
Supplementary Information

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Supplementary Information

1. Synthesis of Ionic Liquids

Trihexyl(tetradecyl)ammonium chloride, [N_{6,6,6,14}][Cl]

Trihexyl(tetradecyl)ammonium bromide (3.3 g, 6.0 mmol) was dissolved in methanol and eluted through a column containing Amberlite-IRA400 (Cl) ion-exchange resin (40 g) at a drop rate of 1 ml/min. Solvent removed and product dried in vacuo at 50 °C to yield an off-white solid (3.0 g, 100%). 1H NMR (400 MHz, CDCl3): δ ppm 0.81 – 0.86 (m, 12H), 1.20 – 1.36 (m, 40H), 1.57 – 1.68 (m, 8H), 3.30 – 3.34 (m, 8H); 13C NMR (100 MHz, CDCl3): δ ppm 13.7, 14.0, 22.1, 22.3, 22.5, 25.9, 26.3, 29.0, 29.2, 29.3, 29.5, 31.1, 31.8, 59.0; IR ν max (CHCl3)/cm⁻¹ 1246, 1468, 2858, 2929; MS (ESI) positive for C_{33}H_{60}N_{13}, M⁺: calcd 466.5346, found 466.5346.

Trihexyl(tetradecyl)ammonium tetrafluoroborate, [N_{6,6,6,14}][BF₄]

To a stirring solution of trihexyl(tetradecyl)ammonium bromide (2.2 g, 4.0 mmol) in chloroform (15 ml) a solution of sodium tetrafluoroborate (0.6 g, 5.4 mmol) was added dropwise at room temperature. Reaction mixture stirred for 16 h. Chloroform (40 ml) and water (15 ml) added, organic layer separated and washed with water (6 x 25 ml). Solvent removed and product dried in vacuo at 50 °C to yield a white solid (1.7 g, 78%). 1H NMR (400 MHz, CDCl3): δ ppm 0.86 – 0.90 (m, 12H), 1.25 – 1.34 (m, 40H), 1.54 – 1.66 (m, 8H), 3.15 – 3.20 (m, 8H); 13C NMR (100 MHz, CDCl3): δ ppm 13.8, 14.1, 25.8, 26.2, 29.0, 29.3, 29.4, 29.6, 31.1, 31.9, 58.6; 19F NMR (377 MHz, CDCl3): δ ppm -151.79 (q, J = 1.1 Hz), -151.73 (br. s); IR ν max (CHCl3)/cm⁻¹ 1059, 1468, 2857, 2929, 2959; MS (ESI) positive for C_{32}H_{68}N_{13}, M⁺: calcd 466.5346, found 466.5333

Trihexyl(tetradecyl)ammonium hexafluorophosphate, [N_{6,6,6,14}][PF₆]

To a stirring suspension of trihexyl(tetradecyl)ammonium bromide (1.9 g, 3.4 mmol) in water (30 ml) an aqueous solution of hexafluorophosphoric acid (60 % w/w, 0.6 ml) was added dropwise using a plastic syringe. Reaction mixture stirred for 16 h at room temperature. Chloroform (55 ml) added and organic layer separated and washed with water (6 x 25 ml). Solvent removed and product dried in vacuo at 50 °C to yield a white, waxy solid (2.0 g, 95 %). 1H NMR (400 MHz, CDCl3): δ ppm 0.86 – 0.91 (m, 12H), 1.26 – 1.34 (m, 40H), 1.54 – 1.65 (m, 8H), 3.12 – 3.16 (m, 8H); 13C NMR (100 MHz, CDCl3): δ ppm 13.8, 14.1, 21.7, 22.3, 22.7, 25.8, 26.1, 29.0, 29.3, 29.4, 29.6, 29.7, 31.0, 31.9, 58.6; 31P NMR (162 MHz, CDCl3): δ ppm -144.38 (spt, J = 713 Hz); 19F NMR (377 MHz, CDCl3): δ ppm -72.30 (d, J = 713 Hz); IR ν max (CHCl3)/cm⁻¹ 848, 1468, 2857, 2929; MS (ESI) positive for C_{33}H_{68}N_{13}, M⁺: calcd 466.5346, found 466.5347.
Trihexyl(tetradecyl)ammonium trifluoromethanesulfonate, [N_{6,6,6,14}][OTf]

To a stirring solution of trihexyl(tetradecyl)ammonium bromide (1.8 g, 3.3 mmol) in chloroform (15 ml) a solution of lithium trifluoromethanesulfonate (0.6 g, 4.0 mmol) in water (15 ml) was added dropwise at room temperature. Reaction mixture stirred for 16 h. Chloroform (40 ml) and water (15 ml) added, organic layer separated and washed with water (6 x 25 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a pale yellow, viscous liquid (1.9 g, 93 %). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.86 – 0.91 (m, 12H), 1.25 – 1.37 (m, 40H), 1.56 – 1.68 (m, 8H), 3.18 – 3.22 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 13.8, 14.1, 21.9, 22.3, 22.6, 25.9, 26.2, 29.0, 29.3, 29.4, 29.6, 31.1, 31.9, 58.8; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -78.18; IR ν max (CHCl$_3$/cm$^{-1}$) 1030, 1164, 1269, 1468, 2857, 2929, 3011; MS (ESI) positive for C$_{32}$H$_{68}$N$_4$, M$: $^+_+$ calcd 466.5346, found 466.5356.

Trihexyl(tetradecyl)ammonium bis(trifluoromethanesulfonimide)limide, [N_{6,6,6,14}][NTf$_2$]

To a stirring solution of trihexyl(tetradecyl)ammonium bromide (1.5 g, 2.7 mmol) dissolved in chloroform (15 ml), a solution of lithium bis(trifluoromethanesulfonimide) (1.0 g, 3.3 mmol) in water (15 ml) was added dropwise. Reaction mixture stirred for 16 h at room temperature. Chloroform (40 ml) and water (15 ml) added, organic layer separated and washed with water (6 x 25 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a pale yellow, viscous liquid (1.9 g, 96 %). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.87 – 0.92 (m, 12H), 1.26 – 1.37 (m, 40H), 1.54 – 1.65 (m, 8H), 3.12 – 316 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 13.7, 14.1, 21.8, 22.3, 22.7, 25.8 26.1, 28.9, 29.3, 29.4, 29.6, 31.0, 31.9, 58.7; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -78.73; IR ν max (CHCl$_3$/cm$^{-1}$) 1059, 1137, 1192, 1351, 1468, 1482, 2858, 2929, 2959; MS (ESI) positive for C$_{32}$H$_{68}$N$_4$, M$: $^+_+$ calcd 466.5346, found 466.5349.

TrIBUTYL(METHYL)AMMONIUM TETRAFLUOROBORATE, [N_{4,4,4,1}][BF$_4$]

To a stirring solution of tributyl(methyl)ammonium bromide (2.9 g, 10.4 mmol) in water (20 ml) a solution of sodium tetrafluoroborate (1.7 g, 15.7 mmol) in water was added dropwise. Reaction mixture stirred vigorously for 16 h at room temperature. Dichloromethane (50 ml) added and organic layer separated and washed with water (6 x 25 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a white solid (2.1 g, 72 %). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.95 – 0.99 (t, J = 7.3 Hz, 9H), 1.35 – 1.44 (m, 6H), 1.60 – 1.68 (m, 6H), 3.01 (s, 3H), 3.22 (m, AA’BB’ system, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 13.4, 19.5, 24.0, 48.2, 61.4; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -151.25 (q, J = 1.1 Hz), -151.73 (br. s); IR ν max (CHCl$_3$/cm$^{-1}$) 1061, 1466, 2879, 2938, 2968, 3045; MS (ESI) positive for C$_{13}$H$_{30}$N$_4$, M$: $^+_+$ calcd 200.2373, found 200.2379.
**Trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonil)imide, [N\textsubscript{4,4,4,1}][NTf\textsubscript{2}]**

To a stirring solution of trihexyl(methyl)ammonium bromide (2.9 g, 10.4 mmol) in chloroform (25 ml) a solution of lithium bis(trifluoromethanesulfonylimide) (3.6 g, 12.5 mmol) in water (25 ml) was added dropwise at room temperature. Reaction mixture was stirred for 16 h. Chloroform (75 ml) and water (25 ml) added, organic layer separated and washed with water (6 x 50 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a colourless, viscous liquid (4.5 g, 91 %). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): δ ppm 0.98–1.01 (t, J = 7.3 Hz, 9H), 1.36 – 1.45 (m, 6H), 1.60 – 1.68 (m, 6H), 2.99 (s, 3H), 3.20 (m, AA’BB’ system, 6H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): δ ppm 13.4, 19.4, 24.1,48.4, 61.7, 118.3, 121.5; \(^{19}\)F NMR (377 MHz, CDCl\textsubscript{3}): δ ppm -78.90; IR ν max (CHCl\textsubscript{3})/cm\(^{-1}\): 1059, 1137, 1192, 1351, 1474, 2879, 2969; MS (ESI) positive for C\textsubscript{13}H\textsubscript{30}N\textsubscript{3}, M\textsuperscript{+}: calcd 200.2373, found 200.2381.

**Trihexyl(tetradecyl)phosphonium tetrafluoroborate, [P\textsubscript{6,6,6,14}][BF\textsubscript{4}]**

Trihexyl(tetradecyl)phosphonium chloride (5.2 g, 10.0 mmol) was suspended in water (15 ml), a solution of sodium tetrafluoroborate (1.3 g, 11.8 mmol) in water (10 ml) was added dropwise at 0 °C with vigorous stirring. Reaction mixture allowed to warm to ambient temperature and stirred for 16 h then extracted with diethyl ether (4 x 25 ml). Combined organic extracts were washed with aqueous 1 % sodium hydroxide solution (2 x 7.5 ml) followed by water (6 x 50 ml). Solvent removed and product dried *in vacuo* at 50 °C to colourless, viscous liquid which solidified on cooling (5.4 g, 96 %). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): δ ppm 0.86 – 0.91 (m, 12H), 1.26 – 1.34 (m, 32H), 1.44 – 1.58 (m, 16H), 2.13 – 2.20 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): δ ppm 13.9, 14.1, 18.5, 18.9, 21.6, 21.7, 22.3, 22.6, 28.9, 29.3, 29.5, 29.6, 30.3, 30.4, 30.6, 30.8, 30.9, 31.9; \(^{31}\)P NMR (162 MHz, CDCl\textsubscript{3}): δ ppm +32.80; \(^{19}\)F NMR (377 MHz, CDCl\textsubscript{3}): δ ppm -151.47 (q, J = 1.4 Hz), -151.41 (br. s); MS (ESI) positive for C\textsubscript{32}H\textsubscript{68}P\textsubscript{14}, M\textsuperscript{+}: calcd 483.5053, found 483.5039. Data in agreement to literature.\(^1\)

**Trihexyl(tetradecyl)phosphonium hexafluorophosphate, [P\textsubscript{6,6,6,14}][PF\textsubscript{6}]**

Trihexyl(tetradecyl)phosphonium chloride (5.4 g, 10.4 mmol) was suspended in water (60 ml), an aqueous solution of hexafluorophosphoric acid (60 % w/w, 2 ml) was added dropwise using a plastic syringe at 0 °C. Reaction mixture allowed to warm to room temperature and stirred for 16 h then extracted with diethyl ether (4 x 25 ml). Combined organic extracts washed with an aqueous 1 % sodium hydroxide solution (2 x 7.5 ml) followed by water (6 x 50 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a white solid (6.1 g, 94 %). \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}): δ ppm 0.86 – 0.91 (m, 12H), 1.26 – 1.34 (m, 32H), 1.43 – 1.58 (m, 16H), 2.07 – 2.15 (m, 8H); \(^{13}\)C NMR (100 MHz, CDCl\textsubscript{3}): δ ppm 13.9, 14.1, 18.4, 18.8, 21.4, 21.5, 22.3, 22.7, 28.8, 29.3, 29.5, 29.6, 29.7, 30.2, 30.3, 30.5, 30.7, 30.9; \(^{31}\)P NMR (162 MHz, CDCl\textsubscript{3}): δ ppm +32.81, -144.31 (spt, J = 713 Hz); \(^{19}\)F NMR (377 MHz, CDCl\textsubscript{3}): δ ppm -72.09 (d, J = 713 Hz); MS (ESI) positive for C\textsubscript{32}H\textsubscript{68}P\textsubscript{14}, M\textsuperscript{+}: calcd 483.5053, found 483.5048. Data in agreement to literature.\(^1\)
**Trihexyl(tetradecyl)phosphonium trifluoromethanesulfonate, [P$_{6,6,6,14}$][OTf]**

To a stirring solution of trihexyl(tetradecyl)phosphonium chloride (7.0 g, 10.5 mmol) in acetone (50 ml) a solution of lithium trifluoromethanesulfonate (2.5 g, 16.2 mmol) in acetone (50 ml) was added dropwise. The reaction mixture was stirred for 16 h at ambient temperature. The solvent was removed and diethyl ether (25 ml) added, lithium chloride and unreacted lithium trifluoromethanesulfonate were removed by filtration. Diethyl ether (125 ml) added to filtrate and washed with water (6 x 50 ml). Solvent removed and product dried in vacuo at 50 °C to yield a colourless, viscous liquid (7.3 g, 86%). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.86 – 0.91 (m, 12H), 1.25 – 1.32 (m, 32H), 1.42 – 1.59 (m, 16H), 2.16 – 2.23 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 13.8, 14.1, 18.6, 21.6, 21.7, 22.3, 22.6, 28.8, 29.2, 29.3, 29.5, 29.6, 30.2, 30.4, 30.6, 30.7, 30.9, 31.9; $^{31}$P NMR (162 MHz, CDCl$_3$): δ ppm +32.84; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -78.25; MS (ESI) positive for C$_{32}$H$_{68}$P$_1$, M$^+$: calcd 483.5053, found 483.5048. Data in agreement to literature. ¹

**Trihexyl(tetradecyl)phosphonium bis(trifluoromethanesulfonylimide), [P$_{6,6,6,14}$][NTf$_2$]**

To a stirring solution of trihexyl(tetradecyl)phosphonium chloride (5.3 g, 10.3 mmol) in acetone (50 ml) a solution of lithium bis(trifluoromethanesulfonimide) (3.5 g, 12.2 mmol) in acetone (50 ml) was added dropwise. The reaction mixture was stirred for 16 h at ambient temperature. The solvent was removed and diethyl ether (25 ml) added, lithium chloride and unreacted lithium bis(trifluoromethanesulfonimide) were removed by filtration. Diethyl ether (125 ml) added to filtrate and washed with water (6 x 50 ml). Solvent removed and product dried in vacuo at 50 °C to yield a colourless, viscous liquid (7.2 g, 94 %). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.85 – 0.91 (m, 12H), 1.25 – 1.37 (m, 32H), 1.45 – 1.59 (m, 16H), 2.17 – 2.24 (m, 8H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 13.9, 14.1, 18.7, 19.2, 21.6, 21.7, 22.3, 22.6, 28.8, 29.2, 29.3, 29.5, 29.6, 30.3, 30.4, 30.6, 30.7, 30.9, 120.0; $^{31}$P NMR (162 MHz, CDCl$_3$): δ ppm +32.99; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -78.75; MS (ESI) positive for C$_{32}$H$_{68}$P$_2$, M$^+$: calcd 483.5053, found 483.5062. Data in agreement to literature. ¹

**Tributyl(methyl)phosphonium tetrafluoroborate, [P$_{4,4,4,1}$][BF$_4$]**

To a stirring solution of tributyl(methyl)phosphonium methylsulfate (6.5 g, 19.9 mmol) in water (15 ml), a solution of sodium tetrafluoroborate (3.3 g, 30.4 mmol) in water (20 ml) was added dropwise at room temperature. Reaction mixture stirred for 16 h. Dichloromethane (100 ml) and water (15 ml) added to reaction mixture. Organic layer separated and washed with water (6 x 50 ml). Solvent removed and product dried in vacuo at 50 °C to yield a white solid (5.1 g, 90 %). $^1$H NMR (400 MHz, CDCl$_3$): δ ppm 0.95 – 0.99 (t, J = 7.1 Hz, 9H), 1.49 – 1.56 (m, 12H), 1.82 (d, J = 13.4 Hz, 3H), 2.14 – 2.22 (m, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ ppm 3.7 (d, J = 52.9 Hz), 13.3, 19.7 (d, J = 49.1 Hz), 23.3 (d, J = 4.6 Hz), 23.7 (d, J = 15.3 Hz); $^{31}$P NMR (162 MHz, CDCl$_3$): δ ppm +32.99; $^{19}$F NMR (377 MHz, CDCl$_3$): δ ppm -150.64 (q, J = 1.2 Hz), -150.59 (br. s); MS (ESI) positive for C$_{13}$H$_{30}$P$_1$, M$^+$: calcd 217.2080, found 217.2080. Data in agreement to literature. ²
Tributyl(methyl)phosphonium bis(trifluoromethanesulfonyl)imide, [P4,4,4,1][NTf2]

To a stirring solution of tributyl(methyl)phosphonium methylsulfate (3.5 g, 10.6 mmol) in chloroform (25 ml) a solution of lithium bis(trifluoromethanesulfonylimide) (3.7 g, 12.7 mmol) in water (25 ml) was added dropwise. Mixture stirred for 16 h at room temperature. Chloroform (75 ml) and water (25 ml) added. Organic layer separated and washed with water (6 x 50 ml). Solvent removed and product dried in vacuo at 50 °C to yield a colourless, viscous liquid (5.1 g, 96 %). 1H NMR (400 MHz, CDCl3): δ ppm 0.95 – 0.98 (t, J = 6.9 Hz, 9H), 1.47 – 1.54 (m, 12H), 1.78 (d, J = 13.1 Hz), 2.08 – 2.16 (m, 6H); 13C NMR (100 MHz, CDCl3): δ ppm 3.9 (d, J = 52.2 Hz), 13.2, 19.9 (d, J = 49.1 Hz), 23.3 (d, J = 4.6 Hz), 23.6 (d, J = 15.3 Hz), 118.2, 121.4; 31P NMR (162 MHz, CDCl3): δ ppm +31.54; 19F NMR (377 MHz, CDCl3): δ ppm -78.89; IR ν max (CHCl3)/cm⁻¹ 932, 1059, 1137, 1192, 1351, 1466, 2877, 2936, 2966; MS (ESI) positive for C13H30P1, M+: calcd 217.2080, found 217.2084.

2. XP spectra of Ionic Liquids

Survey and fitted high resolution spectra for all ionic liquids studied are presented in SI. 1 - 14. C 1s high resolution spectra were fitted according to the models described within the paper. Cl 2p, S 2p and P 2p high resolution spectra were fitted taking into account spin-orbit coupling, whereby the area ratio of 2p1/2:2p3/2 components is set to 1:2. The O 1s and S 2p high resolution spectra for ionic liquids containing the [NTf2]⁻ and [OTf] anions are affected by shake up/off phenomena and a 4 % intensity loss (per oxygen/sulphur atom involved in double bonding) was taken into account when calculating atomic percentages for these elements.
SI.1 $[N_{6,6,6,14}]Cl$ survey and high resolution scans.
SI.2 $[\text{N}_{6,6,6,14}]\text{[BF}_4\text{]}$ survey and high resolution scans.
SI.3 [N\textsubscript{6,6,6,14}][PF\textsubscript{6}] survey and high resolution scans.
SI.4 [N_{6,6,6,14}][OTf] survey and high resolution scans.
Sl. 5 $[\text{N}_{6, 6, 6, 14}]\text{[NTf}_{2}]$ survey and high resolution scans.
Si. 6 [N_4441][BF_4] survey and high resolution scans.
SI.7 [N$_{4,4,4,1}$][NTf$_2$] survey and high resolution scans.
SI. 8 \([P_{6,6,6,14}]\)Cl survey and high resolution scans.
SI. 9 [P$_{6,6,6,14}$][BF$_4$] survey and high resolution scans.
SI. 10 $[P_{6,6,6,14}][PF_6]$ survey and high resolution scans.
Sl. 11 [P_{6,6,6,14}]OTf survey and high resolution scans.
SI. 12 \([P_{6,6,6,14}]\text{NTf}_2\) survey and high resolution scans.
St. 13 [P₄₄₄₁][BF₄] survey and high resolution scans.
Si. 14 $[P_{4,4,4,4}][\text{NTf}_2]$ survey and high resolution scans.