



Synthesis and characterization of dicationic ionic liquids that contain both hydrophilic and hydrophobic anions

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ABSTRACT

A series of dicationic ionic liquids, in which each dication is associated with both a hydrophobic anion and a hydrophilic anion, are synthesized. The thermal properties and solubility in organic solvents of these ILs are characterized. The ionic liquids show interesting properties, which are different from those of dicationic ionic liquids, in which each dication is associated with two identical anions.

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1. Introduction

Compared to molecular organic compounds, ionic liquids (IL) composed of cations and anions exhibit several unique properties, such as extremely low vapor pressure, non-flammability, and high thermal stability.^{1,2} Furthermore, the physical and chemical properties of ILs can be adjusted or tuned by controlling the nature and functionality of the cations and anions.³ Therefore, ILs have been considered for many applications, including the replacement of organic solvents for organic synthesis,^{4,5} enzyme catalyzed reactions,⁶ electrochemistry,⁷ electrolyte for capacitors,⁸ dye-sensitized solar cells (DSSC),⁹ ultra-low-volatility liquid matrixes for matrix-assisted laser desorption/ionization mass spectrometry,¹⁰ and stationary phases in gas chromatography.¹¹

The most popular ILs are composed of an un-symmetrically substituted nitrogen-containing monocation, such as imidazolium or pyridinium with an inorganic anion, such as Cl⁻, Br⁻, PF₆⁻, BF₄⁻, or NTf₂⁻ (bis(trifluoromethanesulfonyl)amide).^{4,5,12,13} In accordance with the nature of cations and anions, ILs can be classified into water-miscible (hydrophilic) and water-immiscible

(hydrophobic).¹² Recently, a type of IL, namely dicationic ILs, in which two monocations are combined into a dication have been reported.^{14–17} The tunability of dicationic ILs has been enhanced by cationic moieties.¹⁵ Dicationic ILs are suitable for applications, such as dye-sensitized solar cells,¹⁸ organic synthesis,¹⁹ and lubricants.^{16,17} In the dicationic ILs reported so far, each dication is associated with two identical anions, which are either hydrophobic or hydrophilic. These ILs are further classified as geminal (the two monocations that form the dication are the same) or unsymmetrical (the monocations are different). There have been no reports on the synthesis of dicationic ILs, in which each dication is associated with two different anions, one hydrophobic and the other hydrophilic. By incorporating both hydrophobic and hydrophilic anions into one dication, a new series of ILs with properties that are different from those of existing geminal dicationic ILs is expected. This paper reports the synthesis of such dicationic ILs, in which each dication is associated with both a hydrophobic and a hydrophilic anion. These ILs are termed heteroanionic ILs in this paper. Since the synthesis protocol for the preparation of geminal ILs^{14,15} cannot be applied to heteroanionic ILs, a different synthetic route is developed. The thermal properties (melting temperature and decomposition temperature) and solubility in organic solvents of these ILs are discussed.

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2. Experimental

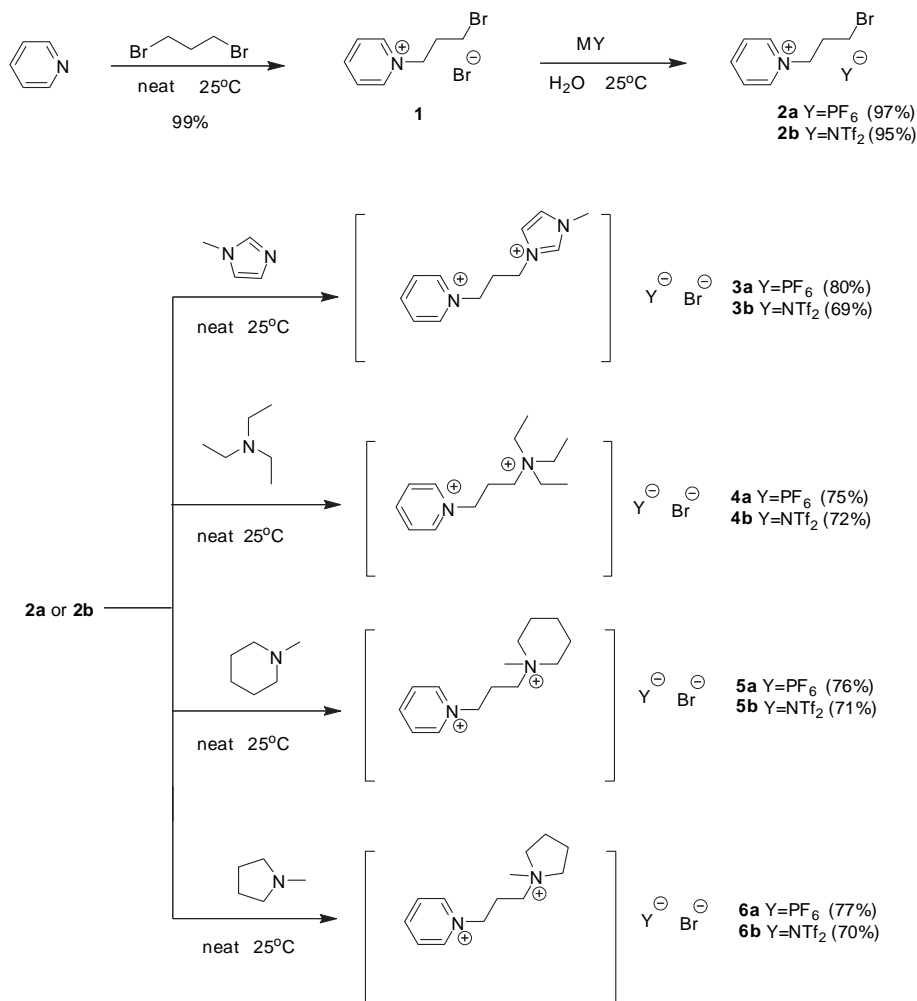
2.1. Chemicals

1,3-Dibromopropane (99.9%) was purchased from Alfa Aesar. Pyridine (98%), 1-methylimidazole (99.9%), triethylamine (98%), 1-methylpiperidine (99.9%), 1-methylpyrrolidine (99.9%), potassium hexafluorophosphate (KPF₆) (99.9%), and lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂) (99.9%) were purchased from Aldrich. Ethyl acetate (ACS grade, ≤0.01% H₂O) was purchased from Baker. All chemicals were purchased from a commercial supplier and used as received.

10 °C/min (the *T*_d was the temperature corresponding to 10% weight loss). Melting points were measured using a capillary melting point apparatus (Buchi B-540) with a heating rate of 10 °C/min. The solubility of ILs was tested using common organic solvents.

2.3. General procedure for the synthesis of heteroanionic dicationic ionic liquids

The general procedure for the synthesis of heteroanionic ILs is shown in Scheme 1. Compound **1** was prepared by stirring pyridine (1.0 mmol) and 1,3-dibromopropane (1.5 mmol) at room tempera-



Scheme 1. Synthesis routes of dicationic ionic liquids that contain both hydrophobic and hydrophilic anions.

2.2. Characterization

After the heteroanion dicationic ionic liquids were synthesized, the ¹H, ¹³C, and ¹⁹F NMR spectra of the purified products were recorded in D₂O (Cambridge Isotope Laboratories Inc., 99.9% D), CDCl₃ (Cambridge Isotope Laboratories Inc., 99.9% D), or DMSO-*d*₆ (Cambridge Isotope Laboratories Inc., 99.9% D) on a Bruker Avance 400 spectrometer at 400, 100, and 282 MHz (compounds **1**, **2a**, and **2b**) were measured by Bruker Avance 200 spectrometer at 200 MHz in ¹H and 50 MHz in ¹³C for **2b**), and at a temperature of 25 °C, respectively. Elemental analyses were conducted using an Elemental analyzer (model: vario EL III). Low resolution mass spectra were obtained using an electrospray ionization Thermo Finnigan API 4000Q-Trap LC-MS/MS. Thermogravimetry analysis (TGA, model: TGA-50, Shimadzu) was conducted at a heating rate of

ture for 4 days. The mixture was washed with ethyl acetate to remove any unreacted reactants, followed by filtration to afford white precipitates of **1**. Compounds **2a** and **2b** were prepared by performing anion exchange for compound **1** with 1.5 mmol KPF₆ (compound **2a**) or LiNTf₂ (compound **2b**) in deionized water at room temperature for 3 h. The products were extracted with ethyl acetate. Compounds **3a–6a** and **3b–6b** were prepared by reacting compound **2a** (for **3a–6a**) or **2b** (for **3b–6b**) with a slight molar excess of 1-methylimidazole for **3a** and **3b**, triethylamine for **4a** and **4b**, 1-methylpiperidine for **5a** and **5b**, and 1-methylpyrrolidine for **6a** and **6b** for 24 h at room temperature. The precipitates were filtrated, washed, and purified by ethyl ether to afford the corresponding salts.

2.3.1. [1-(3-Bromopropyl)pyridinium] bromide (**1**). Yield 99%. ¹H NMR (200 MHz, D₂O): δ 2.58 (quin, *J*=6.6 Hz, 2H), 3.48 (t, *J*=6.6 Hz,

2H), 4.85 (t, $J=6.6$ Hz, 2H), 8.08 (t, $J=6.8$ Hz, 2H), 8.54 (t, $J=7.3$ Hz, 1H), 8.89 (d, $J=6.2$ Hz, 2H).

2.3.2. [1-(3-Bromopropyl)pyridinium] hexafluorophosphate (**2a**). Yield 97%. ^1H NMR (200 MHz, D_2O): δ 2.57 (quin, $J=6.4$ Hz, 2H), 3.48 (t, $J=6.4$ Hz, 2H), 4.75 (t, $J=6.4$ Hz, 2H), 8.07 (t, $J=7.3$ Hz, 2H), 8.55 (t, $J=7.2$ Hz, 1H), 8.88 (d, $J=6.4$ Hz, 2H). LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_8\text{H}_{12}\text{BrF}_6\text{NP}^+$: 346.0; found: 346.0, $[\text{M}-\text{PF}_6]^-$ calcd for $\text{C}_8\text{H}_{11}\text{BrN}^+$: 200.0; found: 200.0. LRMS-ESI (-ve): m/z calcd for $[\text{PF}_6]^-$: 145.0; found: 145.0.

2.3.3. [1-(3-Bromopropyl)pyridinium] [bis(trifluoromethanesulfonyl)amide] (**2b**). Yield 95%. ^1H NMR (200 MHz, CDCl_3): δ 2.60 (quin, $J=6.5$ Hz, 2H), 3.42 (t, $J=6.5$ Hz, 2H), 4.84 (t, $J=6.5$ Hz, 2H), 8.09 (t, $J=7.0$ Hz, 2H), 8.51 (t, $J=7.3$ Hz, 1H), 8.87 (d, $J=6.3$ Hz, 2H). ^{13}C NMR (50 MHz, CDCl_3): δ 28.3, 33.4, 60.6, 120.0, 129.0, 144.6, 146.5. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{12}\text{BrF}_6\text{N}_2\text{O}_4\text{S}_2$: 482.9; found: 482.5, $[\text{M}-\text{NTf}_2]^+$ calcd for $\text{C}_8\text{H}_{11}\text{BrN}^+$: 200.0; found: 200.0. LRMS-ESI (-ve): m/z calcd for $[\text{NTf}_2]^-$: 279.9; found: 280.0.

2.3.4. [1-(1-Pyridinium-yl-propyl)-3-methylimidazolium] (hexafluorophosphate) (bromide) (**3a**). Yield 80%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.55 (quin, $J=7.0$ Hz, 2H), 3.88 (s, 3H), 4.33 (t, $J=7.0$ Hz, 2H), 4.74 (t, $J=7.0$ Hz, 2H), 7.75 (s, 1H), 7.82 (s, 1H), 8.20 (t, $J=6.8$ Hz, 2H), 8.65 (t, $J=7.2$ Hz, 1H), 9.18 (d, $J=6.3$ Hz, 2H), 9.25 (s, 1H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 30.6, 35.8, 45.7, 57.6, 122.2, 123.7, 128.2, 136.9, 144.9, 145.8. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -70.4 (d, $J_{\text{P-F}}=710.4$ Hz). Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{BrF}_6\text{N}_3\text{P}$: C, 33.66; H, 4.00; N, 9.81. Found: C, 33.40; H, 4.03; N, 9.78. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{12}\text{H}_{18}\text{BrF}_6\text{N}_3\text{P}^+$: 428.0; found: 428.0, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{F}_6\text{N}_3\text{P}^+$: 348.1; found: 348.2, $[\text{M}-\text{PF}_6]^-$ calcd for $\text{C}_{12}\text{H}_{17}\text{BrN}_3^+$: 282.1 and 284.1; found: 282.2 and 284.2, $[\text{M}-\text{PF}_6-\text{Br}]^{2+}$ calcd for $\text{C}_{12}\text{H}_{17}\text{N}_3^+$: 203.1; found: 203.2. LRMS-ESI (-ve): m/z calcd for $[\text{PF}_6]^-$: 145.0; found: 145.0, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.5. [1-(1-Pyridinium-yl-propyl)triethylammonium] (hexafluorophosphate) (bromide) (**4a**). Yield 75%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.21 (t, $J=7.1$ Hz, 9H), 2.34–2.47 (m, 2H), 3.22–3.38 (m, 8H), 4.77 (t, $J=7.7$ Hz, 2H), 8.21 (t, $J=7.1$ Hz, 2H), 8.66 (t, $J=7.4$ Hz, 1H), 9.25 (d, $J=6.6$ Hz, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 7.3, 23.7, 52.5, 52.6, 57.4, 128.2, 145.0, 146.0. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -70.4 (d, $J_{\text{P-F}}=709.2$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{26}\text{BrF}_6\text{N}_2\text{P}\cdot\text{H}_2\text{O}$: C, 36.14; H, 6.07; N, 6.02. Found: C, 36.47; H, 6.16; N, 5.98. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{27}\text{BrF}_6\text{N}_2\text{P}^+$: 447.1; found: 447.2, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{14}\text{H}_{26}\text{F}_6\text{N}_2\text{P}^+$: 367.2; found: 367.3, $[\text{M}-\text{PF}_6]^-$ calcd for $\text{C}_{14}\text{H}_{26}\text{BrN}_2^+$: 301.1 and 303.1; found: 301.3 and 303.3, $[\text{M}-\text{PF}_6-\text{Br}]^{2+}$ calcd for $\text{C}_{14}\text{H}_{26}\text{N}_2^+$: 222.2; found: 222.2. LRMS-ESI (-ve): m/z calcd for $[\text{PF}_6]^-$: 145.0; found: 145.0, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.6. [1-(1-Pyridinium-yl-propyl)methylpiperidinium] (hexafluorophosphate) (bromide) (**5a**). Yield 76%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.51–1.60 (m, 2H), 1.75–1.88 (m, 4H), 2.40–2.50 (m, 2H), 3.04 (s, 3H), 3.32–3.45 (m, 4H), 3.47–3.55 (m, 2H), 4.76 (t, $J=7.2$ Hz, 2H), 8.22 (t, $J=7.0$ Hz, 2H), 8.66 (t, $J=7.3$ Hz, 1H), 9.20 (d, $J=6.5$ Hz, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 19.3, 20.5, 23.4, 47.9, 57.7, 60.3, 128.2, 145.0, 145.9. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -70.4 (d, $J_{\text{P-F}}=708.1$ Hz). Anal. Calcd for $\text{C}_{14}\text{H}_{24}\text{BrF}_6\text{N}_2\text{P}\cdot\text{H}_2\text{O}$: C, 36.30; H, 5.66; N, 6.05. Found: C, 36.36; H, 5.50; N, 6.03. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{25}\text{BrF}_6\text{N}_2\text{P}^+$: 445.1; found: 445.1, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{14}\text{H}_{24}\text{F}_6\text{N}_2\text{P}^+$: 365.2; found: 365.2, $[\text{M}-\text{PF}_6]^-$ calcd for $\text{C}_{14}\text{H}_{24}\text{BrN}_2^+$: 299.1 and 301.1; found: 299.4 and 301.4, $[\text{M}-\text{PF}_6-\text{Br}]^{2+}$ calcd for $\text{C}_{14}\text{H}_{24}\text{N}_2^+$: 220.2; found: 220.4. LRMS-

ESI (-ve): m/z calcd for $[\text{PF}_6]^-$: 145.0; found: 145.0, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.7. [1-(1-Pyridinium-yl-propyl)methylpyrrolidinium] (hexafluorophosphate) (bromide) (**6a**). Yield 77%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.07–2.17 (m, 4H), 2.44–2.57 (m, 2H), 3.05 (s, 3H), 3.37–3.63 (m, 6H), 4.76 (t, $J=7.4$ Hz, 2H), 8.22 (t, $J=6.6$ Hz, 2H), 8.66 (t, $J=7.0$ Hz, 1H), 9.22 (d, $J=6.0$ Hz, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 21.2, 25.3, 47.9, 57.7, 59.3, 63.8, 128.2, 145.0, 145.9. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -70.4 (d, $J_{\text{P-F}}=710.6$ Hz). Anal. Calcd for $\text{C}_{13}\text{H}_{22}\text{BrF}_6\text{N}_2\text{P}\cdot\text{H}_2\text{O}$: C, 34.76; H, 5.39; N, 6.24. Found: C, 35.16; H, 5.19; N, 6.28. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{13}\text{H}_{23}\text{BrF}_6\text{N}_2\text{P}^+$: 431.1; found: 431.8, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{F}_6\text{N}_2\text{P}^+$: 351.1; found: 351.4, $[\text{M}-\text{PF}_6]^-$ calcd for $\text{C}_{13}\text{H}_{22}\text{BrN}_2^+$: 285.1 and 287.1; found: 285.4 and 287.4, $[\text{M}-\text{PF}_6-\text{Br}]^{2+}$ calcd for $\text{C}_{13}\text{H}_{22}\text{N}_2^+$: 206.2; found: 206.2. LRMS-ESI (-ve): m/z calcd for $[\text{PF}_6]^-$: 145.0; found: 145.1, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.8. [1-(1-Pyridinium-yl-propyl)-3-methylimidazolium] [bis(trifluoromethanesulfonyl)amide] (bromide) (**3b**). Yield 69%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 2.62 (quin, $J=7.0$ Hz, 2H), 3.91 (s, 3H), 4.39 (t, $J=7.0$ Hz, 2H), 4.80 (t, $J=7.0$ Hz, 2H), 7.75 (s, 1H), 7.86 (s, 1H), 8.21 (t, $J=7.0$ Hz, 2H), 8.67 (t, $J=7.3$ Hz, 1H), 9.23 (d, $J=6.4$ Hz, 2H), 9.28 (s, 1H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 30.9, 36.0, 45.9, 57.8, 119.5 (q, $J=319.7$ Hz), 122.3, 123.9, 128.4, 137.0, 145.0, 145.9. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -79.1. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{BrF}_6\text{N}_4\text{O}_4\text{S}_2\cdot\text{H}_2\text{O}$: C, 28.92; H, 3.29; N, 9.64. Found: C, 28.67; H, 3.34; N, 9.64. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{14}\text{H}_{18}\text{BrF}_6\text{N}_4\text{O}_4\text{S}_2$: 565.0; found: 565.4, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{14}\text{H}_{17}\text{F}_6\text{N}_4\text{O}_4\text{S}_2$: 483.1; found: 482.7, $[\text{M}-\text{NTf}_2]^+$ calcd for $\text{C}_{12}\text{H}_{17}\text{BrN}_3^+$: 282.1 and 284.1; found: 282.4 and 284.4, $[\text{M}-\text{NTf}_2-\text{Br}]^{2+}$ calcd for $\text{C}_{12}\text{H}_{17}\text{N}_3^+$: 203.1; found: 203.4. LRMS-ESI (-ve): m/z calcd for $[\text{NTf}_2]^-$: 279.9; found 279.9, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.9. [1-(1-Pyridinium-yl-propyl)triethylammonium] [bis(trifluoromethanesulfonyl)amide] (bromide) (**4b**). Yield 72%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): 1.22 (t, $J=6.7$ Hz, 9H), 2.34–2.48 (m, 2H), 3.23–3.39 (m, 8H), 4.79 (t, $J=7.3$ Hz, 2H), 8.23 (t, $J=6.8$ Hz, 2H), 8.67 (t, $J=7.1$ Hz, 1H), 9.29 (d, $J=6.3$ Hz, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 7.2, 23.6, 52.4, 52.5, 57.3, 119.5 (q, $J=319.9$ Hz), 128.1, 145.0, 145.9. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -79.0. Anal. Calcd for $\text{C}_{16}\text{H}_{26}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2\cdot\text{H}_2\text{O}$: C, 32.01; H, 4.70; N, 7.00. Found: C, 32.12; H, 4.53; N, 7.05. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{27}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2$: 584.1; found: 583.7, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{16}\text{H}_{26}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: 502.1; found: 501.8, $[\text{M}-\text{NTf}_2]^+$ calcd for $\text{C}_{14}\text{H}_{26}\text{BrN}_2^+$: 301.1 and 303.1; found: 301.4 and 303.4, $[\text{M}-\text{NTf}_2-\text{Br}]^{2+}$ calcd for $\text{C}_{14}\text{H}_{26}\text{N}_2^+$: 222.2; found: 222.4. LRMS-ESI (-ve): m/z calcd for $[\text{NTf}_2]^-$: 279.9; found 279.9, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 80.9.

2.3.10. [1-(1-Pyridinium-yl-propyl)methylpiperidinium] [bis(trifluoromethanesulfonyl)amide] (bromide) (**5b**). Yield 71%. ^1H NMR (400 MHz, $\text{DMSO}-d_6$): δ 1.54–1.64 (m, 2H), 1.69–1.95 (m, 4H), 2.43–2.57 (m, 2H), 3.08 (s, 3H), 3.38–3.46 (m, 4H), 3.53–3.60 (m, 2H), 4.76 (t, $J=7.1$ Hz, 2H), 8.24 (t, $J=7.0$ Hz, 2H), 8.67 (t, $J=7.3$ Hz, 1H), 9.27 (d, $J=6.6$ Hz, 2H). ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$): δ 19.3, 20.5, 23.6, 48.0, 57.7, 60.4, 119.5 (q, $J=320.0$ Hz), 128.2, 145.0, 145.9. ^{19}F NMR (282 MHz, $\text{DMSO}-d_6$): δ -79.1. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2\cdot\text{H}_2\text{O}$: C, 32.11; H, 4.38; N, 7.02. Found: C, 32.02; H, 4.26; N, 7.04. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{25}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2$: 582.0; found: 581.7, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{16}\text{H}_{24}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$: 500.1; found: 500.1, $[\text{M}-\text{NTf}_2]^+$ calcd for $\text{C}_{14}\text{H}_{24}\text{BrN}_2^+$: 299.1 and 301.1; found: 299.4 and 301.4, $[\text{M}-\text{NTf}_2-\text{Br}]^{2+}$ calcd for $\text{C}_{14}\text{H}_{24}\text{N}_2^+$: 220.2; found: 220.3. LRMS-ESI (-ve): m/z calcd for $[\text{NTf}_2]^-$: 279.9; found 280.0, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

2.3.11. [1-(1-Pyridinium-yl-propyl)methylpyrrolidinium] [bis(trifluoromethanesulfonyl)amide] (bromide) (**6b**). Yield 70%. ^1H NMR (400 MHz, DMSO- d_6): δ 2.11–2.19 (m, 4H), 2.50–2.62 (m, 2H), 3.09 (s, 3H), 3.50–3.66 (m, 6H), 4.76 (t, $J=7.3$ Hz, 2H), 8.24 (t, $J=7.1$ Hz, 2H), 8.68 (t, $J=7.4$ Hz, 1H), 9.28 (d, $J=6.6$ Hz, 2H). ^{13}C NMR (100 MHz, DMSO- d_6): δ 21.2, 25.4, 48.0, 57.7, 59.3, 63.9, 119.5 (q, $J=319.7$ Hz), 128.2, 145.0, 145.9. ^{19}F NMR (282 MHz, DMSO- d_6): δ -79.1. Anal. Calcd for $\text{C}_{15}\text{H}_{22}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2 \cdot \text{H}_2\text{O}$: C, 30.83; H, 4.14; N, 7.19. Found: C, 30.69; H, 3.99; N, 6.97. LRMS-ESI (+ve): m/z $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{15}\text{H}_{23}\text{BrF}_6\text{N}_3\text{O}_4\text{S}_2^+$: 568.0; found: 567.6, $[\text{M}-\text{Br}]^+$ calcd for $\text{C}_{15}\text{H}_{22}\text{F}_6\text{N}_3\text{O}_4\text{S}_2^+$: 486.1; found: 485.8, $[\text{M}-\text{NTf}_2]^+$ calcd for $\text{C}_{13}\text{H}_{22}\text{BrN}_2^+$: 285.1 and 287.1; found: 285.4 and 287.4, $[\text{M}-\text{NTf}_2-\text{Br}]^{2+}$ calcd for $\text{C}_{13}\text{H}_{22}\text{N}_2^{2+}$: 206.2; found: 206.3. LRMS-ESI (-ve): m/z calcd for $[\text{NTf}_2]^-$: 279.9; found 279.9, $[\text{Br}]^-$: 78.9 and 80.9; found: 79.0 and 81.0.

3. Results and discussion

3.1. Synthesis of dicationic ionic liquids that contain both hydrophilic and hydrophobic anions

As shown in Scheme 1, the synthesis of compounds **3a–6a** and **3b–6b** involves three steps. First, pyridine is used rather than strong nucleophiles, such as 1-methylimidazole, to react with 1,3-dibromopropane. Pyridine is used because it replaces only one bromine of 1,3-dibromopropane, whereas stronger nucleophiles would replace both bromines. In the second step, the Br^- ion in the product of the first step is anion exchanged with Y^- (PF_6^- and NTf_2^-). The yield of the anion exchange reaction was >95%. In the final step, a second base or nucleophile is used to conduct the $\text{S}_{\text{N}}2$ substitution reaction. The yields of compounds that contain PF_6^- are higher than those that contain NTf_2^- . This is probably due to the larger steric effect of NTf_2^- , which makes it difficult to attack the Br^- group.²⁰

3.2. Thermal stability

The thermal stability of the ILs synthesized in this study was studied using thermogravimetry analysis (TGA). The TGA curves recorded for the heteroanionic ILs are shown in Figure 1 and the thermal decomposition temperatures (T_d) estimated from these curves are collected in Table 1. Comparing the data in Table 1 to values reported in the literature, it was found that the thermal stability of the ILs synthesized in this study is lower than that of previously reported bromide-free dicationic ILs (for example, compound **9**,¹⁴ shown in Table 1) but higher than that of dicationic ILs containing di-bromide anions (for example, compound **7**,¹⁴ also shown in Table 1). This observation indicates that the thermal

stability of ILs may be related to the nucleophilicity of the bromide anion,^{11,21–23} which decreases the stability of the cations with increasing temperature. Table 1 also reveals that, with regard to the cation effect, ILs that contain the ILs that contain the triethylamine and 1-methylpiperidine cationic moiety (compounds **4a,b** and **5a,b**) have lower thermal stability than those that contain imidazolium (compounds **3a** and **3b**) or piperidine (compounds **5a** and **5b**) rings. This behavior is similar to that of most of the IL systems reported in the literature.^{5,23–25} With regard to the anion effect, Table 1 indicates that the thermal stability of PF_6^- -containing ILs does not significantly differ from that of NTf_2^- -containing ILs. This behavior is unusual since it is generally recognized that the PF_6^- anion more easily undergoes thermal decomposition than does the NTf_2^- anion.^{11,13–17,21,23} Possibly, the bromide anions in the ILs have a higher nucleophilicity to attack the electrophilic $\text{S}=\text{O}$ double bonds in NTf_2^- anions in initial weight loss step at elevated temperatures.^{26,27}

3.3. Melting point

The melting points of the organic salts synthesized in this study are collected in Table 1. We classify these organic salts as ionic liquids although the melting point of an ionic liquid should be usually lower than 100 °C. With regard to the cation effect, it can be seen that ILs that contain the imidazolium moiety have the lowest melting point, whereas ILs that contain the six-member ring 1-methylpiperidine moiety exhibit the highest melting point (compounds **5a** and **5b**). As suggested by Welton and Wasserscheid,⁵ this may be attributed to the relative degree of charge dispersion around the cation; imidazolium has good charge dispersion whereas 1-methylpiperidine does not.

Previous reports indicate that the melting point of dicationic ILs was affected by the anions and increased following the order: $\text{Br}^- > \text{PF}_6^- > \text{NTf}_2^-$.¹⁴ For example, compound **7** (162 °C) > **8** (131 °C) > **9** (-4 °C) (shown in Table 1). Matsumoto and Hagiwara²⁸ attributed such behavior to the symmetry of the anions; the bromide anion has the most symmetrical sphere, whereas PF_6^- anion is an octahedron, and NTf_2^- anion has the lowest symmetry in cis or trans forms (it also has S–N–S charge delocalization). Table 1 also shows that, similar to previous reports for other kinds of IL, among the heteroanion dicationic ILs synthesized in this study, the melting points of ILs that contain NTf_2^- anions are lower than those of the corresponding ILs that contain PF_6^- anions.

3.4. Solubility

The solubility of the synthesized heteroanionic ILs in several selected solvents is summarized in Table 2. Early research^{14–17,29}

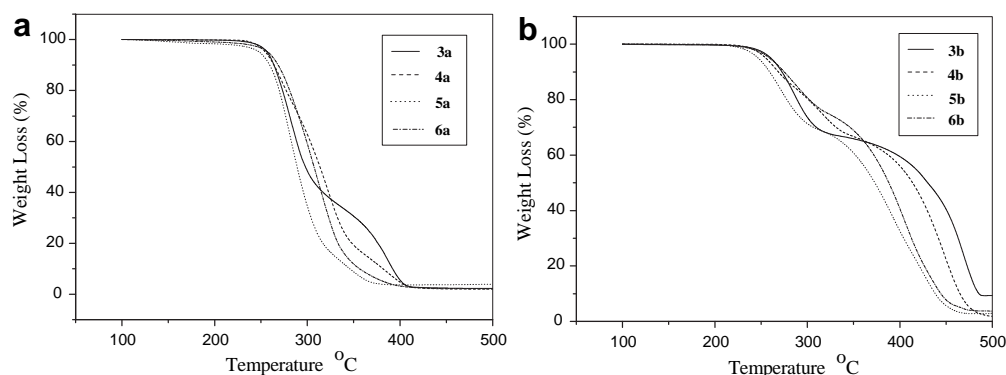


Figure 1. TGA curves of synthesized heteroanionic ionic liquids for (a) PF_6^- and Br^- system, and (b) NTf_2^- and Br^- system.

Table 1
Comparison of melting points and T_d values between the heteroanionic ionic liquids synthesized in this study and dicationic ILs reported in the literature

Structure	Mp (°C)	T_d (°C) ^a	T_d (°C) ^b	Structure	Mp (°C)	T_d (°C) ^a	T_d (°C) ^b
	150–151	252	265		107–108	239	260
	180–181	244	264		92–93	249	274
	186–187	250	259		162 ^c	240	250
	169–170	252	268		131 ^c	320	350
	34–35	246	271		–4 ^c	401	410
	76–77	240	263				

^a T_d onset.

^b T_d in 10% weight loss.

^c Reported in Ref. 14.

Table 2
Comparison of solubility in various organic solvents between heteroanionic ionic liquids synthesized in this study (+: soluble, -: insoluble)

	H ₂ O	MeOH	EtOH	Hexane	Et ₂ O	THF	EtOAc	Acetone	CH ₂ Cl ₂
3a	+	+	+	–	–	–	–	–	–
4a	+	+	+	–	–	–	–	–	–
5a	+	+	+	–	–	–	–	–	–
6a	+	+	+	–	–	–	–	–	–
3b	+	+	+	–	–	–	–	–	–
4b	+	+	+	–	–	–	–	–	–
5b	+	+	+	–	–	–	–	–	–
6b	+	+	+	–	–	–	–	–	–

indicated that the solubility behavior of geminal dicationic ILs was quite similar to that of monocationic ionic liquids, i.e., PF₆[–] and NTf₂[–] salts, such as compounds **8** and **9**, are immiscible with water, MeOH, and EtOH, whereas Br[–] salts are miscible with these solvents.^{14–17} On the other hand, the PF₆[–] and NTf₂[–] salts are soluble in acetone, tetrahydrofuran (THF), and EtOAc. Table 2 indicates that the synthesized heteroanionic ILs are soluble in water, MeOH, and EtOH, but not in acetone, EtOAc, THF, Et₂O, CH₂Cl₂, and hexane (shown in Table 2). Apparently the heteroanionic ILs exhibit solubility behavior, that is, opposite to that of previously reported

geminal dicationic ILs containing PF₆[–] and NTf₂[–] even though the heteroanionic ILs contain PF₆[–] and NTf₂[–]. The presence of Br[–] anions in heteroanionic ILs makes the ILs behave more like Br[–]-containing monocationic and geminal dicationic ILs. Because the solubility of ILs in solvents is affected by factors such as the dielectric constant and polarity of the solvents, hydrogen bonding,³⁰ and π – π interaction, more detailed studies (such as NMR and Raman spectroscopy) are needed to gain more insight into the solubility behavior of the ILs in various solvents.

4. Conclusion

Dicationic ILs that contain hydrophobic and hydrophilic heteroanions were successfully synthesized. The heteroanionic ionic liquids are miscible with water, MeOH, and EtOH but not with acetone, EtOAc, THF, Et₂O, CH₂Cl₂, and hexane. These heteroanionic ILs are also miscible with MeOH/Et₂O and MeOH/EtOAc co-solvents. Currently, application of these ILs as stationary phase for gas chromatography and for solid phase extraction is being investigated and the results will be reported elsewhere. It appears that the Br[–] anions of the synthesized heteroanionic ILs have a strong influence on the properties of these ILs. The tuning of the physical properties of ILs in a dicationic system can be achieved by

using two types of anion. The synthesis and characterization of other heteroanionic ILs with anions other than Br⁻ are in progress.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2010.05.105. These data include MOL files and InChIKeys of the most important compounds described in this article.

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