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XPS of Guanidinium Ionic Liquids: A Comparison of Charge Distribution in Nitrogenous Cations

Supplementary Information

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Supplementary Information

Synthesis of Ionic Liquids

Tetra-butyl-dimethylguanidinium chloride, [$(C_4C_4)_2$dmg][Cl]

To a suspension of phosgene iminium chloride (2.1 g; 13 mmol) in anhydrous dichloromethane (20 ml) at 0 °C (ice bath) was added dropwise a mixture of dibutylamine (4.6 ml; 27.3 mmol) and triethylamine (3.99 ml; 28.6 mmol) in dichloromethane (30 ml). After 30 min at 0 °C (complete solubilisation of the phosgene iminium salt), the reaction was stirred at room temperature for 4 h. The solvent was removed under vacuum and an aqueous solution of NaOH (2 M; 20 ml) was added. The mixture was washed with diethyl ether (2 x 25 ml) and the pH adjusted to 7 by dropwise addition of hydrochloric acid (37%). The water was removed at reduced pressure, the residue extracted with dichloromethane (50 ml), the solvent evaporated and the residue left *in vacuo* overnight. The salt [$(C_4C_4)_2$dmg][Cl] (3.73 g; 82%) was obtained as a slight yellow coloured hygroscopic solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.89 (t, J = 7.20 Hz, 12 H), 1.16 - 1.45 (m, 12 H), 1.46 - 1.76 (m, 4 H), 2.93 - 3.05 (m, 2 H), 3.06 - 3.34 (m, 12 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.53 and 13.59 (rotamers), 19.80 and 19.96 (rotamers), 29.41 and 29.73 (rotamers), 40.86, 49.03 and 49.58 (rotamers), 163.30. ESI-MS (+ve): calcd 312.3373, found 312.3371. Data in agreement to literature.[1]

Tetra-butyl-dimethylguanidinium hexafluorophosphate, [$(C_4C_4)_2$dmg][PF_6]

The [dmg] chloride (3.50 g, 10.1 mmol) was transferred to a round bottom flask followed by the addition of water. HPF_6 (1.67 ml, 12.1 mmol) 60% w/w solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt [$(C_4C_4)_2$dmg][PF_6] (4.51 g; 98%) was obtained as a slight yellow coloured solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.94 (t, J = 7.20 Hz, 12 H), 1.23 - 1.50 (m, 12 H), 1.52 - 1.78 (m, 4 H), 2.97 (s, 6 H), 2.99 - 3.28 (m, 8 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.59, 19.78 and 20.01 (rotamers), 29.31 and 29.66 (rotamers), 40.25, 48.95 and 49.70 (rotamers), 163.50; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -73.23 (d, J = 712.00 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm -144.40 (spt, J = 712.00 Hz). ESI-MS (+ve): calcd 312.3373, found 312.3365. Data in agreement to literature.[1]

Tetra-butyl-dimethylguanidinium tetrafluoroborate, [$(C_4C_4)_2$dmg][BF_4]

The [dmg] chloride (2.00 g, 5.75 mmol) was transferred to a round bottom flask followed by the addition of water. $NaBF_4$ (0.76 g, 6.89 mmol) solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt [$(C_4C_4)_2$dmg][BF_4] (2.20 g; 96%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.94 (t, J = 7.20 Hz, 12 H), 1.20 - 1.50 (m, 12 H), 1.51 - 1.84 (m, 4 H), 2.94 - 3.10 (m, 8 H), 3.13 - 3.27 (m, 6 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.68, 19.87 and 20.08 (rotamers), 29.42 and 29.73 (rotamers), 40.40, 48.96 and 49.70 (rotamers), 163.57; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -153.44 to -153.40 (m), -153.36 (br. s); ESI-MS (+ve): calcd 312.3373, found 312.3366. Data in agreement to literature.[1]

Tetra-butyl-dimethylguanidinium bis(trifluoromethanesulfonyl)imide, $[(C_4C_4)_2dmg][NTf_2]$

The [dmg] chloride (1.50 g, 4.31 mmol) was transferred to a round bottom flask followed by the addition of water. $LiNTf_2$ (1.48 g, 5.17 mmol) solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt $[(C_4C_4)_2dmg][NTf_2]$ (2.53 g; 99%) was obtained as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J = 7.20 Hz, 12 H), 1.21 - 1.50 (m, 12 H), 1.52 - 1.78 (m, 4 H), 2.90 - 3.30 (m, 14 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.56, 19.83 and 20.03 (rotamers), 29.35 and 29.72 (rotamers), 40.40, 49.05 and 49.82 (rotamers), 118.32, 121.52 163.48; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -78.85. IR ν max ($CHCl_3$)/cm^{-1} 3044.85, 2964.48, 2935.97, 2877.12, 1577.81, 1539.40, 1459.45, 1421.33, 1350.51, 1192.11, 1136.39, 1059.89, 889.93. ESI-MS (+ve): calcd 312.3373, found 312.3369. Analysis: Calc. for $C_{21}H_{42}F_6N_4O_4S_2$: N 9.45, C 42.55, H 7.14. Found: N 9.22, C 42.57, H 7.02.

Butyl-methyl-dimethylguanidinium chloride, $[(C_4C_1)_2dmg][Cl]$

To a suspension of phosgene iminium chloride (5.0 g; 30.8 mmol) in anhydrous dichloromethane (40 ml) at 0 °C (ice bath) was added dropwise a mixture of methylbutylamine (7.66 ml; 64.7 mmol) and triethylamine (9.44 ml; 67.8 mmol) in dichloromethane (50 ml). After 30 min at 0 °C (complete solubilisation of the phosgene iminium salt), the reaction was stirred at room temperature for 4 h. The solvent was removed under vacuum and an aqueous solution of NaOH (2 M; 30 ml) was added. The mixture was washed with diethyl ether (2 x 50 ml) and the pH adjusted to 7 by dropwise addition of hydrochloric acid (37%). The water was removed at reduced pressure, the residue extracted with dichloromethane (100 ml), the solvent evaporated and the residue left *in vacuo* overnight. The salt $[(C_4C_1)_2dmg][Cl]$ (6.91 g; 85%) was obtained as a yellow coloured viscous liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.84 (t, J = 7.30 Hz, 6 H), 1.08 - 1.74 (m, 8 H), 2.76 - 3.32 (m, 16 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.44, 19.75, 29.38, 37.97 and 38.24 (rotamers), 40.40 and 40.83 (rotamers), 52.38, 163.30. ESI-MS (+ve): calcd 228.2434, found 228.2433. Data in agreement to literature.[1]

Butyl-methyl-dimethylguanidinium hexafluorophosphate, $[(C_4C_1)_2dmg][PF_6]$

The [dmg] chloride (0.66 g, 2.5 mmol) was transferred to a round bottom flask followed by the addition of water. HPF_6 (0.42 ml, 3.0 mmol) 60% w/w solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for

24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred under *vacuo* overnight at 50 ºC. The salt $[(C_4C_1)_2dmg][PF_6]$ (0.85 g; 91%) was obtained as a slight yellow coloured solid.

^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.94 (t, J = 7.30 Hz, 6 H), 1.15 - 1.87 (m, 8 H), 2.86 - 3.03 (m, 12 H), 3.04 - 3.27 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.56, 19.84, 29.44, 37.63 and 37.83 (rotamers), 40.10 and 40.28 (rotamers), 52.46, 163.61; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -73.20 (d, J = 712.00 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm -144.46 (spt, J = 712.00 Hz). ESI-MS (+ve): calcd 228.2434, found 228.2429. Data in agreement to literature.[1]

Butyl-methyl-dimethylguanidinium tetrafluoroborate, $[(C_4C_1)_2dmg][BF_4]$

The [dmg] chloride (0.83 g, 3.14 mmol) was transferred to a round bottom flask followed by the addition of water. $NaBF_4$ (0.41 g, 3.78 mmol) solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred under *vacuo* overnight at 50 ºC. The salt $[(C_4C_1)_2dmg][BF_4]$ (0.88 g; 89%) was obtained as a slight yellow coloured solid.

^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.93 (t, J = 7.31 Hz), 1.16 - 1.81 (m, 8 H), 2.86 - 3.04 (m, 12 H), 3.04 - 3.28 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.58, 19.83, 29.43, 37.61 and 37.90 (rotamers), 40.07 and 40.31 (rotamers), 52.38, 163.67; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -153.38 (q, J=1.10 Hz), -153.33 (br. s); ESI-MS (+ve): calcd 228.2434, found 228.2438. Data in agreement to literature.[1]

Butyl-methyl-dimethylguanidinium bis(trifluoromethanesulfonyl)imide, $[(C_4C_1)_2dmg][NTf_2]$

The [dmg] chloride (0.44 g, 1.67 mmol) was transferred to a round bottom flask followed by the addition of water. $LiNTf_2$ (0.57 g, 2.00 mmol) solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt $[(C_4C_1)_2dmg][NTf_2]$ (0.81 g; 96%) was obtained as a slight yellow coloured solid.

^1H NMR (400 MHz, $CDCl_3$): δ ppm 0.95 (t, J = 7.31 Hz, 6 H), 1.16 - 1.83 (m, 8 H), 2.87 - 3.04 (m, 12 H), 3.04 - 3.29 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.53, 19.86, 29.29 and 29.46 (rotamers), 37.77, 40.19 and 40.45 (rotamers), 52.57, 115.07, 118.28, 121.46, 124.66, 163.64; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -78.88. IR v max ($CHCl_3$)/cm^{-1} 3044.98, 2964.35, 2936.25, 2876.80, 1569.17, 1467.88, 1408.44, 1349.87, 1192.10, 1135.58, 1060.14, 893.23. ESI-MS (+ve): calcd 228.2434, found 228.2436. Analysis: Calc. for $C_{15}H_{30}F_6N_4O_4S_2$: N 11.02, C 35.43, H 5.95. Found: N 10.79, C 35.47, H 5.84.

Methyl-octyl-dimethylguanidinium chloride, $[(C_8C_1)_2dmg][Cl]$

To a suspension of phosgene iminium chloride (4.06 g; 25 mmol) in anhydrous dichloromethane (40 ml) at 0 °C (ice bath) was added dropwise a mixture of methyloctylamine (9.52 ml; 52.5 mmol) and triethylamine (7.67 ml; 55.0 mmol) in dichloromethane (50 ml). After 30 min at 0 °C (complete solubilisation of the phosgene iminium salt), the reaction was stirred at room temperature for 4 h. The solvent was removed under vacuum and an aqueous solution of NaOH (2 M; 30 ml) was added. The mixture was washed with diethyl ether (2 x 50 ml) and the pH adjusted to 7 by dropwise addition of hydrochloric acid (37%). The water was removed at reduced pressure, the residue extracted with dichloromethane (100 ml), the solvent evaporated and the residue left *in vacuo* overnight. The salt [(C_8C_1)$_2$dmg][Cl] (7.62 g; 81%) was obtained as a slight yellow coloured solid wax.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.79 (t, J = 6.80 Hz, 6 H), 1.05 - 1.29 (m, 20 H), 1.30 - 1.75 (m, 4 H), 2.82 - 3.31 (m, 16 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.81, 22.33, 26.53 and 27.22 (rotamers), 28.88 and 28.94 (rotamers), 31.46, 38.29 and 38.51 (rotamers), 40.83 and 40.97 (rotamers), 52.64, 163.48. IR ν max ($CHCl_3$)/cm^{-1} 2930.23, 2858.44, 2463.14, 1566.44,1466.68, 1407.63, 1378.32, 1246.63, 1062.57, 898.10. ESI-MS (+ve): calcd 340.3686, found 340.3677. Analysis: Calc. for [(mo)$_2$dmg][Cl]·3H_2O ($C_{21}H_{52}ClN_3O_3$): N 9.77, C 58.64, H 12.19. Found: N 9.81, C 58.51, H 11.91.

Methyl-octyl-dimethylguanidinium hexafluorophosphate, [(C_8C_1)$_2$dmg][PF_6]

The [dmg] chloride (1.09 g, 2.9 mmol) was transferred to a round bottom flask followed by the addition of water. HPF_6 (0.48 ml, 3.5 mmol) 60% w/w solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt [(C_8C_1)$_2$dmg][PF_6] (1.38 g; 98%) was obtained as a slight yellow coloured liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.88 (t, J = 6.80 Hz, 6 H), 1.14 - 1.38 (m, 20 H), 1.39 - 1.81 (m, 4 H), 2.84 - 3.01 (m, 12 H), 3.02 - 3.23 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 13.99, 22.52, 26.64, 27.33 and 27.51 (rotamers), 29.06 and 29.09 (rotamers), 31.65, 37.66 and 37.92 (rotamers), 40.08 and 40.33 (rotamers), 52.78, 163.59; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -73.19 (d, J = 712.00 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ ppm -144.45 (spt, J = 712.00 Hz). IR ν max ($CHCl_3$)/cm^{-1} 3045.73, 2930.46, 2858.15, 1569.62, 1467.07, 1408.56, 1249.59, 848.60. ESI-MS (+ve): calcd 340.3686, found 340.3678. Analysis: Calc. for $C_{21}H_{46}F_6N_3P$: N 8.65, C 51.94, H 9.55. Found: N 8.73, C 51.91, H 9.36.

Methyl-octyl-dimethylguanidinium tetrafluoroborate, [(C_8C_1)$_2$dmg][BF_4]

The [dmg] chloride (1.09 g, 2.90 mmol) was transferred to a round bottom flask followed by the addition of water. $NaBF_4$ (0.38 g, 3.49 mmol) solution was added and the mixture stirred at 0 ºC and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 ºC. The salt [(C_8C_1)$_2$dmg][BF_4] (1.14 g; 92%) was obtained as a slight yellow coloured solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.87 (t, J = 6.80 Hz, 6 H), 1.15 - 1.36 (m, 20 H), 1.38 - 1.82 (m, 4 H), 2.86 - 3.03 (m, 12 H), 3.05 - 3.25 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 14.06, 22.60, 26.73, 27.56, 29.15 and 29.18 (rotamers), 31.73, 37.73, and 38.04 (rotamers), 40.17 and 40.43 (rotamers), 52.76, 163.74; ^{19}F NMR (377 MHz, $CDCl_3$): δ ppm -153.45 to -153.39 (m), -153.37 (br. s). IR ν max ($CHCl_3$)/cm^{-1} 3045.06, 2930.44, 2858.04, 1569.74, 1467.01, 1408.54, 1378.30, 1285.67, 1241.62, 1059.85, 898.49. ESI-MS (+ve): calcd 340.3686, found 340.3681. Analysis: Calc. for $C_{21}H_{46}F_4N_3B$: N 9.83, C 59.01, H 10.85. Found: N 9.81, C 59.10, H 10.91.

Methyl-octyl-dimethylguanidinium bis(trifluoromethanesulfonyl)imide, [$(C_8C_1)_2$dmg][NTf_2]

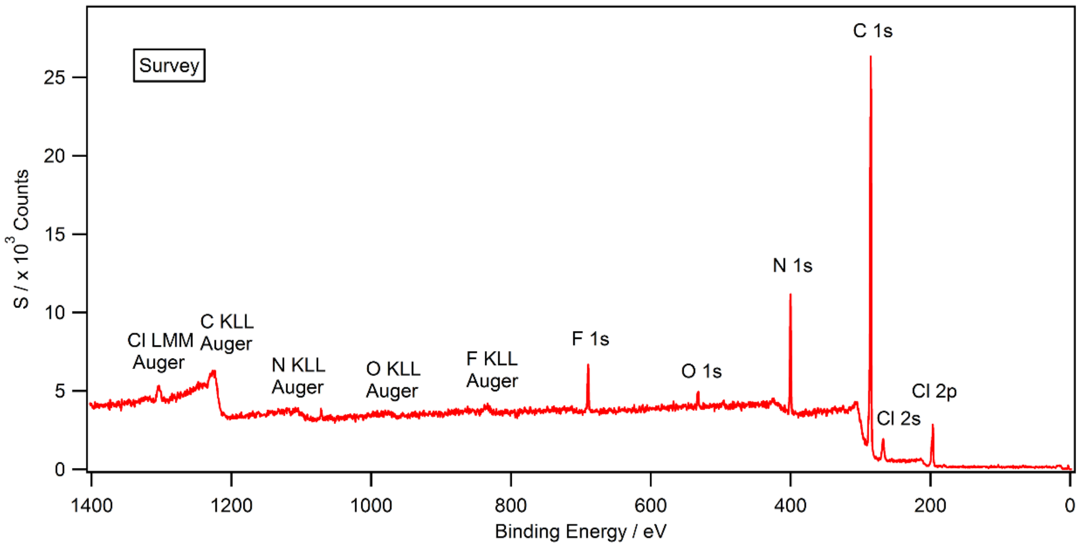
The [dmg] chloride (0.51 g, 1.36 mmol) was transferred to a round bottom flask followed by the addition of water. $LiNTf_2$ (0.47 g, 1.63 mmol) solution was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 hours. Dichloromethane was added to recover the ionic liquid and washed with cold water. The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 °C. The salt [$(C_8C_1)_2$dmg][NTf_2] (0.83 g; 98%) was obtained as a slight yellow coloured liquid.

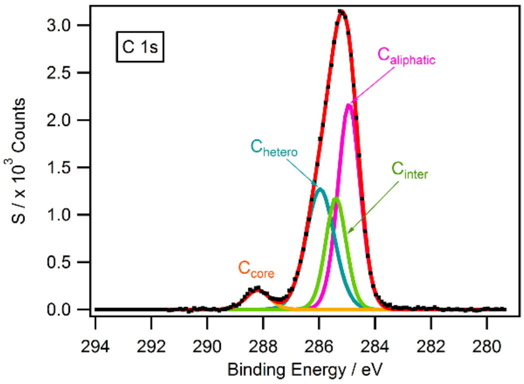
^{1}H NMR (400 MHz, $CDCl_3$): δ ppm 0.88 (t, J =6.80 Hz, 6 H), 1.13 - 1.38 (m, 20 H), 1.40 - 1.81 (m, 4 H), 2.87 - 3.02 (m, 12 H), 3.04 - 3.25 (m, 4 H); ^{13}C NMR (101 MHz, $CDCl_3$): δ ppm 14.04, 22.58, 26.68, 27.55, 29.13, 31.71, 37.81, 40.22 and 40.50 (rotamers), 52.88, 115.11, 118.32, 121.50, 124.70, 163.70; ^{19}F NMR (376 MHz, $CDCl_3$) δ ppm -78.86. IR ν max ($CHCl_3$)/cm^{-1} 3045.02, 2930.60, 2858.25, 1569.12, 1467.12, 1408.37, 1349.59, 1192.12, 1135.42, 1060.19, 897.90. ESI-MS (+ve): calcd 340.3686, found 340.3677. Analysis: Calc. for $C_{23}H_{46}F_6N_4O_4S_2$: N 9.03, C 44.50, H 7.47. Found: N 9.11, C 44.62, H 7.33.

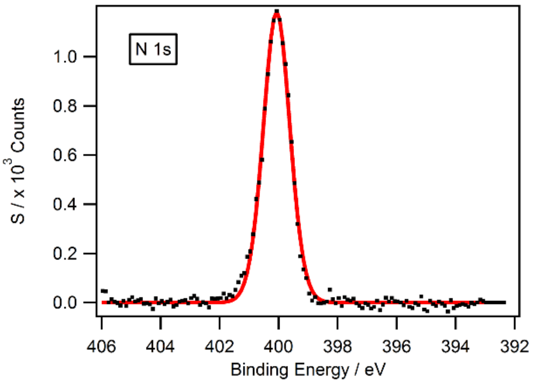
XP spectra of Ionic Liquids

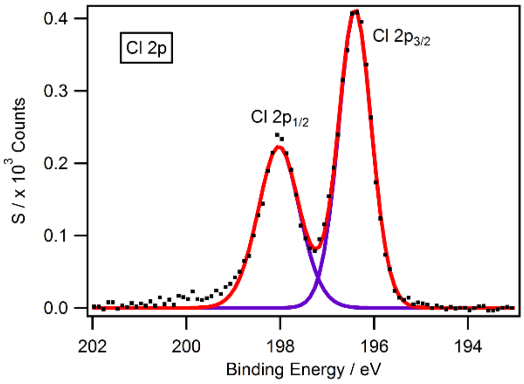
Survey and fitted high resolution spectra for all ionic liquids studied are presented in SI. C 1s high resolution spectra were fitted according to the models described within the paper. Cl 2p, S 2p and P 2p high resolution spectra were fitted taking into account spin-orbit coupling, whereby the area ratio of $2p_{1/2}$:$2p_{3/2}$ components is set to 1:2. The O 1s and S 2p high resolution spectra for ionic liquids containing the $[NTf_2]^-$ anion 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. Likewise, the C_{core} 1s and N 1s high resolution spectra of all cations are affected by shake up/off phenomena and a 20% and 12%, respectively, intensity loss (per carbon/nitrogen atom involved in double bonding) was taken into account when calculating atomic percentages for these elements.[2]

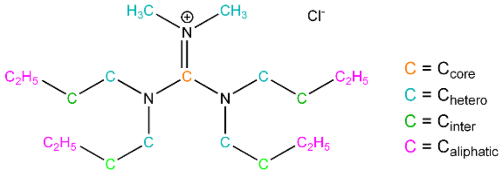
$[(C_4C_4)_2dmg][Cl]$ survey and high resolution scans



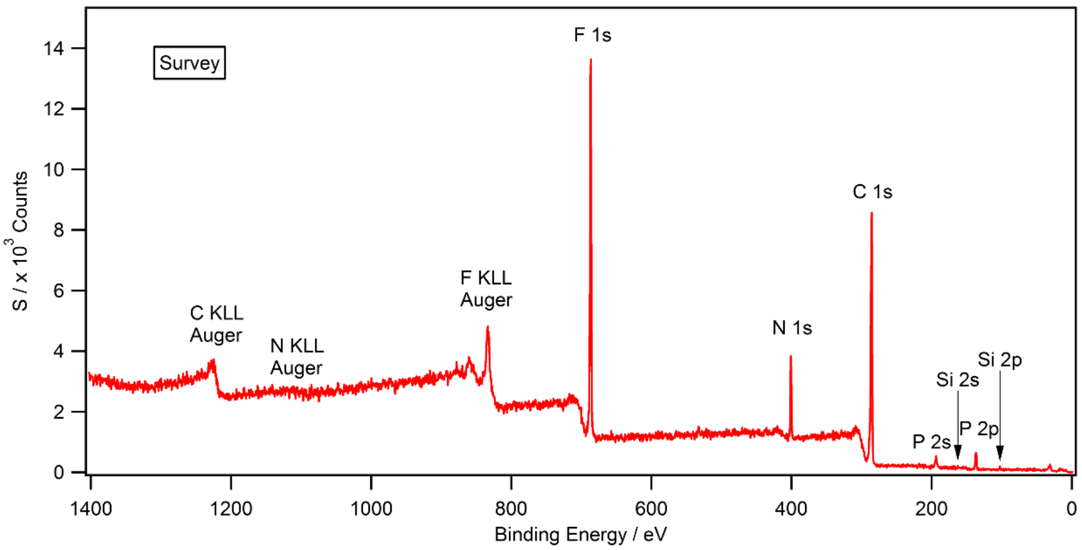


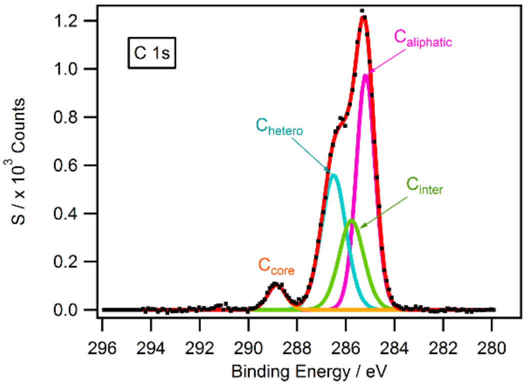


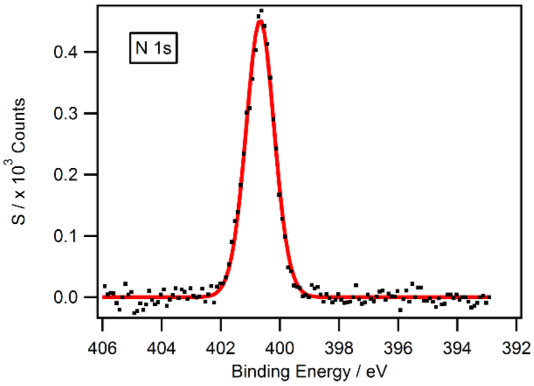


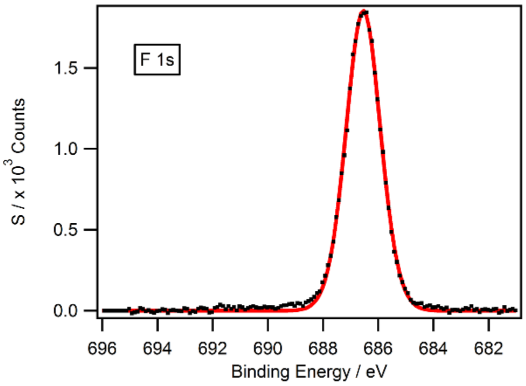


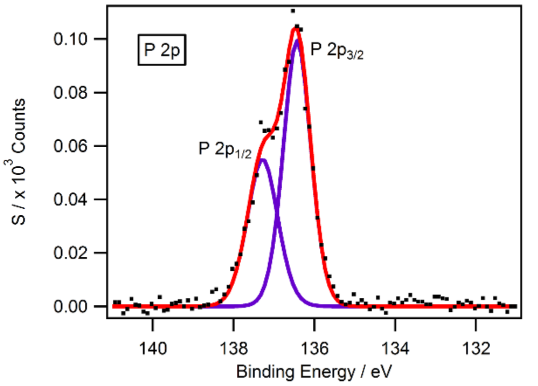
[$(C_4C_4)_2$dmg][PF_6] survey and high resolution scans

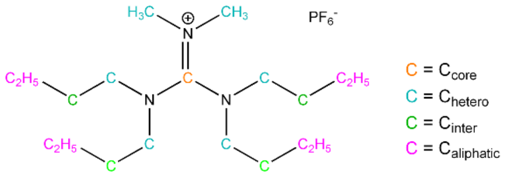




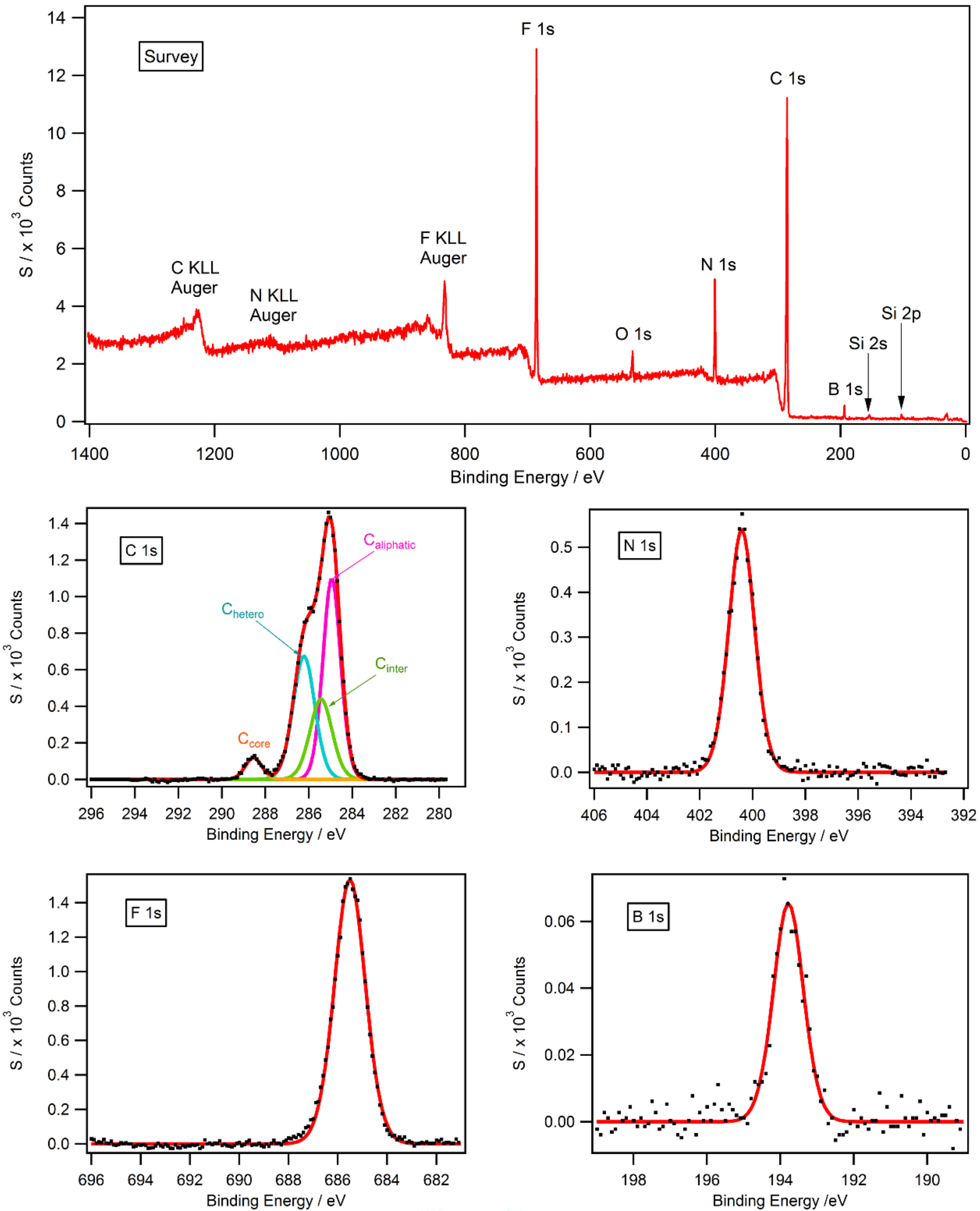


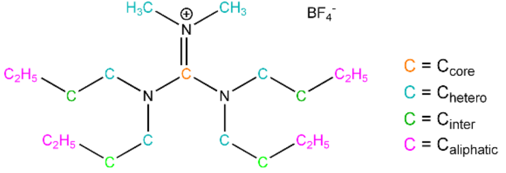




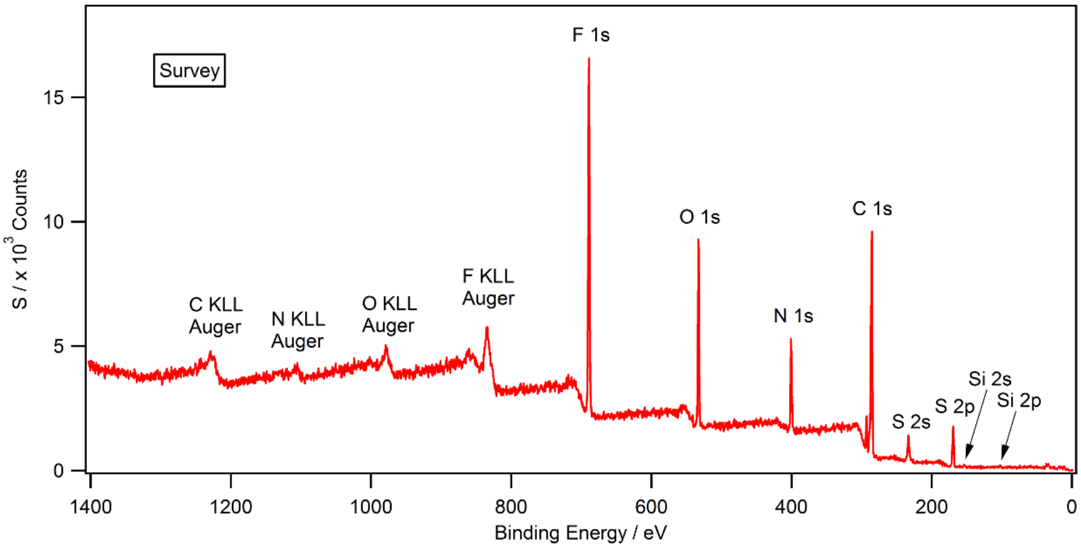


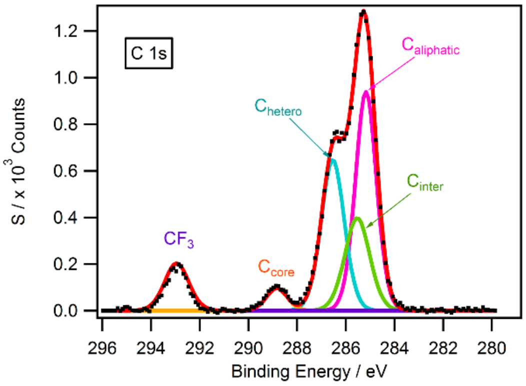
$[(C_4C_4)_2dmg][BF_4]$ survey and high resolution scans

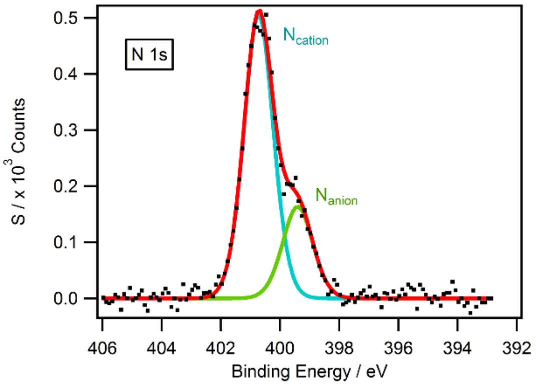


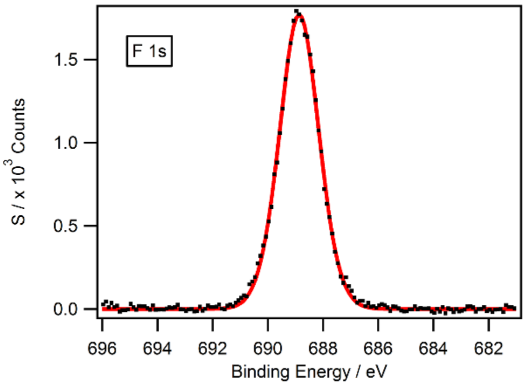


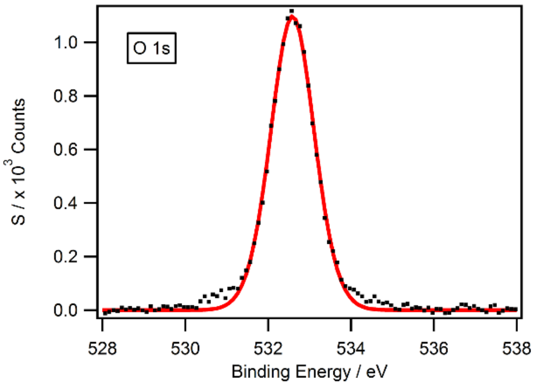
$[(C_4C_4)_2dmg][NTf_2]$ survey and high resolution scans

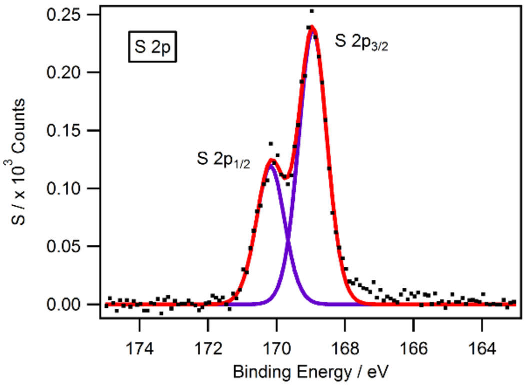


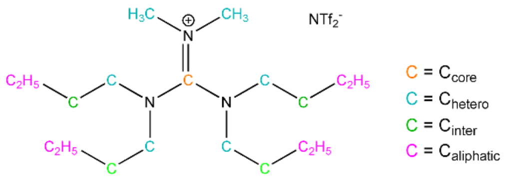




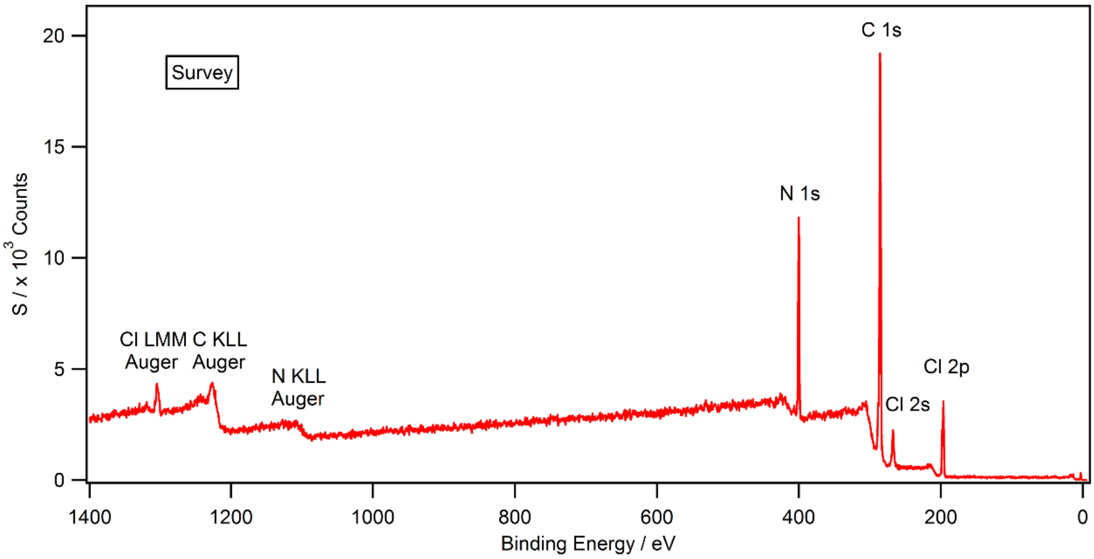


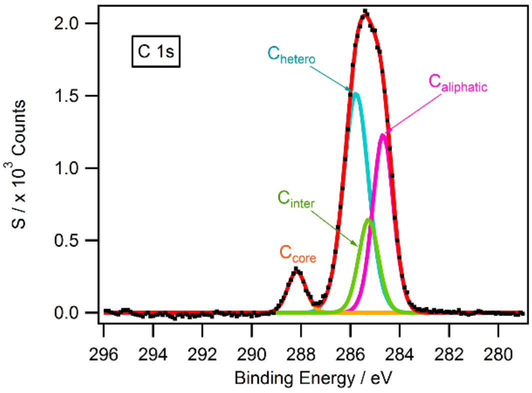


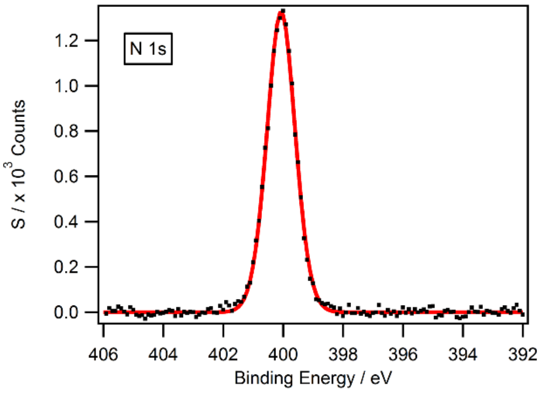


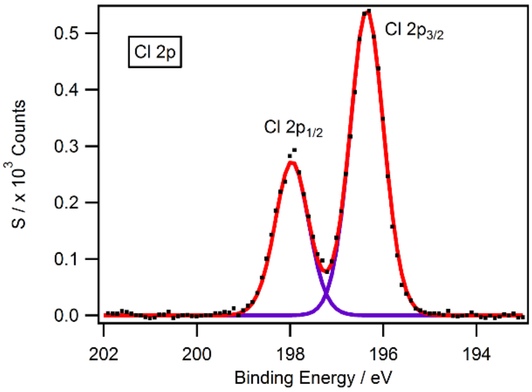


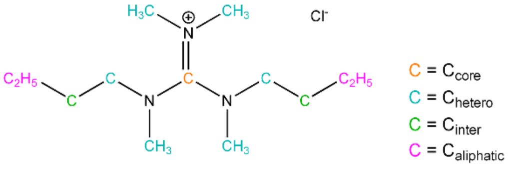
$[(C_4C_1)_2dmg][Cl]$ survey and high resolution scans



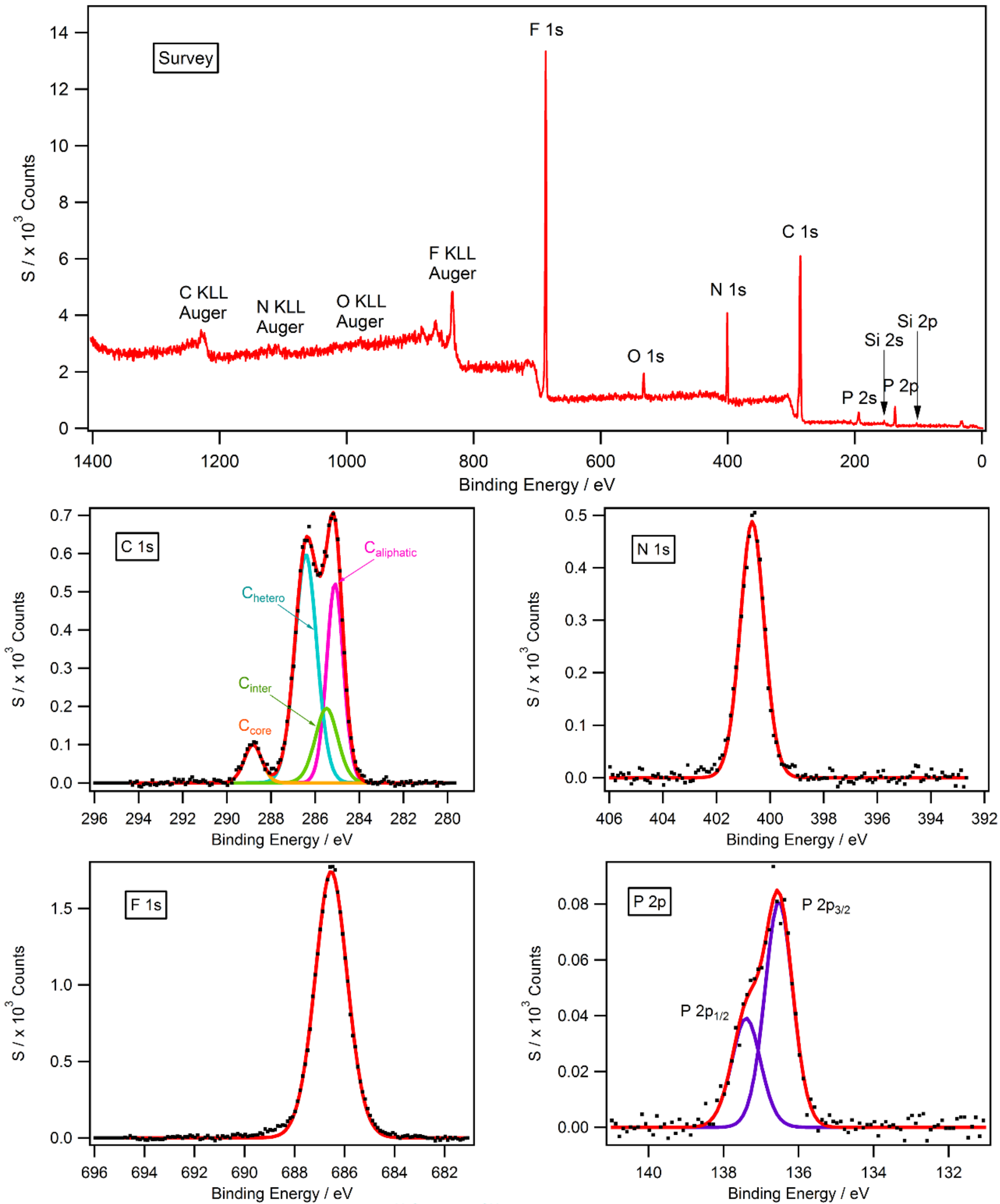


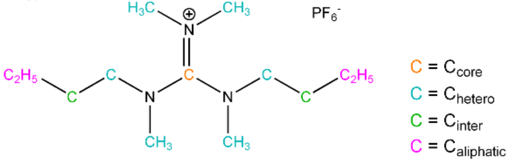




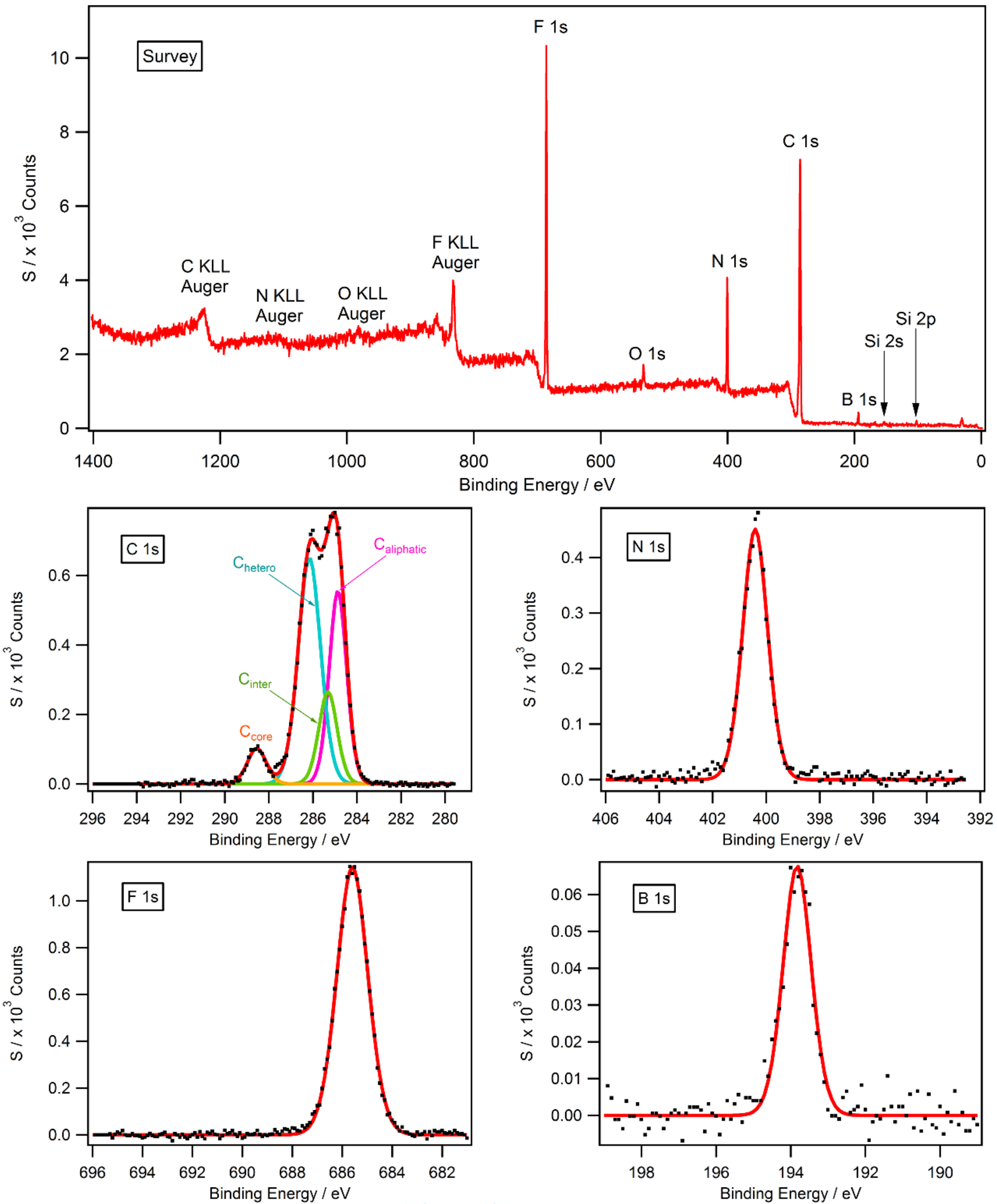


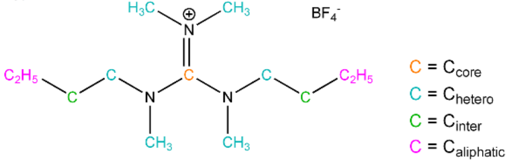
[$(C_4C_1)_2$dmg][PF_6] survey and high resolution scans



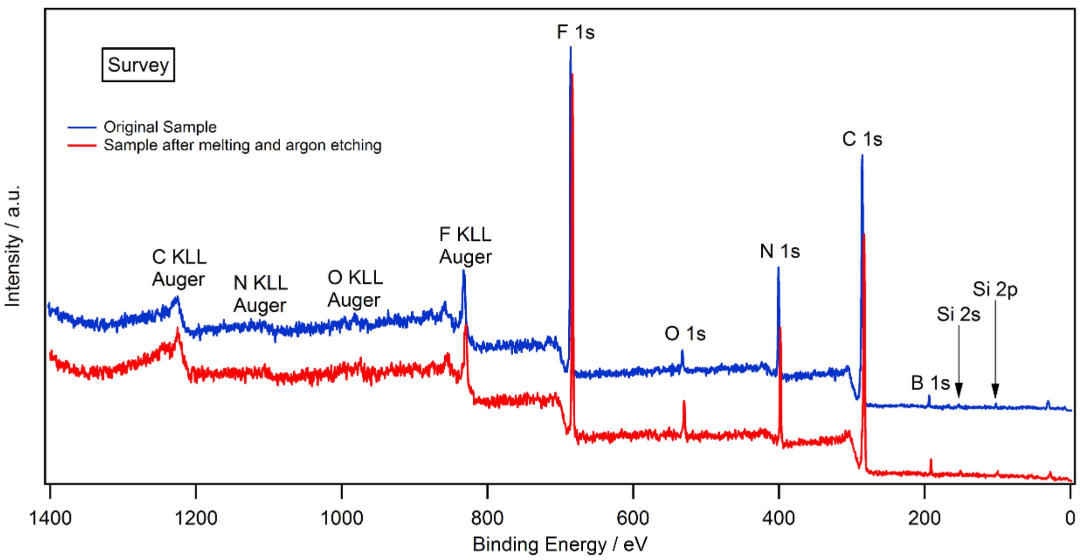


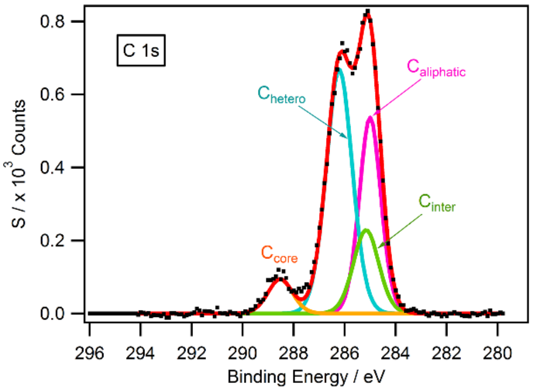
$[(C_4C_1)_2dmg][BF_4]$ survey and high resolution scans

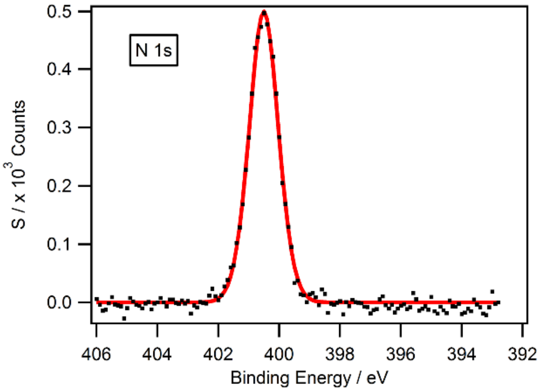


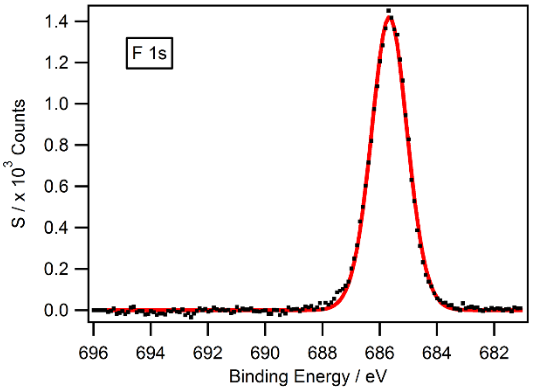


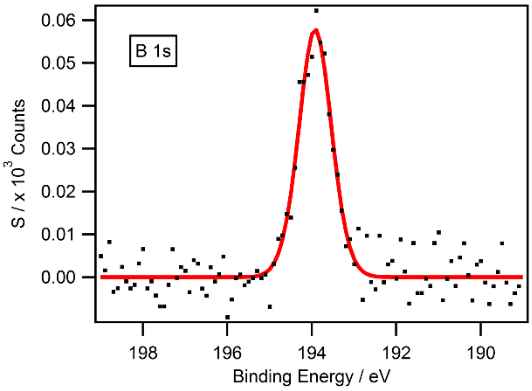
[$(C_4C_1)_2$dmg][BF_4] survey and high resolution scans – melting followed by argon etching



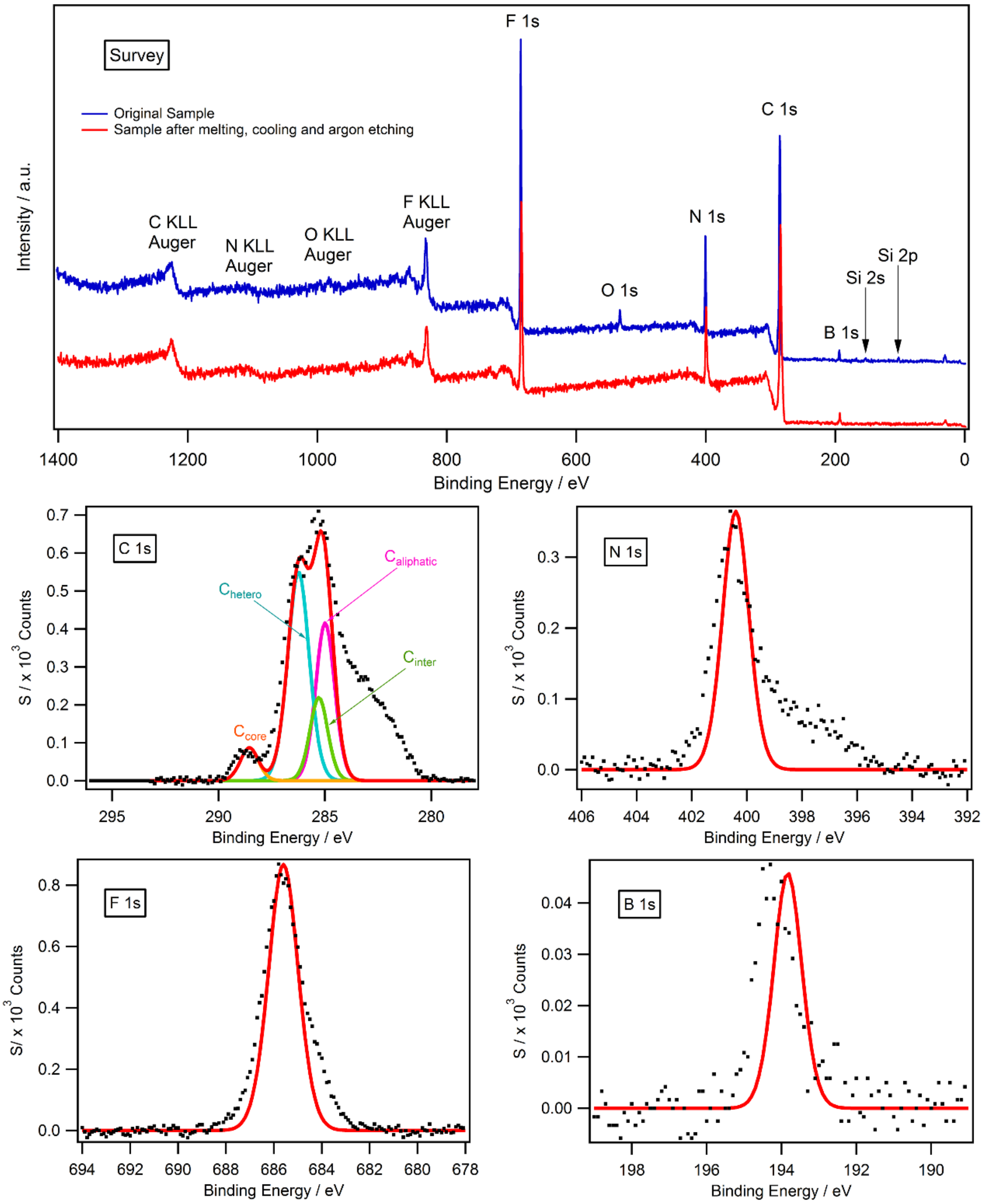








$[(C_4C_1)_2dmg][BF_4]$ survey and high resolution scans – melting, followed by cooling to form a glassy state solid and finally argon etching[1]



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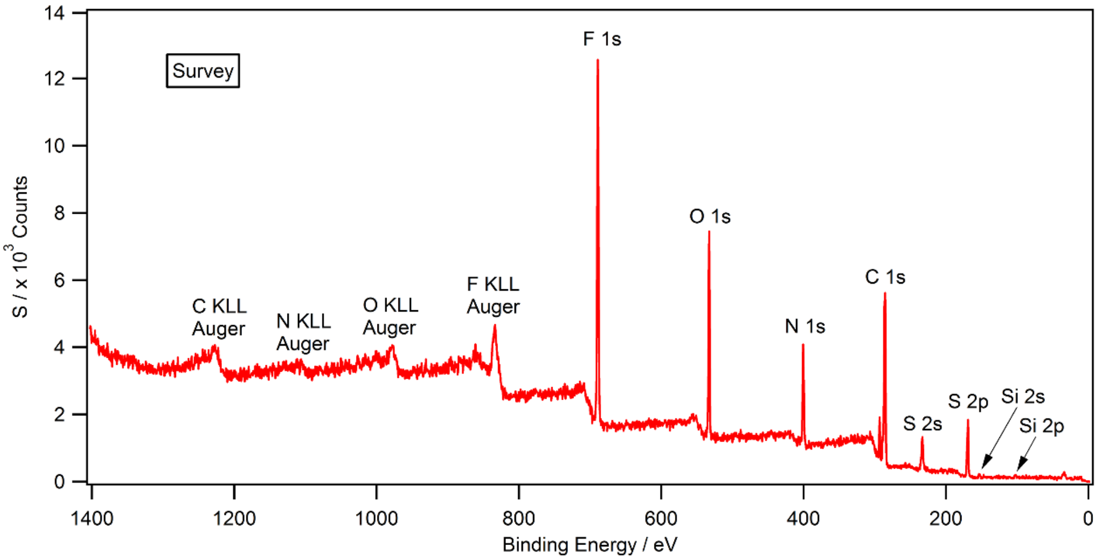
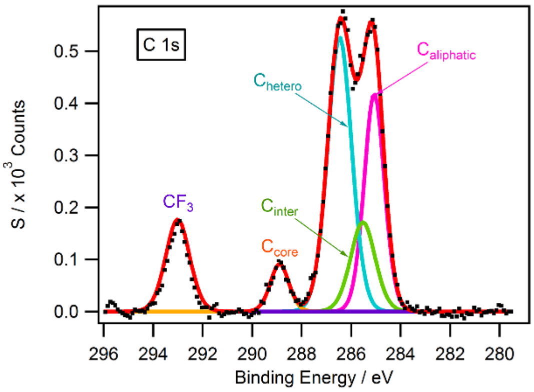
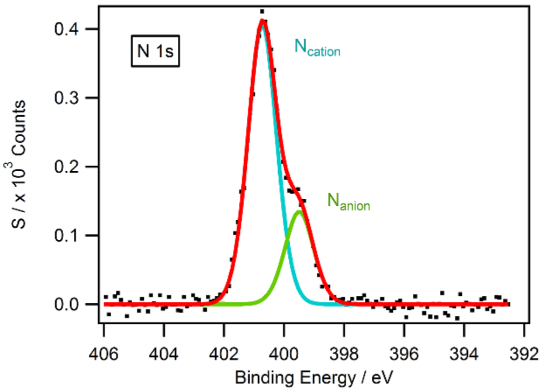
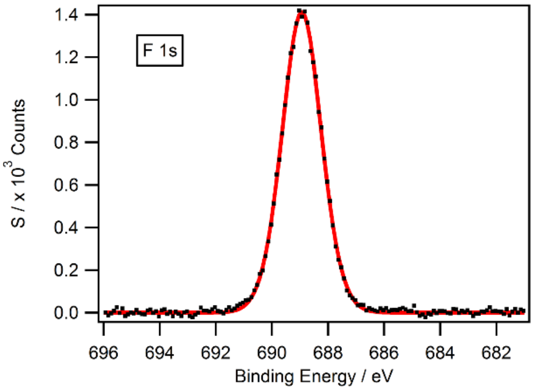
[1] XP spectra charge corrected to F 1s = 685.6 eV and model fitted to match original fitting for $[(C_4C_1)_2dmg][BF_4]$ to highlight extensive peak broadening as a result of the irreversible damage under the argon beam.

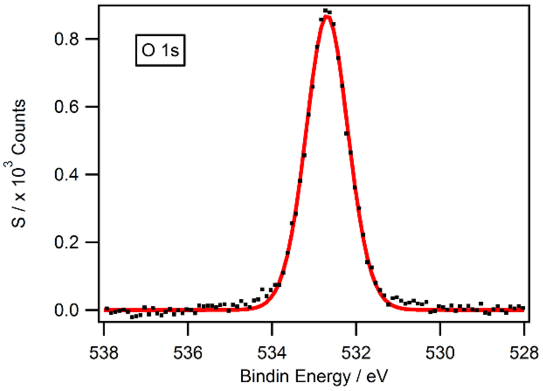
$[(C_4C_1)_2dmg][NTf_2]$ survey and high resolution scans

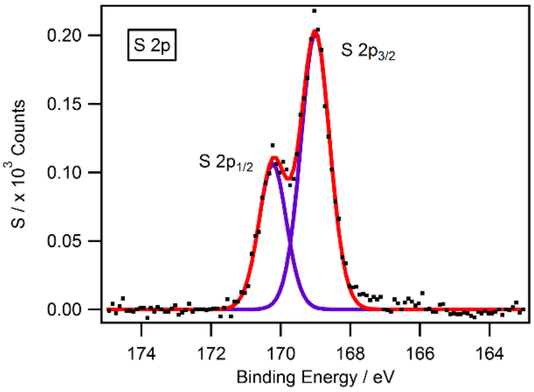


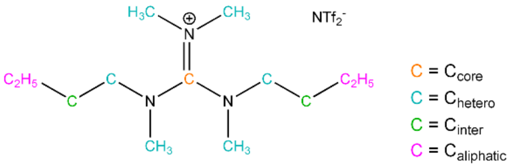




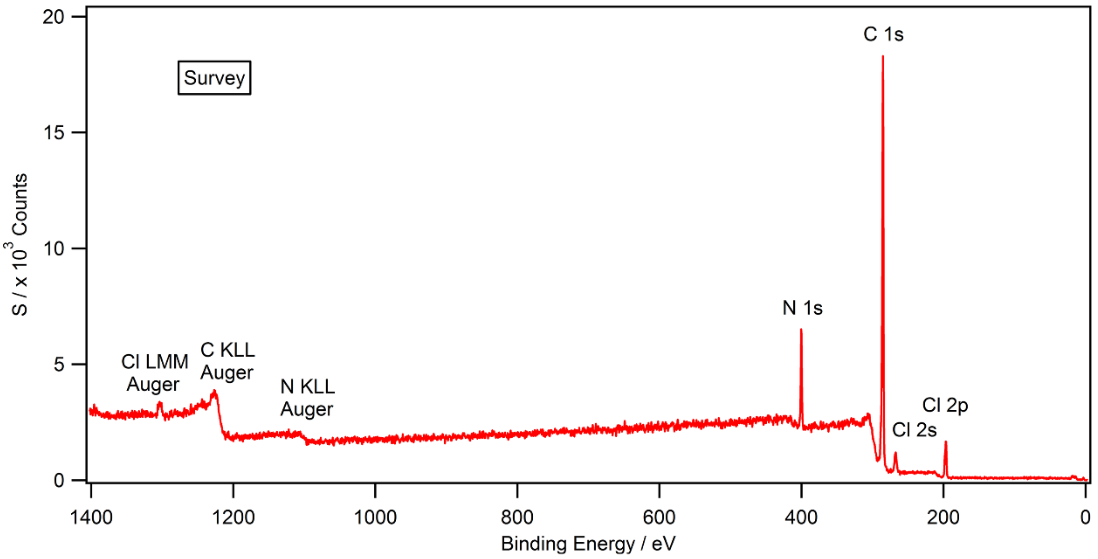


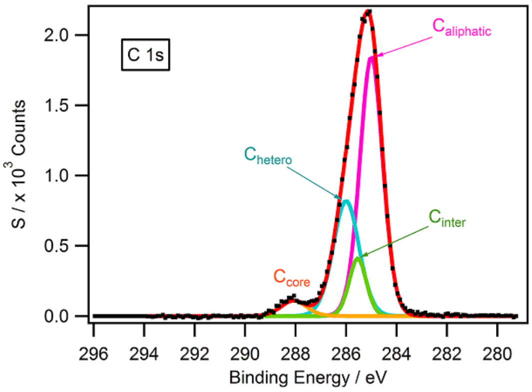


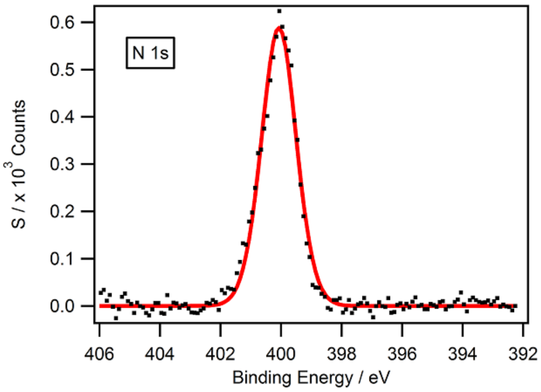


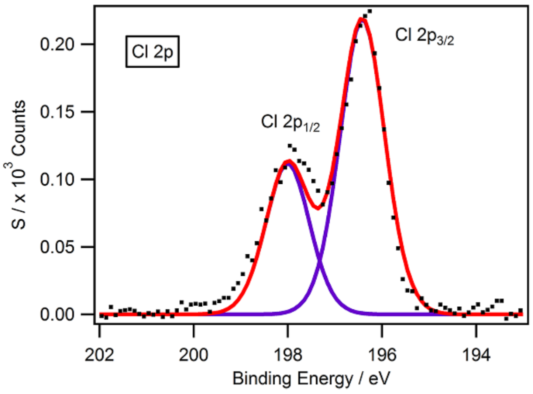


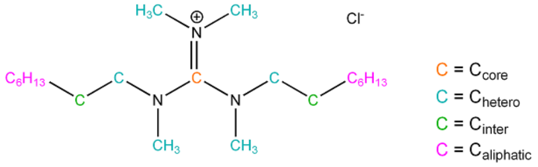
$[(C_8C_1)_2dmg][Cl]$ survey and high resolution scans



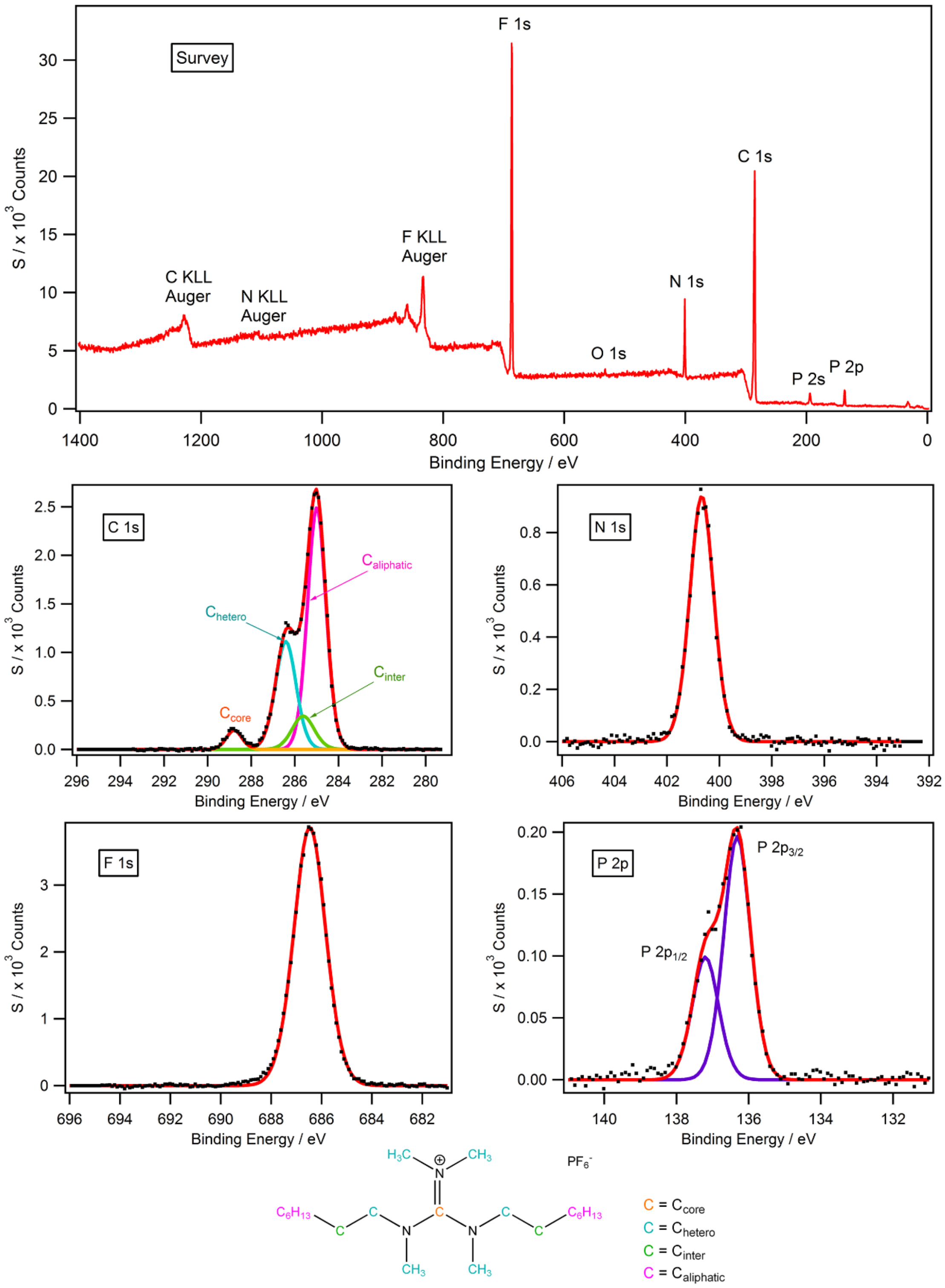




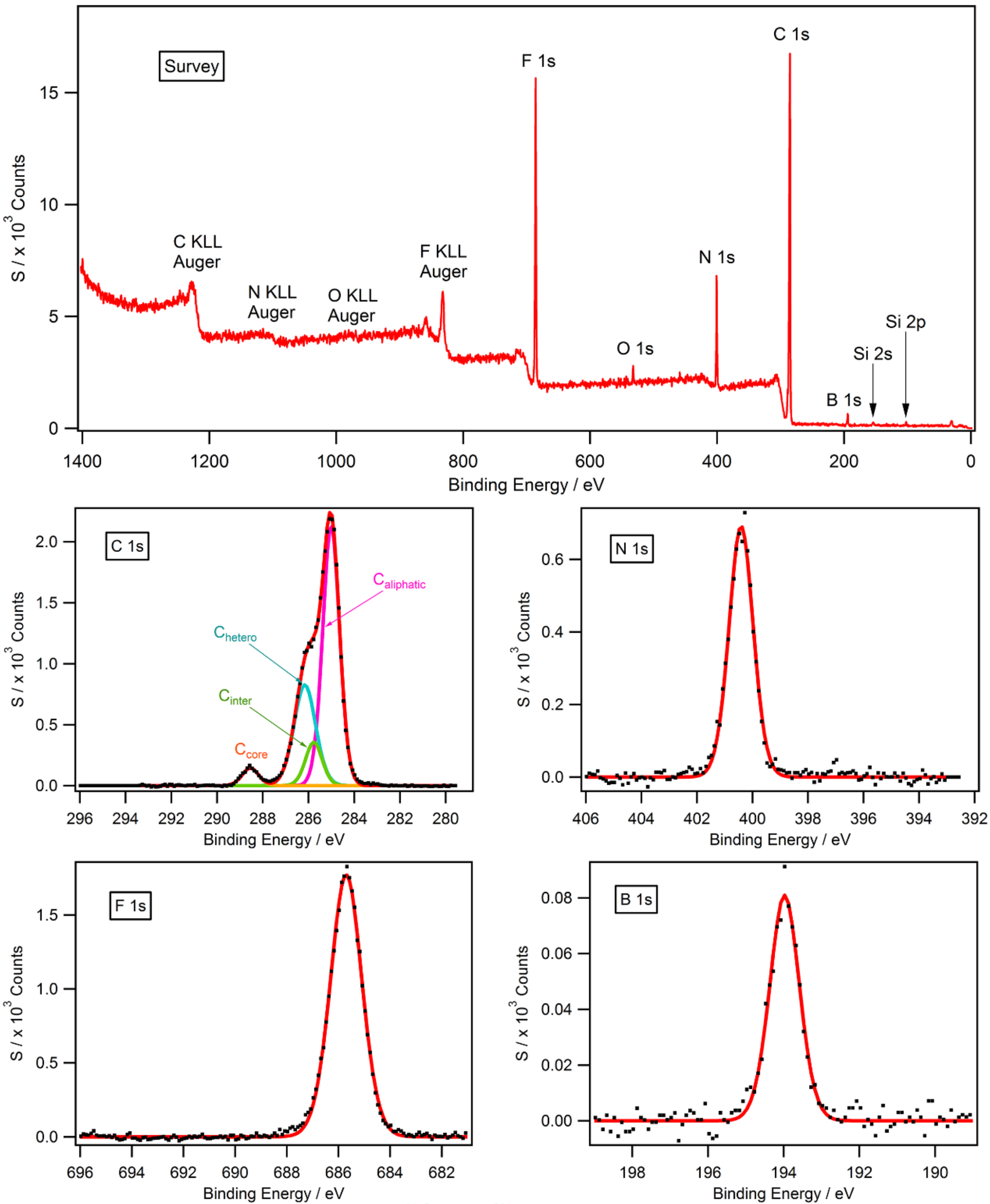


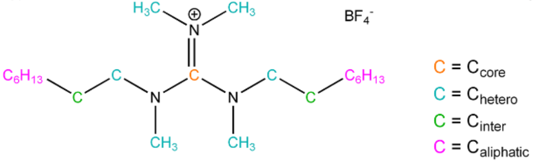


[$(C_8C_1)_2$dmg][PF_6] survey and high resolution scans

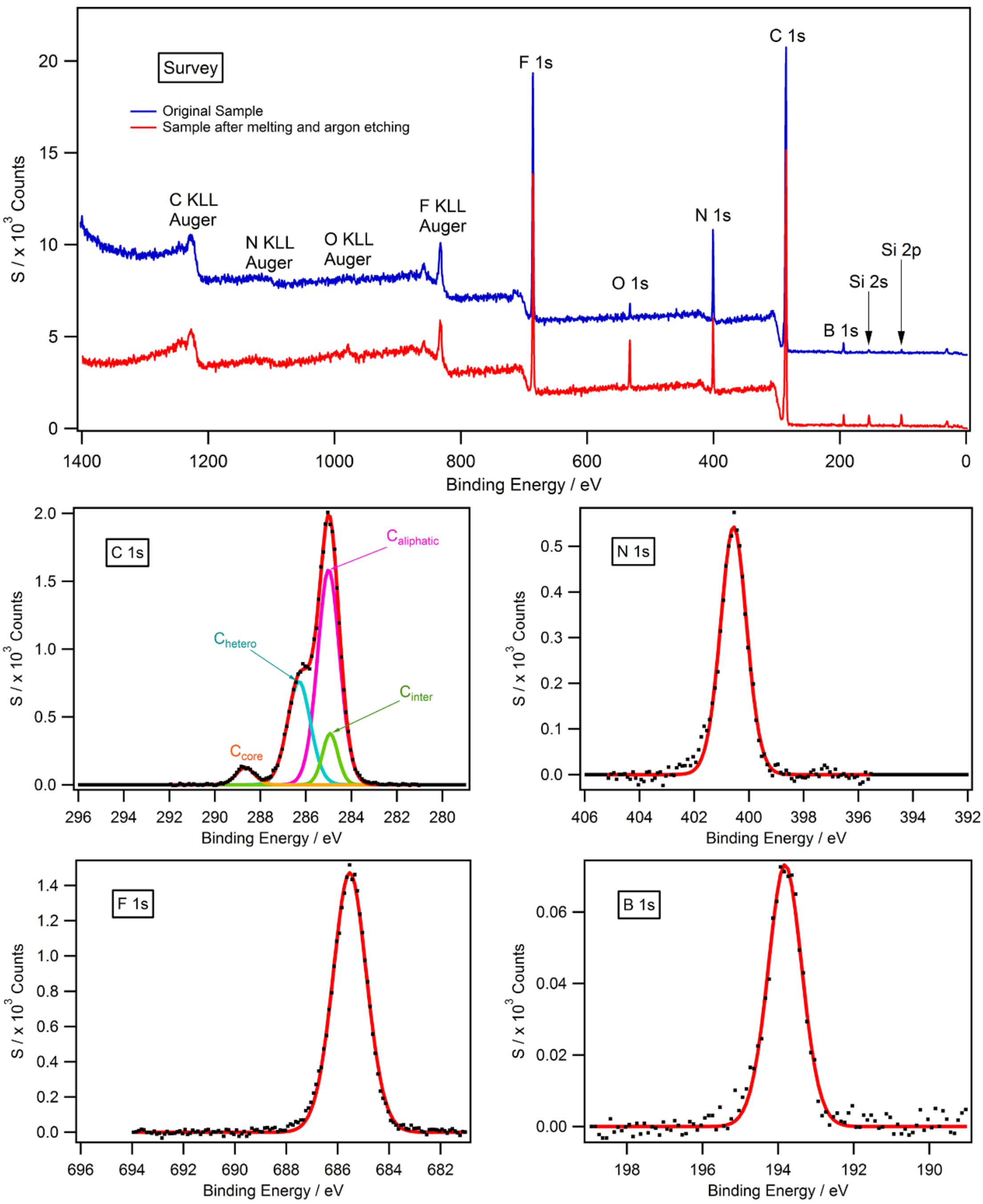


$[(C_8C_1)_2dmg][BF_4]$ survey and high resolution scans

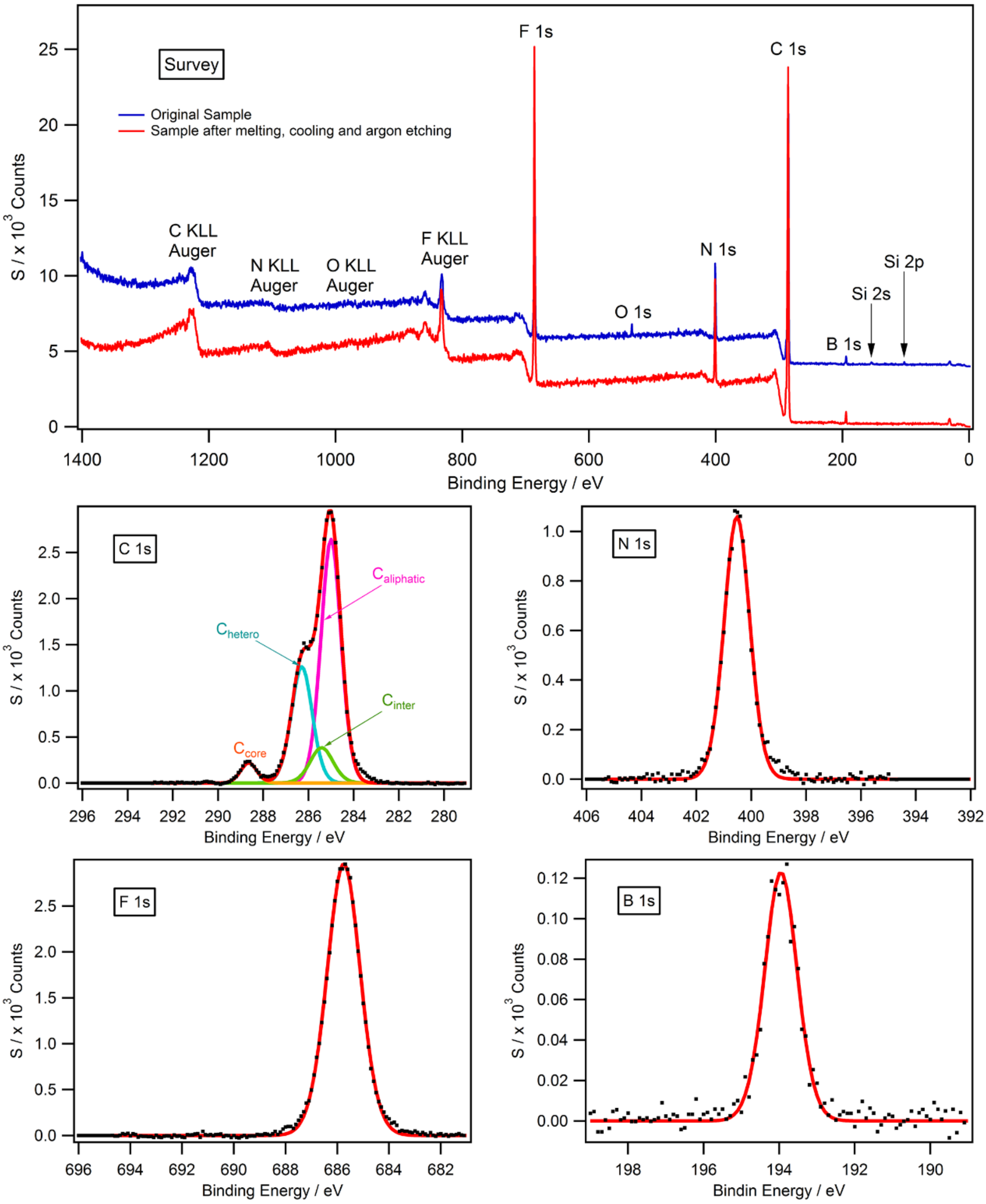




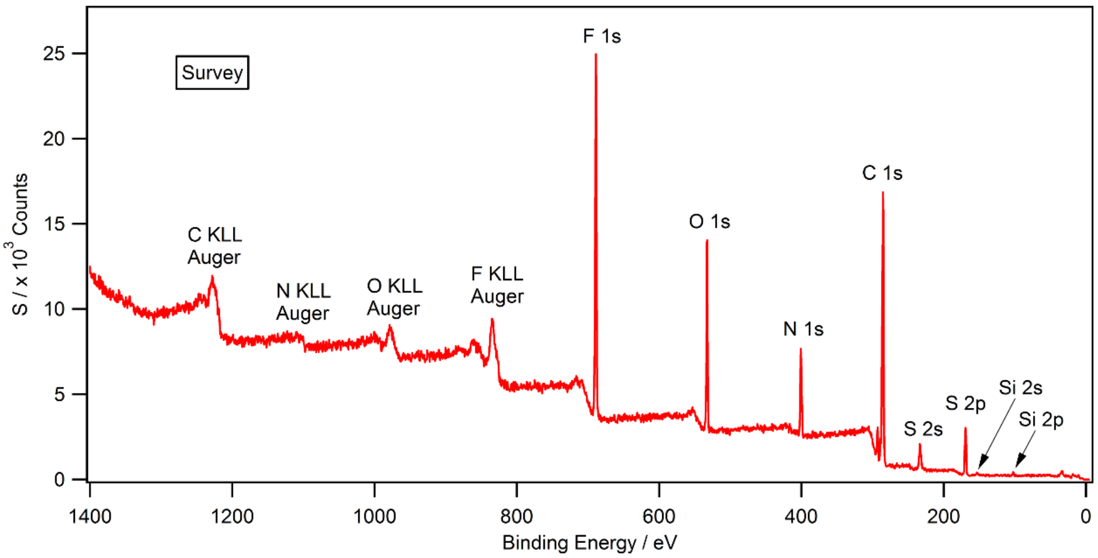
[$(C_8C_1)_2$dmg][BF_4] survey and high resolution scans – melting followed by argon etching

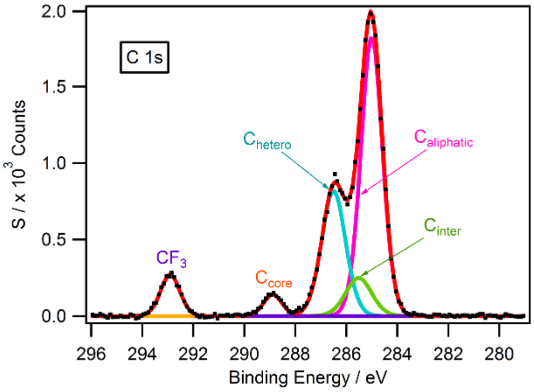


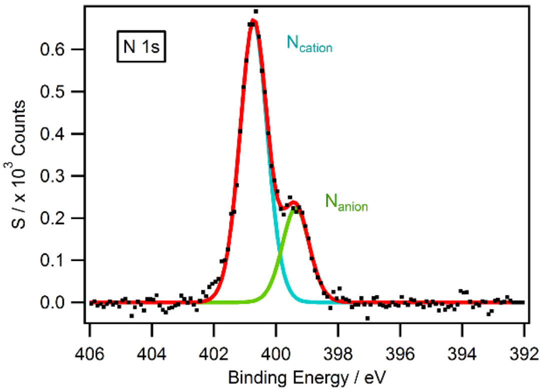
$[(C_8C_1)_2dmg][BF_4]$ survey and high resolution scans – melting, followed by cooling to form a glassy state solid and finally argon etching

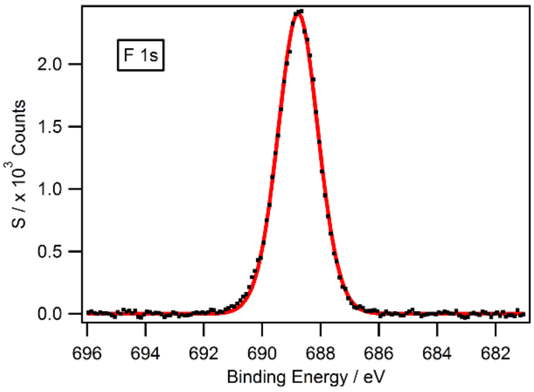


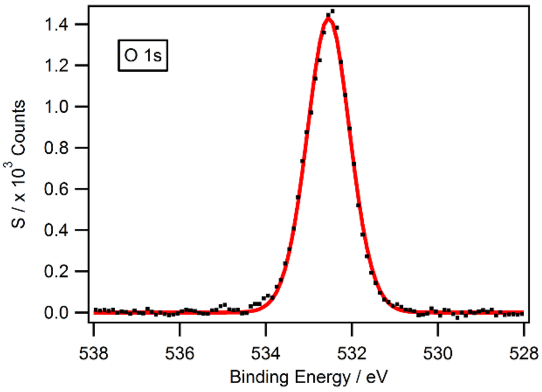
$[(C_8C_1)_2dmg][NTf_2]$ survey and high resolution scans

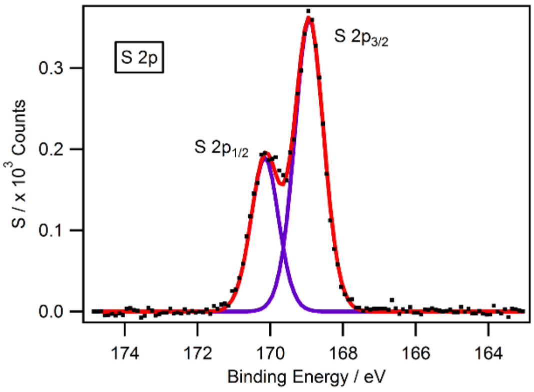


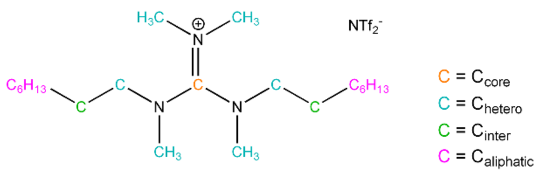












References

1. N. M. M. Mateus, L. C. Branco, N. M. T. Lourenço and C. A. M. Afonso, *Green Chem.*, 2003, **5**, 347-352.
2. E. F. Smith, F. J. M. Rutten, I. J. Villar-Garcia, D. Briggs and P. Licence, *Langmuir*, 2006, **22**, 9386-9392.