^- liquids where R

was varied from butyl to hexyl to octyl to decyl and thymol blue (an indicator dye) as the solute. The pH was varied using CO₂ and NH₃ gases. It was illustrated that the phase preference of the solute could be accomplished by altering the pH and also depending on the alkyl substituent on the ionic liquid this phase preference could be fine tuned for specific solutes. They also showed that in the case of the decyl-substituted ionic liquid which melts slightly above room temperature, the extraction occurred at elevated temperatures. The ionic liquid was then recrystallized out of the mixture and the pure solute was recovered. The overall results obtained were considered to be similar to what would be expected for organic/aqueous extraction data.

Dupont and co-workers¹⁸⁷ studied the partitioning of aqueous ions into an ionic liquid deposited on an electrode surface. 1-methyl-3-(2,6-(*S*)-dimethylocten-2-yl)-imidazolium tetrafluoroborate was deposited as microdroplets and thin films on the surface of carbon micro electrodes and 4.9 mm pyrolytic graphite electrodes respectively. Selective uptake of the ferricyanide ion [Fe(CN)₆]³⁻ into the ionic liquid was observed.

Studies have also been conducted on the extraction of aromatic hydrocarbons from mixtures of aromatic and paraffin.¹⁹⁰ Liquid-liquid equilibrium data was gathered for toluene/heptane/[Emim]I₃ and toluene/heptane/[Bmim]I₃ systems. The conclusion was that these ionic liquids can be used to remove toluene from hexane that contains only small amounts of toluene. A non-random two-liquid physical thermodynamic model was used to correlate the experimental data. It was found that this model represent the ternary systems well and suggested that the predicted data can be quite useful for process design.

(d) Media for transition metal solution chemistry

Room temperature haloaluminate ionic liquids have been used as solvents for transition metal solution chemistry.⁷³ The study of transition metal halide complexes in molecular solvents like water and acetonitrile result in erroneous results because of solvation, solvolysis and dissociative side reactions. However, since water is reactive with the haloaluminate anions and cannot exist in these liquids, they are more suitable for studying

the solution chemistry of transition metal halide complexes. Liquids such as butylpyridinium chloride/aluminum chloride, $[\text{Emim}]\text{AlCl}_4^-$ and $[\text{Emim}]\text{AlBr}_4^-$ were used and were found to “stabilize a number of species that ordinarily exhibit only transient existence in molecular solvents at room temperature.”

(e) Stationary phases for gas chromatography

Armstrong *et al.*¹¹⁵ at the University of Missouri used $[\text{Bmim}]\text{PF}_6$ and $[\text{Bmim}]\text{Cl}$ as stationary phases in gas-liquid chromatography. Their interest stems from the ability of room temperature ionic liquids to solubilize complex organic compounds such as some cyclodextrins and macrocyclic antibiotics. The ionic liquids were coated onto silica capillary columns. The columns were found to exhibit a dual nature, they “acted as nonpolar stationary phases when separating nonpolar or low polarity analytes that are not proton donor or acceptor molecules.” However, analytes containing strong proton donor or acceptor groups are retained strongly and tend to be “spatially resolved, as a group from nonpolar analytes.”

(f) Matrixes for MALDI mass spectrometry

Armstrong *et al.*¹⁹¹ studied several ionic liquids for applications as matrixes for matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS). Matrixes for MALDI “must dissolve (liquid matrix) or co-crystallize (solid matrix) with the sample, strongly absorb the laser light, remain in the condensed phase under high vacuum conditions, stifle both chemical and thermal degradation of the sample and promote the ionization of the sample via any of a number of mechanisms.” Solid matrixes are problematic because it is difficult to obtain a homogenous mixture with the analyte, resulting in poor reproducibility. Liquid matrixes produce homogenous solutions and give better reproducibility but their volatility results in “a dynamic, changing, uncontrolled matrix.”

Ionic liquids with their low vapor pressure and proven ability to dissolve analytes ranging from inorganic to organic to polymeric substances, would therefore combine the advantages of both solid and liquid matrixes. However it is necessary for the ionic liquid to absorb at a desired wavelength in the UV and have available protons to promote ionization. Most of the

conventional ionic liquids investigated, such as [Bmim]Cl, PF_6^- and BF_4^- lacked these properties and did not produce MALDI signals.

However, the ionic liquids that did have the desired properties produced “greater spectral peak intensities and lower limits of detection than comparable solid matrixes.” The authors suggest that both the cationic and anionic portion of the ionic matrix must be chosen with a consideration for the special requirements of UV-MALDI.

(g) Media for photochemical reactions

There are a few reports of photochemical reactions in ionic liquids. The photochemical behavior of anthracene in [EmimCl]AlCl₃ was reported in 1993.¹⁹² The same group reported on the photo-induced electron transfer chemistry of 9-methylanthracene in [EmimCl]/AlCl₃ in 1996.⁸⁵ More recently the photoelectron transfer from excited state ruthenium (II) tris(bipyridyl) to methylviologen was reported in [Bmim]PF₆.¹⁹³ The reaction was reported to occur, within experimental error, at a diffusion controlled rate.

It is impossible to discuss the myriad of investigations where ionic liquids have been utilized as reaction media. The reader is referred to additional references for further media application discussions.¹⁹⁴⁻²⁰⁸

Discussions here range from the nucleophilic conversion of fatty alcohols to alkyl halides²⁰⁶ to the cleavage of ethers¹⁹⁸ and free radical propagation.¹⁹⁹

The imidazolium salts such as [Bmim]PF₆ have been the most investigated as illustrated in the preceding discussion. However, recently as more ionic liquids of differing structural types become available, this trend is changing.

METHODS OF PREPARATION

The first step in the preparation of ionic liquids is the quaternization of the desired amine or phosphine compound. In some cases the quaternary ammonium or phosphonium compounds are commercially available. The synthesis involves reaction of the amine or phosphine compound with the desired monohaloalkane to yield the ammonium or phosphonium halide. The

pyridinium and imidazolium halides are prepared similarly.^{11, 12, 25, 98} In some instances these halides are themselves ionic liquids.

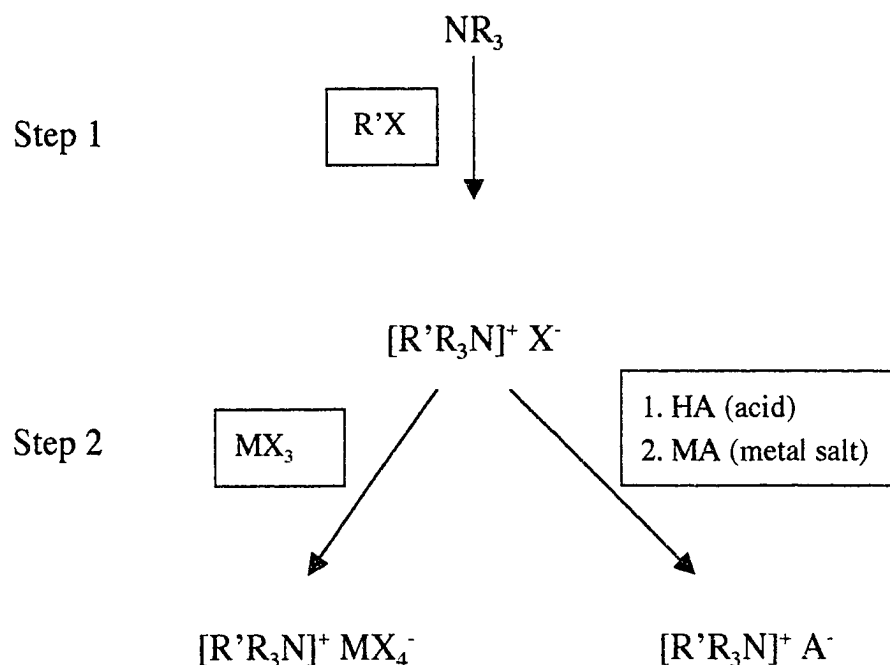


Figure 7: Schematic representation of the synthetic pathway for ionic liquids

The next step is the conversion of the purified halide salts into ionic liquids containing the desired anion. This is achieved by metathesis of the halide salts with a silver or group I metal salt of the anion or acid-base neutralization reactions. Metathesis is often carried out in methanol or methanol-water media.¹⁵ The ionic liquids are then dried in a vacuum oven or using a vacuum pump.

Apart from routine structure analysis and determination, it is essential that ionic liquids are analyzed for residual water content. However there is no mention in the literature of an established acceptable value for residual water content in ionic liquids and some authors do not discuss water determination. Ideally the liquids should be dried until they contain negligible water. In most cases, authors report water contents that range from 100 ppm to 10000 ppm. Water content determination is an important aspect in the synthesis and characterization of ionic liquids because the presence of a significant amount of water results in an ionic solution by definition and not an ionic liquid. The physical properties of the liquids are also greatly influenced by the presence of residual water.

Residual halide content is also problematic and should be monitored to avoid distortion of measured physical values. Seddon *et al.*³² showed that for a series of imidazolium salts with BF_4^- and NO_3^- anions, increasing the chloride ion concentration dramatically altered the viscosity. Samples with higher concentrations of chloride were more viscous.

Syntheses of quaternary ammonium halide salts

Even though the majority of researchers in the field of ionic liquids have focused on the imidazolium, pyrrolodinium or pyridinium cations, there have been some reports on monocationic quaternary ammonium compounds.²⁰⁹

The Engel research group has been concerned with the preparation of several series of structurally unique ammonium and phosphonium compounds for over a decade.²¹⁰ In most cases these compounds have been polycationic (containing multiple positively charged sites) resulting in polyammonium and polyphosphonium salts. Some of these unique structural ammonium types include:

1. Polycationic Strings^{211, 212}- cationic sites arrayed in a regular linear manner along a flexible chain. These include strings containing tertiary amine sites as well as the di(tertiary)amine, 1,4-diazabicyclo[2.2.2]octane (dabco).

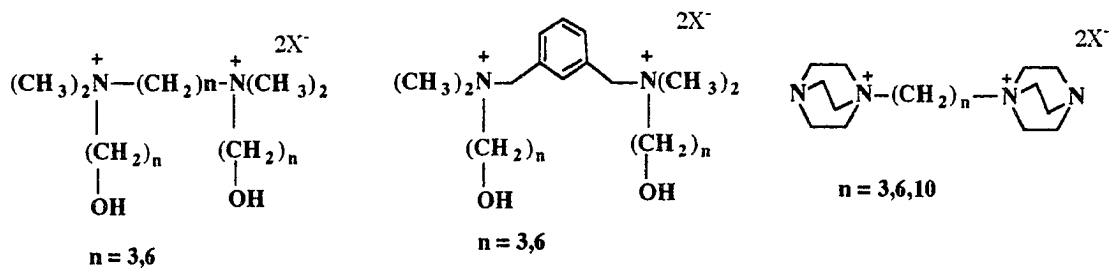


Figure 8: Representative structural types of polyammonium strings

2. Monocationic Strings²⁷ - singly positively charged species derived from pyridine, dimethylaminopyridine (dmap) and mono-substituted dabco species. More recently this category has included imidazolium species.

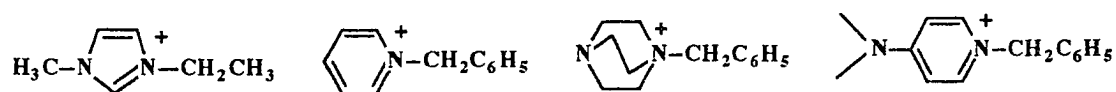


Figure 9: Representative structural types of monocationic ammonium salts

3. Rings²¹³- cyclic structures with cationic sites (from tertiary amine or dabco units) located in ring systems containing olefinic, acetylenic or alkyl linkages and/or ortho-, meta- and para-disubstituted aromatic rings.

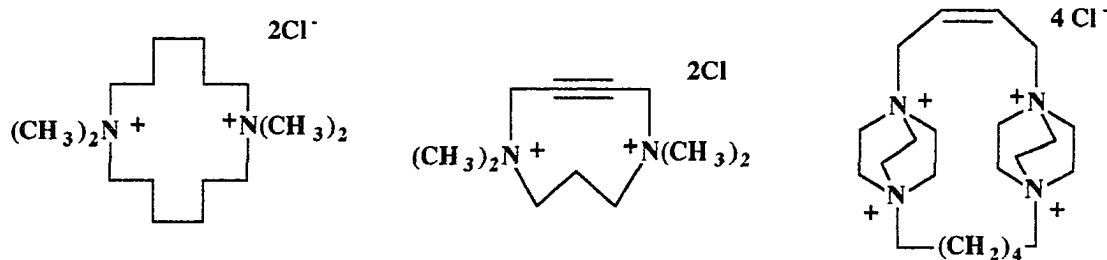


Figure 10: Representative structural types of polyammonium rings

4. Dendrimers^{214,215}/Cyclodextrins²¹⁶- Structurally more complex species.

Dendrimers contain cationic sites at repetitive points in a branching structure, while cyclodextrins with dabco substituents contain an excess of twelve cationic sites.

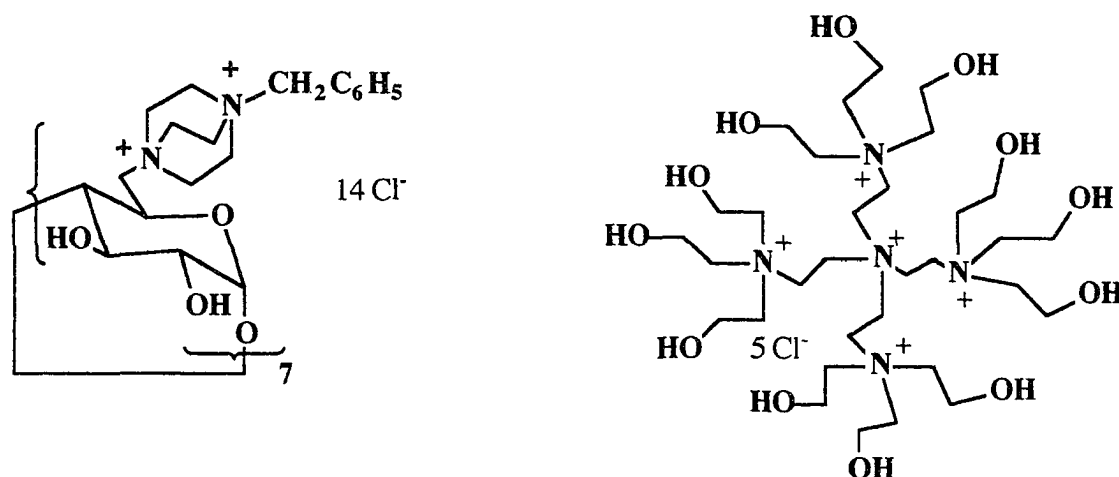


Figure 11: Representative structural types of ammonium dendrimers and cyclodextrins

The interesting results reported by others some years ago on the pyridinium and imidazolium ionic liquids, sparked our interest and inspired us to investigate the potential of our unique ammonium halide salts as ionic liquids. We set out to convert these salts into compounds bearing varying anions, with hopes that some of them would be ionic liquids. Hence began our exciting and challenging work in this new and unexplored field of intriguing compounds that defy most of the rules and expectations of traditional chemistry.

Chapter 2

RESULTS AND DISCUSSION

A. SYNTHESSES

1. Synthesis of polyammonium halide precursors

This laboratory has previously synthesized many of the polyammonium halide precursors utilized for the preparation of ionic liquids in this investigation and detailed procedures are published elsewhere.^{210, 211, 213, 216} In re-synthesizing these halide salts, in some instances slight modifications were made to the established procedures. This was mainly a difference in the choice of reaction solvent to increase precipitation and improve yields. Analogs of the existing halide compounds were also synthesized mainly by introducing different functional groups.

Syntheses of the previously prepared unmodified halide salts will be outlined only briefly. However, the newly prepared salts will be discussed in more detail. The structures of all new compounds were confirmed by ^1H and ^{13}C NMR. The salts described here are by no means a comprehensive list of all of the structural variations of salts prepared by this laboratory. Structural

types that did not yield low melting ionic liquids were not studied further and are not discussed in detail.

1. Strings

(i) Hydroxyl bearing strings

Previous researchers in this laboratory synthesized strings of the type shown in figure 12.^{27,217}

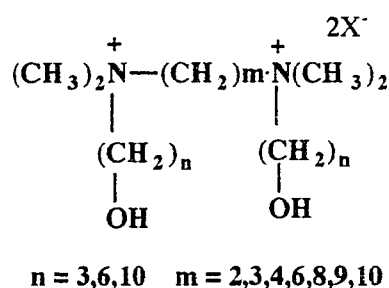


Figure 12: Representative structure of the hydroxyl string category of halide salt previously synthesized

These di-tertiary amines were synthesized by either of two methods.

The following is described for the string where $n = 3$ and $m = 4$:

- (ii) One equivalent of *N, N, N', N'*-tetramethyl-1, 4-butanediamine was dissolved in acetonitrile and placed in a round bottom flask fitted with a stir bar and reflux condenser. Two equivalents of 3-chloro-1-

propanol were added to the reaction mixture under the hood. The reaction was left to stir for 24 hours at 50-60°C. The disubstituted ammonium halide compound was recovered as a white precipitate by suction filtration through a sintered glass funnel. The filtrate was washed with acetonitrile and volatile materials were removed by rotary evaporation at 60°C followed by drying on a high vacuum pump (< 0.5 torr) for a few days. The structure was then determined by ¹H and ¹³C NMR spectroscopy. If residual solvent or impurities were present, the washing and drying steps were repeated. Acetonitrile was substituted for ethanol as the reaction solvent as it was found to promote precipitation.

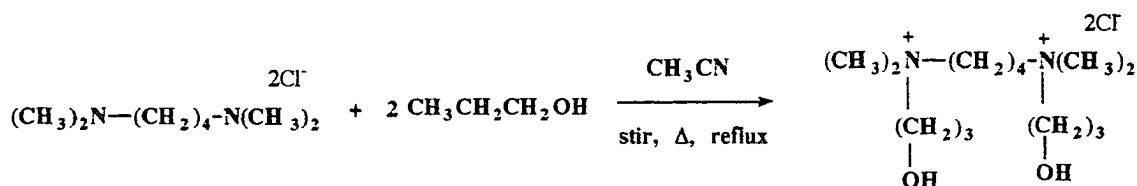


Figure 13: Preparation of a di-tertiary ammonium halide

(ii) The di-tertiary ammonium halide of the type shown in Figure 12 was alternatively prepared by allowing one equivalent of 1,4-dichlorobutane in acetonitrile to react with two equivalents of 3-dimethylamino-1-propanol. The reaction was performed and the product purified as described above.

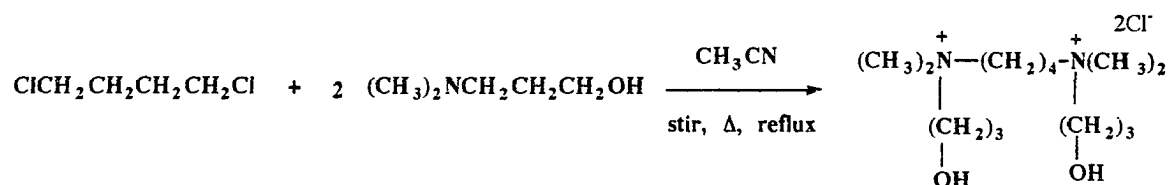


Figure 14: Preparation of a di-tertiary ammonium halide

The ammonium halide precursors were resynthesized using one of the above methods. The string where $m = 5$ and $n = 3$ (SH5), previously unreported, was also synthesized by these methods.

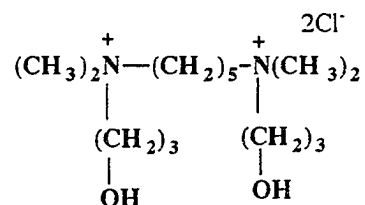


Figure 15: SH5- 4,4,10,10-tetramethyl-4,10-diazonia-tridecan-1,13-diol dichloride

Strings of this type are referred to as “String Hydroxyl N-carbon (SHN)”, where N represents the number of CH₂ units linking the two dimethylamino groups. For example, the compound in Figure 15 is called SH5. These strings are summarized in Table 8.

Analogues of the halides depicted in Table 8 were prepared by incorporating different functional groups in place of the hydroxyl group for comparison of their physical properties, in particular their pulse radiolysis characteristics.

Table 8- Hydroxyl substituted di-tertiary ammonium halides

Structure	Code	Name
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH3	4,4,8,8-tetramethyl-4,8-diazonia-undecan-1,11-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_4 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH4	4,4,9,9-tetramethyl-4,9-diazonia-dodecan-1,12-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_5 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH5	4,4,10,10-tetramethyl-4,10-diazonia-tridecan-1,13-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_6 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH6	4,4,11,11-tetramethyl-4,11-diazonia-tetradecan-1,14-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_8 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH8	4,4,13,13-tetramethyl-4,13-diazonia-hexadecan-1,16-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_9 - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH9	4,4,14,14-tetramethyl-4,14-diazonia-heptadecan-1,17-diol dichloride
$\begin{array}{c} \quad + \quad 2 \text{Cl}^- \quad \\ \text{HO}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_{10} - \text{N} - (\text{CH}_2)_3\text{OH} \\ \quad \quad \quad \end{array}$	SH10	4,4,15,15-tetramethyl-4,15-diazonia-octadecan-1,18-diol dichloride

(iii) **Alkyl bearing strings**

Strings bearing alkyl substituents in place of the hydroxyl substituents were synthesized in the halide form. The reaction was performed as described in (b) above except that instead of adding two equivalents of 3-chloro-1-propanol, 2 equivalents of 1-bromobutane were added. The product was isolated, washed and dried in the same way as previously noted. The structure was then determined by ^1H and ^{13}C NMR spectroscopy. Strings of this type are referred to as "String Alkyl N-carbon (SAN)." Compounds SA3, SA4 and SA6 were prepared this way and are shown in Table 9.

Table 9- Alkyl substituted di-tertiary ammonium halides

Structure	Code	Name
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{C}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_3\text{CH}_3 \\ \quad \quad \quad \end{array}$	SA3	4,4,8,8-tetramethyl-4,8-diazonia-undecane dichloride
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{C}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_4 - \text{N} - (\text{CH}_2)_3\text{CH}_3 \\ \quad \quad \quad \end{array}$	SA4	4,4,9,9-tetramethyl-4,9-diazonia-dodecane dichloride
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{C}(\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_6 - \text{N} - (\text{CH}_2)_3\text{CH}_3 \\ \quad \quad \quad \end{array}$	SA6	4,4,11,11-tetramethyl-4,11-diazonia-tetradecane dichloride

(iv) Ether bearing strings

Strings bearing ether substituents in place of the hydroxyl or alkyl substituents were synthesized in the halide form. The reaction was performed as described above except that instead of adding two equivalents of 3-chloro-1-propanol, 2 equivalents of 2-chloroethylethylether were added. The product was isolated, washed and dried in the same way as described previously. The structure was then determined by ^1H and ^{13}C NMR spectroscopy. Strings of this type are referred to as "String Ether N-carbon (SEN)." Compounds SE3, SE4 and SE6 were prepared this way and are shown in Table 10.

Table 10- Ether substituted di-tertiary ammonium halides

Structure	Code	Name
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{CCH}_2\text{O}(\text{CH}_2)_2 - \text{N} - (\text{CH}_2)_3 - \text{N} - (\text{CH}_2)_2\text{OCH}_2\text{CH}_3 \\ \quad \quad \quad \end{array}$	SE3	3,3,7,7-tetramethyl-3,7-diazonia-diethoxy nonane dichloride
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{CCH}_2\text{O}(\text{CH}_2)_2 - \text{N} - (\text{CH}_2)_4 - \text{N} - (\text{CH}_2)_2\text{OCH}_2\text{CH}_3 \\ \quad \quad \quad \end{array}$	SE4	3,3,8,8-tetramethyl-3,8-diazonia-diethoxy decane dichloride
$\begin{array}{c} \quad + \quad 2 \text{ Cl}^- \quad \\ \text{H}_3\text{CCH}_2\text{O}(\text{CH}_2)_2 - \text{N} - (\text{CH}_2)_6 - \text{N} - (\text{CH}_2)_2\text{OCH}_2\text{CH}_3 \\ \quad \quad \quad \end{array}$	SE6	3,3,10,10-tetramethyl-3,10-diazonia-diethoxy dodecane dichloride

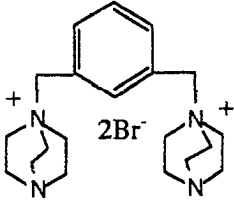
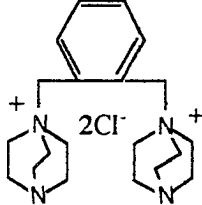
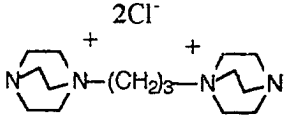
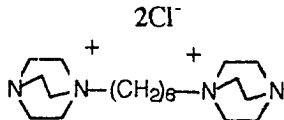
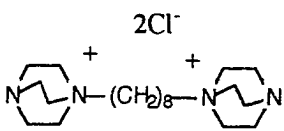
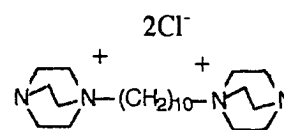
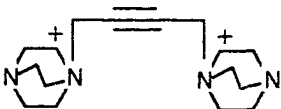
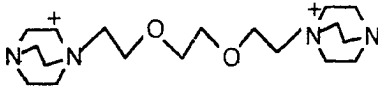
1.4 Dicationic strings containing Dabco and aromatic units

Previous members of this laboratory²¹⁷ synthesized dicationic strings containing one disubstituted dabco unit or two monosubstituted dabco units, such as those shown in Table 11. Strings containing disubstituted aromatic groups, such as those shown in Table 12 were also previously prepared.²¹⁷

The mono dabco dicationic strings were prepared by allowing one equivalent of dabco to react with two equivalents of the appropriate dihaloalkane in acetonitrile. If the desired strings were unsymmetrical, one substituent was first attached in ethyl acetate and then the other, usually in

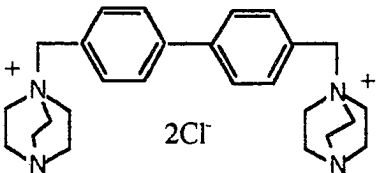
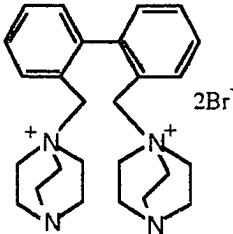
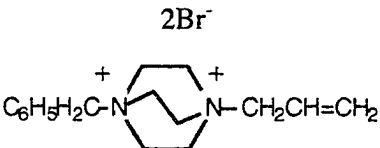
acetonitrile. The didabco strings were prepared by the reaction of four equivalents of dabco with the appropriate dihaloalkane in acetonitrile.

Table 11- Mono- and di-dabco containing dicationic strings

Structure	Code	Name
	MDD	1,3-bis-(1'-azonia-3'-azabicyclo[2.2.2]octane)-methyl-benzene dibromide
	ODD	1,2-bis-(1'-azonia-3'-azabicyclo[2.2.2]octane)-methyl-benzene dibromide
	DD3	4-(3'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-propyl)azonia-1-azabicyclo[2.2.2]octane dichloride
	DD6	4-(6'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-hexyl)azonia-1-azabicyclo[2.2.2]octane dichloride
	DD8	4-(8'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-octyl)azonia-1-azabicyclo[2.2.2]octane dichloride
	DD10	4-(10'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-decyl)azonia-1-azabicyclo[2.2.2]octane dichloride
	DDT	4-(4'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-(Z)-2'-butynyl)azonia-1-azabicyclo[2.2.2]octane dichloride
	DDE2	1,2-di-(2'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-dichloride

MDD- Meta DiDabco; **DD3**- DiDabco 3 carbon; **DD6**- DiDabco 6 Carbon;
DD8- DiDabco 8 carbon; **DD10**- DiDabco 10 Carbon; **DDE2**- DiDabco-2
 ethers; **DDT**- Dabco dabco tripple bond.

Table 11 continued-Mono- and di-dabco containing dicationic strings

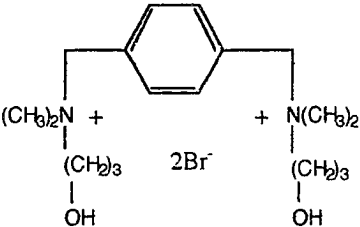
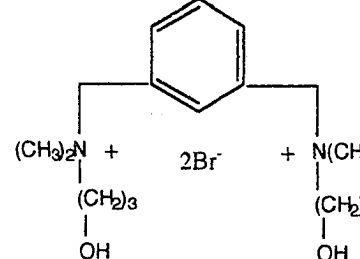
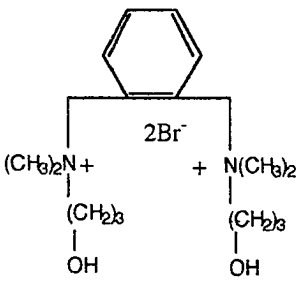
Structure	Code	Name
	PPDD	4,4'-bis(1''-azonia-4''-azabicyclo[2.2.2]octyl)-methyl biphenyl dichloride
	OODD	2,2'-bis(1''-azonia-4''-azabicyclo[2.2.2]octyl)-methyl biphenyl dibromide
	DSBBu	1-benzyl-4-{3'-propenyl}-1,4-diazoniabicyclo[2.2.2]octane dibromide

OODD – Ortho ortho dabco dabco; **PPDD**- para para dabco dabco;

DSBBu- Dabco String Benzyl Butenyl

The aromatic-containing strings are prepared by the reaction of α,α' -dihalo *ortho*-, *para*- or *meta*- xylene with two equivalents of 3-dimethylamino-1-propanol in acetonitrile. These strings are referred to as **OSH** (Ortho String Hydroxyl), **PSH** (Para String Hydroxyl) and **MSH** (Meta String Hydroxyl) respectively and are shown in Table 12.

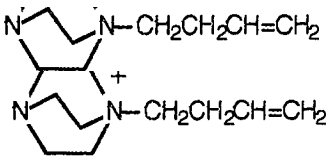
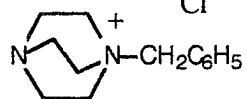
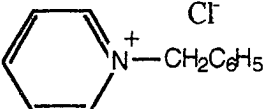
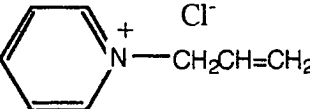
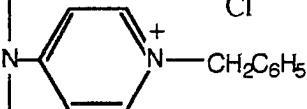
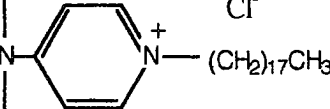
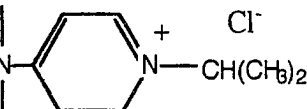
Table 12- Disubstituted aromatic halides

Structure	Code	Name
	PSH	<i>N,N,N',N'</i> -tetramethyl- <i>N,N'</i> -bis(3-hydroxypropyl)-1,4-diazoniummethyl)benzene dibromide
	MSH	<i>N,N,N',N'</i> -tetramethyl- <i>N,N'</i> -bis(3-hydroxypropyl)-1,5-diazoniummethyl)benzene dibromide
	OSH	<i>N,N,N',N'</i> -tetramethyl- <i>N,N'</i> -bis(3-hydroxypropyl)-1,6-diazoniummethyl)benzene dibromide

1.5- Monocationic strings containing Dabco, DMAP and Pyridine

In addition to the dicationic strings discussed above, a series of monocationic strings based on dabco, pyridine and dimethylaminopyridine (DMAP) were also prepared. These are shown in Table 13.

Table 13- Monocationic halide strings

Structure	Code	Name
	DSBu	1-(3-butenyl)-1-azonia-4-azabicyclo[2.2.2]octane bromide
	DSB	1-(benzyl)-1-azonia-4-azabicyclo[2.2.2]octane chloride
	BenPy	<i>N</i> -benzylpyridinium chloride
	AlPy	<i>N</i> -allylpyridinium chloride
	DMAPB	4-dimethylamino-1-benzylpyridinium chloride
	DMAP18	4-dimethylamino-1-octadecylpyridinium chloride
	DMAPI	4-dimethylamino-1-isopropylpyridinium chloride

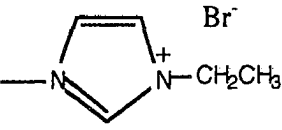
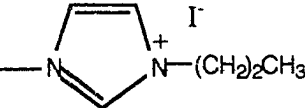
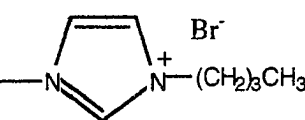
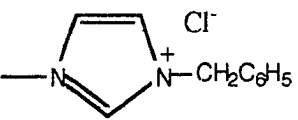
The codes used for compounds in Table 12 refer to the following: **DSBu**- Dabco String Butenyl; **DSB**- Dabco String Benzyl; **BenPy**- Benzyl Pyridinium; **AlPy**-Allyl Pyridinium; **DMAPB**-Dimethylamimopyridine Benzyl; **DMAPI8**-DMAP 18 carbon; **DMAPI**-DMAP Isopropyl; **Emim**- 1-methyl-3-ethyl imidazolium; **C₃mim**- 1-methyl-3-propylimidazolium; **Bmim**- 1-methyl-3-butylimidazolium; **Benmim**- 1-methyl-3-benzylimidazolium.

The monocationic dabco strings were prepared by the reaction of one equivalent of dabco with one equivalent of the halide of the desired structure in ethyl acetate. The pyridinium strings were prepared similarly by the reaction of pyridine with the halide form of the desired structure (1:1) in diethyl ether. The DMAP strings were prepared by the reaction of DMAP with an excess of the halide of the desired structure in acetonitrile under reflux.

1.6 – Monocationic strings containing 1-methylimidazole

Monocationic strings containing 1-methylimidazole were newly prepared and are shown in Table 14.

Table 14- Monocationic imidazolium strings

Structure	Code	Name
	Emim	1-methyl-3-ethyl-imidazolium bromide
	C₃mim	1-methyl-3-propyl-imidazolium iodide
	Bmim	1-methyl-3-butyl-imidazolium bromide
	Benmim	1-methyl-3-benzyl-imidazolium chloride

The imidazolium halides shown in Table 13 were newly prepared.

The procedure was adopted from Wilkes *et al.*¹¹ and Bonhote *et al.*¹⁶ with slight modifications. Emim was prepared by combining one equivalent of 1-methylimidazole with one equivalent of ethyl bromide in acetonitrile. The product [Emim] bromide was recovered as a white solid. The propyl and butyl analog, [C₃mim] and [Bmim], were prepared similarly but without the

addition of any solvent. These are examples of solvent-free reactions and were done in an attempt to employ greener methods for the preparation of ionic liquids. [C₃mim] iodide and [Bmim] bromide were obtained as liquids.

(2) RINGS

In addition to the strings described above, ring structures were also prepared in the halide form.²¹⁷ These are shown in Table 15. The codes used in Table 15 were derived in the following way: **UCD6**: Unsaturated Cyclic Dabco 6 Carbon; **PCD6**: Para Cyclic Dabco 6 Carbon; **MCD6**: Meta Cyclic Dabco 6 Carbon; **MCD10**: Meta Cyclic Dabco 10 Carbon; **C4T4**- cyclic triple bond 4 carbon; **C6T4**- cyclic triple bond 6 carbon; **C3T4**- cyclic triple bond 3 carbon; **C4U4**- cyclic unsaturated 4 carbon; **C66**- cyclic 6 carbon plus 6 carbon; **C69**- cyclic 6 carbon plus 9 carbon; **PCN5**-Para cyclic nitrogen 5 carbon

Table 15: Polycationic ring halides

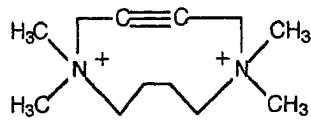
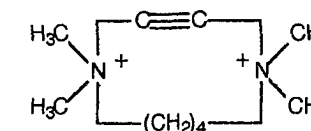
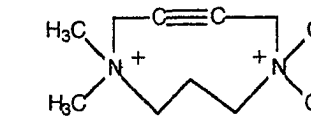
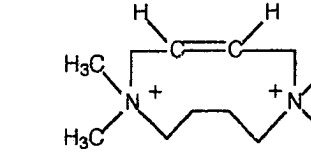
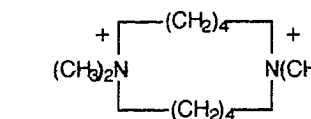
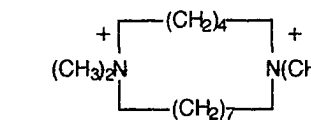
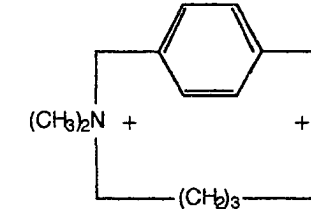
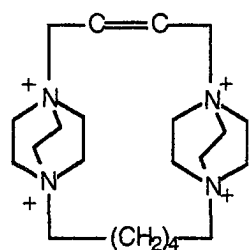
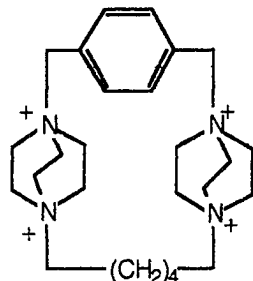
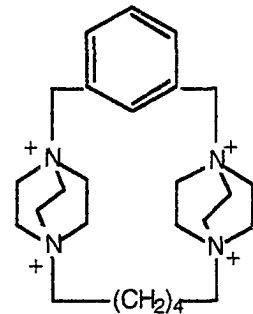
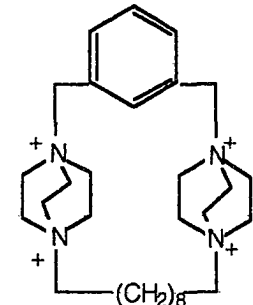
Structure	Code	Name
	C4T4	4,4,9,9-tetramethyl-4,9-diazoniacyclocyneyne dichloride
	C6T4	4,4,11,11-tetramethyl-4,11-diazoniacyclononyne dichloride
	C3T4	4,4,8,8-tetramethyl-4,8-diazoniacyclocyneyne dichloride
	C4U4	4,4,9,9-tetramethyl-4,9-diazoniacyclocdecene dichloride
	C66	1,1,8,8-tetramethyl-1,8-diazoniacyclopentadecane dichloride
	C69	1,1,11,11-tetramethyl-1,11-diazoniacycloheptadecane dichloride
	PCN5	<i>p</i> -2,2,8,8-tetramethyl-1,8-diazoniacyclopentadecane dichloride

Table 15 continued: Polycationic ring halide

Structure	Code	Name
	UCD6	1,4-but-2-enyl-1',4'''-(4{8''-(1''',4'''-diazoniabicyclo[2.2.2]octane)-1''-octyl}azonia-1'-azoniabicyclo[2.2.2]octane tetrachloride
	PCD6	<i>p</i> -xylyl-1,4''-(4{6'-(1'',4''-diazonia-bicyclo[2.2.2]octane)-1'-hexyl}azonia)-bicyclo[2.2.2]octane tetrachloride
	MCD6	<i>p</i> -xylyl-1,4''-(4{6'-(1'',4''-diazonia-bicyclo[2.2.2]octane)-1'-hexyl}azonia)-bicyclo[2.2.2]octane tetrachloride
	MCD10	<i>m</i> -xylyl-1,4''-(4{10'-(1'',4''-diazonia-bicyclo[2.2.2]octane)-1'-decyl}azonia)-bicyclo[2.2.2]octane tetrachloride

(3) Dendrimers and Cyclodextrins

Previous members of this laboratory have also prepared more elaborate structures such as the dendrimer and cyclodextrin²¹⁷ shown in Table 16. These types of materials have not been a point of focus in this investigation.

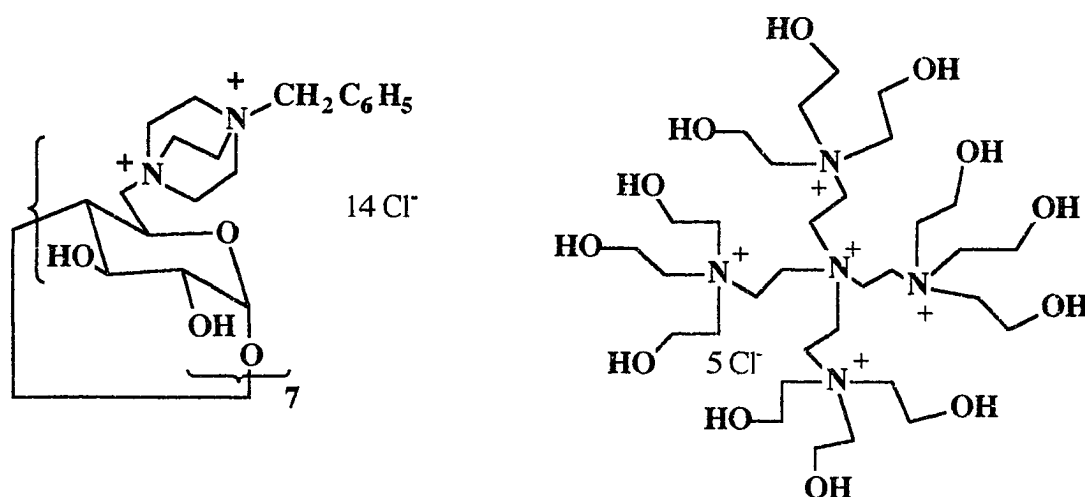


Table 16- Dendrimers and cyclodextrins

This fascinating array of structurally diverse quaternary ammonium salts that were available inspired us to investigate their potential as ionic liquids that would be unlike any previously reported.

Synthesis of ionic liquids

The burgeoning field of ionic liquids involving quaternary ammonium cations and hexafluorophosphate or tetrafluoroborate anions in the late 1990's attracted our attention. Reported species contained only monocationic quaternary ammonium sites incorporated into imidazolium, pyridinium and ammonium type species.^{9, 11, 88, 89} Notable exceptions were the reports of a dicationic imidazolium compound which incorporated two imidazolium units at opposite ends of a long alkyl chain,²¹⁸ and more recently a dicationic compound which contained two imidazolium units separated by diethylether spacers.²¹⁹ Since most of our ammonium halide salts were polycationic, our goal was to synthesize structurally unique polyammonium ionic liquids.

(1) Reaction with Hexafluorophosphoric acid (HPF₆)- The discovery of Liquid Ionic Phosphates (LIPs)

Our first approach towards the conversion of our halide salts into ionic liquids involved a slight modification of the reported¹³ procedure for the preparation of hexafluorophosphate salts as shown in Figure 16.

(PO_4^{3-}) anion. It was found that the two compounds could be separated by washing the water-insoluble solid with water.

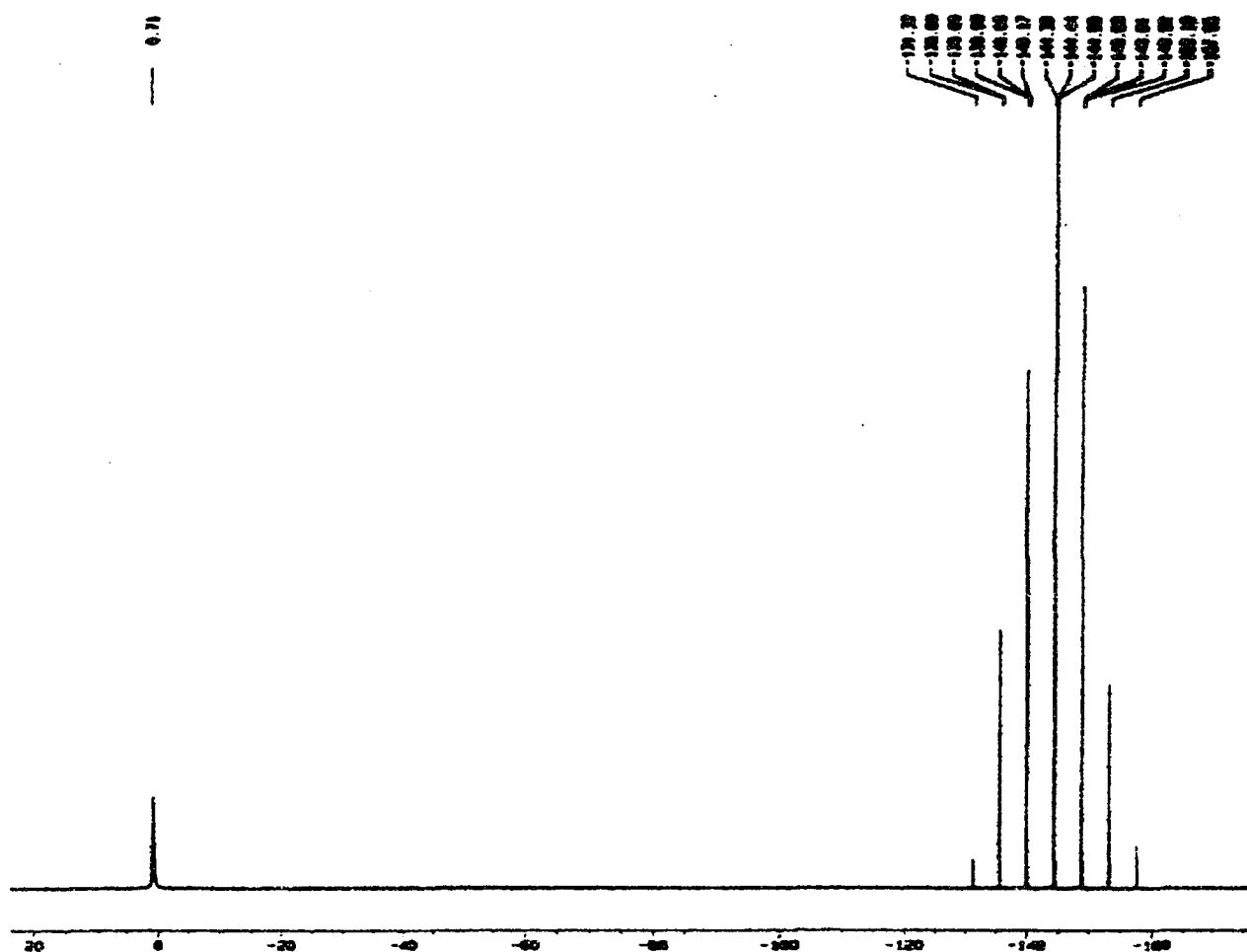


Figure 17: ^{31}P NMR showing both the PO_4^{3-} and PF_6^- anions

Interestingly, the remaining liquid when evaporated under vacuum with heating at 40-50 $^{\circ}\text{C}$ resulted in a viscous colored liquid which exhibited characteristics common to those reported for ionic liquids. ^1H , ^{13}C and ^{31}P NMR of this liquid indicated it to be that of the same cation as obtained with

the solid but bearing the simple phosphate (PO_4^{3-}) anion. The ^{31}P NMR of this liquid is shown in Figure 18.

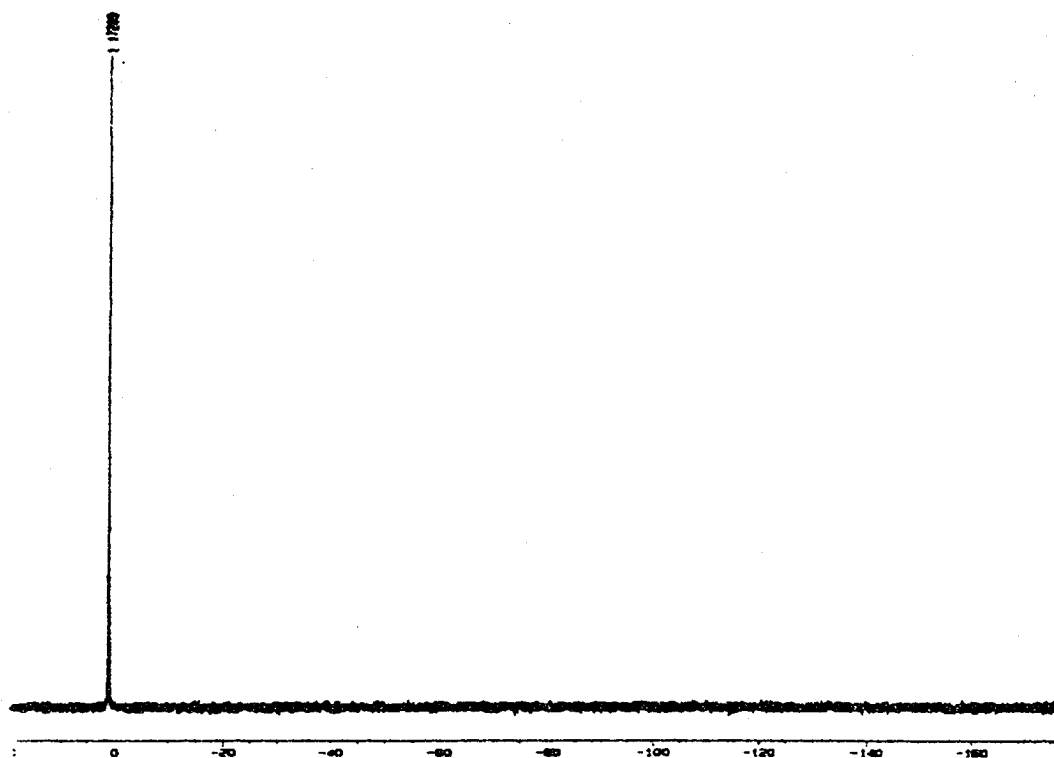


Figure 18: ^{31}P NMR of a newly discovered liquid ionic phosphate

We had discovered a new category of ionic liquids, which we named Liquid Ionic Phosphates (LIPs). Surprisingly, there were no reports in the literature containing ^{31}P NMR data for the PF_6^- containing ionic liquids. The PF_6^- salts of our polycationic species were solids that melted well above room temperature and have not been a point of focus in this investigation.

In order to confirm that the anion of LIPs was indeed PO_4^{3-} and not a protonated form of phosphate, we conducted additional NMR studies. First a coupled ^{31}P spectrum was taken of $[\text{C}_3\text{mim}]$ LIP as shown in figure 19.

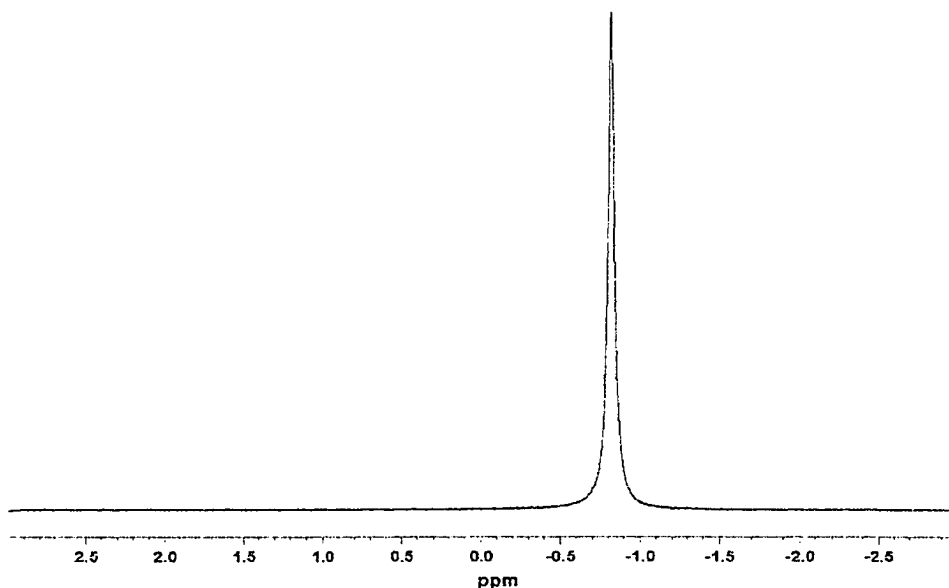


Figure 19: Coupled ^{31}P NMR spectrum of $[\text{Emim}]$ LIP

The lack of splitting in Figure 19 indicates that there are no protons and hence protonated forms of phosphorus present. In addition, Na_3PO_4 was added to $[\text{C}_3\text{mim}]\text{LIP}$ and a ^{31}P NMR spectrum was taken. The argument was that if the anion in LIPs was not PO_4^{3-} then two peaks would be observed due to the presence of another form of phosphate. Interestingly, two peaks were observed in a room temperature spectrum but raising the

temperature to 45°C resulted in one peak. This change was reversible. These NMR's are depicted in Figure 20. This proves that the anion present is indeed PO_4^{3-} but that it is tightly bound and does not exchange easily at room temperature. This is in accord with results reported by Hardacre²⁹⁵ on the order in 1,3-dimethylimidazolium chloride (a liquid) being very similar to that observed in the solid state.

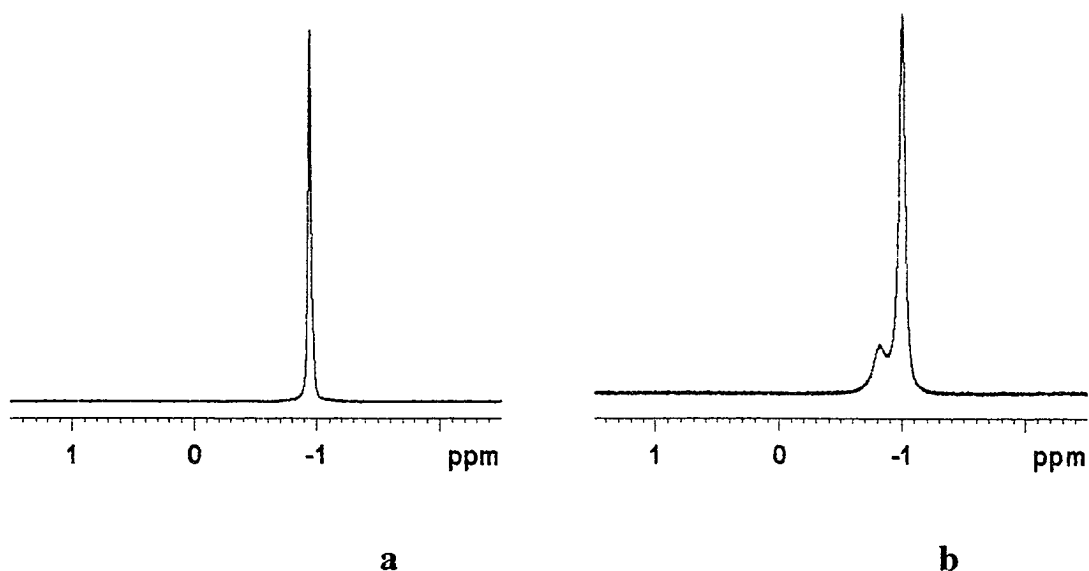


Figure 20: ^{31}P NMR of (a) $[\text{C}_3\text{mim}]\text{LIP}$ at 45°C (b) $[\text{C}_3\text{mim}]\text{LIP}$ at 25°C

We realized that the preparation of LIPs using HPF_6 had particular drawbacks: (1) the PO_4^{3-} species was a minor product and yields of LIPs from this reaction were low (30-40%), (2) HPF_6 is expensive and hazardous

to work with, and (3) the liberation of HF produced during the reaction into the environment was environmentally unfriendly. Hence alternative methods of preparation for LIPs were sought.

2. Anion exchange using an anion exchange resin-Dowex 2x8

Our goal was then to find a less hazardous procedure to prepare LIPs in higher yield with minimum contamination. We decided to try using an anion exchange resin as shown in Figure 21. A column was made with an excess of the insoluble anion exchange resin (Dowex 2x8). The resin was first washed with distilled water and then converted to the phosphate ion form by running a solution of sodium phosphate through it. The parent halide salt was dissolved in water and run onto the column. The column was then washed with copious amounts of water to elute the product. The effluent was then evaporated under vacuum with heating at 40-50 °C to remove water.

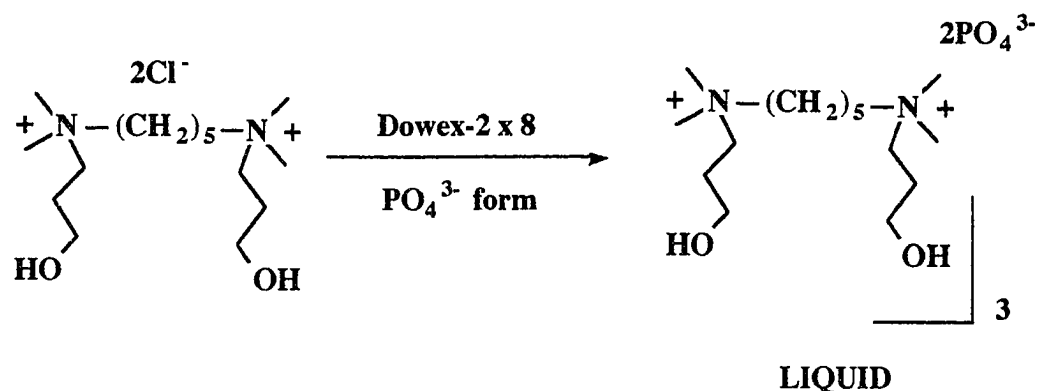


Figure 21: Reaction using Dowex 2x8

This method produced the same liquid ionic phosphate as obtained by reaction with HPF_6 . However the conversion was often incomplete and yields were very low. The conversion was also unsuccessful for some categories of salts and the removal of large quantities of water was time consuming. We decided to pursue alternative methods of preparation for LIPs and discontinued using the resin. (Interestingly, Gordon recently noted that this would be an ideal method for the commercial preparation of ionic liquids with high purity.)⁶

3. Reaction with 85% phosphoric acid (H_3PO_4)

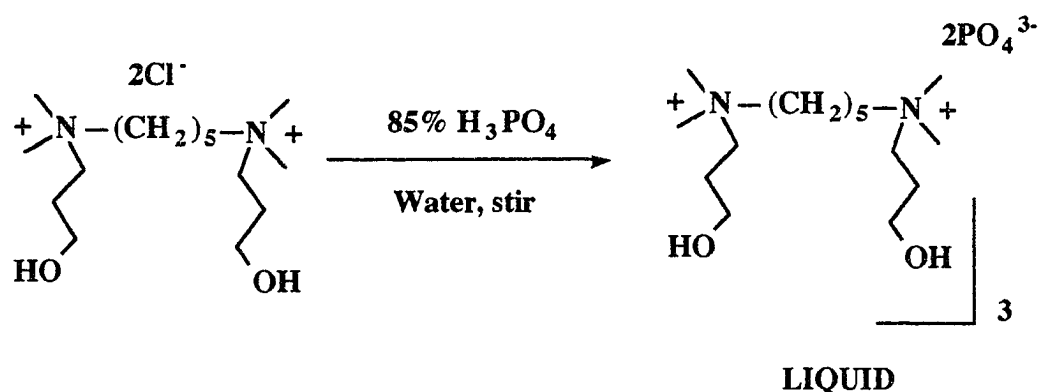


Figure 22: Reaction with 85% phosphoric acid (H_3PO_4)

Our next attempt involved the use of 85% phosphoric acid. The parent halide salt was dissolved in water and stirred with a charge equivalent amount of 85% phosphoric acid overnight as shown in Figure 22. The reaction mixture was then evaporated under vacuum at 40-50 °C to remove all volatile materials (water and the hydrogen halide). LIPs were then placed on a high vacuum pump for 3-7 days. This method generated LIPs in good yield with NMR spectra in accord with their proposed structures. At this point the anhydrous nature of LIPs was qualitatively determined using NMR, and LIPs were presumed to contain 1% or less water. However

subsequent measurements indicated that LIPs contained much more water and anhydrous methods of preparation were sought.

4. Reaction with 98% phosphoric acid and anhydrous methanol or ethanol.

Since the removal of water was a problem, efforts were made to eliminate water from the reaction procedure. 85% phosphoric acid was replaced with 98% phosphoric acid (crystals) and water was replaced with distilled methanol or absolute ethanol as the reaction solvent as shown in Figure 23.

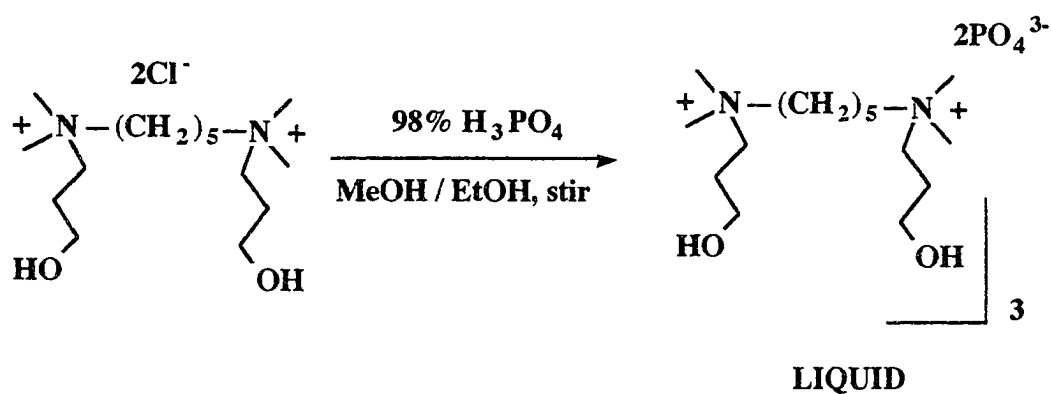


Figure 23: Reaction with 98% phosphoric acid (H_3PO_4)

The methanol or ethanol was first dried with molecular sieves 4A (MS 4A) overnight and the procedure described for reaction with 85% H_3PO_4 repeated. This method was found to work well for the preparation of LIPs with minimum water. However it was later realized that absolute ethanol worked well without the use of molecular sieves. Also if the starting halide salts were insoluble in ethanol, water was used as the reaction solvent. We realized that with a good high vacuum pump water could be removed from LIPs to negligible amounts and that our initial belief that water was tenaciously retained by LIPs was incorrect. LIPs when dried on a high vacuum pump (with a pressure of less than 0.5 torr) for 5-7 days in some instances with heating in an oil bath at 60°C contain negligible amounts of water.

This procedure using either absolute ethanol or water as the solvent with 98% H_3PO_4 , has now been established as the acceptable method for the preparation of LIPs in good yield. This is a greener and cheaper method for the preparation of LIPs which avoids the use of hazardous materials such as

HPF₆. Most of the LIPs analyzed further were synthesized by this latter method and are shown in Table 17.

Table 17: Low melting (< 80°C) Liquid Ionic Phosphates (LIPs)

General structure	LIPs
$ \begin{array}{c} \text{2PO}_4^{3-} \\ \text{(CH}_3\text{)}_2\text{N}^+ - (\text{CH}_2)_n - \text{N}^+(\text{CH}_3)_2 \\ \left \qquad \qquad \qquad \right \\ (\text{CH}_2)_3 \qquad (\text{CH}_2)_3 \\ \left \qquad \qquad \qquad \right \\ \text{OH} \qquad \qquad \text{OH} \\ \left. \qquad \qquad \qquad \right] 3 \\ n = 3,4,5,6,8,9,10 \end{array} $	SH3-LIP SH4-LIP SH5-LIP SH6-LIP SH8-LIP SH9-LIP SH10-LIP
$ \begin{array}{c} \text{2PO}_4^{3-} \\ \text{(CH}_3\text{)}_2\text{N}^+ - (\text{CH}_2)_n - \text{N}^+(\text{CH}_3)_2 \\ \left \qquad \qquad \qquad \right \\ (\text{CH}_2)_2 \qquad (\text{CH}_2)_2 \\ \left \qquad \qquad \qquad \right \\ \text{OCH}_2\text{CH}_3 \quad \text{OCH}_2\text{CH}_3 \\ \left. \qquad \qquad \qquad \right] 3 \\ n = 3,4,6 \end{array} $	SE3-LIP SE4-LIP SE6-LIP
$ \begin{array}{c} \text{PO}_4^{3-} \\ \left[\text{—N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{N}^+ \text{—R} \right] 3 \end{array} $ $\text{R} = \text{CH}_2\text{CH}_3$ $\text{R} = (\text{CH}_2)_2\text{CH}_3$ $\text{R} = (\text{CH}_2)_3\text{CH}_3$ $\text{R} = \text{CH}_2\text{C}_6\text{H}_5$	EMIM-LIP C ₃ MIM-LIP BMIM-LIP BENMIM-LIP
$ \begin{array}{c} \text{PO}_4^{3-} \\ \left[\text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{N}^+ \text{—CH}_2\text{C}_6\text{H}_5 \right] 3 \end{array} $	DSB
$ \begin{array}{c} \text{PO}_4^{3-} \\ \left[\text{C}_6\text{H}_5\text{N}^+ \text{—CH}_2\text{C}_6\text{H}_5 \right] 3 \end{array} $	BenPy
$ \begin{array}{c} \text{PO}_4^{3-} \\ \left[\text{C}_6\text{H}_5\text{N}^+ \text{—CH}_2\text{CH=CH}_2 \right] 3 \end{array} $	AlPy

The seventeen LIPs depicted in Table 17 have been analyzed further and will be discussed later. There are also several categories of LIPs that were either gels or had melting points above 80°C. The viscosity of the gels prevented their analysis by methods that involved placing them into small sample holders (such as fill-type conductivity cells). The cut-off temperature of 80°C for the higher melting salts was chosen because it was very difficult to work above this temperature and temperature-sensitive electrodes used for measuring conductivity could be damaged. These higher melting salts and gels are depicted in Tables 18 and 19.

LIPs based on the imidazolium cation, [Emim], [C₃mim], [Bmim] and [Benmim] were synthesized on a large scale and distributed through Strem Chemicals, Inc.

Table 18: Gel ionic phosphates

Structure	Code
	PSH-LIP
	MSH-LIP
	OSH-LIP

Table 19: High melting LIPs (> 80°C)

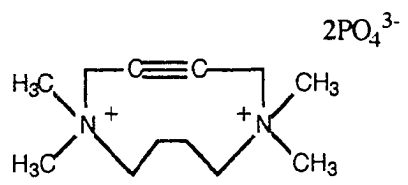
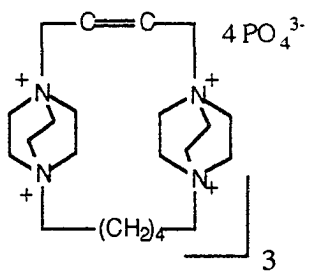
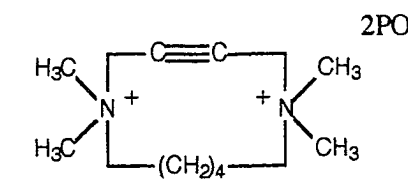
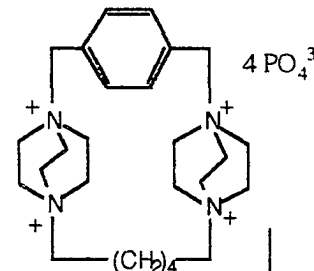
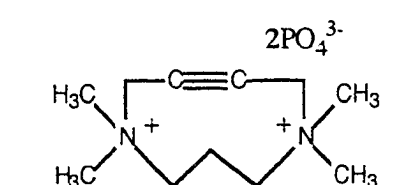
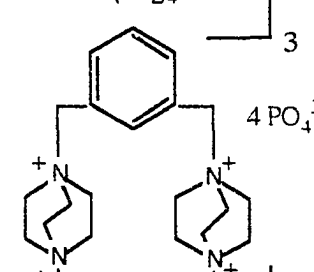
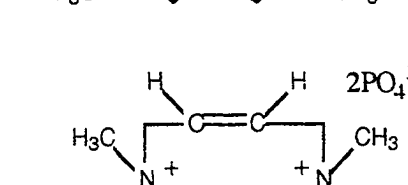
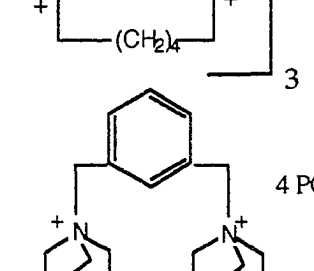
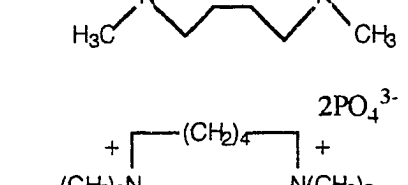
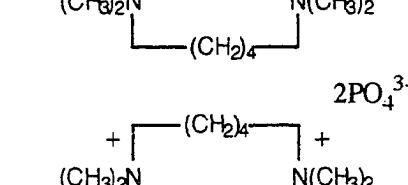
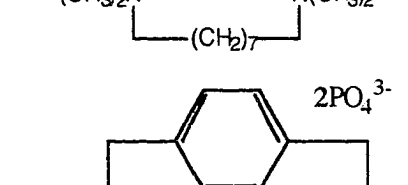
Structure	Code	Structure	Code
	C4T4-LIP		UCD6-LIP
	C6T4-LIP		PCD6-LIP
	C3T4-LIP		MCD6-LIP
	C4U4-LIP		MCD10-LIP
	C66-LIP		
	C69-LIP		
	PCN5-LIP		

Table 19 continued: High melting LIPs (> 80°C)

Structure	Code	Structure	Code
	MDD-LIP		PPDD-LIP
	ODD-LIP		OODD-LIP
	DD3-LIP		DSBBu-LIP
	DD6-LIP		bCD12-LIP
	DD8-LIP		bCD9OH-LIP
	DD10-LIP		
	DDT-LIP		
	DDE2-LIP		

Synthesis of Polyammonium Ionic Liquid Sulfonamides (PILS)

The viscosity and high melting points of the LIPs made it difficult to perform their complete characterization using standard instrumentation. In particular we encountered difficulty when attempting to perform conductivity, density and pulsed radiolysis experiments. Reports on the characteristic of the bis(trifluoromethylsulfonyl)imide (NTf_2^-) anion of lowering the viscosity of room temperature ionic liquids and suggestions by our collaborator James Wishart of Brookhaven National Laboratory (BNL) prompted us to investigate this category of ionic liquid. Recognizing that our structurally unique cations were our stronghold we set out to explore the potential of the array of ammonium strings and rings for forming ionic liquids when combined with the NTf_2^- anion.

Our first attempt towards the preparation of this new category of compounds involved reaction of the polyammonium “string” halide salts with the lithium salt of the NTf_2^- (bistriflamide or sulfonamide) anion in water as shown in Figure 24. This procedure was adopted from Bonhote, *et al.*¹⁶

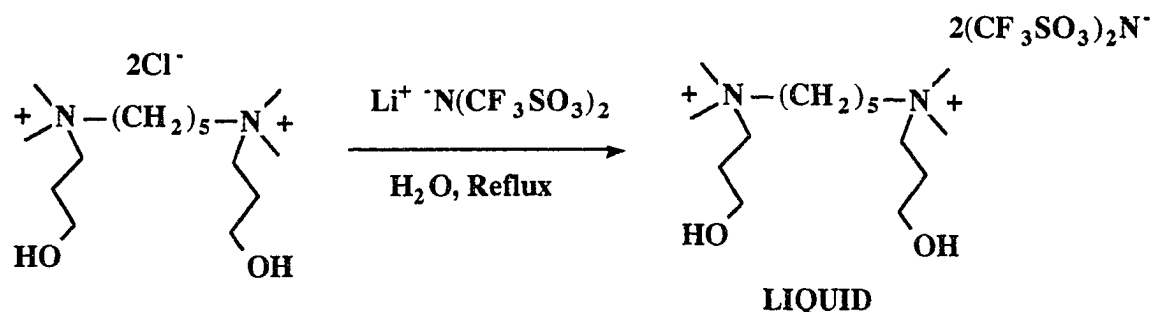


Figure 24: Preparation of sulfonamides

The halide salt was dissolved in water and a charge equivalent amount of the $\text{Li}^+ \text{N}(\text{CF}_3\text{SO}_3)_2$ salt was added. The reaction was stirred for two days under reflux at 60-70°C. The resultant liquid was isolated from the mixture containing two immiscible layers by extraction with ether (3 x 30 mL). The liquid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. ^1H and ^{13}C NMR in $\text{DMSO}-d_6$ indicated the product to be that of the same cation as the halide salt. However an additional quartet in the ^{13}C spectrum centered at 19.45 ppm confirmed the presence of the $(\text{CF}_3\text{SO}_3)_2\text{N}^-$ anion. We named these new ionic liquids,

Polyammonium Ionic Liquid Sulfonamide (PILS). These new species took much less time to dry and could easily be dried to contain less than 0.1% water. The liquids were notably less viscous than their corresponding phosphate analogs.

In cases where the reaction yielded a precipitate instead of two immiscible layers, isolation was performed by filtration followed by rotary evaporation. A series of PILS were prepared as described above and are depicted in Table 20 and Table 21. The lower melting PILS are depicted in Table 20 and the higher melting PILS are shown in Table 21.

Table 20 – Roomtemperature ($\leq 28^{\circ}\text{C}$) PILS

General structure	PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ (\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_n-\text{N}^+(\text{CH}_3)_2 \\ \qquad \qquad \\ (\text{CH}_2)_3 \qquad (\text{CH}_2)_3 \\ \qquad \qquad \\ \text{OH} \qquad \qquad \text{OH} \end{array} $ $n = 3,4,5,6,8,9,10$	SH3-PILS SH4-PILS SH5-PILS SH6-PILS SH8-PILS SH9-PILS SH10-PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ (\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_n-\text{N}^+(\text{CH}_3)_2 \\ \qquad \qquad \\ (\text{CH}_2)_2 \qquad (\text{CH}_2)_2 \\ \qquad \qquad \\ \text{OCH}_2\text{CH}_3 \quad \text{OCH}_2\text{CH}_3 \end{array} $ $n = 3,4,6$	SE3-PILS SE4-PILS SE6-PILS
$ \begin{array}{c} (\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{C}_6\text{H}_5\text{N}^+ \end{array} $	BenPy
$ \begin{array}{c} (\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \qquad \qquad \\ \text{N} \quad \text{C}_6\text{H}_4 \quad \text{N}^+ \\ \qquad \qquad \\ \text{CH}(\text{CH}_3)_2 \end{array} $	DMAPI-PILS
$ \begin{array}{c} (\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \qquad \qquad \\ \text{N} \quad \text{C}_6\text{H}_4 \quad \text{N}^+ \\ \qquad \qquad \\ (\text{CH}_2)_{17}\text{CH}_3 \end{array} $	DMAPI18-PILS

Table 21 – Higher melting PILS

$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ (\text{CH}_3)_2\text{N}^+-(\text{CH}_2)_n-\text{N}^+(\text{CH}_3)_2 \\ \qquad \qquad \\ (\text{CH}_2)_3 \quad (\text{CH}_2)_3 \\ \qquad \qquad \\ \text{CH}_3 \qquad \text{CH}_3 \end{array} $	SA3-PILS SA4-PILS SA6-PILS
$n = 3, 4, 6$	
$ \begin{array}{c} (\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{N}^+ \text{---} \text{N}^+ \text{---} \text{CH}_2\text{CH}=\text{CH}_2 \end{array} $	DSBu-PILS
$ \begin{array}{c} (\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{N}^+ \text{---} \text{N}^+ \text{---} \text{CH}_2\text{C}_6\text{H}_5 \end{array} $	DSB-PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{C}_6\text{H}_5\text{H}_2\text{C} \text{---} \text{N}^+ \text{---} \text{N}^+ \text{---} \text{CH}_2\text{CH}=\text{CH}_2 \end{array} $	DSBBu-PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{N}^+ \text{---} (\text{CH}_2)_6 \text{---} \text{N}^+ \end{array} $	
$ \begin{array}{c} 4(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ \text{N}^+ \text{---} \text{N}^+ \text{---} (\text{CH}_2)_4 \text{---} \text{N}^+ \text{---} \text{N}^+ \end{array} $	MCD6-PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ (\text{CH}_3)_2\text{N}^+ \text{---} (\text{CH}_2)_4 \text{---} \text{N}^+(\text{CH}_3)_2 \end{array} $	C66-PILS
$ \begin{array}{c} 2(\text{CF}_3\text{SO}_3)_2\text{N}^- \\ (\text{CH}_3)_2\text{N}^+ \text{---} (\text{CH}_2)_3 \text{---} \text{OH} \end{array} $	MSH-PILS

The results obtained from the conversion of the different categories of polyammonium halide salts into PILS indicated that the category of strings resulted in the lower melting and less viscous liquids. In particular the strings containing ether and hydroxyl linkages. In general this effect of lowering the viscosity seems to be characteristic of ether containing compounds.

B. Analyses

1. Purity

There seems to be a general consensus that 100% pure ionic liquids should be colorless and halide free.⁶ There is, however, an agreement that the preparation of colorless ionic liquids requires intensive purification procedures which is impractical for preparation on a large scale at a reasonable cost. These procedures often involve washing the haloalkane used for the synthesis with concentrated sulfuric acid, neutralizing with NaHCO_3 and deionized water and then distilling before use. All other starting reagents also need to be distilled before use.⁶ In order to remove the

colored impurities if they are still present after the synthesis, samples are stirred with activated charcoal, filtered and then passed through a column of acidic or neutral alumina. This approach does not necessarily remove all of the color and even after such purification methods the final products are often pale yellow in color. There is some implication that keeping temperatures low during synthesis and isolation reduces the intensity of the color in the final product.

The quantity of the colored impurity is thought to be extremely low and is not detectable by NMR or other analytical methods, including CHN microanalysis. Hence these impurities will not affect many potential applications. The preparation of extremely pure ionic liquids may only be necessary for applications involving photochemical or UV/visible spectroscopic investigations.

The purity of the ionic liquids discussed herein has been mostly determined through the use of NMR. The color of LIPs and PILS range from pale yellow to brown.

2. Halide Content

Analysis of the halide content of PILS was performed qualitatively using a saturated solution of silver nitrate. The absence of halide was confirmed by the absence of a precipitate when a small amount of the “wash solution” of the PILS sample was added to a small amount of the AgNO_3 solution. On the basis of the K_{sp} for AgCl this approach indicates that the concentration of chloride is less than 1.3×10^{-5} mol/kg. Samples were washed with water to remove residual halide.

Analysis of the LIPs for residual halide was more difficult because Ag_3PO_4 forms a precipitate also when AgNO_3 is added. A random number of LIPs were chosen and analyzed by Professor Yan Zheng's group at Queens College, using ion chromatography. They were found to contain less than 120 ppm residual halide. This concentration is sufficiently low for most applications and should not have an effect on the physical properties of these compounds.

3. Water Content

Water content was initially determined using NMR techniques.

However the water contents that will be subsequently discussed were not determined by this method. The lack of a Karl Fischer Titrator earlier in our work on ionic liquids forced us to find alternative methods for the determination of water content. This was achieved using NMR techniques.

(a) Water determination by NMR analysis

Analysis was done using a Bruker 400 MHz NMR. A ^1H NMR spectrum of a standard sample of 0.6 mL deuterium oxide (D_2O) containing 1% of dimethylsilapentanesulfonic acid (DSS) an internal standard was first taken. The sample compound was then dissolved in the same amount of D_2O containing 1% DSS and another ^1H NMR spectrum was taken. Before the samples were run, parameters previously determined for minimum % error were set. The number of scans (NS) was set to 32 and the relaxation delay time (D_1) was set to 10.0s. The peak at 0ppm on both spectra was calibrated to the same value (9.0 for DSS) as shown in Figure 25. The percent water

was then determined quantitatively by subtracting contributions from the standard and OH groups if any were present. The percent water determined by this method was found to be 10-15% greater than that determined using Karl Fischer titration.

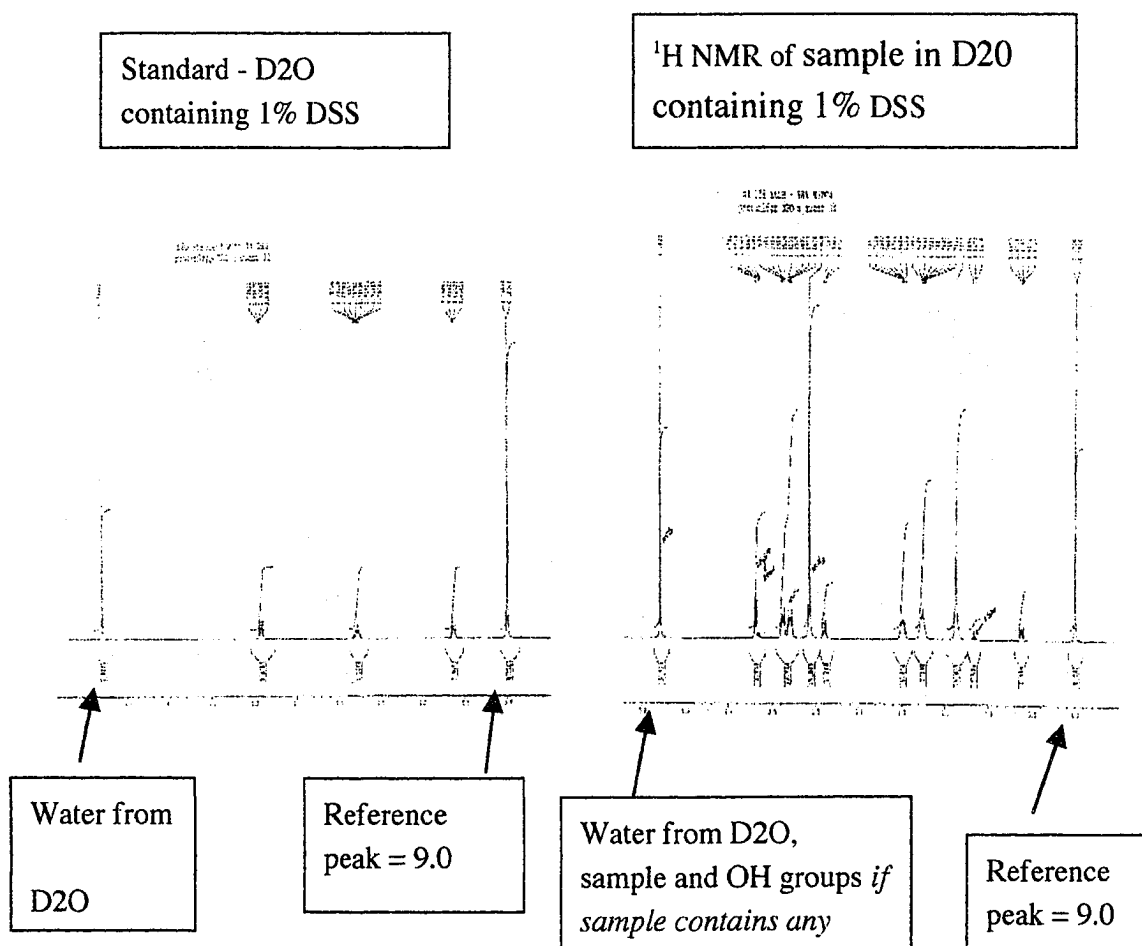


Figure 25: Water determination by NMR analysis

(b) Determination of water by Karl Fischer Titration

Karl Fischer (KF) titration is the standard method for the determination of % water. Fortunately we were able to acquire a KF titrator and all measurements of % water reported were conducted by this method.

Measurements were performed using an EM Science V1B Volumetric Karl Fischer (KF) Titrator. The samples were analyzed by one of two methods depending on their viscosity.

(i) The low viscosity (fluid) samples (~ 0.05 g) were titrated pure without a co-solvent. The percent water was determined in 2-3 minutes. Triplicate measurements were performed.

(ii) The more viscous samples were weighed (~ 0.05 g), dissolved in 1.0 mL of HPLC grade methanol and the entire sample was injected into the sample cell using a 1.0 mL syringe. The % water present per gram methanol was predetermined. The percent water present in the sample was calculated by subtracting the contributions of methanol to the total % water obtained. The percent water was determined in 2-3 minutes. Triplicate measurements were performed.

Once the liquids were dried until they contained less than 1% residual water they were characterized for their physical properties. In actuality they often contained much less than 1% water.

4. Melting Points

Melting points were difficult to determine for all samples. Using the standard melting point apparatus available the melting points were determined for the solid samples. Difficulty was also encountered in determining melting points for samples that were gel-like, waxy or glassy. Hence melting points are only reported for some samples and are shown in Table 22.

In general PILS are less viscous and lower melting than LIPs for corresponding cations. Forsyth *et al.*²²⁰ attributed this to the diffuse negative charge on the sulfonamide anion and the inefficient packing of these large and irregularly shaped ions.

The string category of salts yielded the lower melting ionic liquids for both LIPs and PILS, in particular the ether-containing strings. The

imidazolium and pyridinium compounds are also relatively low melting.

However the dabco- derived compounds are all relatively high melting, particularly the cyclic compounds.

Table 22 – Melting points for LIPs and PILS that are not liquid at 25°C

Sample Code	Melting Point
LIP-SH3	25-27
LIP-SH4	30-33
LIP-SH5	30-33
LIP-SH6	Gel
LIP-SH8	26-28
LIP-SH9	27-28
LIP-SH10	26-28
LIP-SA6	105-110
LIP-C48	33-37
LIP-C66	66-70
LIP-C4U4	94-98
LIP-DSBBu	223-226
LIP-DD3	235-237
LIP-DD6	162-166
LIP-DD10	180-181
LIP-DMAPI	85-90
LIP-DMAP18	65-67
LIP-DMAPB	139-141
LIP-PSH	105-110
LIP-PPDD	295-300
LIP-PCD10	210-214
LIP-MDD	152-156
PILS-SA3	60.05-60.15
PILS-SA4	78-80
PILS-SA6	66.5-68.0
PILS-C66	125-128
PILS-DMAP18	27-28
PILS-DSBBu	113-115
PILS-DSB	43-44
PILS-DD6	115-118

Symmetry and branching in cations tend to increase melting points; this may explain why the cyclic compounds melt at such high temperatures. Lowering of the melting point with increasing the size of the anion has been attributed to weaker coulombic interactions in the crystal lattice. Recent reports by others supports that the NTf₂ (sulfonamide) and dicyanamide [(CN)₂N⁻] anions, lower melting points. Also, pyrrolidinium cations lower melting points.²²⁰ For example *N*-methyl-*N*-propylpyrrolodinium NTf₂ has a melting point of -14 °C compared with the iodide salt of the same cation which melts at 113 °C.²²³ Additional studies on lowering and predicting melting points have been recently reported.^{224, 225} Low melting points have also been attributed to polymorphism, that is the inhibition of crystallization through provision of a large number of similarly stabilized solid state structures.³⁰⁰ This phenomenon was observed by us for the SA3-PILS which melts around 60 °C but supercooled after being heated during analysis.

1. Density

Density measurements were performed using pre-weighed graduated vials to measure out a specific volume of the LIP or PILS. The corresponding mass of the LIP or PILS was then determined and the density calculated. Measurements were done in duplicate and an average density value was calculated. Water was used as a sample to determine the percentage error of this method. The percentage error was calculated to be $\pm 2.52\%$. The densities obtained by this method are shown in Table 23.

The values obtained are in the range of that reported by others⁶ for ionic liquids. The values ranged from 0.9 g/mL to 1.7 g/mL. There is no obvious trend observed for the LIPs and PILS analyzed.

Table 23 – Water, density and conductivity measurements

LIPs	% H₂O	Conductivity[†] (mS/cm)	Density[†] (g/mL)
LIP-SH3	0.0705	0.03356*	1.182
LIP-SH4	0.0929	0.04539*	1.096
LIP-SH5	0.1027	0.03089*	1.218
LIP-SH6	0.1029	0.06659 *	0.9940
LIP-SH8	0.2266	0.01494*	0.9890
LIP-SH9	0.0831	0.05521*	1.194
LIP-SH10	0.1157	0.0433*	1.083
LIP-EMIM	0.1383	0.6913	1.456
LIP-C3MIM	0.6370	0.4850	1.529
LIP-BMIM	0.1400	0.1838	1.263
LIP-BENMIM	0.5000	0.2366	1.393

[†]Refer to page 217 for experimental details

Table 23 continued – Water, density and conductivity measurements

LIPs	% H₂O	Conductivity (mS/cm)	Density (g/mL)
LIP-BENPY	0.1298	0.2269*	1.294
LIP-C66	0.5170	_____	0.852
LIP-ALPY	0.2230	0.7008	1.427
LIP-DSA	0.5777	0.1613	1.242
LIP-SE3	0.6883	0.1612	1.106
LIP-SE6	0.3712	0.5087*	1.096
LIP-OSH	0.0870	_____	1.258
LIP-MSH	0.0794	_____	1.656

Table 23 Continued – Water, density and conductivity measurements

PILS	% H₂O	Conductivity (mS/cm)	Density (g/mL)
PILS-SH3	0.0253	0.01980	2.000
PILS-SH4	0.0213	0.06782	1.473
PILS-SH5	0.4700	0.0431	1.426
PILS-SH6	0.800	0.03157	1.439
PILS-SH8	0.0511	0.07377	1.373
PILS-SH9	0.06290	0.05600	1.345
PILS-SH10	0.00104	0.04831	1.217
PILS-SA3	0.0363	0.4310*	1.395

Table 23 Continued – Water, density and conductivity measurements

PILS	% H₂O	Conductivity (mS/cm)	Density (g/mL)
PILS-SA4	< 0.01	1.230*	1.313
PILS-SA6	< 0.1	1.941*	1.313
PILS-SE3	0.0871	0.1809	1.244
PILS-SE4	0.1642	0.2094	1.277
PILS-SE6	0.1886	1.935	1.361
PILS-BENPY	0.0571	1.226	1.419
PILS-DMAP18	0.1571	0.9824**	1.023
PILS-DMAPI	0.3607	0.4283	1.454

— Sample too viscous to perform measurement

* Measurement performed at 80°C

** Measurement performed at 40 °C

2. Conductivity

Conductivity measurements were performed using a YSI 3200 conductivity meter with a dip-type probe containing platinum black electrodes. The conductivity of samples that were liquid at or below room temperature was measured at 25 °C. Samples that were higher melting were measured at 40 °C and 80 °C depending on their melting points. The results are shown in Table 23.

The values obtained ranged from 0.01 mS/cm for the C66-LIP to 1.9 mS/cm for the SE6-PILS. The conductivity of the string ether-type PILS were the highest and one order of magnitude greater than values obtained for the corresponding LIPs. The SH string-type LIPs exhibited conductivities at 80°C of the same order of magnitude as the corresponding PILS at room temperature. The imidazolium and pyridinium LIPs also exhibited relatively high conductivities.

These conductivity values are similar to those reported for other quaternary ammonium sulfonamides.⁶ Battery electrolytes with conductivities in the range of 1.0-10 mS/cm are considered high.²²⁷

Therefore the ionic liquids reported here in particular the PILS are good potential battery electrolytes.

7. Electrochemical Windows

The electrochemical windows were determined by cyclic voltammetry (CV) using a CH Instruments Electrochemical Analyzer (program: CHI 613A). The reference electrode was Ag / AgCl and the working electrode was Glassy Carbon (3 mm). A Pt wire counter electrode was used. The scan rate was typically 0.1 V/s. These are the typical experimental conditions reported for analyzing ionic liquids by this method.²²⁷⁻²²⁹ The electrochemical windows obtained for LIPs and PILS are shown in Table 24. The electrochemical window values ranged from 2.1 V to 4.4 V. These are considered to be wide windows and similar values have been reported by others.²²⁸ However, many liquids have been reported with electrochemical windows over 4.5V.⁶ The reported range depends on how one defines “window”. Electrochemical windows have been reported for tetraalkylammonium sulfonamide ionic liquids of 4.5-5V.²²⁷ In general the PILS were observed to have wider electrochemical

windows than the LIPs. Windows in this range indicate that these liquids are potentially applicable as battery electrolytes and as media for electrochemical reactions.

Table 24 – Electrochemical windows

Ionic Liquid	Electrochemical Window (V)	Potential Range (V)
LIP-SH3	3.2	1.3 to -1.9
LIP-SH5	3.0	1.0 to -2.0
LIP-SH6	2.5	0.8 to -1.7
LIP-SH8	2.4	0.9 to -1.5
LIP-SH9	3.2	1.3 to -1.9
LIP-SH10	3.2	1.2 to -2.0
LIP-SE3	2.1	0.3 to -1.8
LIP-SE6	2.8	1.0 to -1.8
LIP-EMIM	2.6	1.0 to -1.6
LIP-ALPY	2.8	1.1 to -1.7
LIP-BENPY	3.3	2.3 to -1.0
PILS-SH3	3.3	1.2 to -2.1
PILS-SH4	3.4	0.8 to -2.6
PILS-SH5	2.3	0.5 to -1.8
PILS-SH6	4.4	2.6 to -1.8
PILS-SH8	3.4	1.0 to -2.4
PILS-SH9	3.5	1.0 to -2.5
PILS-SH10	3.4	0.8 to -2.6
PILS-SE3	3.4	0.8 to -2.6
PILS-SE6	3.4	0.8 to -2.6
PILS-BENPY	3.4	2.2 to -1.2

A typical cyclic voltammogram obtained for LIPs and PILS is shown in

Figure 26

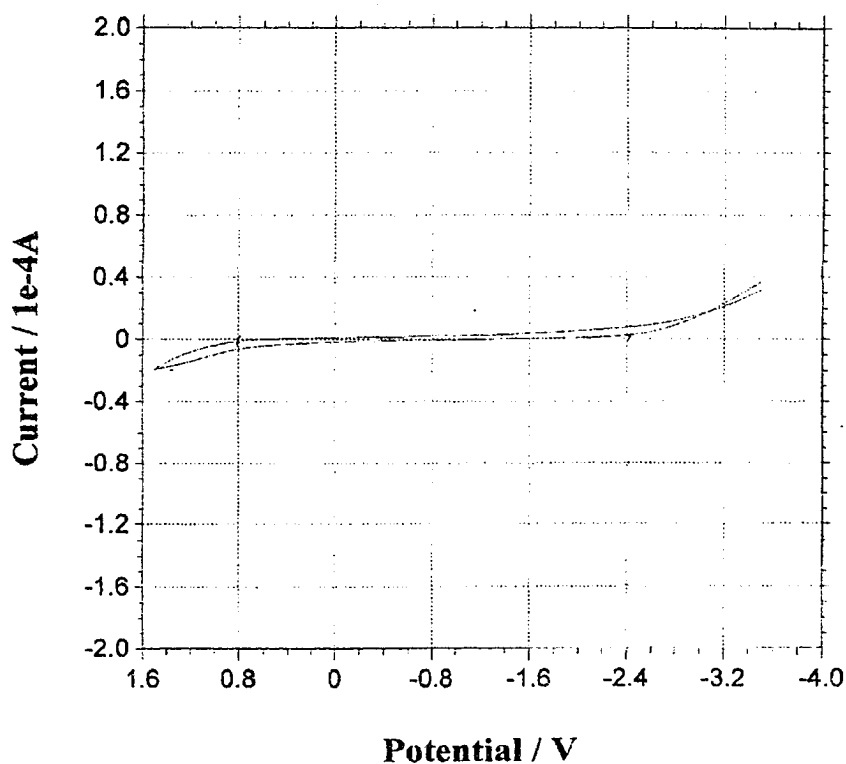


Figure 26 – Cyclic voltammogram of SH4-PILS

8. UV/visible Measurements

UV/visible analysis was performed on 0.1 - 0.4M solutions of LIPs and PILS. LIP samples were made up in water and PILS samples were made up in methanol. Neat samples of ionic liquids without the addition of any sample

were analyzed by smearing a thin film of the liquid in between two quartz plates. The spectrum was identical to that obtained in solution. Measurement in solution was performed because it was simpler. The data obtained is summarized in Table 25.

Table 25 – UV Measurements

Sample	FW	Mass (g)	mmole	conc (M)	Max Wavel.	Abs	E (1/M.cm)
LIP-SH3	935	0.0311	0.0333	0.00333	210	2.16	650
LIP-SH4	977	0.0295	0.0302	0.00302	194	1.57	521
LIP-SH5	1019	0.0364	0.0357	0.00357	194	1.72	482
LIP-SH6	1061	0.0325	0.0306	0.00306	194	1.57	512
LIP-SH8	1146	0.0300	0.0262	0.00262	194	1.59	608
LIP-SH9	1188	0.0298	0.0251	0.00251	210	2.18	869
LIP-SH10	1230	0.0314	0.0255	0.00255	194	1.60	627
LIP-EMIM	428	0.0614	0.143	0.0143	232	2.34	164
LIP-C3MIM	471	0.0550	0.117	0.0117	234	3.15	269
LIP-BMIM	513	0.0674	0.131	0.0131	232	2.37	180
LIP-BENMIM	618	0.0312	0.0505	0.0051	232	2.38	472
LIP-BENPY	606	0.0433	0.0715	0.00715	234	2.54	355
LIP-C66	959	0.0371	0.0387	0.00387	196	1.74	449
LIP-MSH	1121	0.0272	0.0243	0.00243	210	2.20	908
LIP-OSH	1121	0.0424	0.0378	0.00378	232	2.46	649
LIP-PSH	1121	0.0334	0.0298	0.00298	264	2.43	815
LIP-ALPY	455	0.0571	0.125	0.0125	234	2.55	203
LIP-DSA	502	0.0411	0.0819	0.00819	210	2.16	264
LIP-C4T4	779	0.0497	0.0638	0.00638	210	2.55	400
LIP-SE3	1019	0.0311	0.0305	0.00305	194	1.59	522
LIP-SE6	1146	0.0354	0.0309	0.00309	194	1.62	525
LIP-D_CD	5302	0.0330	0.0062	0.00062	262	2.46	3958

Table 25 Continued– UV Measurements

Sample	FW	Mass (g)	mmole	conc (M)	Max Wavel.	Abs	E (1/M.cm)
PILS-SH3	809	0.0396	0.0490	0.00490	200	1.91	390
PILS-SH4	823	0.0397	0.0483	0.00483	200	1.87	388
PILS-SH5	837	0.0435	0.0520	0.00520	200	1.86	358
PILS-SH6	851	0.0746	0.0877	0.00877	202	1.94	222
PILS-SH8	879	0.0428	0.0487	0.00487	200	1.89	389
PILS-SH9	893	0.0466	0.0522	0.00522	210	2.29	439
PILS-SH10	907	0.0314	0.0346	0.00346	194	1.60	462
PILS-SA3	805	0.0397	0.0493	0.00493	200	1.87	378
PILS-SA4	819	0.0384	0.0469	0.00469	200	1.91	406
PILS-SA6	847	0.0666	0.0786	0.00786	200	1.96	249
PILS-SE3	837	0.0464	0.0555	0.00555	210	0.82	148
PILS-SE4	851	0.0444	0.0522	0.00522	214	0.63	120
PILS-SE6	879	0.0474	0.0539	0.00539	206	0.70	129
PILS-BENPY	450	0.0464	0.1030	0.0103	264	2.37	230
PILS-DMAP18	656	0.0300	0.0457	0.00457	304	2.79	610
PILS-DMAPI	445	0.0310	0.0696	0.00696	310	2.80	402

The $\lambda_{\max}$ values obtained were in accord with expected values. Most compounds exhibited only end absorption. Compounds containing aromatic substituents and unsturated linkages exhibited the expected absorption. The availability of data on the maximum absorption is important for applications such as when used as background electrolytes in capillary electrophoresis.²³⁰

9. Solubility and Miscibility properties

The solubility properties of LIPs and PILS were qualitatively investigated in a range of common organic solvents. The results are summarized in Table 26.

The miscibility data indicate that hydrophilic LIPs are miscible with water and also with methanol. In contrast PILS which are hydrophobic are immiscible with water but miscible with acetone, acetonitrile and methanol.

This type of information is particularly important when choosing ionic liquids for use in biphasic systems for extractions and separations.

Table 26 – Solubility / Miscibility data

Sample	Hexane	Toluene	Chloro- form	Methylene Chloride	Ethyl Acetate	Acetone	Aceto- nitrile	Ethanol	Water	Methanol
LIP-SH4	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-SH5	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-SH6	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-SH8	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-SH9	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-SH10	IM	IM	IM	IM	IM	IM	IM	IM	M	M
LIP-BENMIM	IM	IM	SM	SM	IM	IM	M	IM	M	M
LIP-BMIM	IM	IM	SM	SM	IM	IM	M	-	M	M
LIP-C3MIM	IM	IM	M	M	SM	M	M	SM	M	M
LIP-EMIM	IM	IM	IM	M	SM	SM	SM	M	M	M
LIP-OSH	IM	IM	IM	IM	IM	IM	IM	IM	IM	IM
LIP-ALPY	IM	IM	SM	SM	IM	IM	M	IM	M	M
PILS-SH3	IM	IM	IM	IM	M	M	M	SM	IM	M
PILS-SH5	IM	IM	IM	IM	M	M	M	M	IM	M
PILS-SH6	IM	IM	IM	IM	SM	M	M	IM	IM	M
PILS-SH8	IM	IM	IM	M	M	M	M	SM	IM	M
PILS-SH9	IM	IM	IM	IM	M	M	SM	IM	IM	M
PILS-SH10	IM	IM	IM	SM	M	M	M	IM	IM	M
PILS-SA3	IM	IM	SM	M	M	M	M	SM	IM	M
PILS-SA4	IM	SM	IM	M	M	M	M	SM	IM	M
PILS-SA6	IM	IM	IM	SM	M	M	IM	IM	IM	IM
PILS-BENPY	IM	IM	SM	IM	IM	IM	IM	IM	IM	M

M = Miscible

IM = Immiscible

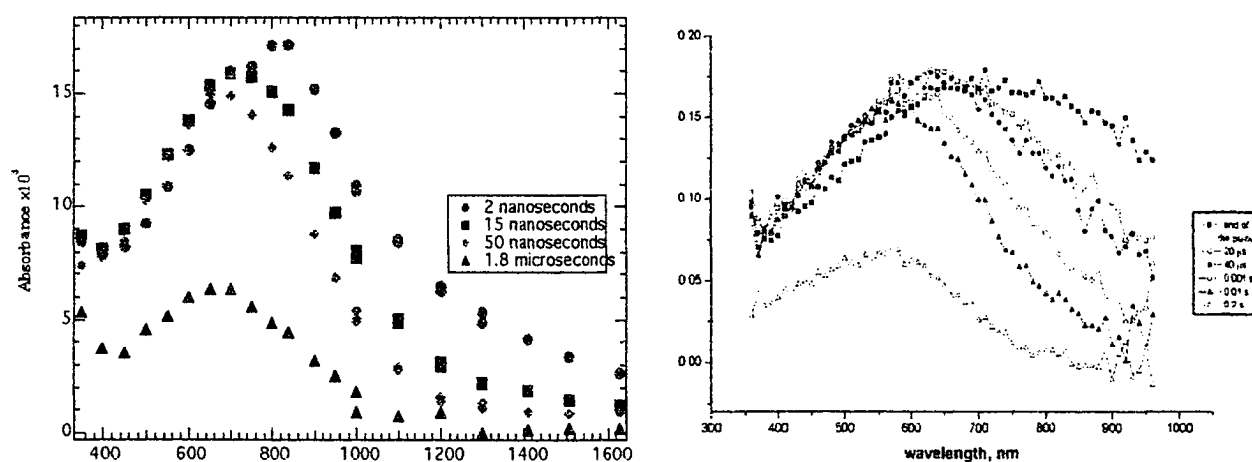
SM = Slightly Miscible

10. Pulse Radiolysis Studies

Pulse radiolysis studies were performed at Brookhaven National Laboratories (BNL) in collaboration with Dr. James Wishart. According to Dr. Wishart,²³¹ “Radiolytic investigations of ionic liquids have two general goals: understanding the chemistry of ionic liquids under ionizing radiation and learning how pulse radiolysis techniques can be used to study general problems of chemical reactivity in ionic liquids.”

Information on the stability of ionic liquids to exposure of high levels of radiation is of importance because it can be used to determine whether ionic liquids are applicable as media for the storage or recycling of radioactive material. A report by Harmon *et al.* of Los Alamos National Laboratory indicates that based on calculations, the stability of plutonium stored in large containers of ionic liquids based on tetrachloroaluminate and tetrafluoroborate is 20 to 100 times greater, respectively, than in water.²³² Others, such as British Nuclear Fuels, Ltd. are investigating the use of electron transfer reactions in ionic liquids to recycle spent nuclear fuels.²³³

A homologous series of PILS was prepared and analyzed by this technique. The goal was to investigate the effect of varying functional groups on pulse radiolysis properties of ionic liquids. Ether- and alcohol- containing strings were analyzed. Figure 27 shows the absorbance spectra generated from pulse radiolysis experiments. The spectrum of the solvated electron at increasing time intervals for SH8-PILS on the left is being compared to that for ethanol on the right.



Ethanol + 6 mol % water, 90 K
Suwalski & Kroh, *RPC 64*, 197

(2002)

Figure 27: Absorbance spectra of the solvated electron in SH8-PILS (left) and in ethanol (right).

It was observed that the spectra of the alcohol containing PILS behaved similarly to of the short chain alcohols as is shown above. Both SH8-PILS and ethanol have absorbance maxima around 700 nm. Results were similar for different alkyl chain length.

The ether PILS investigated yielded interesting results also. Unlike the alcohol-containing PILS they exhibited absorption maxima around 1100 nm. It can be reasoned that the hydroxyl samples with absorption maxima at shorter wavelengths require more energy for the removal of the electron when the sample is irradiated. We believe this is due to the presence of the hydroxyl groups, which orient their positive dipoles in the direction of the electron and trap it. It is expected that there is also some degree of hydrogen bonding in these compounds. Hence these studies give an indication of the degree of order present within the ionic liquids.

11. Self - Diffusion Coefficient Measurements

Diffusion coefficient measurements were performed by Pulsed Gradient Spin Echo (PGSE) NMR techniques. Measurements were performed at Hunter

College, CUNY in collaboration with Dr. Steve Greenbaum and Ms. Sophia

Gustave. These measurements indicate the rate at which the constituent anions and cations of ionic liquids are diffusing. These rates are a good indication of whether species will be potentially useful for fuel cell or battery applications.

The results obtained for the ^1H NMR analysis of PILS are depicted in Table 27.

Table 27 : Diffusion coefficient s from ^1H PGSE NMR experiments

Sample Name	D (cm²/s) x 10⁻⁷
PILS-SH5	0.275
PILS-SH9	0.500
PILS-SE4	0.228
PILS-SH10	0.565
PILS-SH8	0.105
PILS-SH6	0.380
PILS-SH3	0.400
PILS-SH4	0.150
PILS-BENPY	1.725
PILS-DMAP18	0.296
PILS-SA3	0.620
PILS-SE3	0.303

The data in Table 27 indicate that the cations of the PILS are diffusing on the order of 10^{-7} cm²/s. Self diffusion coefficients on the order of 10^{-7} cm²/s are

very high, considering that species in water diffuse on the order of $10^{-5} \text{ cm}^2/\text{s}$.

These values are similar to those obtained by others for ionic liquids⁶ and

suggest that PILS will have potential applications in fuel cells.

Chapter 3

EXPERIMENTAL

A. SYNTHESSES

All chemicals used in syntheses and purification were of commercial reagent quality and were used without further purification.

1. Preparation of halide salts (ionic liquid precursors)

The procedures are outlined for salts that were newly synthesized or resynthesized for this work. The procedures for salts prepared by previous researchers³²³ of this laboratory and used for further work are omitted.

Preparation of 4,4,8,8-tetramethyl-4,8-diazoniaundecan-1,11-diol dibromide

(SH3). 1,3-Dibromopropane (25.0 g, 0.124 mol) was dissolved in acetonitrile (80 mL). To the mixture 3-dimethylamino-1-propanol (25.6 g, 0.248 mol, 2 equivalents) were carefully added. The reaction mixture was left to stir with heat (60-70 °C) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump.

NMR (δ , D₂O) - ¹H: 1.90-2.01, br, 4H; 2.22-3.20, br, 2H; 3.10, s, 12H; 3.33-3.55, m, 8H; 3.60-3.79, m, 4H. ¹³C: 19.07, 27.37, 53.23, 60.45, 62.60, 64.79.

Preparation of 4,4,9,9-tetramethyl-4,9-diazonia-dodecan-1,12-diol dichloride

(SH4). 1,4-Dichlorobutane (30.0 g, 0.236 mol) was dissolved in acetonitrile (150 mL). To the mixture 3-dimethylamino-1-propanol (48.7 g, 0.472 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat (60-70 °C) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump.

NMR (δ , D₂O)- - ¹H: 1.23-1.38, m, 8H; 1.40-1.55, m, 4H; 1.61-1.80, br, 8H; 2.98, s, 12H; 3.17-3.32, br, 8H; 3.45-3.55, t, 4H. ¹³C: 19.97, 22.63, 25.38, 26.03, 31.73, 51.30, 62.31, 63.67, 65.04.

Preparation of 4,4,10,10 tetramethyl-4,10-diazoniatridecane-1,13-diol dichloride

(SH5). 1,5-Dichloropentane (10.5 g, 0.0745 mol) was dissolved in acetonitrile (80 mL). To the mixture 3-dimethylamino-1-propanol (15.4 g, 0.148 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat

(60-70 °C) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump.

NMR (δ , D₂O)- ¹H: 1.39, t, 6H; 1.79, m, 4H; 1.81, m, 4H; 3.02, s, 12H; 3.30, m, 8H; 3.35, t, 4H. ¹³C: 12.37, 20.72, 23.99, 49.73, 57.24, 60.78, 62.74.

Preparation of 4,4,11,11-tetramethyl-4,11-diazonia-tetradecan-1,14-diol

dichloride (SH6). 1,6-dichlorohexane (25.0 g, 0.161 mol) was dissolved in acetonitrile (80 mL). To the mixture 3-dimethylamino-1-propanol (33.3 g, 0.322 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat (60-70 °C) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump. NMR (δ , D₂O)- ¹H: 1.23-1.38, m, 12H; 1.38-1.51, m, 4H; 1.60-1.75, m, 8H; 2.90-3.01, s, 12H; 3.12-3.25, m, 8H; 3.45-3.58, t, 4H. ¹³C: 24.08, 26.83, 27.43, 27.52, 33.20, 34.08, 52.75, 63.95, 65.95, 66.22.

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

dichloride (SH8). 1,8-Dichlorooctane (11.8 g, 0.0643 mol) was dissolved in acetonitrile (80 mL). To the mixture 3-dimethylamino-1-propanol (13.3 g, 0.129 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat (60-70 °C) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump. NMR (δ , D₂O)- ¹H: 1.30, s, 8H; 1.65-1.75, br, 4H; 1.85-1.95, m, 4H; 2.99, s, 12H; 3.15-3.35, d (J = 4Hz), 8H; 3.61, t, 4H. ¹³C: 20.97, 24.49, 25.02, 27.11, 49.77, 58.14, 60.58, 63.35.

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

dichloride (SH9). 1,9-Dichlorononane (16.0 g, 0.0559 mol) was dissolved in acetonitrile (80 mL). To the mixture 3-dimethylamino-1-propanol (11.54 g, 0.112 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat (60-70 °C) under reflux for 72 hours. Precipitation did not occur until after one month. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump. NMR (δ , D₂O)-

^1H : 1.25, br, 14H; 1.68, m, 4H; 1.91, m, 4H; 2.99, s, 12H; 3.23, t ($J = 6$), 4H; 3.31, t ($J = 6$), 4H; 3.61, t ($J = 6$), 4H. ^{13}C : 24.10, 27.20, 27.72, 30.41, 30.58, 52.91, 60.50, 63.71, 66.55.

Preparation of 4,4,15,15-tetramethyl-4,15-diazoniaoctadecan-1,18-diol

dichloride (SH10). 1,10-Dichlorodecane (16.6 g, 0.0787 mol) was dissolved in acetonitrile (100 mL). To the mixture 3-dimethylamino-1-propanol (16.2 g, 0.157 mol, 2 equivalents) was carefully added. The reaction mixture was left to stir with heat (60-70 $^{\circ}\text{C}$) under reflux for 48 hours. The resultant white precipitate was rotary evaporated under reduced pressure and then dried on a high vacuum pump. NMR (δ , D_2O)- ^1H : 1.20, br, 16H; 1.64, m, 4H; 1.87, m, 4H; 2.95, s, 12H; 3.18, t ($J = 4$), 4H; 3.25, t ($J = 4$), 4H; 3.56, t ($J = 6$), 4H. ^{13}C : 22.13, 25.21, 25.75, 28.45, 28.62, 50.92, 58.50, 61.70, 64.54.

Preparation of 3,3,7,7-tetramethyl-3,7-diazoniadiethoxynonane dichloride

(SE3). *N,N,N',N'*-tetramethyl-1,3-Propanediamine (6 g, 0.0460 mol) was dissolved in acetonitrile (50 mL). To the mixture 2-chloroethylethyl ether (10 g,

0.096 mol, 2 equivalents) was added. The reaction was left to stir with heat for 24 hours under reflux. The volatile materials were rotary evaporated under reduced pressure and the resultant white precipitate was left to dry on the high vacuum pump. NMR (δ , D_2O)- ^1H : 1.12, t, 6H; 1.89, m, 2H; 3.12, s, 12H; 3.31-3.53, m, 12H; 3.85, q, 4H. ^{13}C : 14.01, 16.84, 19.30, 43.66, 51.64, 63.43, 66.77.

Preparation of 3,3,8,8-tetramethyl-3,8-diazoniadiethoxydecane dichloride

(SE4). *N,N,N',N'*Tetramethyl-1,3-butanediamine (16.0 g, 0.0693 mol) was dissolved in acetonitrile (75 mL). To the mixture 2-chloroethylethyl ether (15.1 g, 0.138 mol, 2 equivalents) was added. The reaction was left to stir with heat for 24 hours under reflux. The volatiles were rotary evaporated under reduced pressure and the resultant white precipitate was left to dry on the high vacuum pump. NMR (δ , D_2O)- ^1H : 1.11, t, 6H; 1.88, m, 4H; 3.22, s, 12H; 3.48-3.55, m, 12H; 3.83, q, 4H. ^{13}C : 14.04, 24.40, 38.98, 51.35, 56.48, 63.30, 66.85.

Preparation of 3,3,10,10-tetramethyl-3,10-diazoniadiethoxydodecane dichloride

(SE6). *N,N,N',N'*Tetramethyl-1,3-hexanediamine (7.98 g, 0.0460 mol) was dissolved in acetonitrile (50 mL). To the mixture 2-chloroethylethyl ether (10.0 g, 0.138 mol, 2 equivalents) was added. The reaction was left to stir with heat for 24 hours under reflux. The volatile materials were rotary evaporated under reduced pressure and the resultant white precipitate was left to dry on the high vacuum pump. NMR (δ , D_2O)- ^1H : 1.11, t, 6H; 1.35, m, 4H; 1.72, m, 4H; 3.05, s, 12H; 3.31, m, 4H; 3.48, m, 4H; 3.57, q, 4H; 3.85, m, 4H. ^{13}C : 13.41, 21.57, 24.46, 50.68, 62.10, 62.82, 64.43, 66.11.

Preparation of 4,4,8,8-tetramethyl-4,8-diazoniaundecane dichloride (SA3)

*N,N,N',N'*Tetramethyl-1,3-propanediamine (10.6 g, 0.0815 mol) was dissolved in acetonitrile (50 mL). To the mixture 1-bromobutane (22.3 g, 0.163 mol, 2 equivalents) was added. The reaction was left to stir with heat for 24 hours under reflux. The resultant white precipitate was collected by suction filtration, washed with acetonitrile (3 x 30 mL) and placed on the high vacuum pump.

NMR (δ , D_2O)- ^1H : 0.96, t, 6H; 1.34, m, 4H; 1.66, m, 4H; 2.12, m, 2H; 3.04, s, 12H; 3.24-3.35, m, 8H. ^{13}C : 13.36, 16.15, 19.09, 23.65, 50.12, 59.45, 63.39.

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniadodecane dichloride (SA4)

*N,N,N',N'*Tetramethyl-1,4-butanediamine (8.18 g, 0.0567 mol) was dissolved in acetonitrile (50mL). To the mixture 1-bromobutane (15.55 g, 0.114 mol, 2 equivalents) was added. The reaction was left to stir with heat for 72 hours under reflux. The resultant white precipitate was collected by suction filtration, washed with acetonitrile (3 x 30mL) and placed on the high vacuum pump.

NMR (δ , D_2O)- ^1H : 0.95, t, 6H; 1.33, m, 4H; 1.66, m, 8H; 3.01, s, 12H; 3.24-3.34, m, 8H. ^{13}C : 13.38, 18.98, 19.13, 23.63, 50.04, 62.06, 63.01.

Preparation of 4,4,11,11-tetramethyl-4,11-diazoniatetradecane dichloride

(SA6). *N,N,N',N'*Tetramethyl-1,6-hexanediamine (6.33 g, 0.0365 mol) was dissolved in acetonitrile (50 mL). To the mixture 1-bromobutane (10 g, 0.073 mol, 2 equivalents) was added. The reaction was left to stir with heat for 24 hours under reflux. The resultant white precipitate was collected by suction

filtration, washed with acetonitrile (3 x 30mL) and placed on the high vacuum pump. NMR (δ , D_2O)- ^1H : 0.85, t, 6H; 1.32, m, 8H; 1.64, m, 8H; 2.96, s, 12H; 3.18-3.22, m, 8H. ^{13}C : 13.16, 19.22, 22.18, 24.24, 25.53, 50.88, 64.08, 64.25.

Preparation of 1-ethyl-3-methylimidazolium chloride (**Emim**).

1-Methylimidazole (9.90 g, 0.120 mol) was dissolved in ethyl acetate (80 mL). To this mixture was added 1-bromoethane (20 g, 0.181 mol). The reaction was left to stir with heat under reflux for 2 hours. The resultant white precipitate was collected by filtration and dried on the high vacuum pump. NMR (δ , D_2O)- ^1H : 1.31, t, 3H; 3.74, s, 3H; 4.07, q, 2H; 7.34, m, 2H; 8.60, s, 1H. ^{13}C : 14.81, 36.04, 44.86, 121.90, 123.47, 135.53.

Preparation of 1-propyl-3-methylimidazolium chloride (**C₃mim**). (solvent free reaction). To 1-Methylimidazole (20.0 g, 0.244 mol) was added 1-iodopropane (166 g, 0.974 mol, 4 equivalents). The reaction was left to stir with heat (60-70°C) under reflux for 24 hours. The volatiles were rotary evaporated under reduced pressure and the resultant brown liquid was left to dry on the high

vacuum pump. NMR (δ , D_2O)- ^1H : 0.80, t, 3H; 1.78, m, 2H; 3.83, s, 3H; 4.05, t, 2H; 7.36, m, 2H, 8.60, s, 1H. ^{13}C : 10.15, 23.17, 35.95, 51.42, 122.53, 123.81, 139.35.

Preparation of 1-butyl-3-methylimidazolium chloride (**Bmim**). (Solvent free reaction). To 1-Methylimidazole (10.0 g, 0.122 mol) was added 1-bromopropane (66.8 g, 0.487 mol, 4 equivalents). The reaction was left to stir with heat (60-70°C) under reflux for 24 hours. The volatiles were rotary evaporated under reduced pressure and the resultant brown liquid was left to dry on the high vacuum pump. NMR (δ , D_2O)- ^1H : 0.76, t, 3H; 1.17, m, 2H; 1.71, m, 2H; 3.74, s, 3H; 4.04, t, 2H; 7.30, m, 2H; 8.57, s, 1H. ^{13}C : 13.02, 19.11, 31.62, 36.07, 49.65, 122.57, 123.83, 140.18.

Preparation of 1-benzyl-3-methylimidazolium chloride (**Benmim**). (Solvent free reaction). To 1-methylimidazole (20.0 g, 0.244 mol) was added benzyl chloride (30.8 g, 0.244 mol, 1 equivalent). The reaction was left to stir with heat (60-70°C) under reflux for 24 hours. The resultant pale brown liquid was left to

dry on the high vacuum pump. NMR (δ , D_2O)- ^1H : 3.77, s, 3H; 5.18, s, 2H; 7.18-7.31, m, 7H; 8.68, s, 1H. ^{13}C : 35.74, 52.73, 122.15, 123.76, 128.60, 128.76, 129.29, 133.55, 135.89.

Preparation of *N*-benzylpyridinium chloride (BenPy). Pyridine (34.7 g, 0.438 mol) was dissolved in diethyl ether (32.5 g, 1 equivalent). To the mixture was added slowly benzyl chloride (55.6 g, 0.438 mol). A white precipitate was formed after 3 minutes of stirring. The reaction was left to stir for 24 hours. The precipitate was collected by filtration, washed with diethyl ether (3 x 30 mL) and left on the high vacuum pump to dry. NMR (δ , D_2O)- ^1H : 4.71, s, 2H; 7.33, br, 5H; 7.91, m, 2H; 8.39, m, 1H; 8.74, m, 2H. ^{13}C : 67.00, 130.84, 131.55, 132.05, 132.42, 135.18, 146.67, 148.44.

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,6-diazoniamethylbenzene dichloride (OSH). To α,α' -dichloro-*o*-xylene (14.03 g, 0.0801 mol) dissolved in acetonitrile (50 mL) was added slowly 3-dimethylamino-1-propanol (16.5 g, 0.160 mol). The reaction mixture was left to

stir with heat (60°C) under reflux for 48 hours. The resultant white precipitate was isolated by rotary evaporating the mixture under reduced pressure to remove all volatile materials and left on the high vacuum pump to dry. NMR (δ , D₂O)- ¹H: 2.00, m, 4H; 2.95, s, 12H; 3.33, m, 4H; 3.57, m, 4H; 4.52, s, 4H; 7.61, s, 4H. ¹³C: 25.72, 50.51, 58.82, 67.72, 67.82, 130.33, 134.27.

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,5-

diazoniomethyl)benzene dibromide (MSH). To α,α' -dibromo-*m*-xylene (5.0 g, 0.020 mol) dissolved in acetonitrile (75 mL) was added slowly 3-dimethylamino-1-propanol (4.13 g, 0.040 mol). The reaction mixture was left to stir with heat (60°C) under reflux for 48 hours. The resultant white precipitate was isolated by rotary evaporating the mixture under reduced pressure to remove all volatile materials and left on the high vacuum pump to dry. NMR (δ , D₂O)- ¹H: 2.02, m, 4H; 2.96, s, 12H; 3.33, m 4H; 3.59, t, 4H; 4.84, s, 4H; 7.60, m, 4H. ¹³C: 24.36, 49.04, 57.49, 61.42, 66.72, 127.52, 129.47, 134.54, 136.39.

Preparation of 1-(4-butenyl)-1-azonia-4-azabicyclo[2.2.2]octane bromide

(DSBu). To 1,4-diazabicyclo[2.2.2]octane (dabco, 8.30 g, 0.074 mol) dissolved in acetonitrile (75 mL) was added 4-bromo-1-butene (10.0 g, 0.074 mol). The reaction mixture was stirred at room temperature for 48 hours. The resultant white precipitate was collected by suction filtration and dried on the high vacuum pump. NMR (δ , D_2O)- ^1H : 2.54, m, 2H; 3.14, m, 6H; 3.32, m, 2H; 3.39, m, 6H; 5.16, m, 2H; 5.71, m, 1H. ^{13}C : 24.42, 42.70, 50.76, 61.90, 117.20, 130.89.

Preparation of 1-(benzyl)-1-azonia-4-azabicyclo[2.2.2]octane chloride (DSB).

To 1,4-diazabicyclo[2.2.2]octane (dabco, 25.0 g, 0.223 mol) dissolved in acetonitrile (150 mL) was added benzyl chloride (28.21 g, 0.223 mol). The reaction mixture was stirred at room temperature for 48 hours. The resultant precipitate was collected by suction filtration and dried on the high vacuum pump. NMR (δ , D_2O)- ^1H : 2.95-3.12, m, 6H; 3.24-3.28, m, 6H; 4.69, s, 2H; 7.36-7.48, m, 5H. ^{13}C : 46.63, 54.44, 70.86, 127.42, 131.14, 132.33, 132.38.

Preparation of 1-benzyl-4-{6'-butenyl}-1,4-diazoniabicyclo[2.2.2]octane chloride bromide (DSBBu)

1-(Benzyl)-1-azonia-4-azabicyclo[2.2.2]octane chloride (30.6 g, 0.128 mol) was dissolved in acetonitrile. 4-bromo-1-butene was added and the reaction was left to stir with heat under reflux for 48 hours. A white precipitate formed quickly. The precipitate was collected by suction filtration, washed with acetonitrile (3 x 30 mL) and left on the high vacuum pump to dry. NMR (δ , D₂O)- ¹H: 2.53, m, 2H; 3.58, m, 2H; 3.94, br, 12H; 4.73, s, 2H; 5.16, m, 2H; 5.70, m, 1H; 7.52, m, 5H. ¹³C: 26.49, 51.08, 51.74, 64.47, 69.24, 119.80, 125.18, 130.03, 131.61, 131.98, 133.28.

Preparation of 4-(6'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-hexyl)azonia-1-azabicyclo[2.2.2]octane dichloride (DD6). To 1,4-diazabicyclo[2.2.2]octane (dabco, 24.2 g, 0.216 mol) dissolved in acetonitrile (150 mL) was added 1,6-dichlorohexane (13.3 g, 0.108 mol). The mixture was stirred at room temperature for 48 hours. The resultant precipitate was collected by filtration, washed with ethyl acetate and diethyl ether and left on the high vacuum pump

to dry. NMR (δ , D_2O)- ^1H : 1.29, br, 4H; 1.66, br, 4H; 3.00 - 3.16, br, 16H; 3.26, br, 12H. ^{13}C : 27.77, 31.89, 50.85, 58.74, 70.99.

Preparation of 4-(8'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-octyl)azonia-1-azabicyclo[2.2.2]octane dichloride (DD8). To 1,4-diazabicyclo[2.2.2]octane (dabco, 4.92 g, 0.027 mol) dissolved in acetonitrile (50 mL) was added 1,8-dichlorooctane (6.06 g, 0.054 mol). The mixture was stirred at room temperature for 48 hours. The resultant precipitate was collected by filtration, washed with ethyl acetate and diethyl ether and left on the high vacuum pump to dry. NMR (δ , D_2O)- ^1H : 1.24, m, 4H; 1.66, m, 8H; 3.12, m, 12H; 3.25, m, 12H; 3.43, m, 4H. ^{13}C : 23.59, 27.91, 30.44, 46.65, 54.49, 67.04.

Preparation of 4-(10'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-decyl)azonia-1-azabicyclo[2.2.2]octane dichloride (DD10). To 1,4-diazabicyclo[2.2.2]octane (dabco, 21.3 g, 0.189 mol) dissolved in acetonitrile (150 mL) was added 1,10-dichlorodecane (20.0 g, 0.0947 mol). The mixture was stirred at room temperature for 48 hours. The resultant precipitate was collected by filtration,

washed with ethyl acetate and diethyl ether and left on the high vacuum pump to dry. NMR (δ , D_2O)- ^1H : 1.29, br, 4H; 1.66, br, 4H; 3.00 - 3.16, br, 16H; 3.26, br, 12H. ^{13}C : 27.77, 31.89, 50.85, 58.74, 70.99.

Preparation of 4-(4'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'(Z)-2'-

butynyl)azonia-1-azabicyclo[2.2.2]octane dichloride (DDT). To 1,4-

diazabicyclo[2.2.2]octane (dabco, 54.7 g, 0.488 mol) dissolved in acetonitrile (200 mL) was carefully added *cis*-1,4-dichloro-2-butyne (30.0 g, 0.244 mol).

There was rapid formation of a white precipitate. The mixture was stirred at room temperature for 48 hours. The resultant precipitate was isolated by rotary evaporating the mixture under reduced pressure and left on the high vacuum pump to dry. NMR (δ , D_2O)- ^1H : 2.93, m, 12H; 3.21, m, 12H; 4.07, s, 4H. ^{13}C : 44.54, 52.77, 54.13, 80.59.

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniacyclodecene dichloride (C4U4).

cis-1,4-Dichloro-2-butene (10.83 g, 0.0867 mol) was dissolved in acetonitrile (150 mL). *N,N,N',N'*-Tetramethyl-1,4-butanediamine (12.0g, 0.0867mol) was

slowly added with stirring. The reaction mixture was stirred for 24 hours at room temperature. The resultant white precipitate was collected by suction filtration, washed with ethyl acetate and ether (3 x 30 mL), and dried on the high vacuum pump. NMR (δ , D₂O) - ¹H: 1.85, br, 4H; 3.03, s, 12H; 3.42, br, 4H; 4.12, d, 4H; 6.21-6.34, m, 2H. ¹³C: 21.51, 52.89, 62.80, 65.75, 129.12.

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniacyclodecyne dichloride (C4T4).

cis-1,4-Dichloro-2-butyne (4.2 g, 0.0340 mol) was dissolved in acetonitrile (50 mL). *N,N,N',N'*-Tetramethyl-1,4-butanediamine (4.90 g, 0.0340 mol) was slowly added with stirring. The reaction mixture was stirred for 48 hours at room temperature. The resultant white precipitate was collected by suction filtration, washed with ethyl acetate and ether (3 x 30 mL), and dried on the high vacuum pump. (NMR (δ , D₂O) - ¹H: 1.86, br, 4H; 3.16, s, 12H; 3.49, br, 4H; 4.44, s, 4H. ¹³C: 20.87, 51.98, 56.28, 65.41, 81.35.

Preparation of *p*-xylyl-1,4''-(4-{10'-(1'',4''-diazoniabicyclo[2.2.2]octane)-

1'decyl}azonia)-1-azoniabicyclo[2.2.2]octane tetrachloride (PCD10). α,α' -

Dichloro-*p*-xylene (10.83 g, 0.062 mol) was dissolved in acetonitrile (150 mL).

DD10 (27.0 g, 0.062 mol) was slowly added with stirring. The reaction was stirred and heated under reflux for 24 hours. The resultant white precipitate was collected by suction filtration, washed with ethyl acetate and ether (3 x 30 mL), and dried on the high vacuum pump. NMR (δ , D₂O) - ¹H: 1.11-1.36, br, 12H; 1.721, br, 4H; 3.47, br, 4H; 3.75-4.12, br, 24H; 4.82, s, 4H; 7.69, s, 4H. ¹³C: 22.64, 26.39, 29.31, 29.52, 52.12, 52.29, 66.60, 68.94, 129.42, 135.34.

Preparation of *m*-xylyl-1,4''-(4-{10'-(1'',4''-diazoniabicyclo[2.2.2]octane)-

1'decyl}azonia)-1-azoniabicyclo[2.2.2]octane tetrachloride (MCD10). α,α' -

Dichloro-*m*-xylene (5.00 g, 0.0286 mol) was dissolved in acetonitrile (75 mL).

DD10 (12.4 g, 0.0286 mol) was slowly added with stirring. The reaction was stirred and heated under reflux for 24 hours. The resultant white precipitate was collected by suction filtration, washed with ethyl acetate and ether (3 x 30 mL), and dried on the high vacuum pump. NMR (δ , D₂O) - ¹H: 1.18, br, 12H; 1.48,

br, 4H; 3.05, t, 4H; 4.01, br, 24H; 4.86, s, 4H; 7.79, br, 4H. ^{13}C : 21.85, 25.6, 28.49, 28.69, 51.35, 51.53, 65.87, 68.26, 127.02, 131.53, 136.49, 137.50.

Preparation of *m*-xylyl-1,4''-(4-{8'-(1'',4''-diazoniabicyclo[2.2.2]octane)-

1'octyl}azonia)-1-azoniabicyclo[2.2.2]octane tetradichloride (**MCD8**). α,α' -

Dichloro-*m*-xylene (7.13 g, 0.0407 mol) was dissolved in acetonitrile (75 mL).

DD8 (16.54 g, 0.0407 mol) was slowly added with stirring. The reaction

mixture was heated and stirred under reflux for 24 hours. The resultant white

precipitate was collected by suction filtration, washed with ether (3 x 30 mL),

and dried on the high vacuum pump. NMR (δ , D_2O) - ^1H : 1.32, br, 8H; 1.75, br,

4H; 3.51, t, 4H; 3.94, br, 12H; 4.02, br, 12H; 4.78, s, 4H, 7.76, br, 4H. ^{13}C :

20.66, 24.29, 27.13, 50.35, 51.31, 64.40, 67.08, 125.83, 130.34, 135.30, 136.30.

Preparation of *m*-xylylene-1,4''-(4-{6'-(1'',4''-diazoniabicyclo[2.2.2]octane)-

1'hexyl}azonia)-1-azoniabicyclo[2.2.2]octane tetrachloride (**MCD6**). α,α' -

Dichloro-*m*-xylene (5.24 g, 0.030 mol) was dissolved in acetonitrile (75 mL).

DD6 (11.4 g, 0.030 mol) was slowly added with stirring. The reaction mixture

was heated and stirred under reflux for 48 hours. The resultant white precipitate was collected by suction filtration, washed with ether (3 x 30 mL), and dried on the high vacuum pump. NMR (δ , D₂O) - ¹H: 1.39, br, 4H; 1.79, br, 4H; 3.52, t, 4H; 3.94, br, 12H; 4.02, br, 12H; 4.86, s, 4H, 7.78, br, 4H. ¹³C: 21.75, 25.17, 46.10, 51.58, 65.42, 68.24, 127.01, 128.71, 136.47, 137.51.

2. Preparation of Liquid Ionic Phosphates (LIPs)

Preparation of 4,4,8,8-tetramethyl-4,8-diazoniaundecan-1,11-diol phosphate

(SH3-LIP)

To **SH3** dibromide (18.98 g, 0.0465 mol) dissolved in water (100 mL) was added 99% phosphoric acid crystals (3.04 g, 0.0310 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials. The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%.

NMR (δ , D₂O) - ¹H: 1.90-2.01, br, 4H; 2.22-3.20, br, 2H; 3.10, s, 12H; 3.33-

3.55, m, 8H; 3.60-3.79, m, 4H. ^{13}C : 19.07, 27.37, 53.23, 60.45, 62.60, 64.79.

^{31}P : 0.25.

Preparation of 4,4,9,9-tetramethyl-4,9-diazonia-dodecan-1,12-diol phosphate

(SH4-LIP). To **SH4** dichloride (20.0 g, 0.0602 mol) dissolved in water (100 mL) was added 99% phosphoric acid crystals (3.93 g, 0.0401 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials. The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%. .

NMR (δ , D_2O)-- ^1H : 1.23-1.38, m, 8H; 1.40-1.55, m, 4H; 1.61-1.80, br, 8H; 2.98, s, 12H; 3.17-3.32, br, 8H; 3.45-3.55, t, 4H. ^{13}C : 19.97, 22.63, 25.38, 26.03, 31.73, 51.30, 62.31, 63.67, 65.04. ^{31}P : 1.18.

Preparation of 4,4,10,10 tetramethyl-4,10-diazoniatridecane-1,13-diol phosphate

(SH5-LIP). To **SH5** dichloride (10.0 g, 0.0289 mol) dissolved in ethanol (100 mL) was added 85% phosphoric acid crystals (3.22 g, 0.0193 mol, 2/3

equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials.

The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%.

NMR (δ , D₂O)- ¹H: 1.39, t, 6H; 1.79, m, 4H; 1.81, m, 4H; 3.02, s, 12H; 3.30, m, 8H; 3.35, t, 4H. ¹³C: 12.37, 20.72, 23.99, 49.73, 57.24, 60.78, 62.74. ³¹P: 0.16.

Preparation of 4,4,11,11-tetramethyl-4,11-diazonia-tetradecan-1,14-diol

phosphate (SH6-LIP). To **SH6** dichloride (12.6 g, 0.0350 mol) dissolved in ethanol (100 mL) was added 99% phosphoric acid crystals (2.28 g, 0.0233 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials.

The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%.

NMR (δ , D₂O)- ¹H: 1.23-1.38, m, 12H; 1.38-1.51, m, 4H; 1.60-1.75, m, 8H; 2.90-3.01, s, 12H; 3.12-3.25, m, 8H; 3.45-3.58, t, 4H. ¹³C: 24.08, 26.83, 27.43, 27.52, 33.20, 34.08, 52.75, 63.95, 65.95, 66.22. ³¹P: 1.06.

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

phosphate (SH8-LIP). To **SH8** dichloride (10.0 g, 0.0258 mol) dissolved in ethanol (100 mL) was added 99% phosphoric acid crystals (1.69 g, 0.0172 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials. The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 1.30, s, 8H; 1.65-1.75, br, 4H; 1.85-1.95, m, 4H; 2.99, s, 12H; 3.15-3.35, d (J = 4Hz), 8H; 3.61, t, 4H. ¹³C: 20.97, 24.49, 25.02, 27.11, 49.77, 58.14, 60.58, 63.35. ³¹P: 0.05.

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

phosphate (SH9-LIP). To **SH9** dibromide (10.0 g, 0.0203 mol) dissolved in ethanol (100 mL) was added 99% phosphoric acid crystals (1.32 g, 0.0135 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials.

The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C) for 5-7 days, or until the water content was reduced to less than 0.5%. .

NMR (δ , D₂O)- ¹H: 1.25, br, 14H; 1.68, m, 4H; 1.91, m, 4H; 2.99, s, 12H; 3.23, t (J = 6), 4H; 3.31, t (J = 6), 4H; 3.61, t (J = 6), 4H. ¹³C: 24.10, 27.20, 27.72, 30.41, 30.58, 52.91, 60.50. 63.71, 66.55. ³¹P: 1.20.

Preparation of 4,4,15,15-tetramethyl-4,15-diazoniaoctadecan-1,18-diol

phosphate (SH10). To **SH10** dichloride (7.48 g, 0.0180 mol) dissolved in ethanol (100 mL) was added 99% phosphoric acid crystals (1.17 g, 0.0120 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials.

The resultant viscous liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%.

NMR (δ , D₂O)- ¹H: 1.20, br, 16H; 1.64, m, 4H; 1.87, m, 4H; 2.95, s, 12H; 3.18, t (J = 4), 4H; 3.25, t (J = 4), 4H; 3.56, t (J = 6), 4H. ¹³C: 22.13, 25.21, 25.75, 28.45, 28.62, 50.92, 58.50, 61.70, 64.54. ³¹P: 1.19.

Preparation of 3,3,7,7-tetramethyl-3,7-diazoniadiethoxynonane phosphate

(SE3-LIP). To **SE3** dichloride (6.14 g, 0.0177 mol) dissolved in water (50 mL)

was added 99% phosphoric acid crystals (1.16 g, 0.0118 mol, 2/3 equivalents).

The mixture was stirred at room temperature for 24 hours and then rotary

evaporated under reduced pressure to remove all volatile materials. The

resultant viscous liquid was dried on the high vacuum pump with heat (60-

70°C), for 5-7 days or until the water content was reduced to less than 0.5%.

NMR (δ , D₂O)- ¹H: 1.12, t, 6H; 1.89, m, 2H; 3.12, s, 12H; 3.31-3.53, m, 12H;

3.85, q, 4H. ¹³C: 14.01, 16.84, 19.30, 43.66, 51.64, 63.43, 66.77. ³¹P: 0.09.

Preparation of 3,3,10,10-tetramethyl-3,10-diazoniadiethoxydodecane phosphate

(SE6-LIP). To **SE6** dichloride (6.48 g, 0.0166 mol) dissolved in water (75 mL)

was added 99% phosphoric acid crystals (1.09 g, 0.0111 mol, 2/3 equivalents).

The mixture was stirred at room temperature for 24 hours and then rotary

evaporated under reduced pressure to remove all volatile materials. The

resultant viscous liquid was dried on the high vacuum pump with heat (60-

70°C), for 5-7 days or until the water content was reduced to less than 0.5%.

NMR (δ , D_2O)- ^1H : 1.11, t, 6H; 1.35, m, 4H; 1.72, m, 4H; 3.05, s, 12H; 3.31, m, 4H; 3.48, m, 4H; 3.57, q, 4H; 3.85, m, 4H. ^{13}C : 13.41, 21.57, 24.46, 50.68, 62.10, 62.82, 64.43, 66.11. ^{31}P : 0.22.

Preparation of 1-ethyl-3-methylimidazolium phosphate (**Emim-LIP**). To

[**Emim**] bromide (14.4 g, 0.0749 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid crystals (2.45 g, 0.0250 mol, 2/3 equivalents). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure to remove all volatile materials. The resultant viscous pale yellow liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D_2O)- ^1H : 1.31, t, 3H; 3.74, s, 3H; 4.07, q, 2H; 7.34, m, 2H; 8.60, s, 1H. ^{13}C : 14.81, 36.04, 44.86, 121.90, 123.47, 135.53. ^{31}P : 1.07.

Preparation of 1-propyl-3-methylimidazolium phosphate (**C₃mim-LIP**) – a

solvent free reaction. The liquid [**C₃mim**] iodide (63.0 g, 0.250 mol) was heated to 60-70°C and 99% phosphoric acid crystals (8.17 g, 0.083 mol, 1/3

equivalent) was added. The mixture was heated and stirred under reflux for 24 hours. The resultant brown liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 0.80, t, 3H; 1.78, m, 2H; 3.83, s, 3H; 4.05, t, 2H; 7.36, m, 2H, 8.60, s, 1H. ¹³C: 10.15, 23.17, 35.95, 51.42, 122.53, 123.81, 139.35. ³¹P: 1.24.

Preparation of 1-butyl-3-methylimidazolium phosphate (**Bmim-LIP**)- a solvent free reaction. The liquid [**Bmim**] bromide (25.4 g, 0.145 mol) was heated to 60-70°C and 99% phosphoric acid crystals (4.74 g, 0.083 mol, 1/3 equivalent) was added. The mixture was heated and stirred under reflux for 24 hours. The resultant brown liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 0.76, t, 3H; 1.17, m, 2H; 1.71, m, 2H; 3.74, s, 3H; 4.04, t, 2H; 7.30, m, 2H; 8.57, s, 1H. ¹³C: 13.02, 19.11, 31.62, 36.07, 49.65, 122.57, 123.83, 140.18. ³¹P: 0.03.

Preparation of 1-benzyl-3-methylimidazolium phosphate (**Benmim-LIP**).-a

solvent free reaction. The liquid [**Benmim**] chloride (50.6 g, 0.243 mol) was heated to 60-70°C and 99% phosphoric acid crystals (7.93 g, 0.0809 mol, 1/3 equivalent) was added. The mixture was heated and stirred under reflux for 24 hours. The resultant viscous pale brown liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 3.77, s, 3H; 5.18, s, 2H; 7.18-7.31, m, 7H; 8.68, s, 1H. ¹³C: 35.74, 52.73, 122.15, 123.76, 128.60, 128.76, 129.29, 133.55, 135.89. ³¹P: 1.18.

Preparation of *N*-benzylpyridinium phosphate (**BenPy-LIP**). To **BenPy**

chloride (13.03 g, 0.0633 mol) dissolved in water (50 mL) was added 99% phosphoric acid (2.10 g, 0.0211 mol, 1/3 equivalent). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant colorless fluid liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 4.71, s, 2H; 7.33, br, 5H; 7.91,

m, 2H; 8.39, m, 1H; 8.74, m, 2H. ^{13}C : 67.00, 130.84, 131.55, 132.05, 132.42, 135.18, 146.67, 148.44. ^{31}P : 1.10.

Preparation of *N*-allylpyridinium phosphate (**AlPy-LIP**). To *N*-allylpyridinium chloride (**AlPy**) bromide (15.7 g, 0.0786 mol) dissolved in water (50 mL) was added 85% phosphoric acid (3.02 g, 0.0262 mol, 1/3 equivalent). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant brown liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D_2O)- ^1H : 5.14, d ($J = 6$), 2H; 5.44, m, 2H; 6.05, m, 1H; 8.01, m, 2H; 8.48, m, 1H; 8.76, m, 2H. ^{13}C : 62.61, 122.36, 122.50, 129.15, 143.46, 145.17. ^{31}P : 1.02.

Preparation of 1-(4-butenyl)-1-azonia-4-azabicyclo[2.2.2]octane phosphate (**DSBu-LIP**). To **DSBu** chloride (9.08 g, 0.0448 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (1.46 g, 0.0149 mol, 1/3 equivalent). The reaction mixture was stirred at room temperature for 24 hours and then rotary

evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 2.54, m, 2H; 3.14, m, 6H; 3.32, m, 2H; 3.39, m, 6H; 5.16, m, 2H; 5.71, m, 1H. ¹³C: 24.42, 42.70, 50.76, 61.90, 117.20, 130.89. ³¹P: 0.20.

Preparation of 1-(benzyl)-1-azonia-4-azabicyclo[2.2.2]octane phosphate (**DSB-**

LIP). To **DSB** chloride (20.9 g, 0.0876 mol) dissolved in ethanol (100 mL) was added 99% phosphoric acid (2.86 g, 0.0292 mol, 1/3 equivalent). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 2.95-3.12, m, 6H; 3.24-3.28, m, 6H; 4.69, s, 2H; 7.36-7.48, m, 5H. ¹³C: 46.63, 54.44, 70.86, 127.42, 131.14, 132.33, 132.38. ³¹P: 1.10.

Preparation of 1-benzyl-4-{6'-butenyl}-1,4-diazoniabicyclo[2.2.2]octane

phosphate (DSBBu-LIP). To **DSBBu** chloride (4.25 g, 0.0129 mol) dissolved in water (100 mL) was added 99% phosphoric acid (0.843 g, 0.00861 mol, 2/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 2.53, m, 2H; 3.58, m, 2H; 3.94, br, 12H; 4.73, s, 2H; 5.16, m, 2H; 5.70, m, 1H; 7.52, m, 5H. ¹³C: 26.49, 51.08, 51.74, 64.47, 69.24, 119.80, 125.18, 130.03, 131.61, 131.98, 133.28. ³¹P: 1.19.

Preparation of 1-benzyl-4-{6'-methyl}-1,4-diazoniabicyclo[2.2.2]octane

phosphate (MDSB-LIP). **MDSB** chloride iodide 1.00 g, 0.00263 mol) was dissolved in water (6.0 mL) and cooled in an ice bath. Hexafluorophosphoric acid (60%, 1.65 g, 0.0113 mol) was added dropwise with stirring. The reaction was stirred for 24 hours. The mixture was suction filtered and the liquid was collected and rotary evaporated under reduced pressure. The viscous liquid

obtained was dried on the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D₂O)- ¹H: 3.29, s, 3H; 3.95, s, 12H; 4.77, s, 2H; 7.52, br, 5H. ¹³C: 78.26, 80.24, 80.91, 96.38, 132.18, 157.25, 159.16, 160.56. ³¹P: 1.13.

Preparation of 4-dimethylamino-1-octadecylpyridinium phosphate (DMAP18-

LIP). To 4-dimethylamino-1-octadecylpyridinium bromide (DMAP18)

bromide (6.00 g, 0.0132 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (0.431 g, 0.00439 mol, 1/3 equivalent). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 0.83, t, 3H; 1.21, br, 32H; 3.43, s, 6H; 4.17, m, 2H; 7.75, AA'BB', 4H. ¹³C: 13.77, 18.42, 22.06, 25.39, 27.49, 28.13, 28.46, 28.71, 28.87, 28.95, 29.01, 29.05, 30.36, 31.28, 32.23, 33.11, 34.71, 55.95, 56.56, 107.60, 141.92, 155.77. ³¹P: 0.14.

Preparation of 4-dimethylamino-1-benzylpyridinium phosphate (**DMAPB-LIP**).

To 4-dimethylamino-1-benzylpyridinium bromide (**DMAPB**) (8.95 g, 0.0240 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (0.920 g, 0.00799 mol, 1/3 equivalent). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H; 3.03, s, 6H; 5.09, s, 2H; 6.69-6.71, m, 5H, 7.88, AA'BB', 4H. ¹³C: 39.41, 59.69, 107.71, 122.53, 129.90, 132.15, 133.73, 141.23, 156.26. ³¹P: 0.08.

Preparation of 4-dimethylamino-1-isopropylpyridinium phosphate (**DMAPI-LIP**).

To 4-dimethylamino-1-isopropylpyridinium bromide (**DMAPI**) (4.00 g, 0.0137 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (0.5266 g, 0.004568 mol, 1/3 equivalent). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump

with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. ^1H : 1.42, d, 6H; 3.14, s, 6H; 4.59, sept, 1H; 76.62, AA'BB', 4H. ^{13}C : 21.82, 39.31, 59.30, 107.66, 139.76, 155.89. ^{31}P : 0.14.

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniacyclodecyne phosphate (C4T4-

LIP). To C4T4 chloride (3.87 g, 0.0145 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (0.947 g, 0.00967 mol, 2/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D_2O)- ^1H : 1.86 (4 H, br), 3.16 (12 H, s), 3.49 (4 H, br), 4.44 (4 H, s). ^{13}C : 20.87, 51.98, 56.28, 65.41, 81.35. ^{31}P : 1.20

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniacyclodecene phosphate (C4U4-

LIP). To C4U4 (2.00 g, 0.0067 mol) dissolved in ethanol (75 mL) was added 99% phosphoric acid (0.439 g, 0.0045 mol, 2/3 equivalents). The reaction

mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O) - ¹H: 1.85, br, 4H; 3.03, s, 12H; 3.42, br, 4H; 4.12, d, 4H; 6.21-6.34, m, 2H. ¹³C: 21.51, 52.89, 62.80, 65.75, 129.12. ³¹P: 1.18.

Preparation of 4,4,11,11-tetramethyl-4,11-diazoniacyclododecyne phosphate

(C6T4-LIP). To C6T4 dichloride (1.00 g, 0.00337 mol) was dissolved in water (20 mL) and cooled in an ice bath. Hexafluorophosphoric acid (60%, 0.298 g, 0.00337 mol) was added dropwise with stirring. The reaction was stirred for 24 hours. The mixture was suction filtered and the liquid was collected and rotary evaporated under reduced pressure. The viscous liquid obtained was dried on the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D₂O)- ¹H: 1.39 (4 H, br), 1.77 (4 H, br), 3.13 (12 H, s), 4.39 (4 H, s). ¹³C: 21.23, 24.28, 49.61, 53.45, 63.94, 78.87. ³¹P: 2.91

Preparation of 4-(3'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-octyl)azonia-1-

azabicyclo[2.2.2]octane phosphate (DD3-LIP). **DD3** dibromide (4.03 g, 0.0102

mol) was dissolved in water (50 mL) and eluted through a column of Dowex

2x8 anion exchange resin (203.4 g, 0.203 equivalent) in the phosphate form.

The sample was collected in 800 mL water, rotary evaporated under reduced pressure and dried on the high vacuum pump. A solid was obtained after drying.

NMR (δ , D₂O)- ¹H: 2.19, m, 2H; 3.12, m, 12H; 3.22, t, 4H; 3.31, m, 12H. ¹³C:

16.15, 45.06, 53.34, 61.38; ³¹P: 1.27.

Preparation of 4-(6'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-hexyl)azonia-1-

azabicyclo[2.2.2]octane phosphate (DD6-LIP). **DD6** dichloride (1.00 g,

0.00264 mol) was dissolved in water (50 mL) and eluted through a column of

Dowex 2x8 anion exchange resin (52.77 g, 0.053 equivalent) in the phosphate

form. The sample was collected in 200 mL water, rotary evaporated under

reduced pressure and dried on the high vacuum pump. A solid was obtained

after drying. NMR (δ , D₂O)- ¹H: 1.29, br, 4H; 1.66, br, 4H; 3.00 - 3.16, br, 16H;

3.26, br, 12H. ¹³C: 27.77, 31.89, 50.85, 58.74, 70.99. ³¹P:128.

Preparation of 4-(4' {1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-(Z)-2'-

butenyl)azonia-1-azabicyclo[2.2.2]octane phosphate (DDT-LIP). To **DDT**

dichloride (2.14 g, 0.00615 mol) dissolved in water (50 mL) was added 85%

phosphoric acid (0.473 g, 0.00410 mol). The mixture was stirred at room

temperature for 24 hours and then rotary evaporated under reduced pressure at

60-70°C. The resultant liquid was dried on the high vacuum pump with heat

(60-70°C), for 5-7 days or until the water content was reduced to less than

0.5%. A solid was obtained after drying. NMR (δ , D₂O)- ¹H: 2.93, m, 12H;

3.21, m, 12H; 4.07, s, 4H. ¹³C: 44.54, 52.77, 54.13, 80.59. ³¹P: 1.05.

Preparation of 1,2-di-(2'-{1''-azonia}-4''-azabicyclo[2.2.2]octyl)ethoxyethane

phosphate (DDE2-LIP). To **DDE2** dichloride (2.97 g, 0.00724 mol) dissolved

in water (50 mL) was added 85% phosphoric acid (0.557 g, 0.00483 mol, 2/3

equivalent). The mixture was stirred at room temperature for 24 hours and then

rotary evaporated under reduced pressure at 60-70°C. The resultant colorless

viscous liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7

days or until the water content was reduced to less than 0.5%. A colorless solid

was obtained after drying. NMR (δ , D_2O)- ^1H : 3.14, t ($J = 7$), 12H; 3.44, m, 18H; 3.66, s, 4H; 3.93, br, 4H. ^{13}C : 46.22, 55.08, 65.30, 65.37, 71.63. ^{31}P : 1.10.

Preparation of 4,4'-bis(1''-azonia-4''-azatricyclo[2.2.2]octyl)methyl-biphenyl phosphate (PPDD-LIP). To **PPDD** dichloride (4.07 g, 0.00856 mol) was dissolved in water (50 mL) and eluted through a column of Dowex 2x8 anion exchange resin (171.3 g, 0.1713 equivalent) in the phosphate form. The sample was collected in 200 mL water, rotary evaporated under reduced pressure and dried on the high vacuum pump. A solid was obtained after drying. NMR (δ , D_2O)- ^1H : 3.14, m, 12H; 3.44, m, 12H; 4.51, s, 4H; 7.64, AA'BB', 8H. ^{13}C : 44.66, 52.47, 68.25, 124.25, 126.33, 128.16, 134.09. ^{31}P : 1.25.

Preparation of 2,2'-bis(1''-azonia-4''-azabicyclo[2.2.2]octyl)methyl biphenyl phosphate (OODD-LIP). To **Oodd** dibromide (4.66 g, 0.0085 mol) dissolved in water (50 mL) was added 85% phosphoric acid (0.650 g, 0.0057 mol, 2/3 equivalent). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was

dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A white glassy solid was obtained after drying. NMR (δ , DMSO)- ^1H : 3.18-3.43, br, 24H; 4.03, br, 4H; 7.49-7.74, br, 8H. ^{13}C : 45.32, 52.72, 67.08, 124.35, 131.05, 133.75, 134.19, 136.18, 142.96. ^{31}P : 1.28.

Preparation of 1,6-bis-(1'-azonia-4'-azabicyclo[2.2.2]octane)methyl-benzene phosphate (ODD-LIP). ODD dibromide (2.00 g, 0.0074 mol) was dissolved in water (20 mL) and cooled in an ice bath. Hexafluorophosphoric acid (60%, 4.61 g, 0.031 mol) was added dropwise with stirring. The reaction was stirred for 24 hours. The mixture was suction filtered and the liquid was collected and rotary evaporated under reduced pressure. The viscous liquid obtained was dried on the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D_2O)- ^1H : 3.55, br, 12H; 3.81, br, 12H; 3.84, s, 4H; 7.45-7.78, m 4H. ^{13}C : 44.87, 51.23, 64.55, 129.35, 133.19, 137.27, 149.93. ^{31}P : 1.20.

Preparation of 1,5-bis-(1'-azonia-4'-azabicyclo[2.2.2]octane)methyl-benzene

phosphate (MDD-LIP). To **MDD** dichloride (7.05 g, 0.018 mol) dissolved in water (50 mL) was added 85% phosphoric acid (1.36 g, 0.0118 mol, 2/3 equivalent). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A colorless gummy solid was obtained after drying. NMR (δ , D₂O)- ¹H: 3.53, br, 12H; 3.74, br, 12H; 3.94, s, 4H; 7.61-7.68, m 4H. ¹³C: 43.21, 50.11, 67.07, 126.17, 129.55, 135.01, 136.31. ³¹P: 1.18.

Preparation of *p*-2,2,8,8-tetramethyl-2,8-diazoniadecylenylbenzene phosphate

(PCN5-LIP). The **PCN5** dibromide (1.56 g, 0.0038 mol) was dissolved in water (10 mL) and cooled in an ice bath. Hexafluorophosphoric acid (60%, 0.56 g, 0.038 mol) was added dropwise with stirring. The reaction was stirred for 24 hours. The mixture was suction filtered and the liquid was collected and rotary evaporated under reduced pressure. The viscous liquid obtained was dried on

the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D₂O)- ¹H: 1.40, br, 4H; 1.86, br, 4H; 2.96, s, 12H; 3.29, br, 4H; 4.26, s, 4H. 7.61, s, 4H. ¹³C: 21.52, 24.72, 48.99, 64.26, 66.41, 129.11, 133.03. ³¹P: 1.28.

Preparation of 1,1,8,8-tetramethyl-1,8-diazoniacyclotetradecane phosphate

(C66-LIP). To C66 dichloride (20.0 g, 0.061 mol) dissolved in ethanol (150 mL) was added 99% phosphoric acid (3.99 g, 0.0407 mol, 2/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 1.32, br, 4H, 1.68, br, 4H, 2.94, br, 6H, 3.19, br, 4H; ¹³C: 21.91, 25.95, 50.36, 64.09. ³¹P: 1.59.

Preparation of 1,1,8,8-tetramethyl-1,8-diazoniacycloheptadecane phosphate

(C69-LIP). To C69 dibromide (2.95 g, 0.00905 mol) was dissolved in water (14 mL) and cooled in an ice bath. Hexafluorophosphoric acid (60%, 5.68 g,

0.0389 mol, 4.3 equivalents) was added dropwise with stirring. The reaction was stirred for 24 hours. The mixture was suction filtered and the liquid was collected and rotary evaporated under reduced pressure. The viscous liquid obtained was dried on the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D₂O)- ³¹P: 0.39.

Preparation of 1,4-but-2-eneyl-1',4''-(4'8''-(1'',4''-

diazoniabicyclo[2.2.2]octane)-1''-octyl} azonia-1'-azoniabicyclo[2.2.2]octane phosphate (UCD6-LIP). To UCD6 tetrachloride (2.00 g, 0.00400 mol)

dissolved in water (75 mL) was added 99% phosphoric acid (0.523 g, 0.00533 mol, 4/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)-
¹H: 1.41, br, 4H; 1.81, br, 4H; 3.52-3.81, m, 4H; 4.00, br, 24H; 4.49, br, 4H;
 6.44, br, 2H.. ¹³C: 17.60, 21.72, 41.34, 43.22, 53.24, 57.00, 142.61. ³¹P: 1.22.

Preparation of *p*-xylyl-1,4''-(4-{6'-(1'',4''-diazoniabicyclo[2.2.2]octane)-1'-hexyl}azonia)-1-azoniabicyclo[2.2.2]octane (PCD6-LIP). To **PCD6** dichloride dibromide (1.43 g, 0.002 mol) dissolved in water (50 mL) was added 85% phosphoric acid (3.08 g, 0.0267 mol, 4/3 equivalent). The mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A colorless plastic-like solid was obtained after drying. NMR (δ , D₂O)- ¹H: 1.38, br, 4H; 1.78, br, 4H; 3.43, br, 4H; 3.93, br, 12H; 4.03, br, 12H; 4.84, s, 4H; 7.17, s, 4H. ¹³C: 21.80, 25.18, 44.32, 51.36, 51.61, 65.42, 128.65, 134.58. ³¹P: 1.25.

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,6-diazoniamehyl)benzene phosphate (OSH-LIP). To **OSH** dichloride (6.19 g, 0.0162 mol) dissolved in water (75 mL) was added 85% phosphoric acid (1.25 g, 0.0108 mol, 2/3 equivalents). The reaction mixture was stirred at room

temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant viscous yellow liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 2.00, m, 4H; 2.95, s, 12H; 3.33, m, 4H; 3.57, m, 4H; 4.52, s, 4H; 7.61, s, 4H. ¹³C: 25.72, 50.51, 58.82, 67.72, 67.82, 130.33, 134.27. ³¹P: 1.16.

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,5-diazoniameethyl)benzene phosphate (MSH-LIP). To **MSH** dichloride (80.0 g, 0.211 mol) dissolved in water (75 mL) was added 85% phosphoric acid (16.26g, 0.141 mol, 2/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant viscous yellow liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , D₂O)- ¹H: 2.02, m, 4H; 2.96, s, 12H; 3.33, m 4H; 3.59, t, 4H; 4.84, s, 4H; 7.60, m, 4H. ¹³C: 24.36, 49.04, 57.49, 61.42, 66.72, 127.52, 129.47, 134.54, 136.39. ³¹P: 1.17.

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,4-

diazoniomethyl)benzene phosphate (PSH-LIP). To **PSH** dichloride (4.53 g,

0.0119 mol) dissolved in water (75 mL) was added 85% phosphoric acid

(0.777 g, 0.00793 mol, 2/3 equivalents). The reaction mixture was stirred at

room temperature for 24 hours and then rotary evaporated under reduced

pressure at 60-70°C. The resultant viscous yellow liquid was dried on the high

vacuum pump with heat (60-70°C), for 5-7 days or until the water content was

reduced to less than 0.5%. NMR (δ , D₂O) – ¹H: 2.01, m, 4H; 2.95, s, 12H; 3.38,

m, 4H; 3.59, m, 4H; 7.65, s, 4H. ¹³C: 25.76, 50.54, 58.84, 67.75, 67.83, 130.35,

134.31. ³¹P: 1.16.

Preparation of **bCD-D9OH-LIP**. To **bCD-D9OH** heptachloride heptatosylate

(2.40 g, 5.66 x 10⁻⁴ mol) was dissolved in water (15 mL) and cooled in an ice

bath. Hexafluorophosphoric acid (60%, 2.49 g, 0.0170 mol) was added

dropwise with stirring. The reaction was stirred for 24 hours. The mixture was

suction filtered and the liquid was collected and rotary evaporated under

reduced pressure. The viscous liquid obtained was dried on the vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A solid was obtained after drying. NMR (δ , D₂O) – ¹H: 1.34, br, 58H; 1.48, br, 14H; 3.37, t, (J =7.5 Hz), 18H; 3.50-3.81, brm, 140H; 5.02 d, 7H. ¹³C: 21.74, 22.17, 25.18, 25.72, 28.50, 28.56, 31.59, 44.20, 51.33, 60.37, 61.79, 65.30, 72.17, 72.28, 73.64, 103.38. ³¹P: 0.19.

Preparation of bCD-D12-LIP. To bCD-D12 tetradecylchloride (8.88 g, 2.17 x 10⁻³ mol) was dissolved in water (75 mL) was added 85% phosphoric acid (1.17 g, 0.0100 mol, 2/3 equivalents). The reaction mixture was stirred at room temperature for 24 hours and then rotary evaporated under reduced pressure at 60-70°C. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. A white solid was obtained after drying. NMR (δ , D₂O)- ¹H: 0.85, t (J =5), 21H; 1.16, br, 126H; 1.60, br, 14H; 3.25, t (J =9 Hz), 14H; 3.48-3.78, brm, 126H, 4.96 d (J =3.5 Hz), 7H. ¹³C: 13.74, 21.02, 21.72, 22.34, 25.82,

28.64, 28.76, 28.87, 28.92, 29.04, 31.48, 44.20, 51.20, 51.86, 60.02, 65.25, 72.17, 73.61, 81.26, 102.38. ^{31}P : 1.10.

3. Preparation of Polyammonium Ionic Liquid Sulfonamides (PILS)

Preparation of 4,4,8,8-tetramethyl-4,8-diazoniaundecan-1,11-diol

bis(trifluoromethylsulfonyl)imide (SH3-PILS). To **SH3** dibromide (10.0 g, 0.0245 mol) dissolved in water (200 mL) was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (14.07 g, 0.0490 mol, 2 equivalents).

The reaction mixture was stirred at 60-70°C under reflux for 2 days. The

resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with

AgNO_3 for residual halide and washed with water if halide was present. The

resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-

7 days or until the water content was reduced to less than 0.5%. NMR (δ ,

DMSO-d_6) - ^1H : 1.90-2.01, br, 4H; 2.22-3.20, br, 2H; 3.10, s, 12H; 3.33-3.55,

m, 8H; 3.60-3.79, m, 4H. ^{13}C : 19.07, 27.37, 53.23, 60.45, 62.60, 64.79, 19.45,q.

Preparation of 4,4,9,9-tetramethyl-4,9-diazonia-dodecan-1,12-diol

bis(trifluoromethylsulfonyl)imide (SH4-PILS). To **SH4** (10.0 g, 0.0330 mol)

dissolved in water (100 mL) was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (18.9 g, 0.0660 mol, 2 equivalents). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant

liquid was extracted from the two immiscible layers formed, in a separatory

funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for

residual halide and washed with water if halide was present. The resultant liquid

was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until

the water content was reduced to less than 0.5%. NMR (δ , DMSO-*d*₆) - ¹H:

1.23-1.38, m, 8H; 1.40-1.55, m, 4H; 1.61-1.80, br, 8H; 2.98, s, 12H; 3.17-3.32,

br, 8H; 3.45-3.55, t, 4H. ¹³C: 19.97, 22.63, 25.38, 26.03, 31.73, 51.30, 62.31,

63.67, 65.04, 19.45, q

Preparation of 4,4,10,10 tetramethyl-4,10-diazoniatridecane-1,13-diol

bis(trifluoromethylsulfonyl)imide (SH5-PILS). To **SH5** (8.00 g, 0.0329 mol)

dissolved in water (100 mL) was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (18.9 g, 0.0658 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 1.39, t, 6H; 1.79, m, 4H; 1.81, m, 4H; 3.02, s, 12H; 3.30, m, 8H; 3.35, t, 4H. ¹³C: 12.37, 20.72, 23.99, 49.73, 57.24, 60.78, 62.74, 19.45, q

Preparation of 4,4,11,11-tetramethyl-4,11-diazonia-tetradecan-1,14-diol

bis(trifluoromethylsulfonyl)imide (SH6-PILS). To SH6 dichloride (10.0 g, 0.0412 mol) dissolved in water (100 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (23.6 g, 0.0820 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for

residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO- d_6) - ^1H : 1.23-1.38, m, 12H; 1.38-1.51, m, 4H; 1.60-1.75, m, 8H; 2.90-3.01, s, 12H; 3.12-3.25, m, 8H; 3.45-3.58, t, 4H. ^{13}C : 24.08, 26.83, 27.43, 27.52, 33.20, 34.08, 52.75, 63.95, 65.95, 66.22, 19.45, q

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

bis(trifluoromethylsulfonyl)imide (SH8-PILS). To **SH8** dichloride(10.0 g, 0.0389 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (22.3 g, 0.0778 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO- d_6) - ^1H :

1.30, s, 8H; 1.65-1.75, br, 4H; 1.85-1.95, m, 4H; 2.99, s, 12H; 3.15-3.35, d ($J=4\text{Hz}$), 8H; 3.61, t, 4H. ^{13}C : 20.97, 24.49, 25.02, 27.11, 49.77, 58.14, 60.58, 63.35, 19.45, q

Preparation of 4,4,13,13-tetramethyl-4,13-diazoniahexadecan-1,16-diol

bis(trifluoromethylsulfonyl)imide (SH9-PILS). To **SH9** dibromide (10.0 g, 0.0203 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (11.7 g, 0.0406 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d_6) - ^1H : 1.25, br, 14H; 1.68, m, 4H; 1.91, m, 4H; 2.99, s, 12H; 3.23, t ($J=6$), 4H; 3.31, t ($J=6$), 4H; 3.61, t ($J=6$), 4H. ^{13}C : 24.10, 27.20, 27.72, 30.41, 30.58, 52.91, 60.50, 63.71, 66.55, 19.45, q

Preparation of 4,4,15,15-tetramethyl-4,15-diazoniaoctadecan-1,18-diol

bis(trifluoromethylsulfonyl)imide (SH10-PILS). To **SH10** dichloride (20.0 g, 0.0480 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (27.6 g, 0.096 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 1.20, br, 16H; 1.64, m, 4H; 1.87, m, 4H; 2.95, s, 12H; 3.18, t (J = 4), 4H; 3.25, t (J = 4), 4H; 3.56, t (J = 6), 4H. ¹³C: 22.13, 25.21, 25.75, 28.45, 28.62, 50.92, 58.50, 61.70, 64.54, 19.45, q

Preparation of 3,3,7,7-tetramethyl-3,7-diazoniadiethoxynonane

bis(trifluoromethylsulfonyl)imide (SE3-PILS). To **SE3** dichloride (14.2 g,

0.0409 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (23.5 g, 0.0818 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 1.12, t, 6H; 1.89, m, 2H; 3.12, s, 12H; 3.31-3.53, m, 12H; 3.85, q, 4H. ¹³C: 14.01, 16.84, 19.30, 43.66, 51.64, 63.43, 66.77, 19.45, q

Preparation of 3,3,8,8-tetramethyl-3,8-diazoniadiethoxydecane

bis(trifluoromethylsulfonyl)imide (SE4-PILS). To SE4 dichloride (13.0 g, 0.0361 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (20.7 g, 0.0722 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory

funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ, DMSO-d₆) - ¹H:1.11, t, 6H; 1.88, m, 4H; 3.22, s, 12H; 3.48-3.55, m, 12H; 3.83, q, 4H. ¹³C:14.04, 24.40, 38.98, 51.35, 56.48, 63.30, 66.85, 19.45, q

Preparation of 4,4,11,11-tetramethyl-4,11-diazoniatetradecane

bis(trifluoromethylsulfonyl)imide (SE6-PILS). To SE6 dichloride (9.70 g, 0.0248 mol) dissolved in water (200 mL) was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (14.3 g, 0.0497 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ, DMSO-d₆) -

^1H : 1.11, t, 6H; 1.35, m, 4H; 1.72, m, 4H; 3.05, s, 12H; 3.31, m, 4H; 3.48, m, 4H; 3.57, q, 4H; 3.85, m, 4H. ^{13}C : 13.41, 21.57, 24.46, 50.68, 62.10, 62.82, 64.43, 66.11, 19.45, q

Preparation of 4,4,8,8-tetramethyl-4,8-diazoniaundecane

bis(trifluoromethylsulfonyl)imide (SA3-PILS). To **SA3** dibromide (10.0 g, 0.0247 mol) dissolved in water (100 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (14.2 g, 0.0495 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d_6) - ^1H : 0.96, t, 6H; 1.34, m, 4H; 1.66, m, 4H; 2.12, m, 2H; 3.04, s, 12H; 3.24-3.35, m, 8H. ^{13}C : 13.36, 16.15, 19.09, 23.65, 50.12, 59.45, 63.39, 19.45, q

Preparation of 4,4,9,9-tetramethyl-4,9-diazoniadodecane

bis(trifluoromethylsulfonyl)imide (SA4-PILS). To SA4 dibromide (17.5 g, 0.0417 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (24.0 g, 0.0835 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 0.95, t, 6H; 1.33, m, 4H; 1.66, m, 8H; 3.01, s, 12H; 3.24-3.34, m, 8H. ¹³C: 13.38, 18.98, 19.13, 23.63, 50.04, 62.06, 63.01, 19.45, q

Preparation of 4,4,11,11-tetramethyl-4,11-diazoniatetradecane

bis(trifluoromethylsulfonyl)imide (SA6-PILS). To SA6 dibromide (7.25 g, 0.0163 mol) dissolved in water (200 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (9.33 g, 0.0325 mol, 2 equivalents). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 0.85, t, 6H; 1.32, m, 8H; 1.64, m, 8H; 2.96, s, 12H; 3.18-3.22, m, 8H. ¹³C: 13.16, 19.22, 22.18, 24.24, 25.53, 50.88, 64.08, 64.25, 19.45, q

Preparation of *N*-benzylpyridinium bis(trifluoromethylsulfonyl)imide (**BenPy-PILS**). To **BenPy** chloride (30.5 g, 0.150 mol) dissolved in water (250 mL) was added *N*-lithiobis(trifluoromethylsulfonyl)imide (42.6 g, 0.150 mol, 1 equivalent). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant colorless liquid was extracted from the two immiscible layers formed, in a separatory funnel using ether (3 x 30 mL). The liquid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The resultant liquid was dried on the high vacuum pump with heat (60-

70°C), for 5-7 days or until the water content was reduced to less than 0.5%.

NMR (δ , DMSO- d_6) - ^1H : 4.71, s, 2H; 7.33, br, 5H; 7.91, m, 2H; 8.39, m, 1H;

8.74, m, 2H. ^{13}C : 67.00, 130.84, 131.55, 132.05, 132.42, 135.18, 146.67,

148.44, 19.45, q

Preparation of 4-dimethylamino-1-octadecylpyridinium

bis(trifluoromethylsulfonyl)imide (DMAP18-PILS). To DMAP18 bromide

(9.60 g, 0.0211 mol) dissolved in ethanol (200 mL) was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (6.06 g, 0.0211 mol, 1 equivalent). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant

colorless liquid was extracted from the two immiscible layers formed, in a

separatory funnel using ether (3 x 30 mL). The liquid was then tested with

AgNO_3 for residual halide and washed with water if halide was present. The

resultant liquid was dried on the high vacuum pump with heat (60-70°C), for 5-

7 days or until the water content was reduced to less than 0.5%. NMR (δ ,

DMSO- d_6) - ^1H : 0.83, t, 3H; 1.21, br, 32H; 3.43, s, 6H; 4.17, m, 2H; 7.75,

AA'BB', 4H. ^{13}C : 13.77, 18.42, 22.06, 25.39, 27.49, 28.13, 28.46, 28.71, 28.87,

28.95, 29.01, 29.05, 30.36, 31.28, 32.23, 33.11, 34.71, 55.95, 56.56, 107.60, 141.92, 155.77, 19.45, q.

Preparation of 1-benzyl-4-{6'-butenyl}-1,4-diazoniabicyclo[2.2.2]octane

bis(trifluoromethylsulfonyl)imide (DSBBu-PILS). To DSBBu (19.3 g, 0.0510

mol) dissolved in 250 mL water was added added *N*-

lithiobis(trifluoromethylsulfonyl)imide (29.3 g, 0.102 mol, 1 equivalent). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant

white solid was collected by rotary evaporating the mixture under reduced

pressure. The solid was then tested with AgNO₃ for residual halide and washed

with water if halide was present. The resultant solid was dried on the high

vacuum pump for 5-7 days or until the water content was reduced to less than

0.5%. NMR (δ , DMSO-d₆) -¹H: 2.53, m, 2H; 3.58, m, 2H; 3.94, br, 12H; 4.73,

s, 2H; 5.16, m, 2H; 5.70, m, 1H; 7.52, m, 5H. ¹³C: 26.49, 51.08, 51.74, 64.47,

69.24, 119.80, 125.18, 130.03, 131.61, 131.98, 133.28, 19.45, q

Preparation of 1,1,8,8-tetramethyl-1,8-diazoniacyclotetradecane

bis(trifluoromethylsulfonyl)imide (C66-PILS). To 1,1,8,8-tetramethyl-1,8-diazoniacyclotetradecane dichloride (**C66**) (2.00 g, 0.0061 mol) dissolved in 250 mL water was added *N*-lithiobis(trifluoromethylsulfonyl)imide (3.50 g, 0.0122 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant green solid was collected by rotary evaporating the mixture under reduced pressure. The solid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The solid was dried on the high vacuum pump for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-*d*₆) - ¹H D₂O δ , 1.32, br, 4H, 1.68, br, 4H, 2.94, br, 6H, 3.19, br, 4H; ¹³C: 21.91, 25.95, 50.36, 64.09, 19.45, q

Preparation of 1-(4-butenyl)-1-azonia-4-azabicyclo[2.2.2]octane

bis(trifluoromethylsulfonyl)imide (DSBu-PILS). To **DSBu** (3.00 g, 0.0149 mol) dissolved in 100 mL water was added *N*-lithiobis(trifluoromethylsulfonyl)imide (4.30 g, 0.0149 mol, equivalent). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant

solid was collected by rotary evaporating the mixture under reduced pressure.

The solid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The solid was dried on the high vacuum pump for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d_6) - ^1H : 2.54, m, 2H; 3.14, m, 6H; 3.32, m, 2H; 3.39, m, 6H; 5.16, m, 2H; 5.71, m, 1H. ^{13}C : 24.42, 42.70, 50.76, 61.90, 117.20, 130.89, 19.45, q

Preparation of 1-(benzyl)-1-azonia-4-azabicyclo[2.2.2]octane

bis(trifluoromethylsulfonyl)imide (DSB-PILS). To **DSB** (1.50 g, 0.0149 mol) dissolved in 100 mL water was added *N*-lithiobis(trifluoromethylsulfonyl)imide (1.80 g, 0.0149 mol, equivalent). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant solid was collected by rotary evaporating the mixture under reduced pressure. The solid was then tested with AgNO_3 for residual halide and washed with water if halide was present. The solid was dried on the high vacuum pump for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d_6) - ^1H : 2.95-3.12, m, 6H; 3.24-

3.28, m, 6H; 4.69, s, 2H; 7.36-7.48, m, 5H. ^{13}C : 46.63, 54.44, 70.86, 127.42,

131.14, 132.33, 132.38, 19.45, q

Preparation of *m*-xylylene-1,4''-(4-{6'-(1'',4''-diazoniabicyclo[2.2.2]octane)-

1'hexyl}azonia)-1-azoniabicyclo[2.2.2]octane

bis(trifluoromethylsulfonyl)imide (MCD6-PILS). To **MCD6** (3.00 g, 0.0049

mol) dissolved in 100 mL water was added *N*-

lithiobis(trifluoromethylsulfonyl)imide (5.65 g, 0.0196 mol, 4 equivalents). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant

solid was collected by rotary evaporating the mixture under reduced pressure.

The solid was then tested with AgNO_3 for residual halide and washed with

water if halide was present. The solid was dried on the high vacuum pump for

5-7 days or until the water content was reduced to less than 0.5%. NMR (δ ,

DMSO-d_6) - ^1H : 1.39, br, 4H; 1.79, br, 4H; 3.52, t, 4H; 3.94, br, 12H; 4.02, br,

12H; 4.86, s, 4H, 7.78, br, 4H. ^{13}C : 21.75, 25.17, 46.10, 51.58, 65.42, 68.24,

127.01, 128.71, 136.47, 137.51, 19.45, q

Preparation of *N,N,N',N'*-tetramethyl-*N,N'*-bis(3-hydroxypropyl) 1,5-diazoniamethyl)benzene bis(trifluoromethylsulfonyl)imide (**MSH-PILS**). To

MSH (2.00 g, 0.0043 mol) dissolved in 100 mL water was added *N*-lithiobis(trifluoromethylsulfonyl)imide (2.40 g, 0.0086 mol, 2 equivalents). The reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant solid was collected by rotary evaporating the mixture under reduced pressure. The solid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The solid was dried on the high vacuum pump for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-*d*₆) - ¹H: 2.02, m, 4H; 2.96, s, 12H; 3.33, m 4H; 3.59, t, 4H; 4.84, s, 4H; 7.60, m, 4H. ¹³C: 24.36, 49.04, 57.49, 61.42, 66.72, 127.52, 129.47, 134.54, 136.39, 19.45, q

Preparation of 4-(6'-{1''-azonia-4''-azabicyclo[2.2.2]octyl}-1'-hexyl)azonia-1-azabicyclo[2.2.2]octane bis(trifluoromethylsulfonyl)imide (**DD6-PILS**). To

DD6 (5.00 g, 0.013 mol) dissolved in 100 mL water was added *N*-lithiobis(trifluoromethylsulfonyl)imide (7.60 g, 0.026 mol, 2 equivalents). The

reaction mixture was stirred at 60-70°C under reflux for 2 days. The resultant solid was collected by rotary evaporating the mixture under reduced pressure. The solid was then tested with AgNO₃ for residual halide and washed with water if halide was present. The solid was dried on the high vacuum pump for 5-7 days or until the water content was reduced to less than 0.5%. NMR (δ , DMSO-d₆) - ¹H: 1.29, br, 4H; 1.66, br, 4H; 3.00 - 3.16, br, 16H; 3.26, br, 12H. ¹³C: 27.77, 31.89, 50.85, 58.74, 70.99, 19.45, q

B. ANALYSES

1. NMR Analysis

A Bruker 400 MHz Nuclear Magnetic Resonance Spectrometer was used to perform ¹H, ¹³C and ³¹P NMR measurements for structure determination. NMR spectra of LIPs were measured in D₂O and NMR spectra of PILS were measured in DMSO-d₆.

2. Water Content Analysis

(a) Karl Fischer Titration

These measurements were performed using an EM Science V1B Volumetric Karl Fischer (KF) Titrator. Aquastar Comp. 2 KF reagent was used. The sample cell contained 40 mL of anhydrous methanol. The samples were analyzed by one of two methods depending on their viscosity.

(i) The low viscosity (fluid) samples were used pure without a co-solvent. A pipet containing a pure sample was weighed and a small amount (~ 0.05 g) of the sample was placed into the sample cell of the titrator. The pipet was weighed again, the two weights were entered on the titrator and the difference calculated. The percent water was determined in 2-3 minutes. Triplicate measurements were performed.

(ii) The more viscous samples were weighed (~ 0.05 g), dissolved in 1.0 mL of HPLC grade methanol and placed in a 1.0 mL syringe. The syringe and sample were weighed, the entire sample was injected into the KF sample cell, the syringe was re-weighed and the difference in weight was used to calculate the

mass of ionic liquid plus methanol being titrated. The % water present per gram methanol was predetermined. The percent water present in the sample was calculated by subtracting the mass of the ionic liquid dissolved in methanol from the total weight of the methanolic solution injected. The contributions of methanol to the total % water obtained was then calculated and the % water present in the ionic liquid sample was determined.

(b) Water Determination by NMR Analysis

A Bruker 400 MHz NMR was used. A standard sample of 0.6 mL deuterium oxide (D_2O) containing 1% of dimethylsilapentanesulfonic acid (DSS) an internal standard was used. A ^1H NMR spectrum of the standard was taken. The sample compound was dissolved in the same amount of D_2O containing 1% DSS and a ^1H NMR spectrum was taken. Before the samples are run, parameters previously determined for minimum % error are set. The number of scans (NS) was set to 32 and the relaxation delay time (D_1) was set to 10.0s. The peak at 0ppm on both spectra is calibrated to the same value (9.0 for DSS).

The percent water was then determined quantitatively by subtracting contributions from the standard and OH groups if any are present.

3. Melting Points

Melting points were determined using one of two methods depending on their physical state. (i) Samples that were solids at room temperature were placed in capillary tubes and analyzed using a Mel-Temp melting point apparatus.

(ii) Samples that were gel-like, waxy or glassy were analyzed using a Fisher Scientific Eimer and Amend melting point apparatus.

4. Density

Density measurements were performed using pre-weighed graduated vials to measure out a specific volume of the LIP or PILS. The corresponding mass of the LIP or PILS was then determined and the density calculated. Measurements were done in duplicate and an average density value was calculated. Water was used as a sample to determine the percentage error of this method.

$$\text{Density} = \text{Mass/Volume}$$

Equation 2

5. Specific Conductivity

Specific conductivity measurements were performed using a Yellow Springs Instrument (YSI) model 3200 conductivity bridge. Some measurements were done using a fill type probe/cell and others with a dip type probe/cell, both containing platinum black electrodes. The conductance cell was calibrated at 25 °C using an aqueous 0.02M KCl reference solution. A constant temperature bath was used to maintain the temperature of the sample during measurement at 25 °C or 80 °C. All measurements were made at 1kHz. Measurements were done in triplicate and an average conductivity value was calculated.

6. Electrochemical Windows

Measurements were done by cyclic voltammetry (CV) using a CH Instruments Electrochemical Analyzer (program: CHI 613A). A Ag / AgCl reference electrode (RE) was used with a Glassy Carbon (3 mm) working electrode (WE) and a Pt wire counter electrode (CE).

Measurements were conducted on pure samples of LIPs and PILS. The electrodes were inserted into the glass sample vials (cells) such that they were not in contact with each other. Some samples were heated before the experiment so that they were in a liquid state. The scan rate was typically 0.1 V/s.

7. UV/VIS Measurements

Measurements were done using a Hewlett Packard 8452A Diode Array Spectrophotometer. UV samples were made up by dissolving (0.03-0.07) g of each sample in 10mL of water or methanol resulting in (0.1- 0.4) M solutions. The spectra of LIPs were measured in water and that of PILS were measured in methanol. Measurements were performed in 1 cm quartz cuvettes. These measurements were repeated and were found to be reproducible.

8. Solubility / Miscibility

Measurement of solubility / miscibility was conducted qualitatively by dissolving small amounts of each ionic liquid in a variety of common organic solvents.

9. Pulse Radiolysis

Fast transient absorption pulse radiolysis experiments were performed at the Brookhaven National Laboratory (BNL), Laser Electron Accelerator Facility (LEAF), in collaboration with Dr. James Wishart. A homologous series of PILS were synthesized to study the effect of varying functional groups on their pulse radiolysis characteristics. Experimental conditions were similar to those described by Wishart and Neta for monocationic quaternary ammonium sulfonamides.¹¹⁹ The LEAF RF photocathode electron accelerator was used to generate 8.7 MeV electron pulses of less than 150 ps. duration. Radiolytic doses of 6-25 Gy were used. The analyzing light was provided by a pulsed xenon arc lamp. The analyzing wavelength was selected using narrow (10 nm) band pass filters, 40 nm –wide filters were used at wavelengths ≥ 1100 nm. Transient

absorption signals were collected with FND-100 silicon (≤ 1050 nm) or GAP-500 InGaAs (≥ 900 nm) photodiodes, digitized with a Tektronix TDS-680B oscilloscope using custom software running on a DC VAX station 4000 computer. The data were analyzed with Igor Pro software (WaveMetrics, Inc.,) using routines developed at BNL. The temperature varied for the different experiments (depending on the melting points of the samples). The samples were analyzed in septum-capped 1 cm spectrophotometer cuvettes and purged with argon with gentle warming (50°C) for 20 minutes.

10. Self Diffusion Coefficient Measurements

Self diffusion coefficient measurements were performed by ^{31}P , ^{19}F , and ^1H Pulsed Gradient Spin-Echo (PGSE) NMR experiments, which uses the Hahn spin echo pulse sequence ($\pi/2-\tau-\pi$) conducted with a Nalorac Z-Spec gradient probe. The NMR spectra were measured on a Chemagnetics CMX-300 spectrometer used in conjunction with a Japan Magnet Technology $B_0 = 7.1$ T superconducting magnet. For a diffusing species in the presence of a magnetic field the application of square-shaped magnetic field gradient pulses of

magnitude g results in attenuation of the echo amplitude A . This attenuation may be represented by:

$$A(g) = \exp[-\gamma^2 D \delta^2 (\Delta - (\delta/3))] \quad \text{Equation 3}$$

where D is the self-diffusion coefficient for a range of gradient strengths from 0.2 to 1.2 T/m, γ is the nuclear gyromagnetic ratio, Δ is the time interval between two gradient pulses and δ is the duration of the single gradient pulse. For the ionic liquids investigated, the experimental parameters Δ and δ ranged from 7 to 10 and 15 to 50, respectively for ^{19}F . Uncertainties in self-diffusion measurements are ~3-5%. Spectra and self-diffusion coefficients were obtained at 30°C with a pulse width of 10 μs . Spectral information was obtained by transforming the resulting free induction decay (FID) of a single $\pi/2$ pulse sequence. All reported self-diffusion coefficients are an average of the various components observed in the corresponding spectrum. These measurements were done in collaboration with Ms. Sophia Gustave and Dr. Steve Greenbaum at Hunter College, CUNY.

Conclusions

The results presented here indicate the successful preparation and characterization of two new categories of ionic liquids, a hydrophilic category and a hydrophobic category. The characteristics determined are similar to those reported for other categories of ionic liquids. It is clear that the PILS in particular will have potential applications in batteries and possibly in fuel cells. Both LIPs and PILS are promising for media applications.

The recent recognition and admission by the ionic liquid community about the hazards of halide-containing ionic liquids provided a new incentive for the preparation of halide-free ionic liquids. The PF_6^- containing ionic liquids liberate hazardous HF into the environment when they are hydrolyzed and have been described as model systems. Even though the literature overflows with media applications of these compounds, they will never find commercial applications as they go against the goals of *Green Chemistry*.

While the sulfonamide anions contain fluorine, they do not release HF into the environment. However, even though liquids of this type have attractive properties such as lower melting points and viscosities, they suffer from the disadvantage of being very expensive to synthesize. This could prevent their utilization commercially.

In light of these findings, LIPs (phosphates) are particularly attractive. They are halide-free and are very cheap and easy to synthesize and hence they would be ideal for large-scale production. They are also not hazardous to the environment and hence are truly *green* solvents. Our achievement in this work of finding a cheaper and less hazardous way to synthesize ionic liquids is a necessity for all categories of ionic liquids if they are to succeed commercially and become practical replacements for the solvents we currently use.

Future Work

There is much to be done in this exciting and challenging field of research. As Wilkes said, “the applications will be limited only by our imagination.”⁶ The first approach should be to modify the synthetic procedures so that they are also in the category of *Green Chemistry*. Recent work focused on the microwave²³⁴ and halide free^{18,338} preparation of ionic liquids is a step in this direction. The preparation of ionic liquids that incorporate biodegradable compounds and chiral ionic liquids derived from natural amino acids have also been reported,^{235,236} and is in keeping with this argument. Cheap synthetic procedure should also be a priority. Now that a lot of the ground breaking work has been done, it will be easier to carefully select anions and cations that will give the optimum characteristics desired.

Focusing specifically on future studies associated with LIPs and PILS:

1. Synthesizing unsymmetrical cations and combining them with sulfonamide and dicyanamide anions to yield low melting and less viscous liquids. Also using the pyrrolidinium cations with the phosphate anions for the aforementioned result.

2. The preparation of cyclic structures containing ether linkages would be interesting to investigate for their extraction properties of metal ions.

This was recently described for imidazolium linked by ethers for the extraction of mercury (11).¹¹⁹
3. The preparation and properties of phosphonium ionic liquids would also be a good study. Liquids of these types are now available commercially.²³⁷
4. In addition the determination of melting points by differential scanning calorimetry (DSC) studies are necessary.
5. The measurement of viscosity should also be performed.
6. The practical application of LIPs and PILS as alternative media should also be investigated. LIPs with ether linkages are particularly attractive for investigating Diels-Alder reactions.

There will not be a lack of interesting research to conduct in this area for a long time to come.

References

1. DeSimone, J. M. *Science*, (2002) 297, 798-803
2. Wu, B.; Reddy, R. G.; Rogers, R. D. *Proceedings of SolarForum 2001, Solar Energy: The power to choose*, (2001) April 21-25
3. Morrow, T. I.; Maginn, E. J. *J. Phys. Chem. B.*, (2002) 106 (49), 12807-12813
4. Ye, C.; Liu, W.; Chen, Y.; Yu, L. *Chem. Commun.*, (2001) 2244-2245
5. Wasserscheid P.; Keim, W. *Angew.Chem. Int. Ed.* (2000) 39, 3772-3789
6. Wasserscheid, P., Welton, T., (Eds.), *Ionic Liquids in Synthesis*, Wiley-VCH, Weinheim, Germany (2003)
7. Erbedinger, M.; Mesiano, A.J.; Russell, A.J. *Biotechnol. Prog.* (2000) 16, 1129-1131
8. Wilkes, J. S. *Green Chemistry*, (2004) 4, 73-80

9. Fannin, A.A.; Floreani, D. A.; King, L. A.; Landers, J. S.; Piersma, B. J.; Stech, D. J.; Vaughn, R. L.; Wilkes, J. S.; Williams, J. L. *J. Phys. Chem.*, (1984) 88, 2614-2621
10. Karpinski, Z.J.; Osteryoung, R.A.; *Inorg. Chem.*, (1984) 23, 1491-1494
11. Wilkes, J.S.; Levisky, J.A.; Wilson, R.A. *Inorg. Chem.* (1982) 21, 1263-1264
12. Cheek, G. T.; Osteryoung, R. A. *Inorg. Chem.*, (1982) 21, 3581-3584
13. Fuller, J.; Carlin, R. T.; De Long, H. C.; Haworth, D. *J. Chem. Soc. Commun.* (1994) 299-300
14. Freemantle, M.. *Chem. Eng. News*, (1998), August 24, 76, 34
15. Wilkes, J.S.; Zaworotko, M. *J. Chem. Soc., Chem. Commun*, (1992), 965-967
16. Bonhote, P.; Dias, A. P.; Papageorgiou, N.; Kalyanasundaram, K.; Gratzel, M. *Inorg. Chem.*, (1996) 35, 1168-1178

17. Chauvin, Y.; Mussman, L.; Olivier, H.; *J. Angew. Chem. Int. Ed. Engl.* 1995, 34, 2698-2700
18. Wasserscheid, P.; Bosmann, A.; VanHal, R. *Applications of new halogen-free ionic liquids in catalysis*. Paper # 119 (IEC) presented at the 224th ACS Meeting, Boston, July 17th (2002).
19. Hamill, J.T.; Hardacre, C.; Nieuwenhuyzen, M.; Seddon, K.R.; Thompson, S.A.; Ellis, B. *Chem. Commun.*, (2000) 1929-1930
20. Zhao, H.; Malhotra, S. V. *Aldrichimica Acta*, (2002), 35, 3, 75-83
21. Ford, W.T.; Hauri, R.J.; Hart, D.J. *J. Org. Chem.* (1973) 38, 3916-3918
22. Hasan, M.; Kozhevnikob, I.; Siddiqui, M.; Steiner, A.; Winterton, N. *Inorg. Chem.*, (1999) 38, (25) 5637-5641
23. Larsen, A. S.; Holbrey, J. D.; Tham, F.S.; Reed, C. A. *J. Am. Chem. Soc.*, (2000) 122, 7264-7272

24. Williams, S.D.; Shoebrechts, J.P.; Selkirk, J.C.; Mamantov, G. *J. Amer. Chem. Soc.* (1987) 109, 2219-2220
25. Sanders, J. R.; Ward, E. H.; Hussey, C. L. *J. Electrochem. Soc.*, (1986) 133, 325-330
26. Lall, S.; Mancheno, D.; Castro, S.; Behaj, V.; Cohen, J.I.; Engel, R. *Chem. Commun.*, (2001), 2413
27. Lall, S.; Behaj, V.; Mancheno, D.; Cassiano, R.; Thomas, M.; Rikin, A.; Gaillard, J.; Raju, R.; Scumpia, A.; Castro, S.; Engel, R.; Cohen, J. *Synthesis*, (2002) 11, 1530-1540
28. <http://www.ionicliquids-merck.de>
29. Pringle, J. M.; Golding, J.; Forsyth, C. M.; Deacon, G. B.; Forsyth, M.; McFarlane, D. R. *J. Mater. Chem.*, (2002), 12, 3475-3480
30. Laher, T.M.; Hussey, C.L. *Inorg. Chem.*, (1982) 4079-4083
31. Walden, P., *Bull. Acad. Imper. Sci.(St. Petersburg)*, (1914), 1800

32. Seddon, K. R., Stark, A., Torres, M-J, *Pure Appl. Chem.*, 72, (2000)
2275-2287
33. Hussey, C. L.; King, L. A.; Wilkes, J. S. *J. Electroanal. Chem.*,
(1979) 102 321-322
34. Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.*, (1979) 101, 323-
327
35. Arnett, E. M.; Wolf, J. F. *J. Am. Chem. Soc.*, (1975) 97, 3264-3265
36. Koch, V.R.; Miller, L.L.; Osteryoung, R.A. *J. Am. Chem. Soc.*, (1976)
98, 5277-5284
37. Chowdhry, V.; Westheimer, F. H. *J. Am. Chem. Soc.*, (1978) 310-312
38. Singh, P.; Rajeshwar, K.; DuBow, J.; Job, R. *J. Am. Chem. Soc.*,
(1980) 102, 4676-4681
39. Robinson, J.; Osteryoung, R. A. *J. Am. Chem. Soc.*, (1980) 102, 4415-
4420

40. Oye, H. A.; King, L. A. *Inorg. Nucl. Chem. Letters.*, (1980) 16, 547-550
41. Gale, R.J.; Singh, P.; Job, R. *J. Organometal. Chem.*, (1980) 199, C44-C46
42. Hussey, C.L.; Laher, T.M. *Inorg. Chem.*, (1981) 20, 4201-4206
43. Carpio, R.A.; King, L.A.; Lindstrom, R.E.; Nardi, J.C.; Hussey, C.L. *J. Electrochem. Soc.*, (1979) 126, 1644-1650
44. Gordon, J. E., *J. Am. Chem. Soc.*, 30 (1965) 2760-2763
45. Gordon, J.E.; Selwyn, J.E.; Thorne, R.L. (1966), 1925-1930
46. Starks, C.M. *J. Am. Chem. Soc.* (1971), 93, 195-199
47. Gordon, J.E.; SubbaRao, G.N. *J. Am. Chem. Soc.* (1978) 100, 7445-7454
48. Luer, G. D.; Bartak, D. E. *J. Org. Chem.*, (1982) 47, 1238-1243
49. Laher, T. M.; Hussey, C. L. *Inorg. Chem.*, (1983) 22, 1279-1283

50. Scheffler, T.B.; Hussey, C.L.; Seddon, K.R.; Kent, C.M.; Armitage, P.D. *Inorg. Chem.*(1983), 22, 2099-2100
51. Sahami S.; Osteryoung R.A. *Anal. Chem.*, (1983) 55, 1970-1973
52. Gale, R.J.; Motyl, K.M.; Job, R. *Inorg. Chem.* (1983) 22, 130-133
53. Karpinski, Z.J.; Nanjundiah, C.; Osteryoung, R.A. *Inorg. Chem.*, (1984) 23, 3358-3364
54. Lipsztajn, M.; Osteryoung, R.A.; *Inorg. Chem.*, (1984) 23, 1735-1739
55. Sahami, S.; Osteryoung, R.A. *Inorg. Chem.*, (1984) 23, 2511-2518
56. Haaboush, D.A.; Osteryoung, R.A. *Inorg. Chem.*, (1984) 23, 1726-2734
57. Pickup, P. G.; Osteryoung, R. A; *J. Am. Chem. Soc.*, (1984) 106, 2294-2299
58. Lipsztajn, M.; Osteryoung, R. A. *Inorg. Chem.*, (1985) 24, 716-719
59. Pickup, P. G.; Osteryoung R. A. *Inorg. Chem.*, (1985) 24, 2707-2712

60. Lipsztajn, M.; Osteryoung, R.A. *Inorg. Chem.*, (1985) 24, 3492-3494
61. Schoebrechts, J. P.; Gilbert, B. *Inorg. Chem.*, (1985) 24, 2105-2110
62. Dietrich, M.; Mortensen, J.; Heinze, J. *Angew. Chem. Int. Ed. Engl.*
(1985) 24, 508-509
63. Woodcook, C.; Shriver, D.F. *Inorg. Chem.*, (1986) 25, 2137-2142
64. Gray, J.L.; Maciel, G.E. *J. Am. Chem. Soc.*, (1981) 103, 7147-7151
65. Tait, S.; Osteryoung, R. A. *Inorg. Chem.*, (1984) 23, 4352-4360
66. Angell, C. A.; Bennett, P. D. *J. Am. Chem. Soc.*, (1982) 104, 6304-
6309
67. Karpinski, Z. J.; Osteryoung, R. A. *Inorg. Chem.*, (1984) 23, 4561-
4565
68. Bennett, P. D.; Angel, C. A. *Inorg. Chem.*, (1985) 24, 3030-3035
69. Karpinski, Z.J.; Osteryoung, R.A. *Inorg. Chem.*, (1985) 24, 2259-
2264

70. Wilkes, J.S.; Levisky, J.A.; Wilson, R.A. *Inorg. Chem.* (1982) 21, 1263-1264
71. Boon, J.A.; Levisky, J.A.; Pflug, J.L.; Wilkes, J.S. *J. Org. Chem.*, (1986) 51, 480-483
72. Wilkes, J.S.; Hussey, C.L.; Sanders, J.R.; *Polyhedron* (1986) 5 1567-1571
73. Hussey, C. L. *Pure & Appl. Chem.*, (1988) 60, 1763-1772
74. Das, B.; Carlin, R.; Osteryoung, R.A. *Inorg. Chem.*, (1989) 28, 421-426
75. Zawodzinski, T.A. Jr.; Kurland, R.; Osteryoung, R.A. *J. Phys. Chem.*, (1987) 91, 962-966
76. Fischer, T.; Sethi, A.; Welton, T.; Wolf, J. *Tet. Lett.*, (1999) 40, 793-796
77. Noel, M.A.M.; Trulove, P.C.; Osteryoung, R.A. *Anal. Chem.*, (1991) 63, 2892-2896

78. Tang, J.; Allendoerfer, R.D.; Osteryoung, R.A. *J. Phys. Chem.*, (1992) 96, 3531-3536
79. Quigley, R.; Barnard, P.A.; Hussey, C.L.; Seddon, K.R. *Inorg. Chem.*, (1992) 31, 1255-1261
80. Tang, J.; Shimizu, K.; Osteryoung, R.A. *Inorg. Chem.*, (1992) 31, 2328-2333
81. Song, S.; Tang, J.; Kajitani, M.; Shimizu, K.; Osteryoung, R. A. *J. Organometallic Chem.*, (1993) 445, 211-217
82. Quarmby, I. C.; Osteryoung, R. A. *J. Am. Chem. Soc.*, (1994) 116, 2649-2650
83. Gerhard. A.; Cobranchi, D.P.; Garland ,B.A.; Highley, A.M.; Huang, Y.; Konya, G.; Zahl, A.; Van Eldik, R.; Petrucci, S.; Eyring, E.M. *J. Phys. Chem.*, (1994) 98, 7923-7928
84. Hussey, C. L.; Quigley, R.; Seddon, K. R. *Inorg. Chem.*, (1995) 34, 370-377

85. Lee, C.; Winston, T.; Unni, A.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.*, (1996) 118, 4919-4924
86. Surette, J.K.D.; Green, L.; Singer, R.D. *Chem. Commun.*, (1996) 2753-2754
87. Adams, C.J.; Earle, M.J.; Roberts, G.; Seddon, K.G. *Chem. Commun.* (1998) 2097-2098
88. Carmichael, H. *Chemistry in Britain.*, (2000), January, 36-38
89. Freemantle, M. *Chem. Eng. News*, (2000), May 15, 20, 78, 37- 50
90. Freemantle, M. *Chem. Eng. News*, (2001), January 1, 1, 79, 21-25
91. Freemantle, M. *Chem. Eng. News*, (1999), May 10, 77, 19
92. Davis, J.; Forrester, K. *Tet. Lett.*, (1999) 40, 1621-1622
93. Dzyuba, S. V.; Bartsch, R. A. *Angew. Chem. Int. Ed.* (2003) 42, 2, 148-150

94. Scurto, A. M.; Aki, S. N. V. K.; Brennecke, J. F. *Chem. Commun.*, (2003), 572-573
95. Gutowski, K. E.; Broker, G. A.; Willauer, H. D.; Huddleston, J. G.; Swatloski, R. P.; Holbrey, J. D.; Rogers, R. D. *J. Am. Chem. Soc.*, (2003) 125, 22, 6632-6633
96. Lu, J.; Liotta, C. L.; Eckert, C. A. *J. Phys. Chem. A*, (2003) 107 (19), 3995-4000
97. Welton, T.; *Chem Rev.*, (1999) 99, 2071-2083
98. Hagiwara, R.; Ito, Y. *J. Fluorine Chemistry*, (2000) 105, 221-227
99. Freemantle, M. *Chem. Eng. News*, (2000), May 15, 78, 37- 50
100. Sun, J.; Forsyth, M.; McFarlane, D. R. *J. Phys. Chem. B.*, (1998) 102, 8858-8864
101. MacFarlane, D.R.; Golding, J.; Forsyth, S.; Forsyth, M. Deacon; G. B. *Chem. Commun.*, (2001) 1430-1431

102. Petrovic, C.; Mamantov, G.; Sorlle, M.; Lietzke, M.H.; Smith, G.P. *J.*

Phys. Chem., (1982) 86, 4598-4605

103. Fuller, J.; Breda, A. C.; Carlin, R. T.; *J. Electroanal. Chem.*, (1998)

459, 29-34

104. Noda, A.; Watanabe, M. *Electrochimica Acta.*, (2000) 45, 1265-1270

105. Hagiwara, R., Hirashige, T., Tsuda, T., Ito, Y., *J. Electrochem. Soc.*,

149, (2002) D1-D6

106. Claridge, T. D. W. *High Resolution Techniques in Organic*

Chemistry, Pergamon, Oxford, UK (1999) 369

107. McFarlane, D.R.; Sun, J.; Golding, J.; Meakin, P.; Forsyth, M.

Electrochimica Acta., (2000) 45, 1271-1278

108. Mukhopandhyay, I.; Freyland, W. *Langmuir*, (2003) 19, 1951-1953

109. Endres, F. *ChemPhysChem.* (2002) 3, 144-154

110. Favre, F.; Olivier-Bourbigou, H.; Commereuc, D.; Saussine, L.
Chem. Commun., (2001) 1360-1361
111. Gordon, C. *Applied Catalysis A: General* (2001) 222, 101-117
112. Muldoon, M. J.; Gordon, C. M.; Dunkin, I. R. *J. Chem. Soc., Perkin Trans. 2*, (2001), 433-435
113. Fletcher, K. A.; Storey, I. A.; Hendricks, A. E.; Pandey, S.; Pandey S.
Green Chemistry, (2001), 3, 210-215
114. Sheldon R. *Chem. Commun.*, (2001) 2399-2407
115. Armstrong, D.W.; He, L.; Liu, Y. *Anal. Chem.*, (1999) 71, 3873-3876
116. Anderson, J.L.; Ding, J.; Welton, T.; Armstrong, D. W. *J. Am. Chem. Soc.*, (2002) 124, 14247-14254
117. Grodkowski, J.; Neta, P. *J. Phys. Chem. A* (2002) 106 (46), 11130-11134

118. Grodkowski, J.; Neta, P. *J. Phys. Chem. A* (2002) 106 (22), 5468-5473
119. Wishart, J. F.; Neta, P. *J. Phys. Chem. B*, (2003) 107 (30), 7261-7267
120. Slocum, D.W.; Edgecombe, A.L.; Fowler, J.S.; Gibbard, H.F.; Phillips, J. *Organometallics.*, (1990) 9, 307-311
121. Billard, I.; Moutiers, G.; Labet, A.; El Azzi, A.; Gaillard, C.; Mariet, C.; Lutzenkirchen, K. *Inorganic Chemistry*, (2003) 42 (5), 1726-1733
122. Quarmby, I. C.; Mantz, R. A.; Goldenberg, L. M.; Osteryoung, R. A. *Anal. Chem.*, (1994) 66, 3558-3561
123. Howarth, J.; Hanlon, K.; Fayne, D.; McCormac, P. *Tetrahedron. Lett.* (1997) 38, 3097-3100
124. Fischer, T.; Sethi, A.; Welton, T.; Wolf, J. *Tet. Lett.*, (1999) 40, 793-796
125. Lee, C.W. *Tet. Lett.*, (1999) 40, 2461-2464

126. Wheeler, C.; West, K. N.; Liotta, C. L.; Eckert, C. A. *Chem. Commun.*, (2001) 887-888
127. Van Der Eycken, E.; Appukkuttan, P.; De Borggraeve, W.; Dehaen, W.; Dallinger, D.; Kappe, C. O. *J. Org. Chem.*, (2002) 67 (22), 7904-7907
128. De Bellefon, C.; Pollet, E.; Grenouillet, P. *J. Mol. Catal. A.*, (1999) 145, 121-126
129. Freemantle, M. *Chem. Eng. News*, (1999), March 1, 77, 9
130. Freemantle, M. *Chem. Eng. News*, (1999), January 11, 77, 2
131. Dupont, J.; De Souza, R.F.; Suarez, P.A.Z. *Chem. Rev.*, (2002), 102, 3667-3692
132. Forsyth, S. A.; MacFarlane, D.R.; Thompson, R. J.; Von Itzstein, M. *Chem. Commun.*, (2002), 714-715
133. Song, C. E.; Jung, D.; Roh, E. J.; Lee, S.; Chi, D. Y. *Chem. Commun.*, (2002), 3038-3039

134. Branco, L. C.; Afonso, C. A. M. *Chem. Commun.*, (2002), 3036-3037
135. Dyson, P. J.; McIndoe, J. S.; Zhao, D. *Chem. Commun.*, (2003), 508-509
136. Gaillon, L.; Bedioui, F. *Chem. Commun.*, (2001), 1458-1459
137. Freemantle, M. *Chem. Eng. News*, (2001), September 11, 79, 36
138. Bosmann, A.; Francio, G.; Janssen, E.; Solinas, M.; Leitner, W.; Wasserscheid, P. *Angew. Chem. Int. Ed.*, (2001), 40, 14, 2697-2699
139. Kawanami, H.; Sasaki, A.; Matsui, K.; Ikushima, Y. *Chem. Commun.*, (2003), 896-897
140. Liu, F.; Abrams, M. B.; Baker, R. T.; Tumas, W. *Chem. Commun.*, (2001), 433-434
141. Reetz, M. T.; Wiesenhofer, W.; Francio, G.; Leitner, W. *Chem. Commun.*, (2002), 992-993

142. Lozano, P.; de Diego, T.; Carrie, D.; Vaultier, M.; Iborra, J. L. *Chem. Commun.*, (2002), 692-693
143. Dullius, J.; Suarez, P. A. Z.; Einloft, S.; DeSouza, R. F.; Dupont, J.; Fischer, J.; De Zian, A. *Organometallics*, (1998) 17, 815-819
144. Song, C. E.; Chim, W. H.; Roh, E. J.; Lee S.; Choi, J. H. *Chem. Commun.*, (2001) 1122-1123
145. Wasserscheid, P.; Gordon, C. M.; Hilgers, C.; Muldoon, M. J.; Dunkin, I. R. *Chem. Commun.*, (2001) 1186-1187
146. Wasserscheid, P.; Waffenschmidt, H. *J. Mol. Catal. A.*, Chemical 164 (2000) 61-67
147. Kaar, J. L.; Jesionowski, A. M.; Berberich, J. A.; Moulton, R.; Russell, A. J. *J. Am. Chem. Soc.*, (2003) 125, 4125-4131
148. Kielbasinski, P.; Albrycht, M.; Luczak, J.; Mikolajczyk, M. *Tetrahedron: Asymmetry*, (2002) 13, 735-738

149. Deshmukh, R. R.; Rajagopal, R.; Srinivisan, K.V. *Chem. Commun.*, (2001) 1544-1545
150. Mathews, C.J.; Smith, P.J.; Welton, T.; White, A.J.P.; Williams, D.J. *Organometallics*, (2001) 20, 3848-3850
151. Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis Jr. J. H. *J. Am. Chem. Soc.*, (2002) 124, 5962-5963
152. Freemantle, M. *Chem. Eng. News*, (2001), May 28, 79, 22
153. Boxwell, C.J.; Dyson, P.J.; Ellis, D.J.; Welton, T. *J. Am. Chem. Soc.*, (2002) 124, 9334-9335
154. Dupont, J.; Fonseca, G. S.; Umpierre, A. P.; Fichtner, P. F. P.; Teixeira, S. R. *J. Am. Chem. Soc.*, (2002) 124, 4228-4229
155. Mehnert, C. P.; Mozeleski, E. J.; Cook, R. A. *Chem. Commun.*, (2002), 3010-3011

156. Brown, R. A.; Pollet, P.; McKoon, E.; Eckert, C. A.; Liotta, C. L.; Jessop, P. G. *J. Am. Chem. Soc.*, (2001) 123, 1254-1255
157. Jessop, P. G.; Stanley, R. R.; Brown, R. A.; Eckert, C. A.; Liotta, C. L.; Ngo, T. T.; Pollet, P. *Green Chemistry*, (2003) 5, 123-128
158. Carmichael, A.; Haddleton, D.; Bon, S.; Seddon, K. *Chem. Commun.*, (2000) 1237-1238
159. Freemantle, M. *Chem. Eng. News*, (2000), July 78, 29
160. Ross, J.; Chen, W.; Xu, L.; Xiao, J. *Organometallics* (2001) 20, 138-142
161. Zhang, H.; Hong, K.; Jablonsky, M.; Mays, J. W. *Chem. Commun.*, (2003), 1356-1357
162. Freemantle, M. *Chem. Eng. News*, (2002), March 4, 38-39
163. Freemantle, M. *Chem. Eng. News*, (2002), March 4, 80, 9
164. Semeril, D.; Olivier-Bourbigou, H.; Bruneau, C.; Dixneuf, P. H. *Chem. Commun.*, (2002), 146-147

165. Laali, K. K.; Gettwert, V. J. *J. Org. Chem.*, (2001) 66, 35-40
166. Howarth, J.; Paraic, J.; Dai, *Tetrahedron Letters*, (2000) 41, 10319-10321
167. Fadeev, A. G.; Meagher, M. M. *Chem. Commun.*, (2001) 295-296
168. Calo, V.; Nacci, A.; Lopez, L.; Napola, A. *Tetrahedron Letters*, (2001) 42, 4701-4703
169. Calo, V.; Nacci, A.; Monopoli, A.; Laera, S.; Cioffi, N. *J. Org. Chem.*, (2003) ASAP
170. McNulty, J.; Capretta, A.; Wilson, J.; Dyck, J.; Adjabeng, G.; Robertson, A. *Chem. Commun.*, (2002), 1986-1987
171. Peng, J.; Deng, Y. *Tetrahedron Letters*, (2001) 42, 403-405
172. Ren, R. X.; Ou, W. *Tetrahedron Letters*, (2001) 42, 8445-8446
173. Ren, R. X.; Zueva, L. D.; Ou, W. *Tetrahedron Letters*, (2001) 42, 8441-8443

174. Kim, D. W.; Song, C. E.; Chi, D. Y. *J. Am. Chem. Soc.*, (2002) 124, 10278-10279
175. Fraile, J. M.; Garcia, J. I.; Herrerias, C.I.; Mayoral, J. A.; Carrie, D.; Vaultier, M. *Tetrahedron: Asymmetry*, (2000) 12, 1891-1894
176. Qiao, K.; Deng, Y. *J. Mol. Catal. A.*, (2001) 171, 81-84
177. Peng, J.; Deng, Y. *Tetrahedron. Lett.* (2001) 42, 5917-5919
178. Ligabue, R. A.; Dupont, J.; De Souza. R. F. *J. Mol. Catal. A.*, (2001) 169, 11-17
179. Davis, J.H.; Forrester, K. *Tet. Lett.*, (1999) 40, 1621-1622
180. Qiao, K.; Deng, Y. *J. Mol. Catal. A.*, (2001) 171, 81-84
181. Huddleston, J.G.; Willauer, H.D.; Swaltloski, R.P.; Visser, A. E.; Rogers, R.D. *Chem. Commun.* (1998) 1765-1766
182. Muldoon, M. J.; McLean, A. J.; Gordon, C. M.; Dunkin, I. R. *Chem. Commun.*, (2001) 2364-2365

183. Freemantle, M. *Chem. Eng. News*, (2001), April 2, 79, 14
184. Anthony, J. L.; Maginn, E. J.; Brennecke, J. F. *J. Phys. Chem. B.*,
(2001) 105, 10942-10949
185. Chun, S.; Dzyuva, S. V.; Bartsch, R. A. *Anal. Chem.*, (2001) 73,
3737-3741
186. Dietz, M. L.; Dzielawa, J. A. *Chem. Commun.*, (2001) 2124-2125
187. Wadhawan, J.D.; Schroder, U.; Neudeck, A.; Wilkins, S.J.; Compton,
R.G.; Marken, F.; Consorti, C.S.; De Souza, R.F.; Dupont, J. J.
Electroanal. Chem., (2000) 493, 75-83
188. Visser, A. E.; Swatloski, R.P.; Rogers, R.D. *Green Chemistry* (2000)
Feb. 1- 4
189. Bates, E. D.; Mayton, R. D.; Ntai, I.; Davis Jr. J. H. *J. Am. Chem.
Soc.*, (2002) 124 (6) 926-927
190. Selvan, M.S.; Mckinley, M.D.; Dubois, R.H.; Atwood, J.L. *J. Chem.
Eng. Data* (2000) 45, 841-845

191. Armstrong, D. W.; Zhang, L.; He, L.; Gross, M. *Anal. Chem.*, (2001) 73, 3679-3686
192. Hondrogiannis, G.; Lee, C. W.; Pagni, R. M.; Mamantov, G. *J. Am. Chem. Soc.*, (1993) 115, 9828-9829
193. Gordon, C.; McLean, J. *Chem. Commun.*, (2000) 1395-1396
194. Ritchie, J. E.; Murray, R. W. *J. Phys. Chem. B.*, (2001) 105 (46), 11523-11528
195. Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Sheppard, O.; Hardacre, C.; Rogers, R. D. *Chem. Commun.*, (2003), 476-477
196. Lagrost, C.; Carrie, D.; Vaultier, M.; Hapiot, P. *J. Phys. Chem. A.*, (2003) 107, 745-752
197. Yadav, J. S.; Reddy, B. V. S.; Ganeshwar, D. *New J. Chem.*, (2003) 27, 202-204
198. Driver, G.; Johnson, K. E. *Green Chemistry*, (2003) 5, 163-169

199. Harrison, S.; MacKenzie, S. R.; Haddleton, D. M. *Chem. Commun.*, (2002), 2850-2851
200. Bradley, D. *AlchE*, (2000)
201. Kawano, R.; Watanabe, M. *Chem. Commun.*, (2003), 330-331
202. Scott, J. L.; MacFarlane, D. R.; Raston, C. L.; Teoh, C. M. *Green Chemistry*, (2000) 2, 123-126
203. Bradley, A. E.; Hatter, J. E.; Nieuwenhuyzen, M.; Pitner, W. R.; Seddon, K. R.; Thied, R. C. *Inorg. Chem.* (2002) 41, 1692-1694
204. Adams, C. J.; Bradley, A. E.; Seddon, K. R. *Aust. J. Chem.* (2001) 54, 679-681
205. Mann, B. E.; Guzman, M. H. *Inorganica Chimica Acta*, (2002) 330, 143-148
206. Nguyen, H-P.; Matondo, H.; Baboulene, M. *Green Chemistry*, (2003) 5, 303-305

207. Barhdadi, R.; Courtinard, C.; Nedelec, J. Y.; Troupel, M. *Chem. Commun.*, (2003), 1434-1435
208. Ren, R. X. *Unpublished Research*, Wesleyan University, (2003)
209. Abbott, A. P.; Capper, G.; Davies, D. L.; Munro, H. L.; Rasheed, R. K.; Tambyrajah, V. *Chem. Commun.*, (2001) 2010-2011
210. Cohen, J. I.; Engel, R. *Current Organic Chemistry*, 6, 1453-1467 (2002).
211. Cohen, J. I.; Traficante, L.; Schwartz, P. W.; Engel, R. *Tetrahedron Lett.*, 39, 8617 (1998).
212. Fabian, J.; October, T.; Cherestes, A.; Engel, R. *Synlett*, 1007(1997).
213. Cohen, J. I.; Shteto, V.; Engel, R. *Synthesis*, 1263 (2000).
214. Engel, R. *Advances in Dendritic Macromolecules*, 2, 73-99 (1995).
215. Cherestes, A.; October, T.; Engel, R. *Heteroatom Chem.*, 9, 485 (1998).

216. Cohen, J. I.; Castro, S.; Han, J-A.; Behaj, V.; Engel, R. *Heteroatom Chem.*, 11, 546 (2000).
217. Cohen, J. I. *Thesis*, "Polycationic Organic Salts – Syntheses and Investigations," Ph.D. Dissertation, CUNY, (2001)
218. Reichert, W. M., Visser, A. E., Swatloski, R. P., and Rogers, R. D., (March 2000), Paper # 85 presented at the 219th National Meeting of the American Chemical Society, I&EC Division, San Francisco, CA, USA.
219. Holbrey, J. D.; Visser, A. E.; Spear, S. K.; Reichert, W. M.; Swatloski, R.P.; Broker, G. A.; Rogers, R. D. *Green Chemistry*, (2003) 5, 129-135
220. Forsyth, C. M.; MacFarlane, D. R.; Golding, J. J.; Huang, J.; Sun, J.; Forsyth, M. *Chem. Mater.* (2002) 14, 2103-2108
221. Hardacre, C.; Holbrey, J. D.; McMath, S. E. J.; Bowron, D. T.; Soper, A. K. *J. Chem. Phys.* (2003) 118, 1, 273-278

222. Golding, J.; Hamid, N.; MacFarlane, D. R.; Forsyth, M.; Forsyth, C.; Collins, C.; Huang, J. *Chem. Mater.*, (2001) 13, 558-564
223. Kazarian, S. G.; Sakellarios, N.; Gordon, C. M. *Chem. Commun.*, (2003), 1314-1315
224. Eike, D. M.; Brennecke, J. M.; Maginn, E. J. *Green Chemistry*, (2003) 5, 323-328
225. Holbrey, J. D.; Reichert, W. M.; Nieuwenhuyzen, M.; Johnson, S.; Seddon, K. R.; Rogers, R. D. *Chem. Commun.*, (2003) ASAP
226. Afanas'ev, V. N.; Grechin, A. G. *Russian Chemical Reviews*, (2002) 71, 9, 775-787
227. Sun, J.; McFarlane, D. R.; Forsyth, M. *Electrochimica Acta*, 48 (2003) 1707-1711
228. McFarlane, D. R.; Forsyth, S. A.; Golding, J.; Deacon, G. B. *Green Chemistry*, (2002) 4, 444-448

229. Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.; Pitner, W. R.; Seddon, K. R.; Rogers, R. D. *Green Chemistry*, (2002) 4, 407-413
230. Yanes, E. G.; Gratz, S. R.; Baldwin, M. J.; Robinson, S. E.; Stalcup, A. M. *Anal. Chem.*, (2001) 73, 3838-3844
231. Wishart, J. F. *Radiation Chemistry of Ionic Liquids: Reactivity of Primary Species* in "Ionic Liquids as Green Solvents: Progress and Prospects" Rogers, R. D. and Seddon, K. R., Eds.; *ACS Symp. Ser.* 856, Ch. 31, pp. 381-395, American Chemical Society, Washington, DC, (2003).
232. Harmon, C. D.; Smith, W. H.; Costa, D. A.; *Radiat. Phys. Chem.* 60 (2001) 157-159
233. Fields, M. *et al.*; *World Patent*, vol. WO 99(1999) 14160
234. Deetlefs, M.; Seddon, K. R. *Green Chemistry*, (2003) 5, 181-186
235. Gathergood, N.; Scammells, P. J. *Aust. J. Chem.* (2002) 55, 557-560

236. Bao, W.; Wang, Z.; Li, Y. *J. Org. Chem.*, (2002)

237. Bradaric, C. J.; Downard A.; Kennedy C.; Robertson A. J.; Zhou Y.

Green Chemistry, (2003) 5, 143-152

238. Holbrey, J. D.; Reichert, W. M.; Swatloski, R. P.; Broker, G. A.;

Pitner, W. R.; Seddon, K. R.; Rogers, R. D. *Green Chemistry*, (2002)

4, 407-413