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Trigonal Tricationic Ionic Liquids: Molecular Engineering of Trications to Control Physicochemical Properties

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Simple modification of traditional ionic liquids (ILs) by varying their cations and anions can produce ILs with variable and tunable physicochemical properties that make them much more versatile and useful for a variety of applications.[1] Their uses traverse many areas of chemistry and biochemistry, including novel solvent systems in organic syntheses and catalysis,[2,3] enzyme-catalyzed reactions,[4] electrochemical studies,[5] electrolyte materials for double-layer capacitors, dye-sensitized solar cells, liquid−liquid extractions,[6,7] liquid matrixes for matrix-assisted laser desorption/ionization mass spectrometry,[8] additives in HPLC and capillary electrophoresis, and stationary phases in GC.[9–12] The tunable properties include but are not limited to melting point, viscosity, density, thermal and chemical stability, hydrophilicity/lipophilicity, and miscibility with water and organic solvents, as well as extractability for various organic compounds and metal ions.

Multifunctional ionic liquids (especially dicationic and dianionic ILs) have been shown to have a greater range of physical properties than most traditional, singly charged ILs.[13,14] Consequently, they have been shown to be exceptional high temperature and selective gas chromatographic stationary phases [13,15] and have been prepared as a new class of high temperature lubricants.[16] They often have greater thermal stability, lower volatility, and more flexibility in tuning/varying their physiochemical properties. In particular, varying the cationic or anionic moieties to produce unsymmetrical dicationic (or dianionic) moieties allows greater variety and control of virtually all IL properties.[14]

The question arises, can ever more complex multifunctional ILs (tricationic, trianionic, tetracationic, etc.) be beneficial? As the number of charged groups and the molecular weight of these multifunctional salts increases it becomes increasingly difficult to produce them in liquid forms (at ambient temperature). In addition, the synthetic/manufacturing process can become increasingly complex which raises their production cost. Hence it is possible to reach a point of diminishing returns in the quest for ever larger and more complicated multifunctional ionic liquids.

However, unsymmetrical tricationic ionic liquids reported have shown good thermal stabilities and were tested for antimicrobial activity.[17] In this work, we present a much extended study to demonstrate that symmetrical, trigonal tricationic ionic liquids can be molecularly tailored to a greater extent than the traditional ILs. This is achieved by synthesizing novel symmetrical tricationic ionic liquids using four major types of central cores having five or more different cationic moieties for each center. We also demonstrate that this sort of molecular structure alterations could be used to further tune their physical properties such as melting point, viscosity, density, thermal stability, hydrophilicity/lipophilicity, refractive index, and miscibility with water and organic

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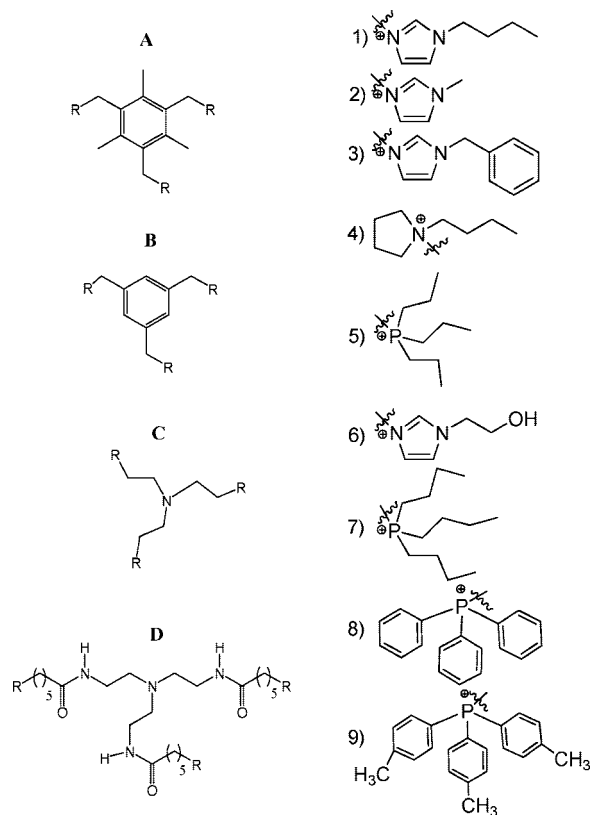(17) Pernak, J.; Skrzypczak, A.; Lota, G.; Frackowiak, E. *Chem. Eur. J.* **2007**, *13*, 3106–3112.

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A

B

C

D

1)

2)

3)

4)

5)

6)

7)

8)

9)

Figure 1. Structures of trications examined.

solvents. A final important consideration is the fact that there have been no prior IL studies involving these symmetrical trications.

The four main symmetrical tricationic core moieties, **A**, **B**, **C**, and **D**, are shown in Figure 1. These central structures were selected to range from the more rigid mesitylene core (**A**) to the more flexible tri(2-hexanamido)ethylamine (**D**).

Application of tricationic liquids can be obtained by attributing any of five different charge carrying groups (**R1**, **R2**, **R3**, **R4**, and **R5**) to the desired core. This allows study of the molecular structure dependence of the trication salts to their physicochemical properties. Several other tricationic ILs were also synthesized using a central core-**C** with **R6**, **R7**, **R8**, and **R9** charge carrying moieties. The counteranions studied include bis(trifluoromethylsulfonyl)imide (NTf_2^-), hexafluorophosphate (PF_6^-), tetrafluoroborate (BF_4^-), and trifluoromethanesulfonate (TfO^-)

All four NTf_2^- salts synthesized with the flexible central-tri(2-hexanamido)ethylamine core (**D1** to **D4**) provided melting temperatures below 0 °C. The more rigid mesitylene core (**A**) provided all NTf_2^- salts that were solids at ambient temperatures. The melting temperatures of the NTf_2^- salts having **B** and **C** cores, with intermediate flexibilities, were dependent on the nature of the charge carrying moieties **1**, **2**, **3**, **4**, and **5**. Except for **C2**-NTf_2 all tricationic NTf_2^- salts having the **B** and **C** cores with their charge carrying moieties having imidazolium systems provided melting temperatures below 0 °C. The phosphonium charge carrying moiety provided an RTIL only with the most flexible central core (**D**). With central core structures **A**, **B**, and **C**, all salts are solids at room temperature (compare ILs-**B5**, **A5**, and **C5**).

Tricationic salts with PF_6^-, BF_4^-, and TfO^- counteranions and the moderately rigid central core (**B**) and moderately flexible core (**C**) associated with butylimidazolium charge carrying moiety were evaluated. Melting temperatures of these along with the NTf_2^- salts were compared. A general trend of melting temperatures for the tricationic ILs with same trication with varying anions is observed as follows: $NTf_2^- < TfO^- < BF_4^- < PF_6^-$. The melting point trends observed for these tricationic ILs is similar to that observed for previously reported imidazolium based dicationic ILs.[13] However, the trend is different from that observed in traditional imidazolium based monocationic ILs.[1]

The densities of the synthesized tricationic ILs range from 1.20 to 1.69 g/cm³. The highest density is observed for IL-**A2** having three methylimidazolium cationic moieties associated with mesitylene core (**A**) having NTf_2^- counteranions (1.69 g/cm,³ IL-**A2**). The lowest density was observed for compound IL-**C5** which has nitrogen core (**C**) with three tripropylphosphinium cationic moieties (**5**) and NTf_2^- anions (1.20 g/cm³, IL-**C5**). For similar cationic moieties with NTf_2^- anions, ionic liquids having mesitylene cores are more dense than those with the other three types of cores. The general trend that can be discerned from the data in Table 1 is that the densities of imidazolium based ionic liquids decreases with increasing length of the hydrocarbon chain at the no. 3 position of imidazole (compare 1.53 g/cm³ for IL-**B1** to 1.56 g/cm³ for IL-**B2**, 1.55 g/cm³ for IL-**A1** to 1.69 g/cm³ for IL-**A2**, 1.41 g/cm³ for IL-**C1** to 1.56 g/cm³ for IL-**C2**, and 1.49 g/cm³ for IL-**D1** to 1.59 g/cm³ for IL-**D2**). Similar trends have been previously reported for a large series of mono- and dicationic ionic liquids.[13,18,19] Furthermore, it is clear from the data obtained given in Table 1 that for ionic liquids with similar cationic moieties, densities are also affected by the nature of the counteranions in the order $NTf_2^- > PF_6^- > TfO^- > BF_4^-$. This trend is similar to that observed for both di- and monocationic ILs.[1,13]

The kinematic viscosities of the 9 room temperature ionic liquids (IL-**B1**, IL-**B2**, IL-**B3**, IL-**C1**, IL-**C3**, IL-**D1**, IL-**D2**, IL-**D3**, IL-**D4**,) were measured at 30 °C and are given in Table 1. The tricationic ionic liquids are much more viscous than traditional monocationic ionic liquids and dicationic ionic liquids.[1] The viscosities are remarkably high for ILs containing charged benzylimidazolium charge moieties (20000−45000 cSt for IL-**B3**, IL-**C3**, IL-**D3**). This may be due to the presence of additional aromatic moieties compared to the other cationic groups.[14] Ionic liquids with higher viscosities are preferred for some applications, such as stationary phases for gas−liquid chromatography.[10,11] Viscosities of ionic liquids with imidazolium based moieties and NTf_2^- anions show increasing in viscosities with increasing alkyl chain at the 3-position of imidazole (compare 2320 cSt for IL-**B1** to 1280 cSt for IL-**B2**, 10200 cSt for IL-**D1** to 7760 cSt for IL-**D2**). An analogous trend has been observed with traditional monocationic and dicationic ionic liquids.[6,13,14,19]

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Table 1. Physicochemical Properties of Tricationic ILs Synthesized

ionic liquid	MW (g/mol)	melting point (°C)	D^a (g/cm³)	refractive index	viscosity^b (cSt)	thermal stability^c (°C) 99% w	95% w	miscibility with heptane^d	miscibility with water^d
A1-NTf2	1372.3	66−69	1.55			300	359	I	I
A2-NTf2	1246.0	82−85	1.69			338	370	I	I
A3-NTf2	1474.3	60−62	1.59			339	365	I	I
A5-NTf2	1480.4	123−126	1.31			288	398	I	I
B1-NTf2	1330.2	−24.6^e	1.53	1.467	2320	344	401	I	I
B2-NTf2	1203.9	−38.6^e	1.56	1.467	1280	364	414	I	I
B3-NTf2	1432.2	−87.4^e	1.55	1.588	20000−25000	262	361	I	I
B4-NTf2	1339.3	62−64	1.44			344	371	I	I
B5-NTf2	1438.3	89−91	1.24			397	430	I	I
C1-NTf2	1311.2	−47.5^e	1.41	1.451	1580	308	363	I	I
C2-NTf2	1184.9	36−37^e	1.56			338	393	I	I
C3-NTf2	1413.2	−6.7^e	1.51	1.493	25000−30000	348	381	I	I
C4-NTf2	1320.3	57−58^e	1.47			297	337	I	I
C5-NTf2	1419.3	103−104	1.20			310	395	I	I
C6-NTf2	1275.0	−38.5^e	1.64	1.460	7980	344	392	I	I
C7-NTf2	1545.5	133−135	1.26			361	406	I	I
C8-NTf2	1725.5	82−84^e	1.53			235	269	I	I
C9-NTf2	1851.7	17.1^e	1.37			396	398	I	I
D1-NTf2	1650.6	−54.1^e	1.49	1.466	10200	262	335	I	I
D2-NTf2	1524.4	−16.4^e	1.59	1.465	7760	279	351	I	I
D3-NTf2	1752.7	−15.6^e	1.54	1.495	40000−45000	212	337	I	I
D5-NTf2	1758.8	−31.4^e	1.48	1.466	35000−40000	284	388	I	I
A1-Pf6	924.6	141−143	1.49			246	320	I	I
A1-Tfo	937.0	63−65	1.47			316	380	I	M
A1-Bf4	750.1	130−133	1.41			302	357	I	M
C1-Pf6	905.6	195−197	1.33			309	344	I	I
C1-Tfo	917.9	64.2^{e,f}	1.33			253	349	I	M
C1-Bf4	731.1	101−104	1.21			274	297	I	M

^{a} Measured using pycnometer. ^{b} Measured using a capillary viscometer at 30 °C. ^{c} Thermogravimetric analysis (TGA), 99% w = temperature at 1% mass decrease of sample, 95% w = temperature at 5% mass decrease of sample. ^{d} I = immiscible, M = miscible ^{e} Phase transition temperature determined by using differential scanning calorimetry(DSC). ^{f} Amorphous solid.

Thermal stabilities of all 28 tricationic salts were measured by thermogravimetric analysis (TGA) and are given in Table 1. Thermal stabilities (5% weight loss) of 17 tricationic ionic liquids with NTf_2^- counteranion range from 355 to 430 °C which is higher than monocationic ionic liquids and similar to dicationic ionic liquids. All central cores carrying phosphonium cationic moieties show the highest thermal stabilities compared to the others (430 °C for IL-**B5**, 398 °C for IL-**A5**, 395 °C for IL-**C5**, and 405 °C for IL-**D5**) followed by methylimidazolium cationic moieties (414 °C for IL-**B2**, 370 °C for IL-**A2**, 393 °C for IL-**C2**, and 351 °C for IL-**D2**). Furthermore the data show that ILs with NTf_2^- anion possess highest thermal stabilities followed by ILs with TfO⁻ as counteranion.

The miscibility of all ionic liquids with both water (polar) and heptane (nonpolar) solvents were evaluated (Table 1). Tricationic ionic liquids illustrate similar solubility behavior as monocationic and dicationic ionic liquids.[2,14,20,21] None of the ionic liquids were soluble in heptane. Refractive index values were recorded for those samples that were liquids at room temperature. All values are in the general region observed for monocationic and dicationic ionic liquids[14,20] and lie between 1.451 and 1.588.

In summary, we have demonstrated the effect of molecular structure modifications on the physicochemical properties of a series of 28 new symmetrical tricationic ILs. We observed that the physicochemical properties of tricationic ILs often can be varied and controlled to a greater extent than simple, more conventional ILs. For bis(trifluoromethylsulfonyl)-imide tricationic ionic liquids, the viscosity generally increased to 4- to 5-fold higher than those reported earlier, when benzylimidazolium is used as the cationic moiety. The thermal stabilities of most of the tricationic ionic liquids (often > 400 °C) are greater than that of traditional monocationic ionic liquids. It is also clear that the melting point of tricationic ILs are contingent on the flexibility of the central core system; for example, ILs (Core **D**) with more flexible structure have low melting points compared to ILs (Core **A**) having more rigid structures. The solubility of tricationic ionic liquids in water and heptane appears very similar to that of the traditional monocationic and dicationic ionic liquids and depends largely on the selected anion.

Supporting Information Available: Experimental procedures and NMR data (PDF). This material is available free of charge via the Internet http://pubs.acs.org.

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