SUPPORTING INFORMATION

Diol-functionalized Imidazolium-based Room-temperature Ionic Liquids with Bis(trifluoromethanesulfonimide) Anions that Exhibit Variable Water Miscibility

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General Considerations

Unless otherwise noted, all reagents were purchased from commercial suppliers and were used without further purification, with the exception of 1-ethyl- and 1-propylimidazole, which were prepared following a literature procedure.[1] ^{1}H NMR spectra were recorded on a 400 MHz Varian instrument and ^{13}C NMR were recorded at 100 MHz on the same instrument. NMR spectra are reported in ppm and were referenced to the solvent peak and processed using ACD Labs 5.0 software. ESI mass spectra were recorded using the Applied Biosystems QSTAR Hybrid LC/MS/MS System mass spectrometer. K^+ content was determined using an Applied Research Laboratories 3410+ inductively coupled plasma-optical emission spectrometer. Cl^- content was determined using a Dionex Series 4500i Ion Chromatograph. Water content was measured using a Mettler Toledo DL32 Karl Fischer Coulometer. Elemental analyses were conducted by Galbraith Laboratories (Knoxville, TN).

1-(2,3-Dihydroxypropyl)-3-methylimidazolium Chloride (1)

1-Methylimidazole (8.21 g, 100 mmol) and 3-chloro-1,2-propanediol (11.05 g, 100.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The residue was then dissolved in CH_3OH, transferred to a tared flask and concentrated to afford the product as a viscous brown oil (19.3 g, 100%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 3.19 - 3.29 (m, 1 H) 3.36 - 3.48 (m, 1 H) 3.77 (dd, *J*=6.78, 4.21 Hz, 1 H) 3.87 (s, 3 H) 4.10 (dd, *J*=13.74, 7.69 Hz, 1 H) 4.32 (dd, *J*=13.74, 3.11 Hz, 1 H) 5.13 (br. s., 1 H) 5.53 (d, *J*=5.13 Hz, 1 H) 7.72 (t, *J*=1.74 Hz, 1 H) 7.74 (t, *J*=1.74 Hz, 1 H) 9.18 (s, 1 H).

1-(2,3-Dihydroxypropyl)-2,3-dimethylimidazolium Chloride (2)

1,2-Dimethylimidazole (9.61 g, 100 mmol) and 3-chloro-1,2-propanediol (11.05 g, 100.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The product was then stirred in refluxing ether for 24 h and filtered to afford a brown solid (20.29 g, 100%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-

1. Bara, J. E.; Lessmann, S.; Gabriel, C. J.,; Hatakeyama, E. S.; Noble, R. D.; Gin, D. L. *Ind. Eng. Chem. Res.* **2007**, 46, 5397-5404.

d_6) 2.60 (s, 3 H) 3.20 - 3.33 (m, 1 H) 3.36 - 3.49 (m, 2 H) 3.78 (s, 3 H) 4.08 (dd, *J*=14.11, 7.88 Hz, 1 H) 4.27 (dd, *J*=14.11, 3.11 Hz, 1 H) 5.14 (t, *J*=5.50 Hz, 1 H) 5.50 (d, *J*=5.68 Hz, 1 H) 7.63 (d, *J*=2.01 Hz, 1 H) 7.66 (d, *J*=2.20 Hz, 1 H).

1-(2,3-Dihydroxypropyl)-3-ethylimidazolium Chloride (3)
1-Ethylimidazole (2.40 g, 25.0 mmol) and 3-chloro-1,2-propanediol (2.76 g, 25.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The residue was then dissolved in CH_3OH, transferred to a tared flask and concentrated to afford the product as a viscous brown oil (4.88 g, 94%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 1.41 (t, *J*=7.24 Hz, 3 H) 3.23 (dd, *J*=11.17, 6.96 Hz, 1 H) 3.37 - 3.47 (m, 1 H) 3.70 - 3.86 (m, 1 H) 4.11 (dd, *J*=13.74, 7.69 Hz, 1 H) 4.22 (q, *J*=7.33 Hz, 2 H) 4.33 (dd, *J*=13.74, 3.11 Hz, 1 H) 5.19 (br. s., 1 H) 5.59 (br. s., 1 H) 7.78 (t, *J*=1.74 Hz, 1 H) 7.85 (t, *J*=1.74 Hz, 1 H) 9.33 (t, *J*=1.56 Hz, 1 H).

1-(2,3-Dihydroxypropyl)-3-propylimidazolium Chloride (4)
1-Propylimidazole (2.75 g, 25.0 mmol) and 3-chloro-1,2-propanediol (2.76 g, 25.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The residue was then dissolved in CH_3OH, transferred to a tared flask and concentrated to afford the product as a viscous brown oil (5.20 g, 95%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 0.84 (t, *J*=7.42 Hz, 3 H) 1.74 - 1.86 (m, 2 H) 3.22 (dd, *J*=11.17, 6.96 Hz, 1 H) 3.42 (dd, *J*=10.99, 4.95 Hz, 1 H) 4.07 - 4.20 (m, 3 H) 4.33 (dd, *J*=13.74, 3.11 Hz, 1 H) 5.15 (br. s., 1 H) 5.56 (br. s., 1 H) 7.78 (t, *J*=1.74 Hz, 1 H) 7.82 (t, *J*=1.83 Hz, 1 H) 9.29 (t, *J*=1.47 Hz, 1 H).

1-(2,3-Dihydroxypropyl)-3-butylimidazolium Chloride (5)
1-Butylimidazole (12.42 g, 100.0 mmol) and 3-chloro-1,2-propanediol (11.05 g, 100.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The residue was then dissolved in CH_3OH, transferred to a tared flask, and concentrated to afford the product as a viscous brown oil (23.27 g, 92%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 0.89 (t, 3 H) 1.17 - 1.31 (m, 2 H) 1.69 - 1.83 (m, 2 H) 3.19 - 3.28 (m, 1 H) 3.37 - 3.46 (m, 1 H) 3.78 (dd, *J*=7.05, 4.49 Hz, 1 H) 4.12 (dd, *J*=13.83, 7.60 Hz, 1 H) 4.20 (t, *J*=7.14 Hz, 2 H) 4.33 (dd, *J*=13.74, 3.11 Hz, 1 H) 5.16 (br. s., 1 H) 5.56 (d, *J*=5.31 Hz, 1 H) 7.78 (t, *J*=1.74 Hz, 1 H) 7.83 (t, *J*=1.74 Hz, 1 H) 9.30 (t, *J*=1.47 Hz, 1 H).

1-(2,3-Dihydroxypropyl)-3-benzylimidazolium Chloride (6)
1-Benzylimidazole (3.95 g, 25.0 mmol) and 3-chloro-1,2-propanediol (2.76 g, 25.0 mmol) were stirred in a 130 ^{o}C oil bath for 48 h, after which the flask was placed under vacuum and stirring continued at 130 ^{o}C for another 48 h. The residue was then dissolved in CH_3OH and transferred to a tared flask and concentrated to afford the product as a viscous brown oil (6.50 g, 97%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 3.18 - 3.30 (m, 1 H) 3.37 - 3.49 (m, 1 H) 3.73 - 3.86 (m, 1 H) 4.15 (dd, *J*=13.74, 7.69 Hz, 1 H) 4.36 (dd, *J*=13.74, 3.11 Hz, 1 H) 5.21 (t, *J*=5.50 Hz, 1 H) 5.49 (s, 2 H) 5.62 (d, *J*=5.50 Hz, 1 H) 7.32 - 7.50 (m, 5 H) 7.80 (t, *J*=1.83 Hz, 1 H) 7.86 (t, *J*=1.83 Hz, 1 H) 9.49 (t, *J*=1.56 Hz, 1 H).

1-(2,3-Dihydroxypropyl)-3-methylimidazolium Bis(trifluoromethanesulfonimide) (7)

1-(2,3-Dihydroxypropyl)-3-methylimidazolium chloride (**1**, 1.71 g, 8.88 mmol) and KTf_2N (2.83 g, 8.88 mmol) were stirred in CH_3CN (10 mL) for 24 h, then filtered through Celite and concentrated to give an orange/brown oil (3.92 g, 100%). ^1H NMR: δ_H ppm (400 MHz; DMSO-d_6) 3.20 - 3.30 (m, 1 H) 3.43 (dd, *J*=10.90, 4.67 Hz, 1 H) 3.77 (dd, *J*=6.69, 4.49 Hz, 1 H) 3.86 (s, 3 H) 4.06 (dd, *J*=13.74, 8.06 Hz, 1 H) 4.29 (dd, *J*=13.74, 2.93 Hz, 1 H) 4.95 (br. s., 1 H) 5.33 (d, *J*=4.95 Hz, 1 H) 7.66 - 7.69 (m, 2 H) 9.05 (s, 1 H). ^{13}C NMR: δ_C ppm (100 MHz; DMSO-d_6) 35.69, 52.17, 62.72, 119.51 (q, CF_3, *J*=322.64 Hz), 123.17, 123.20, 137.09. HRMS: Calc'd for $C_{16}H_{26}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 594.1127. Found: 594.1096. Elemental Analysis: Calc'd: C, 24.72%; H, 3.00%; N, 9.61%; Found: C, 24.54%; H, 2.88%, N, 9.37%. H_2O content: 423 ppm.

1-(2,3-Dihydroxypropyl)-2,3-dimethylimidazolium Bis(trifluoromethanesulfonimide) (8)
1-(2,3-Dihydroxypropyl)-2,3-dimethylimidazolium chloride (**2**, 4.13 g, 20.0 mmol) and $LiTf_2N$ (6.32 g, 22.0 mmol) were dissolved in water (50 mL) and stirred for 24 h. The mixture was then diluted with EtOAc (100 mL) and washed with water (5 x 25 mL) until no precipitate formed in the aqueous layer upon adding $AgNO_3$. The EtOAc layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as an orange/brown oil (5.87 g, 64%). ^1H NMR: δ_H ppm (400 MHz; DMSO-d_6) 2.58 (s, 3 H) 3.29 (dd, *J*=10.99, 6.59 Hz, 1 H) 3.44 (dd, *J*=10.99, 4.95 Hz, 1 H) 3.76 (s, 4 H) 4.04 (dd, *J*=14.56, 7.60 Hz, 1 H) 4.23 (dd, *J*=14.29, 3.11 Hz, 1 H) 4.94 (br. s., 1 H) 5.23 (br. s., 1 H) 7.55 (d, *J*=2.20 Hz, 1 H) 7.59 (d, *J*=2.01 Hz, 1 H). ^{13}C NMR: δ_C ppm (100 MHz; DMSO-d_6) 9.62, 34.79, 50.95, 62.85, 70.30, 119.69 (q, CF_3, *J*=317.42 Hz), 121.96, 122.14, 145.18. HRMS: Calc'd for $C_{18}H_{30}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 622.1440. Found: 622.1438. Elemental Analysis: Calc'd: C, 26.61%; H, 3.35%; N, 9.31%; Found: C, 26.12%; H, 2.98%, N, 9.11%. H_2O content: 443 ppm.

1-(2,3-Dihydroxypropyl)-3-ethylimidazolium Bis(trifluoromethanesulfonimide) (9)
1-(2,3-Dihydroxypropyl)-3-ethylimidazolium chloride (**3**, 2.85 g, 13.8 mmol) and KTf_2N (4.40 g, 13.8 mmol) were stirred in CH_3CN (10 mL) for 24 h, then filtered through Celite and concentrated to give an orange/brown oil (6.25 g, 100%). ^1H NMR: δ_H ppm (400 MHz; DMSO-d_6) 1.42 (t, *J*=7.24 Hz, 3 H) 3.26 (dd, *J*=10.90, 6.69 Hz, 1 H) 3.43 (dd, *J*=10.99, 4.95 Hz, 1 H) 3.77 (br. s., 1 H) 4.06 (dd, *J*=13.74, 8.06 Hz, 1 H) 4.21 (q, *J*=7.33 Hz, 2 H) 4.29 (dd, *J*=13.83, 3.02 Hz, 1 H) 4.95 (br. s., 1 H) 5.33 (br. s., 1 H) 7.70 (t, *J*=1.74 Hz, 1 H) 7.78 (t, *J*=1.74 Hz, 1 H) 9.12 (t, *J*=1.56 Hz, 1 H). ^{13}C NMR: δ_C ppm (100 MHz; DMSO-d_6) 15.17, 44.16, 52.27, 62.78, 69.64, 119.51 (q, CF_3, *J*=321.87 Hz), 121.68, 123.33, 136.29. HRMS: Calc'd for $C_{18}H_{30}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 622.1440. Found: 622.1432. Elemental Analysis: Calc'd: C, 26.61%; H, 3.35%; N, 9.31%; Found: C, 26.20%; H, 3.08%, N, 9.03%. H_2O content: 452 ppm.

1-(2,3-Dihydroxypropyl)-3-propylimidazolium Bis(trifluoromethanesulfonimide) (10)
1-(2,3-Dihydroxypropyl)-3-propylimidazolium chloride (**4**, 3.40 g, 15.4 mmol) and $LiTf_2N$ (4.85 g, 16.9 mmol) were dissolved in water (40 mL) and stirred for 24 h. The mixture was then diluted with EtOAc (100 mL) and washed with water (5 x 25 mL) until no precipitate formed in the aqueous layer upon adding $AgNO_3$. The EtOAc layer was then dried over anhydrous $MgSO_4$, filtered and concentrated to give the product as an orange/brown oil (4.27 g, 60%). ^1H NMR: δ_H ppm (400 MHz; DMSO-d_6) 0.85 (t, *J*=7.42 Hz, 3 H) 1.71 - 1.88 (m, 2 H) 3.25 (dd, *J*=10.99, 6.78 Hz, 1 H) 3.43 (dd, *J*=10.99, 4.95 Hz, 1 H) 3.78 (br. s., 1 H) 3.99 - 4.11 (m, 1 H) 4.14 (t, *J*=7.05 Hz, 2 H) 4.30 (dd, *J*=13.83, 3.02 Hz, 1 H) 4.96 (br. s., 1 H) 5.34 (br. s., 1 H) 7.71 (t, *J*=1.74 Hz, 1 H) 7.77 (t, *J*=1.74 Hz, 1 H) 9.12 (t, *J*=1.47 Hz, 1 H). ^{13}C NMR: δ_C ppm (100

MHz; DMSO-d_6) 10.37, 22.97, 50.36, 52.32, 62.81, 69.67, 119.59 (q, CF_3, J=322.07 Hz), 122.00, 123.43, 136.69. HRMS: Calc'd for $C_{20}H_{34}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 650.1753. Found: 650.1726. Elemental Analysis: Calc'd: C, 28.39%; H, 3.68%; N, 9.03%; Found: C, 28.06%; H, 3.15%, N, 8.60%. H_2O content: 459 ppm.

1-(2,3-Dihydroxypropyl)-3-butylimidazolium Bis(trifluoromethanesulfonimide) (11)
1-(2,3-Dihydroxypropyl)-3-butylimidazolium chloride (**5**, 5.09 g, 20.0 mmol) and $LiTf_2N$ (6.32 g, 22.0 mmol) were dissolved in water (50 mL) and stirred for 24 h. The mixture was then diluted with EtOAc (100 mL) and washed with water (5 x 25 mL) until no precipitate formed in the aqueous layer upon adding $AgNO_3$. The EtOAc layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as an orange/brown oil (4.27 g, 44%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 0.90 (t, 3 H) 1.20 - 1.32 (m, 2 H) 1.71 - 1.85 (m, 2 H) 3.20 - 3.31 (m, 1 H) 3.38 - 3.50 (m, 1 H) 3.71 - 3.85 (m, 1 H) 4.07 (dd, J=13.83, 7.97 Hz, 1 H) 4.18 (t, J=7.14 Hz, 2 H) 4.30 (dd, J=13.83, 3.02 Hz, 1 H) 4.95 (br. s., 1 H) 5.34 (d, J=5.13 Hz, 1 H) 7.70 (t, J=1.74 Hz, 1 H) 7.77 (t, J=1.74 Hz, 1 H) 9.12 (t, J=1.47 Hz, 1 H). ^{13}C NMR: δ_C ppm (100 MHz; DMSO-d_6) 13.28, 18.83, 31.47, 48.58, 52.29, 62.80, 69.64, 119.54 (q, CF_3, J=322.24 Hz), 121.98, 123.39 136.68. HRMS: Calc'd for $C_{22}H_{38}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 678.2066. Found: 678.2042. Elemental Analysis: Calc'd: C, 30.06%; H, 3.99%; N, 8.76%; Found: C, 29.94%; H, 3.83%, N, 8.47%. H_2O content: 379 ppm.

1-(2,3-Dihydroxypropyl)-3-benzylimidazolium Bis(trifluoromethanesulfonimide) (12)
1-(2,3-Dihydroxypropyl)-3-benzylimidazolium chloride (**6**, 2.04 g, 7.60 mmol) and $LiTf_2N$ (2.40 g, 8.30 mmol) were dissolved in water (20 mL) and stirred for 24 h. The mixture was then diluted with EtOAc (100 mL) and washed with water (5 x 25 mL) until no precipitate formed in the aqueous layer upon adding $AgNO_3$. The EtOAc layer was then dried over anhydrous $MgSO_4$, filtered, and concentrated to give the product as an orange/brown oil (3.76 g, 95%). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 3.26 (dd, J=10.35, 7.05 Hz, 1 H) 3.44 (dd, J=10.90, 4.85 Hz, 1 H) 3.72 - 3.85 (m, 1 H) 4.10 (dd, J=13.92, 8.06 Hz, 1 H) 4.32 (dd, J=13.74, 2.93 Hz, 1 H) 4.96 (br. s., 1 H) 5.37 (d, J=4.95 Hz, 1 H) 5.44 (s, 2 H) 7.35 - 7.48 (m, 5 H) 7.72 (t, J=1.74 Hz, 1 H) 7.79 (t, J=1.74 Hz, 1 H) 9.26 (t, J=1.56 Hz, 1 H). *^{13}C NMR:* δ_C ppm (100 MHz; DMSO-d_6) 51.88, 52.39, 62.80, 69.56, 119.53 (q, CF_3, J=321.87 Hz), 122.09, 123.76, 128.22, 129.03, 134.95, 136.81. HRMS: Calc'd for $C_{28}H_{34}F_6N_5O_8S_2$ $[A^+][A^+][B^-]$: 746.1753. Found: 746.1760. Elemental Analysis: Calc'd: C, 34.67%; H, 3.35%; N, 8.18%; Found: C, 35.09%; H, 3.11%, N, 7.85%. H_2O content: 483 ppm.

1,3-*Bis*-(2-hydroxyethyl)-imidazolium Bis(trifluoromethanesulfonimide) (13)
1-(2-hydroxyethyl)-imidazole (5.68 g, 50.7 mmol) was dissolved in CH_3CN (45 mL), then 2-bromoethanol (6.97 g, 55.8 mmol) was added and the reaction heated to reflux and stirred for 16 h. After several hours, a white precipitate formed. The flask was then cooled, the solid filtered and washed with Et_2O (250 ml) and dried under vacuum to produce 10.51 g of a white powder. 10.00 g of this white powder were dissolved in deionized H_2O (50 mL) and $LiTf_2N$ (13.33 g, 46.42 mmol) was added. A yellow oil immediately formed at the bottom of the flask and reaction was stirred for several hours at room temperature. The oil was taken up in EtOAc (200 mL) and washed with deionized H_2O (5 x 100 mL). The fourth and fifth aqueous washings were free of halides as confirmed lack of precipitate upon addition of by addition of $AgNO_3$. The organic phase was dried over anhydrous $MgSO_4$, followed by addition of activated carbon. This

mixture was filtered through basic Al_2O_3, which was washed with EtOAc (100 mL). The filtrate was concentrated, and the product dried under vacuum at 65 ^{o}C overnight to produce **13** as a pale yellow, gel-like solid. (8.55 g, 46.3 %). ^{1}H NMR: δ_H ppm (400 MHz; DMSO-d_6) 3.74 (t, *J*=4.49 Hz, 4 H) 4.15 - 4.32 (m, 4 H) 5.17 (br. s., 2 H) 7.72 (d, *J*=1.65 Hz, 2 H) 9.10 (s, 1 H).