Electronic Supplementary Material (ESI) for ChemComm.

Tuning cation-anion interactions in ionic liquids by changing the conformational flexibility of the cation.

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Supplementary Information

Materials

Chemical precursors were obtained from commercial suppliers and used without further purification unless otherwise stated. All compounds were dried *in vacuo* ($p \leq 10^{-2}$ mbar) at 50 °C and stored under argon before being fully characterised by ^{1}H, ^{13}C and ^{19}F NMR (recorded at room temperature on a Bruker DPX-400 MHz or DPX-300 MHz spectrometer); ESI-MS (Bruker MicroTOF 61 spectrometer) and XPS (Kratos Axis Ultra spectrometer). For syntheses which involved anion exchange chemistries, ion chromatography (Dionex ICS-3000, IonPack AS15, 4 x 250 mm analytical column) showed that residual halide was below the detection limits of the instrument (< 10 ppm).

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 %). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): 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 ($CHCl_3$)/cm^{-1} 1246, 1468, 2858, 2929; MS (ESI) positive for $C_{32}H_{68}N_1$, M^+: calcd 466.5346, found 466.5346. Data in agreement to literature.[1]

Trihexyl(tetradecyl)ammonium tetrafluoroborate, $[N_{6,6,6,14}][BF_4]$

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) 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 white solid (1.7 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$): 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); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.8, 14.1, 25.8, 26.2, 29.0, 29.3, 29.4, 29.6, 31.1, 31.9, 58.6; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -151.79 (q, J = 1.1 Hz), -151.73 (br. s); IR ν max ($CHCl_3$)/cm^{-1} 1059, 1468, 2857, 2929,2959; MS (ESI) positive for $C_{32}H_{68}N_1$, M^+: calcd 466.5346, found 466.5333. Data in agreement to literature.[1]

Trihexyl(tetradecyl)ammonium bis(trifluoromethane)sulfonimide, $[N_{6,6,6,14}][NTf_2]$

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(trifluoromethane)sulfonimide (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 $C_{32}H_{68}N_1$, M$^+$: calcd 466.5346, found 466.5349. Data in agreement to literature.[1]

1-octyl-1-methylpyrrolidinium bromide, [C_8C_1Pyrr][Br]

To a stirring solution of 1-methylpyrrolidine (20 ml, 188.0 mmol) in ethyl acetate (15 ml), 1-bromooctane (40 ml, 232.0 mmol) was added dropwise at room temperature. Reaction mixture heated to 40 °C and stirred for 24 h. Solvent removed and crude white solid recrystallized from acetonitrile/ethyl acetate and dried *in vacuo* at 50 °C to yield a white solid (33.0 g, 63 %)

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.83 (t, *J* = 7.0 Hz, 3H), 1.19 – 1.38 (m, 10H), 1.69 – 1.77 (m, 2H), 2.23 – 2.30 (m, 4H), 3.27 (s, 3H), 3.59 – 3.63 (m, AA'BB' system, 2H), 3.75 – 3.86 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 13.9, 21.5, 22.4, 24.0, 26.3, 28.9, 29.1, 31.5, 48.6, 64.1, 64.3; MS (ESI) positive for $C_{13}H_{28}N_1$, M$^+$: calcd 198.2216, found 198.2210. Data in agreement to literature.[2]

1-octyl-1-methylpyrrolidinium chloride, [C_8C_1Pyrr][Cl]

1-octyl-1-methylpyrrolidinium bromide (7.2 g, 25.9 mmol) was dissolved in methanol (100 ml) and eluted through a column containing Amberlite-IRA400 (Cl) ion-exchange resin (80 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 (5.7 g, 93 %).

^{1}H NMR (300 MHz, $CDCl_3$): δ ppm 0.79 (t, *J* = 7.0 Hz, 3H), 1.16 – 1.36 (m, 10H), 1.63 – 1.74 (m, 2H), 2.17 – 2.28 (m, 4H), 3.23 (s, 3H), 3.53 – 3.58 (m, AA'BB' system, 2H), 3.71 – 3.84 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ ppm 13.9, 21.5, 22.3, 23.9, 26.2, 28.8, 29.0, 31.4, 48.2, 63.9, 64.1; M$^+$: calcd 198.2216, found 198.2222. Data in agreement to literature.[3]

1-octyl-1-methylpyrrolidinium tetrafluoroborate, [C_8C_1Pyrr][BF_4]

To a solution of 1-octyl-1-methylpyrrolidinium bromide (6.8 g, 24.5 mmol) in water (25 ml), a solution of sodium tetrafluoroborate (3.2 g, 29.1 mmol) in water (25 ml) was added dropwise. Reaction mixture stirred overnight at room temperature. Dichloromethane (75 ml) was added and organic layer separated and washed with water (4 x 50 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a white solid (6.4 g, 91 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.87 (t, *J* = 7.0 Hz, 3H), 1.26 – 1.35 (m, 10H), 1.70 – 1.78 (m, 2H), 2.22 – 2.28 (m, 4H), 3.06 (s, 3H), 3.31 – 3.35 (m, AA'BB' system, 2H), 3.48 – 3.60 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.0, 21.6, 22.5, 23.8, 26.3, 29.0, 29.0, 31.6, 48.2, 64.3, 64.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -151.53 (q, *J* = 1.1 Hz), -151.48 (br. s); MS (ESI) positive for $C_{13}H_{28}N_1$, M$^+$: calcd 198.2216, found 198.2220. Data in agreement to literature.[4]

1-octyl-1-methylpyrrolidinium bis(trifluoromethane)sulfonimide, $[C_8C_1Pyrr][NTf_2]$

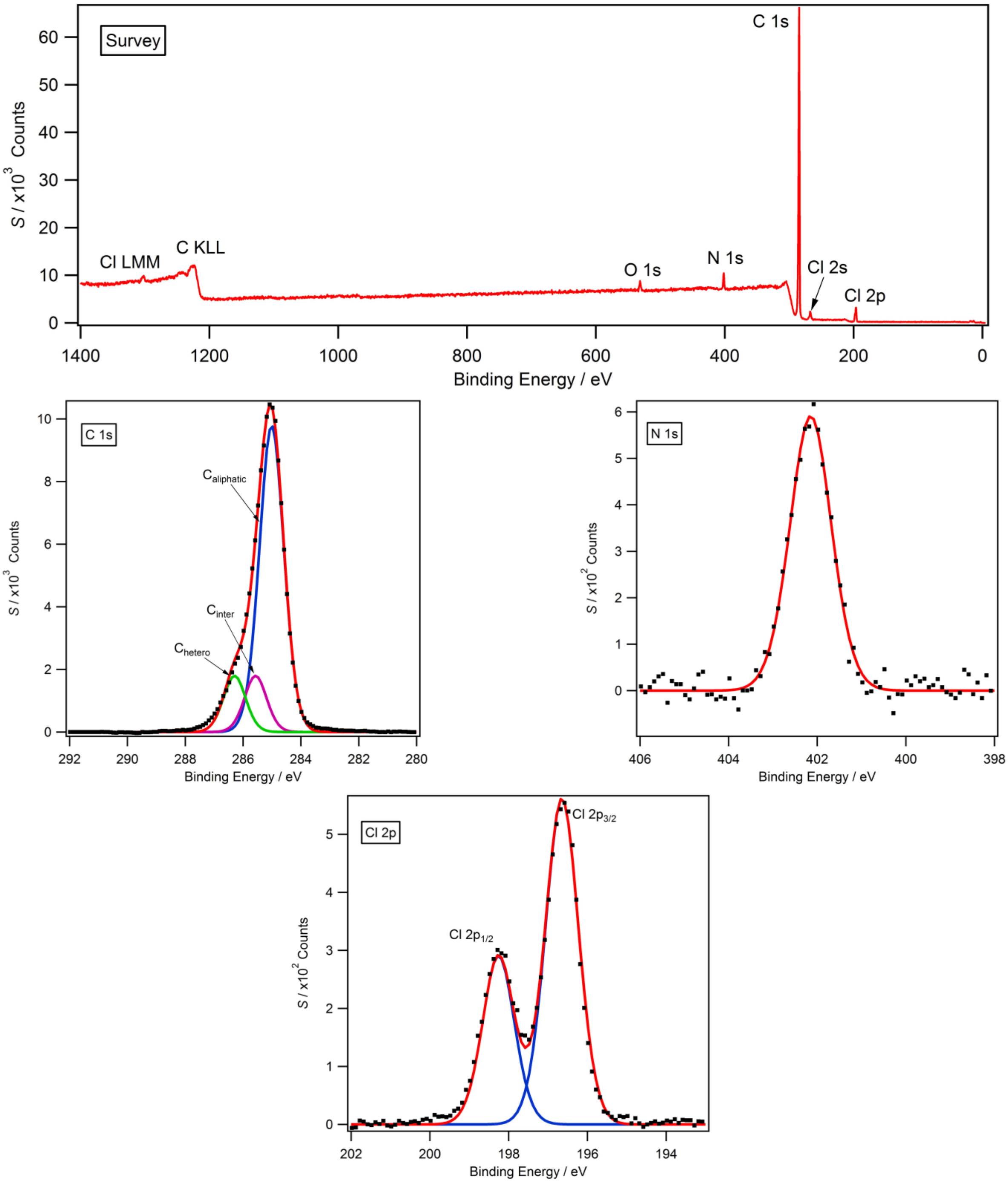
To a solution of 1-octyl-1-methylpyrrolidinium bromide (5.8 g, 20.8 mmol) in water (25 ml), a solution of lithium bis(trifluoromethane)sulfonimide (7.2 g, 25.1 mmol) in water (25 ml) was added dropwise. Reaction mixture stirred overnight at room temperature. Dichloromethane (75 ml) was added and organic layer separated and washed with water (4 x 50 ml). Solvent removed and product dried *in vacuo* at 50 °C to yield a white solid (9.4 g, 94 %).

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.88 (t, *J* = 7.0 Hz, 3H), 1.28 – 1.35 (m, 10H), 1.70 – 1.78 (m, 2H), 2.25 – 2.28 (m, 2H), 3.04 (s, 3H), 3.27 – 3.32 (m, AA'BB' system, 2H), 3.49 – 3.56 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ ppm 14.0, 21.5, 22.5, 23.8, 26.1, 28.9, 31.5, 48.4, 64.5, 64.8, 86.1; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -78.94; MS (ESI) positive for $C_{13}H_{28}N_1$, M^+: calcd 198.2216, found 198.2222; MS (ESI) negative for $C_2F_6N_1O_4S_2$, M^-: calcd 279.9178, found 279.9175. Data in agreement to literature. [4]

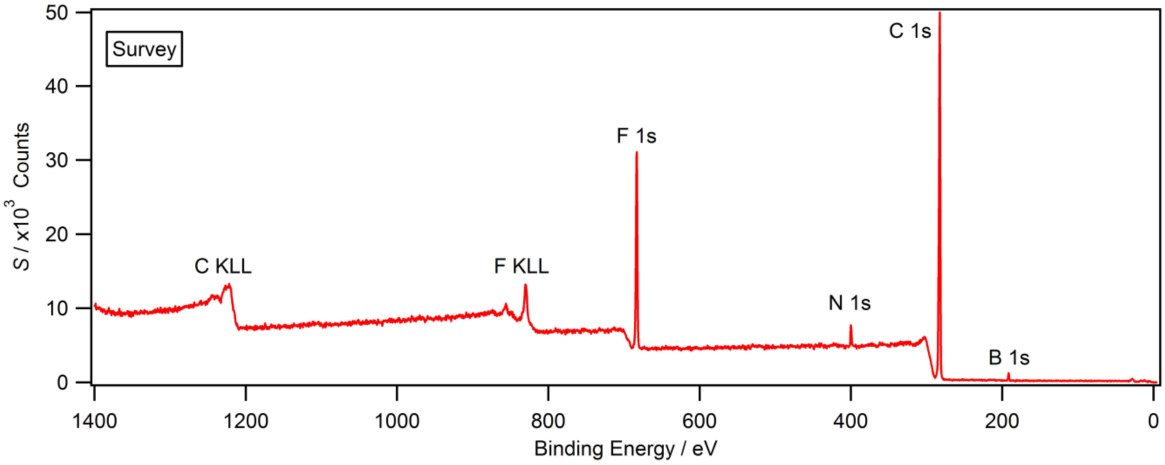
1.2 XP Spectra of ionic liquids

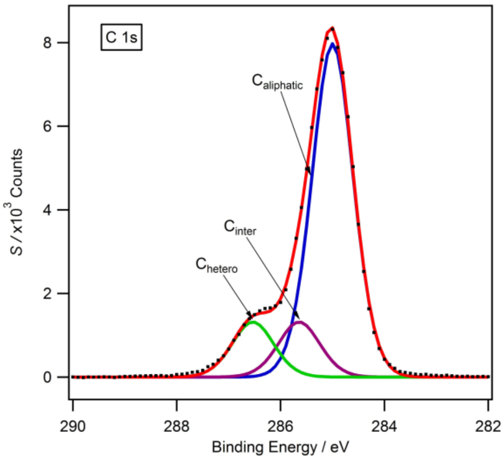
Survey and fitted high resolution spectra for all ionic liquids studied are presented in SI. 1 - 6. C 1s high resolution spectra were fitted according to previously described models.[5, 6] Cl 2p and S 2p high resolution spectra were fitted taking into account spin-orbit coupling, whereby the area ratio of $2p_{1/2}$:$2p_{3/2}$ components is set to 1:2.

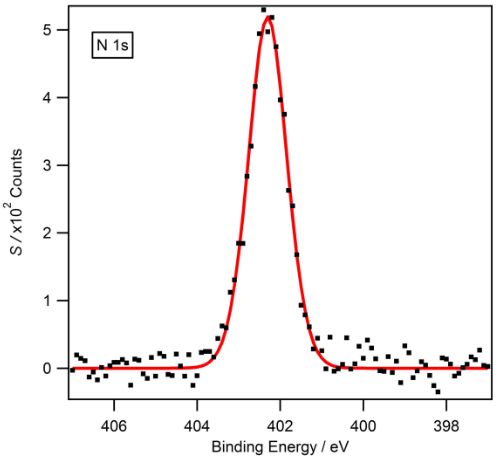
SI.1 $[N_{6,6,6,14}][Cl]$ survey and high resolution scans. A weak O 1s signal is observed which is likely to be a result of laboratory grease and is not expected to affect the recorded binding energies.

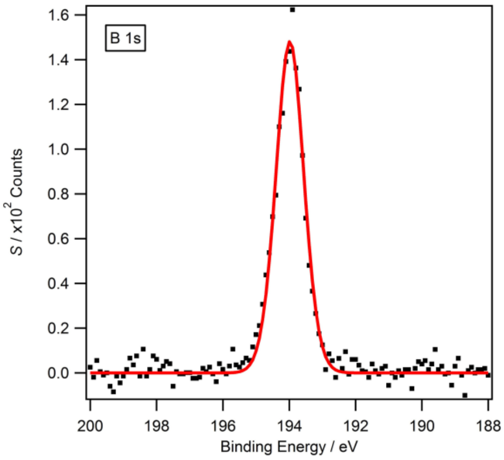


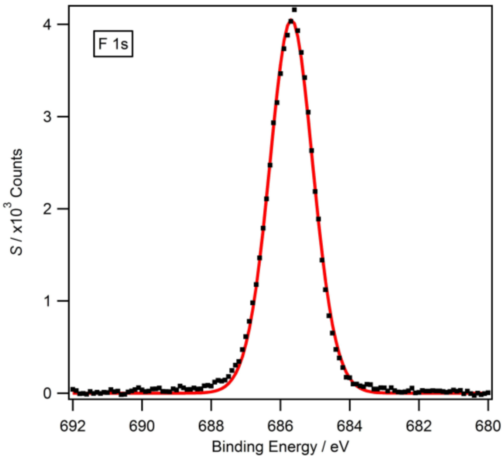
SI.2 $[N_{6,6,6,14}][BF_4]$ survey and high resolution scans.



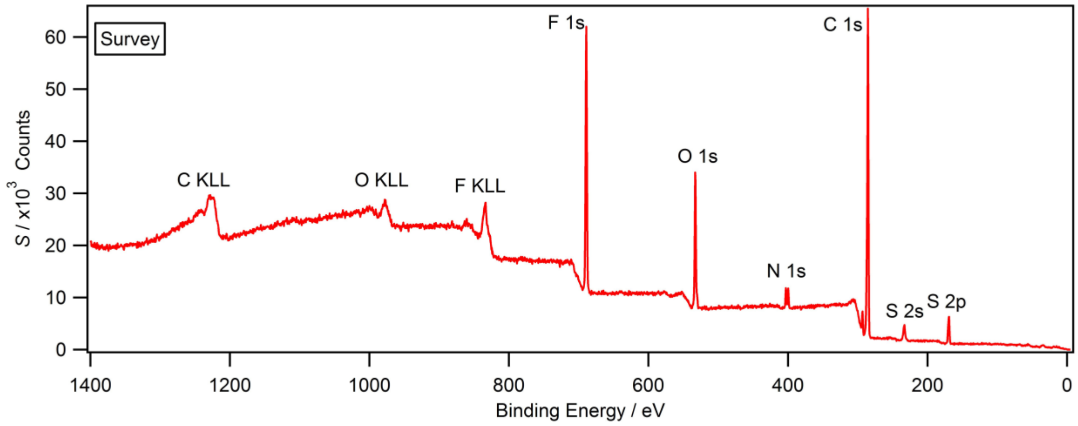


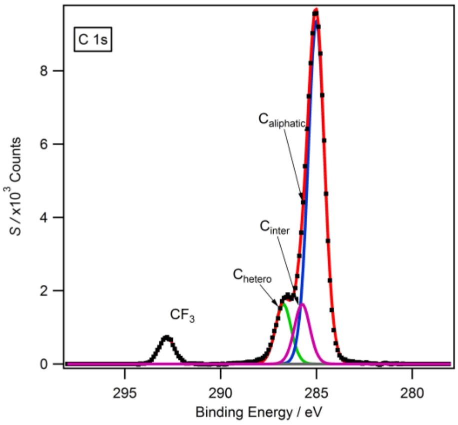


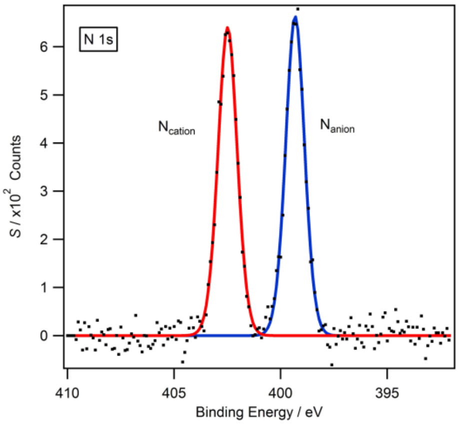


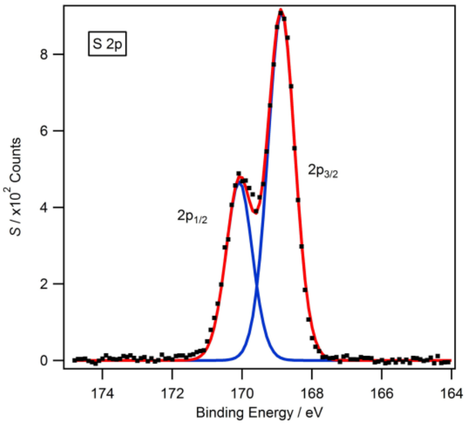


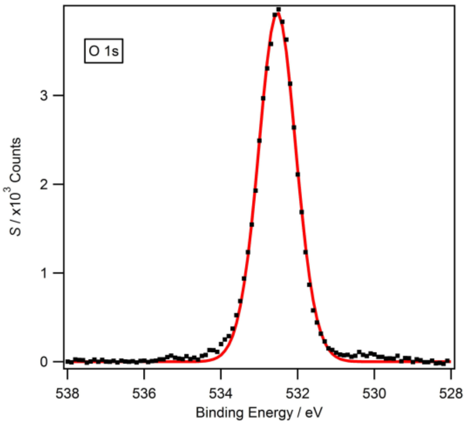
SI.3 [$N_{6,6,6,14}$][NTf_2] survey and high resolution scans.

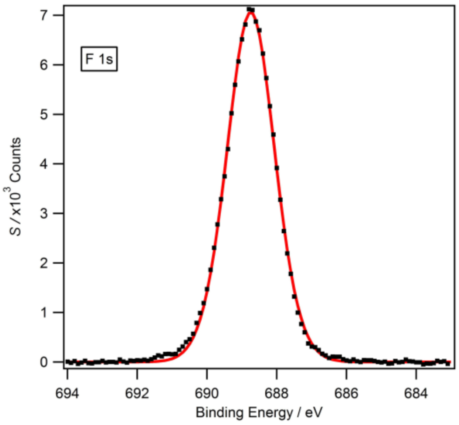




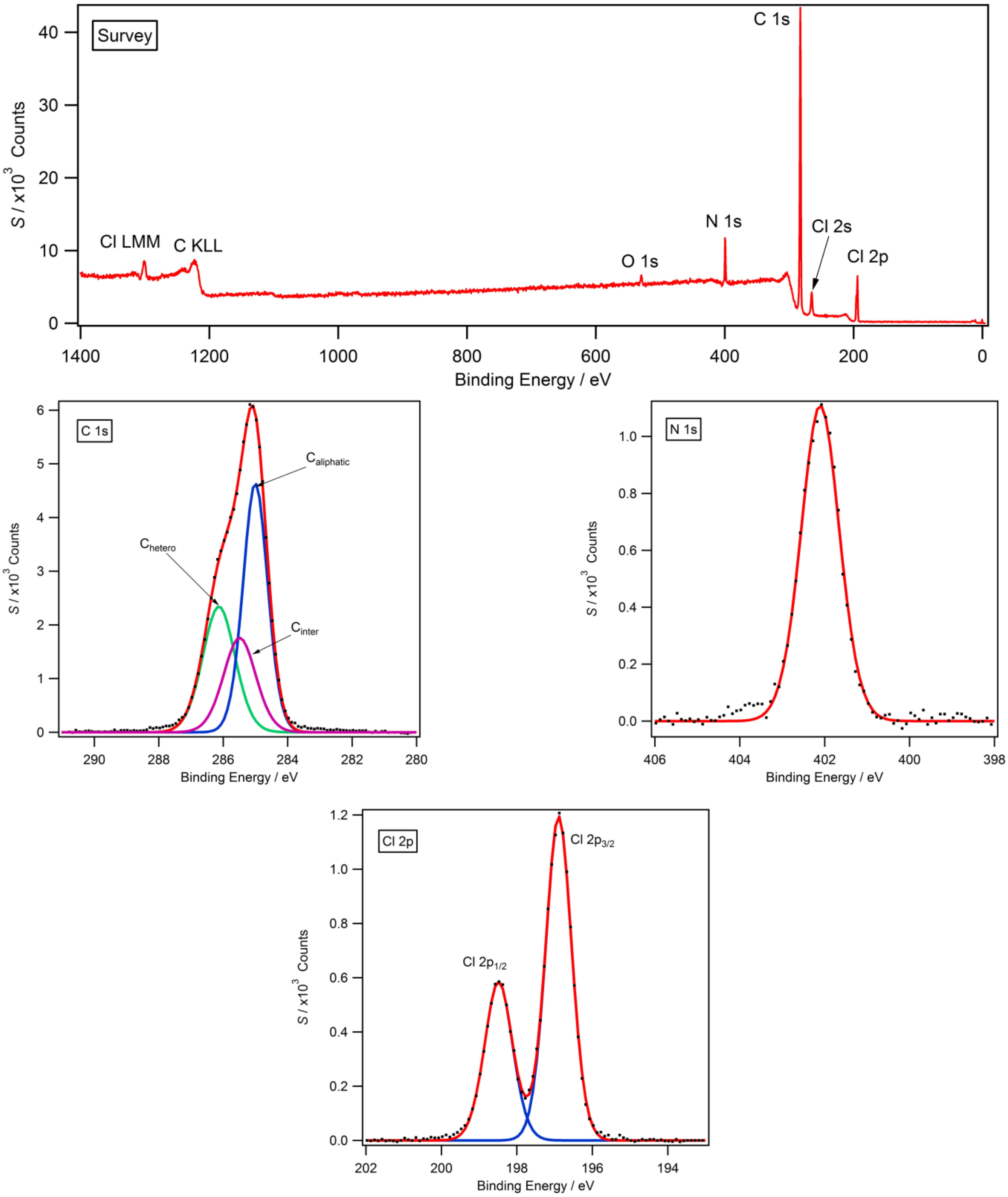




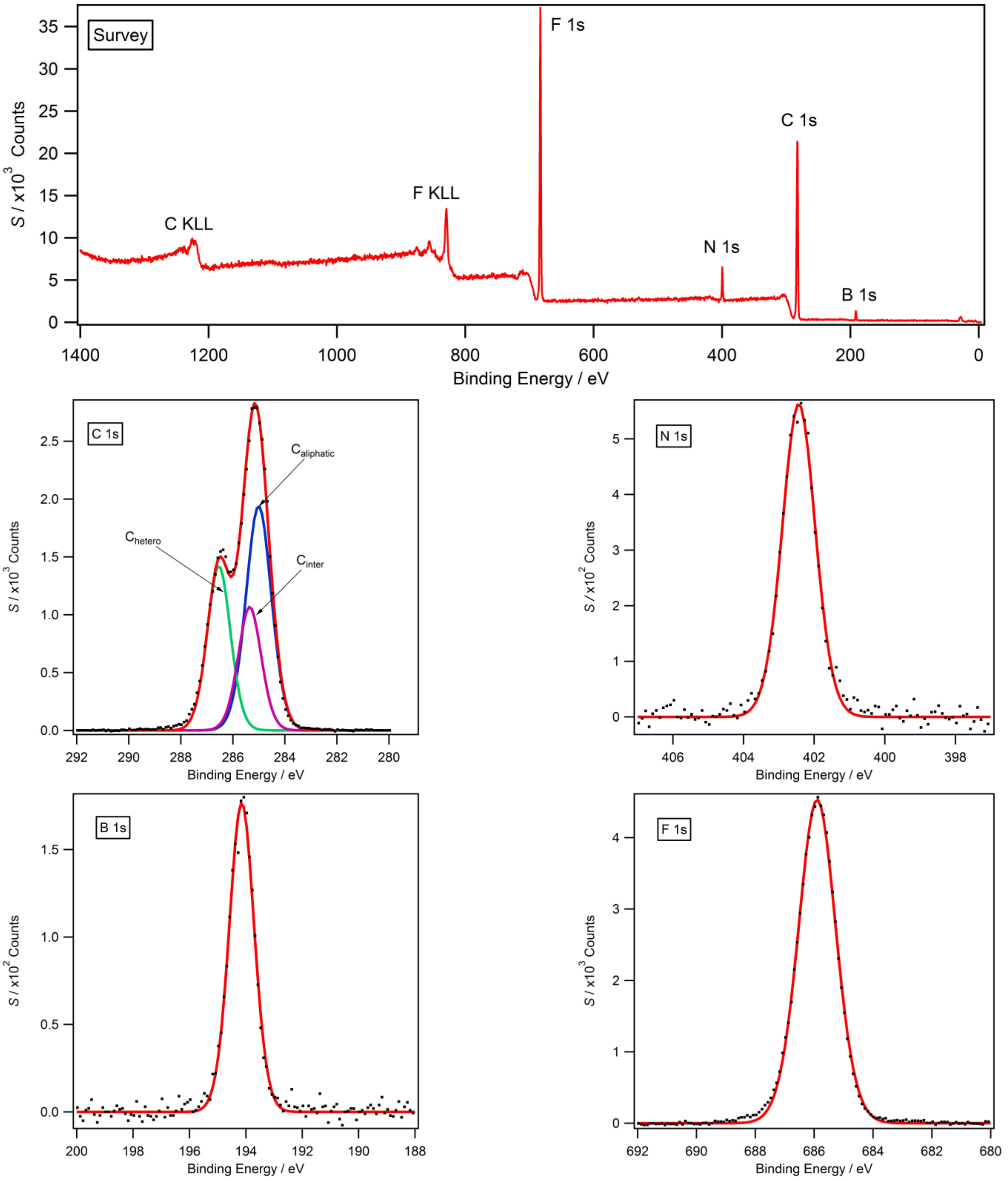




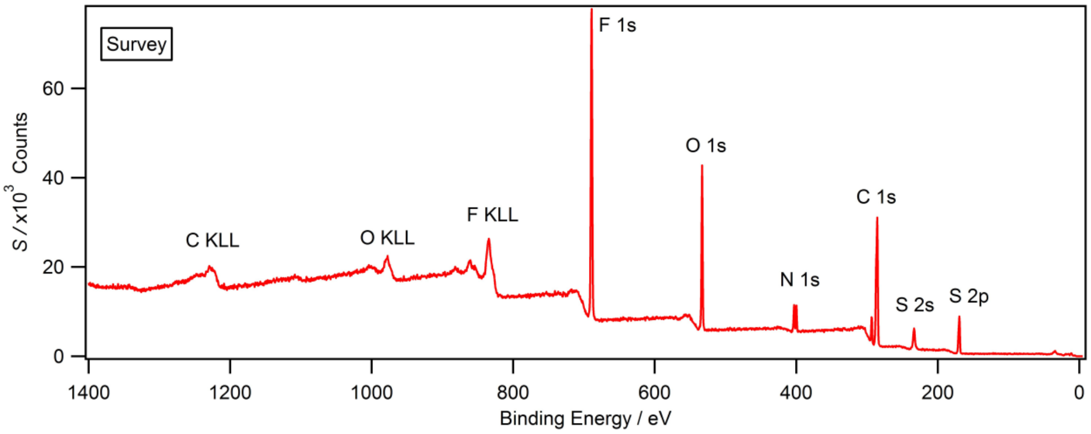
SI.4 [C_8C_1Pyrr][Cl] survey and high resolution scans. A weak O 1s signal is observed which is likely to be a result of laboratory grease and is not expected to affect the recorded binding energies.

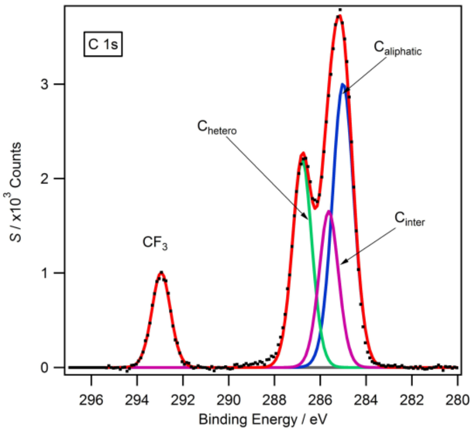


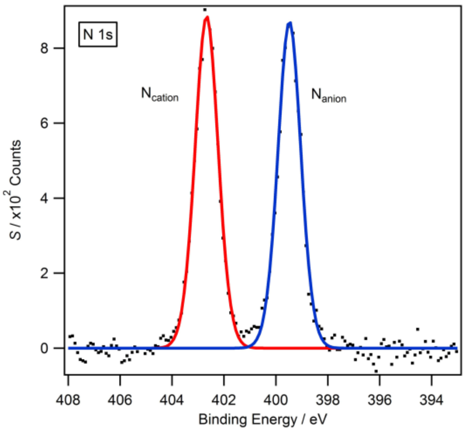
SI.5 [C_8C_1Pyrr][BF_4] survey and high resolution scans.

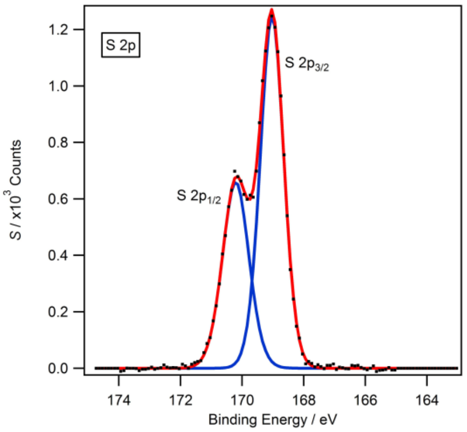


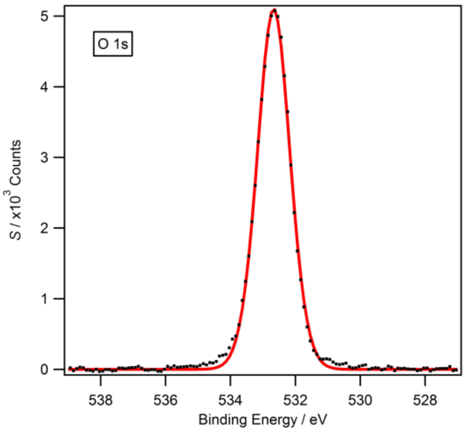
SI.6 [C_8C_1Pyrr][NTf_2] survey and high resolution scans.

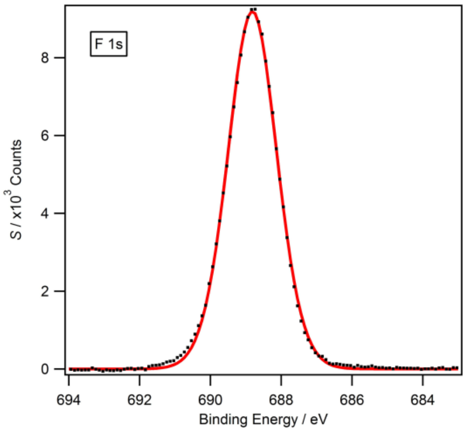












1. A. D. Ballantyne, A. K. Brisdon and R. A. W. Dryfe, *Chem. Commun.*, 2008, 4980-4982.
2. K. Goossens, K. Lava, P. Nockemann, K. Van Hecke, L. Van Meervelt, K. Driesen, C. Gorller-Walrand, K. Binnemans and T. Cardinaels, *Chem. Eur. J.*, 2009, **15**, 656-674.
3. G. Cravotto, E. C. Gaudino, L. Boffa, J. M. Leveque, J. Estager and W. Bonrath, *Molecules*, 2008, **13**, 149-156.
4. M. Guncheva, M. Dimitrov, F. Napoly, M. Draye and B. Andrioletti, *J. Mol. Catal. B: Enzym.*, 2014, **102**, 72-80.
5. S. Men, K. R. J. Lovelock and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15244-15255.
6. R. K. Blundell and P. Licence, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15278 - 15288.