

Supporting Information

Resolving X-Ray Photoelectron Spectra of Ionic Liquids with Difference Spectroscopy

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1. Synthesis

1.1 Materials

All materials were purchased from Sigma-Aldrich or VWR and used as received except for 1-Methylimidazole which was distilled from CaH₂ before use. Unless otherwise stated, all chemistry was performed using standard Schlenk techniques with anhydrous solvents purchased from Sigma-Aldrich or dried by activated alumina towers (H₂O = 3-10 ppm). All non-functionalised ILs and [C_nC₁-4-ClIm][NTf₂] (where n = 2 or 8) were prepared according to existing published procedures.¹ Non-functionalised ILs were tested for residual halide impurities by ion chromatography (IC) as previously reported,² while the washings of all chlorinated ILs were tested for residual halides with an aqueous 0.1 M AgNO₃ solution. All IC traces were negative for bromide or chloride ions (detection limit ≤10 ppb) and all AgNO₃ tests were negative for residual halide ions. NMR experiments were recorded using a Bruker DPX-300 spectrometer with operating frequencies of 300 (¹H), 75 (¹³C), 282 (¹⁹F) and 121 (³¹P) MHz. Chemical shifts (δ) are reported in parts per million (ppm) and spectra are referenced to the residual solvent peaks of commercial deuterated solvents. For this work DMSO-d₆ (δH 2.50 and δC 39.51 ppm), MeOD-d₄ (δH 3.31/4.87 and δC 49.1 ppm), CDCl₃ (δH 7.27 and δC 77.0 ppm) and D₂O (δH 4.75 ppm) were used at room temperature. Coupling constants (J) are presented in Hz. Electrospray ionisation mass spectrometry (ESI-MS) was recorded on a Bruker microTOF MS with both positive and negative ionisation sources. Solutions were made using analytical grade solvents in either acetonitrile or methanol.

1.2 Methods

1-Butyl-2-pyridone (C₄-2-OPy)

In air, 2-Hydroxypyridine (2.00 g, 21.0 mmol), potassium carbonate (5.81 g, 42.1 mmol, 2.0 eq.), tetrabutylammonium bromide (0.68 g, 2.10 mmol, 0.1 eq.) and 1-bromobutane (4.32 g, 3.40 mL, 31.6 mmol, 1.5 eq.) were added to toluene (200 mL) and 1-2 mL of water was added. A reflux condenser was added to the reaction vessel and the mixture was heated to 50 °C and left to stir for 1 hr. The temperature was raised to 130 °C and mixture was left to reflux for 2 hr. After cooling, the insoluble material was removed by filtration and the solvent was evaporated to give a crude yellow oil. The crude product was then purified by column chromatography (hexane:ethyl acetate, 30:70) to give a yellow oil (2.06 g, 64.8%). ¹H NMR (CHLOROFORM-d, 400MHz): δ = 7.15 - 7.35 (m, 2 H), 6.52 (d, J=9.0 Hz, 1 H), 6.05 - 6.17 (m, 1 H), 3.89 (t, J=7.1 Hz, 2 H), 1.58 - 1.77 (m, 2 H), 1.26 - 1.45 (m, 2 H), 0.92 ppm (t, J=7.3 Hz, 3 H). ¹³C NMR (CHLOROFORM-d, 101MHz): δ = 162.5, 139.0, 137.4, 120.9, 105.7, 49.5, 31.2, 19.7, 13.6 ppm.

Data consistent with previous reports.^{3,4}

1-Octyl-2-pyridone (C₈-2-OPy)

The same procedure used to prepare C₄-2-OPy was used to prepare C₈-2-OPy from 2-hydroxypyridine (4.85 g, 50.0 mmol), potassium carbonate (13.8 g, 100.0 mmol, 2.0 eq.), tetrabutylammonium bromide (1.63 g, 5.00 mmol, 0.1 eq.) and 1-bromooctane (14.5 g, 13.0 mL, 75.0 mmol, 1.5 eq.) to give a crude yellow product which was purified by column chromatography (hexane:ethyl acetate, 30:70) to give a yellow oil (7.69 g, 74.2%). ¹H NMR (CHLOROFORM-d, 300MHz): δ = 7.19 - 7.33 (m, 2 H), 6.53 (d, *J*=9.1 Hz, 1 H), 6.12 (td, *J*=6.7, 1.4 Hz, 1 H), 3.89 (t, *J*=7.5 Hz, 2 H), 1.63 - 1.81 (m, 2 H), 1.13 - 1.41 (m, 10 H), 0.85 ppm (t, *J*=6.7 Hz, 3 H). ¹³C NMR (CHLOROFORM-d, 75MHz): δ = 162.5, 139.1, 137.4, 121.0, 105.7, 49.8, 31.6, 29.2, 29.1, 29.0, 26.5, 22.5, 14.0 ppm.

Data consistent with previous reports.^{3,5}

1-Butyl-2-chloropyridinium bis(trifluoromethanesulfonyl)imide ([C₄-2-CIPy][NTf₂])

C₄-2-OPy (2.00 g, 13.2 mmol) was introduced to a dried schlenk flask under an inert atmosphere and phosphorus oxychloride (17.2 g, 10.5 mL, 112.4 mmol, 8.5 eq.) was slowly added. The mixture was heated to 110 °C and left to stir for 2 hrs. After cooling, the phosphorus oxychloride was evaporated and the resulting viscous brown liquid was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 2 hr. Water (50 mL) was slowly added, ensuring the temperature remained below 40 °C. A solution of Li[NTf₂] (4.55 g, 15.8 mmol, 1.2 eq.) in water (10 mL) was added dropwise and the mixture was left to stir for 2 hr. A small portion of DCM was added and the mixture was stirred vigorously. The aqueous layer was removed and the organic layer was further washed with water (3 x 30 mL). The solvent was evaporated to give a light brown liquid (4.14 g, 69.5%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ¹H NMR (DMSO-d₆, 300MHz): δ = 9.20 (dd, *J*=6.2, 1.6 Hz, 1 H), 8.60 (td, *J*=8.1, 1.6 Hz, 1 H), 8.38 (dd, *J*=8.1, 1.3 Hz, 1 H), 8.13 (ddd, *J*=7.6, 6.2, 1.3 Hz, 1 H), 4.70 (t, *J*=7.7 Hz, 2 H), 1.78 - 1.99 (m, 2 H), 1.29 - 1.54 (m, 2 H), 0.94 ppm (t, *J*=7.3 Hz, 3 H). ¹³C NMR (DMSO-d₆, 75MHz): δ = 147.6, 147.2, 146.1, 130.3, 126.6, 119.5 (q, *J*_{CF} = 322 Hz, 2C, CF₃), 59.6, 30.8, 18.8, 13.3 ppm. ¹⁹F NMR (DMSO-d₆, 282 MHz) δ = -78.73 (s, 6 F, CF₃) ppm. HRMS (ESI) *m/z*: [M]⁺ Calcd for [C₉H₁₃ClN]⁺ 170.0731; Found 170.0740.

1-Octyl-2-chloropyridinium bis(trifluoromethanesulfonyl)imide ([C₈-2-CIPy][NTf₂])

The same procedure used to prepare [C₄-3-CIPy][NTf₂] was used to prepare [C₈-2-CIPy][NTf₂] from C₈-2-OPy (2.00 g, 9.65 mmol), phosphorus oxychloride (12.6 g, 82.1 mmol, 8.5 eq.) and Li[NTf₂] (3.33 g, 11.6 mmol, 1.2 eq.) to give a light brown liquid (3.47 g, 71.0%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ¹H NMR (CHLOROFORM-d, 300MHz): δ = 8.95 (dd, *J*=6.2, 1.7 Hz, 1 H), 8.49 (td, *J*=8.1, 1.7 Hz, 1 H), 8.09 (dd, *J*=8.1, 1.3 Hz, 1 H), 8.00 (ddd, *J*=7.7, 6.2, 1.3 Hz, 1 H), 4.74 (t, *J*=7.8 Hz, 2 H), 1.90 - 2.08 (m, 2 H), 1.19 - 1.51 (m, 10 H), 0.79 - 0.94 ppm (m, 3 H). ¹³C NMR (CHLOROFORM-d, 75MHz): δ

= 147.6, 147.3, 146.4, 130.5, 127.1, 119.7 (q, $J_{CF} = 322$ Hz, 2C, CF₃), 61.1, 31.5, 29.8, 28.8, 28.7, 26.0, 22.5, 13.9 ppm. ¹⁹F NMR (DMSO-*d*₆, 282 MHz) $\delta = -78.91$ (s, 6 F, CF₃) ppm. HRMS (ESI) m/z : [M]⁺ Calcd for [C₁₃H₂₁ClN]⁺ 226.1357; Found 226.1355. Anal. Calcd for C₁₅H₂₁ClF₆N₂O₄S₂: C, 35.54; H, 4.18; N 5.53. Found: C, 35.63; H, 3.88; N, 5.44.

1-Butyl-3-chloropyridinium bromide ([C₄-3-ClPy]Br)

3-Chloropyridine (10.0 g, 88.1 mmol) and 1-bromobutane (14.5 g, 11.35 mL, 105.7 mmol, 1.2 eq.) were combined under an inert atmosphere at room temperature. The mixture was heated to 90 °C and left to stir for 48 hr. After cooling, diethyl ether (100 mL) was added and the mixture was agitated until it solidified. The solid was isolated by filtration and recrystallised from methanol/diethyl ether to give a hygroscopic brown solid (16.9 g, 76.8%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ¹H NMR (DMSO-*d*₆, 300MHz): $\delta = 9.59 - 9.67$ (m, 1 H), 9.25 (d, $J=6.1$ Hz, 1 H), 8.77 - 8.84 (m, 1 H), 8.22 (dd, $J=8.4, 6.1$ Hz, 1 H), 4.68 (t, $J=7.5$ Hz, 2 H), 1.83 - 2.00 (m, 2 H), 1.20 - 1.39 (m, 2 H), 0.89 ppm (t, $J=7.4$ Hz, 3 H). ¹³C NMR (DMSO-*d*₆, 75MHz): $\delta = 145.1, 144.1, 143.7, 133.9, 128.7, 60.7, 32.5, 18.7, 13.3$ ppm. HRMS (ESI) m/z : [M]⁺ Calcd for [C₉H₁₃ClN]⁺ 170.0731; Found 170.0738.

1-Octyl-3-chloropyridinium bromide ([C₈-3-ClPy]Br)

3-Chloropyridine (10.0 g, 88.1 mmol) and 1-bromooctane (20.4 g, 18.3 mL, 1.2 eq.) were combined under an inert atmosphere at room temperature. The mixture was heated to 80 °C and left to stir for 48 hr. After cooling, ethyl acetate (100 mL) was added and the viscous liquid was agitated until it solidified. The solid was collected and recrystallised from methanol/diethyl ether to give a hygroscopic brown solid (22.9 g, 84.8%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ¹H NMR (DMSO-*d*₆, 300MHz): $\delta = 9.61$ (s, 1 H), 9.23 (d, $J=6.1$ Hz, 1 H), 8.74 - 8.86 (m, 1 H), 8.22 (dd, $J=8.5, 6.1$ Hz, 1 H), 4.66 (t, $J=7.5$ Hz, 2 H), 1.80 - 2.02 (m, 2 H), 1.15 - 1.43 (m, 10 H), 0.84 ppm (t, $J=7.1$ Hz, 3 H). ¹³C NMR (DMSO-*d*₆, 75MHz): $\delta = 145.6, 144.7, 144.2, 134.4, 129.2, 61.5, 31.6, 31.1, 28.9, 28.8, 25.8, 22.5, 14.4$ ppm. HRMS (ESI) m/z : [M]⁺ Calcd for [C₁₃H₂₁ClN]⁺ 226.1357; Found 226.1364.

1-Octyl-3-chloropyridinium tetrafluoroborate ([C₈-3-ClPy][BF₄])

[C₈-3-ClPy]Br (5.00 g, 16.3 mmol) was dissolved in water (100 mL) and the solution was heated to 40 °C. A solution of sodium tetrafluoroborate (2.15g, 19.6 mmol, 1.2 eq.) in water (10 mL) was added dropwise and the mixture was left to stir for 2 hr. After cooling, a small portion of DCM was added and the mixture was left to stir overnight. The aqueous layer was separated, and the organic layer was

washed with water (5 x 30 mL). The organic solvent was removed to give a viscous light brown liquid (4.21 g, 82.4%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ^1H NMR (CHLOROFORM- d , 300MHz): δ = 8.76 - 8.89 (m, 2 H), 8.39 - 8.51 (m, 1 H), 8.08 (dd, $J=8.4, 6.5$ Hz, 1 H), 4.66 (t, $J=7.5$ Hz, 2 H), 1.91 - 2.10 (m, 2 H), 1.16 - 1.42 (m, 10 H), 0.86 ppm (t, $J=6.7$ Hz, 3 H). ^{13}C NMR (CHLOROFORM- d , 75MHz): δ = 145.3, 143.4, 143.3, 136.1, 129.4, 63.0, 31.6, 31.5, 28.9, 28.9, 26.0, 22.5, 14.0 ppm. ^{19}F NMR (282 MHz, DMSO- d_6) δ ppm -151.2 (br. s, 4 F, BF_4), -151.3 ppm (q, $J_{\text{BF}} = 1.51$ Hz, 4 F, BF_4). HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{13}\text{H}_{21}\text{ClN}]^+$ 226.1357; Found 226.1361.

1-Butyl-3-chloropyridinium bis(trifluoromethanesulfonyl)imide ($[\text{C}_4\text{-3-CIPy}][\text{NTf}_2]$)

The same procedure used to prepare $[\text{C}_8\text{-3-CIPy}][\text{BF}_4]$ was used to prepare $[\text{C}_4\text{-3-CIPy}][\text{NTf}_2]$ from $[\text{C}_4\text{-3-CIPy}]\text{Br}$ (5.00 g, 19.95 mmol) and $\text{Li}[\text{NTf}_2]$ (6.90 g, 23.9 mmol, 1.2 eq.) to give a light brown liquid (5.98 g 66.5%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ^1H NMR (CHLOROFORM- d , 300MHz): δ = 8.71 - 8.80 (m, 2 H), 8.43 - 8.49 (m, 1 H), 8.00 (dd, $J=8.4, 6.1$ Hz, 1 H), 4.59 (t, $J=7.7$ Hz, 3 H), 1.89 - 2.08 (m, 2 H), 1.29 - 1.50 (m, 2 H), 0.94 ppm (t, $J=7.3$ Hz, 3 H). ^{13}C NMR (CHLOROFORM- d , 75MHz): δ = 145.3, 143.0, 136.5, 129.2, 119.7 (q, $J_{\text{CF}} = 322$ Hz, 2C, CF_3), 63.0, 33.3, 30.9, 19.1, 13.2 ppm. ^{19}F NMR (DMSO- d_6 , 282 MHz) δ = -78.92 (s, 6 F, CF_3) ppm. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_9\text{H}_{13}\text{ClN}]^+$ 170.0731; Found 170.0741.

1-Octyl-3-chloropyridinium bis(trifluoromethanesulfonyl)imide ($[\text{C}_8\text{-3-CIPy}][\text{NTf}_2]$)

The same procedure used to prepare $[\text{C}_8\text{-3-CIPy}][\text{BF}_4]$ was used to prepare $[\text{C}_8\text{-3-CIPy}][\text{NTf}_2]$ from $[\text{C}_8\text{-3-CIPy}]\text{Br}$ (5.00 g, 16.3 mmol) and $\text{Li}[\text{NTf}_2]$ (5.62 g, 19.6 mmol, 1.2 eq.) to give a light brown liquid (7.04 g 85.2%) that was dried at 70 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr. ^1H NMR (CHLOROFORM- d , 300MHz): δ = 8.78 - 8.86 (m, 2 H), 8.44 (ddd, $J=8.4, 1.9, 1.2$ Hz, 1 H), 8.06 (dd, $J=8.4, 6.0$ Hz, 1 H), 4.63 (t, $J=7.8$ Hz, 2 H), 1.91 - 2.10 (m, 2 H), 1.15 - 1.47 (m, 10 H), 0.87 ppm (t, $J=6.8$ Hz, 3 H). ^{13}C NMR (CHLOROFORM- d , 75MHz): δ = 145.3, 143.2, 143.1, 136.5, 129.2, 119.7 (q, $J_{\text{CF}} = 322$ Hz, 2C, CF_3), 63.1, 31.5, 31.4, 28.8, 28.7, 25.8, 22.5, 13.9 ppm. ^{19}F NMR (DMSO- d_6 , 282 MHz) δ = -78.95 (s, 6 F, CF_3) ppm. HRMS (ESI) m/z : $[\text{M}]^+$ Calcd for $[\text{C}_{13}\text{H}_{21}\text{ClN}]^+$ 226.1357; Found 226.1375.

1-Octyl-4-(trifluoromethyl)pyridinium bromide ($[\text{C}_8\text{-4-(CF}_3\text{)Py}]\text{Br}$)

Bromooctane (5.76 mL, 29.4 mmol) was added dropwise to 4-(Trifluoromethyl) pyridine (3.4 mL, 35.3 mmol) and allowed to stir at 80 °C for 72hrs under an inert atmosphere. The reaction mixture was dried under vacuum at 70 °C for 24 hr, yielding a yellow viscous liquid of 1-octyl-4-(trifluoromethyl) pyridinium bromide (5.4g, 54%). ^1H NMR (DMSO- d_6 , 400 MHz): δ = 10.04 (d, $J = 6.3$ Hz, 2H), 9.24 (d, $J = 6.3$ Hz, 2H), 5.29 (t, $J = 7.5$ Hz, 2H), 3.09 - 3.03 (m, 2H), 1.97 - 1.71 (m, 10H), 1.41 ppm (t, $J = 7.1$ Hz, 3H). ^{19}F NMR (DMSO- d_6 , 376 MHz) δ -63.85. ^{13}C NMR (126 MHz, Chloroform- d) δ 146.73, 125.32,

63.71, 31.70, 31.67, 28.96, 28.85, 26.07, 22.63, 14.09 ppm. HRMS (ESI) m/z : $[M]^+$ Calcd for $[C_{14}H_{21}F_3N]^+$ 260.1621; Found 260.1617.

1-Octyl-4-(trifluoromethane)pyridinium bis(trifluoromethanesulfonyl)imide ($[C_8-4-(CF_3)Py][NTf_2]$)

$[C_8-4-(CF_3)Py]Br$ (3.1g, 9.3mmol) was dissolved in water (20 mL) and the solution was cooled to 0 °C. A solution of $Li[NTf_2]$ (3.2g, 1.1mmol) in water (10 mL) was added dropwise and the mixture was stirred at 0 °C and gradually allowed to warm to room temperature overnight. The lower IL layer was separated and washed with hot water (6 x 5 mL) and then dried at 50 °C and $\approx 8 \times 10^{-2}$ mbar for 24 hr to give a light brown liquid (1.38g, 44%). 1H NMR (DMSO- d_6 , 400 MHz) δ 9.42 (d, $J = 6.4$ Hz, 2H), 8.65 (d, $J = 6.3$ Hz, 2H), 4.70 (t, $J = 7.6$ Hz, 2H), 2.04 – 1.86 (m, 2H), 1.50 – 1.13 (m, 10H), 0.85 ppm (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (DMSO- d_6 , 126 MHz) δ 147.06, 124.91, 121.39 (q, $J = 273.6$ Hz), 119.47 (q, $J = 320.3$ Hz), 61.63, 31.13, 30.76, 28.41, 28.35, 25.36, 22.03, 13.88 ppm. ^{19}F NMR (DMSO- d_6 , 376 MHz) δ -64.08, -78.82. HRMS (ESI) m/z : $[M]^+$ Calcd for $[C_{14}H_{21}F_3N]^+$ 260.1621; Found 260.1625.

1-Butyl-3-methyl-4-chloroimidazolium bis(trifluoromethanesulfonyl)imide ($[C_nC_1-4-ClIm][NTf_2]$)

Synthesised according to existing procedures;⁶ data consistent with previous reports. 1H NMR (DMSO- d_6 , 300 MHz) δ 9.24 (d, $J = 1.7$ Hz, 1H), 8.09 (t, $J = 1.7$ Hz, 1H), 4.15 (t, $J = 7.1$ Hz, 2H), 3.77 (s, 3H), 1.84 - 1.65 (m, 2H), 1.41 - 1.12 (m, 2H), 0.90 ppm (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 136.9, 121.4, 119.5 (q, $J = 322.1$ Hz), 119.4, 49.4, 33.7, 31.0, 18.6, 13.2 ppm. ^{19}F NMR (DMSO- d_6 , 282 MHz) δ -78.73 ppm. HRMS (ESI) m/z : $[M]^+$ Calcd for $[C_8H_{14}ClN_2]^+$ 173.0840; Found 173.0825.

1-Octyl-3-Methyl-4-chloroimidazolium bis(trifluoromethanesulfonyl)imide ($[C_nC_1-4-ClIm][NTf_2]$)

Synthesised according to existing procedures;⁶ data consistent with previous reports. 1H NMR (DMSO- d_6 , 300 MHz) δ 9.24 (d, $J = 1.8$ Hz, 1H), 8.08 (t, $J = 1.8$ Hz, 1H), 4.14 (t, $J = 7.2$ Hz, 2H), 3.78 (s, 3H), 1.95 - 1.59 (m, 2H), 1.44 - 1.08 (m, 10H), 0.86 ppm (t, $J = 6.7$ Hz, 3H). ^{13}C NMR (DMSO- d_6 , 75 MHz) δ 136.8, 121.4, 119.5 (q, $J = 322.3$ Hz), 119.4, 49.7, 33.7, 31.2, 29.0, 28.4, 28.3, 25.4, 22.0, 13.9 ppm. ^{19}F NMR (DMSO- d_6 , 282 MHz) δ -78.78 ppm. HRMS (ESI) m/z : $[M]^+$ Calcd for $[C_{12}H_{22}ClN_2]^+$ 229.1466; Found 229.1475.

2. XPS Peak Fittings

Photoemission spectra were fitted using CasaXPS software (v. 2.3.19) with GL(30) curves. All heteroatom XP spectra (N 1s, O 1s, F 1s, B 1s, S 2p, Cl 2p) were fitted with a two-point linear background. The C 1s spectra were fitted with a spline linear background to allow incorporation of the $-CF_3$ photoemissions from the $[NTf_2]^-$ anions and measurement of the shake-up signal. The FWHM of

all C 1s peaks are constrained to 0.8-1.2 eV, except for large C^{ali} components (i.e. C₈) which are constrained to 0.8-1.5 eV. Peak position constraints were not used in any of the fittings presented in this work, but area constraints were used to maintain correct peak ratios. Relative sensitivity factors (RSF) used in the determination of atomic percentages were taken from the Kratos library.⁷

2.1 Previous Carbon 1s Fitting Models Published by Our Group

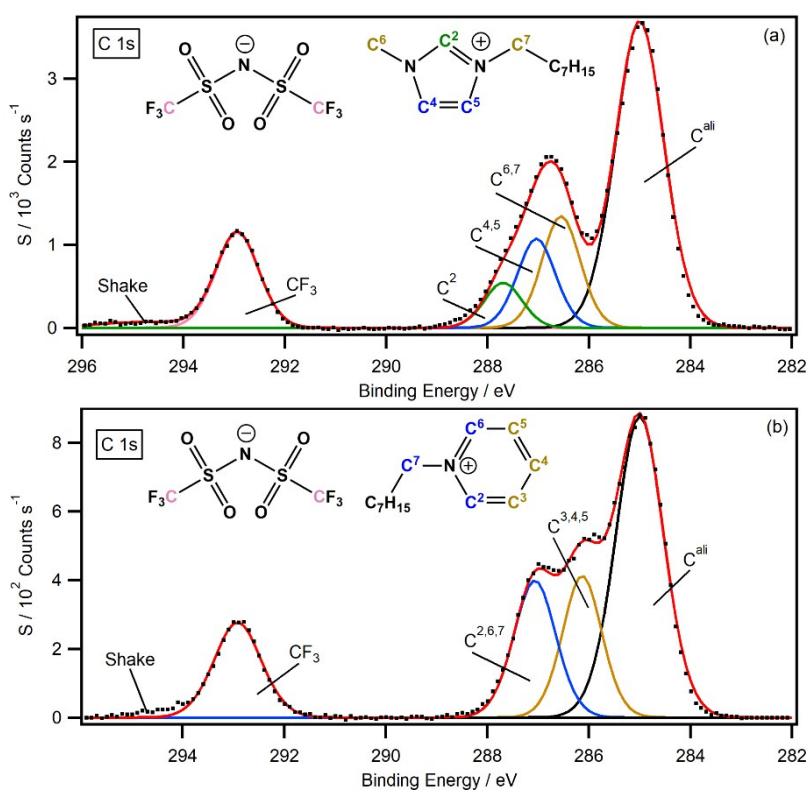


Figure S1 The C 1s peak fitting models published by our group at the University of Nottingham for a) $[C_8C_1Im][NTf_2]$, a common imidazolium IL, and b) $[C_8Py][NTf_2]$, a common pyridinium IL.

Imidazolium C 1s:

Figure S1a shows how the imidazolium C 1s peak fitting model developed by our group is able to accurately reproduce the photoemission spectra of $[C_8C_1Im][NTf_2]$. The model is also able to fit many other imidazolium C 1s spectra,^{8–12} demonstrating its robustness. In **Figure S1a**, each component is colour coded to the chemical structure: C² (green), C^{4,5} (blue), C^{6,7} (orange) and C^{ali} (black). The CF₃ peak and the shake-up signal are also labelled on the plot. After accounting for a 20% signals reduction from each sp² carbon from shake up/off losses,¹³ the area ratios were set to 2: 0.8 : 1.6 : 1.8 : 7 (CF₃ : C² : C^{4,5} : C^{6,7} : C^{ali}) for each $[C_8C_1Im][NTf_2]$ carbon. Note: ratios change depending on the type and

number of chemical states present in each sample. The B.E.s are $C^2 = 287.7$ eV, $C^{4,5} = 287.1$ eV, $C^{6,7} = 286.6$ eV, and $C^{ali} = 285.0$ eV, which are consistent with previous reports.⁹

Pyridinium C 1s:

Figure S1b shows how the pyridinium C 1s peak fitting model developed within our group can also accurately fit the photoemission spectra of the $[C_8Py][NTf_2]$ C 1s photoemission. The $C^{2,6,7}$ (blue) component represents the carbon atoms bound to the nitrogen heteroatom. The $C^{3,4,5}$ (orange) component represents the carbon atoms from the back of the pyridinium ring and the C^{ali} (black) component represents the carbons of the long aliphatic tail. The $C^{2,6,7}$ component (287.1 eV) appears at a higher B.E. due to the charge withdrawal from the electropositive cationic nitrogen atom. The $C^{3,4,5}$ component (286.0 eV) appears at a slightly lower B.E. as there is no neighbouring electropositive heteroatom. The C^{ali} component (285.0 eV) appears at the lowest B.E. due to the electron rich environment of the long aliphatic tail. The C^{ali} component has been used to charge correct the spectrum. The FWHMs of the components have been constrained to 0.8-1.2 eV for $C^{2,6,7}$ and $C^{3,4,5}$ and 0.8-1.5 eV for C^{ali} . The larger FWHM window for C^{ali} is due to the overlapping of multiple C 1s photoemissions. Peak areas are also constrained to the relative proportions of the carbon environments. For example, $[C_8Py][NTf_2]$ has the following components $C^{2,6,7}:C^{3,4,5}:C^{ali}$ in the following ratio 3:3:7. Measurements of the shake-up signals from the C 1s regions of pyridinium ILs have found that sp^2 pyridinium carbon atoms appear to lose an average of 10% of their signal.¹⁴ Therefore, after accounting for shake up/off losses, the ratio of the areas now becomes 2.8:2.7:7. This model has been found to accurately represent a range of pyridinium IL XP spectra.

3. List of Difference Spectra

The following difference spectra are reported in the main text. Structural representations are also shown for each set of difference spectra, with the respective positive and negative signals of the difference highlighted in red. Anions are omitted from all structural representations, except for the F 1s difference spectra (difference 6) which shows the -CF₃ F 1s photoemission of the cation by removing -CF₃ F 1s photoemissions of the [NTf₂]⁻ anions:

- Difference 1 = [C₄Py-2-Cl][NTf₂] C 1s - [C₄Py][NTf₂] C 1s
- Difference 2 = [C₈Py-2-Cl][NTf₂] C 1s - [C₈Py][NTf₂] C 1s

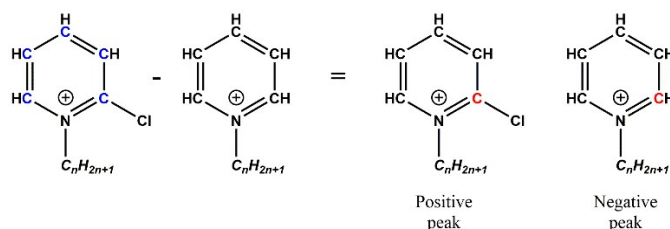


Figure S2 Structural representation of the C 1s difference spectra 1 and 2, showing the positive and negative carbon peak identity (red).

- Difference 3 = [C₄Py-3-Cl][NTf₂] C 1s - [C₄Py][NTf₂] C 1s
- Difference 4 = [C₈Py-3-Cl][NTf₂] C 1s - [C₈Py][NTf₂] C 1s
- Difference 5 = [C₈Py-3-Cl][BF₄] C 1s - [C₈Py][BF₄] C 1s

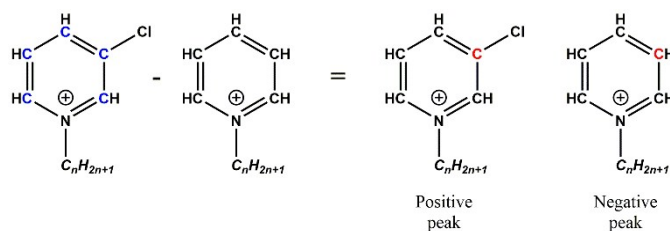


Figure S3 Structural representation of the C 1s difference spectra 3, 4 and 5, showing the positive and negative carbon peak identity (red).

- Difference 6 = [C₈Py-4-(CF₃)][NTf₂] C 1s - [C₈Py][NTf₂] C 1s

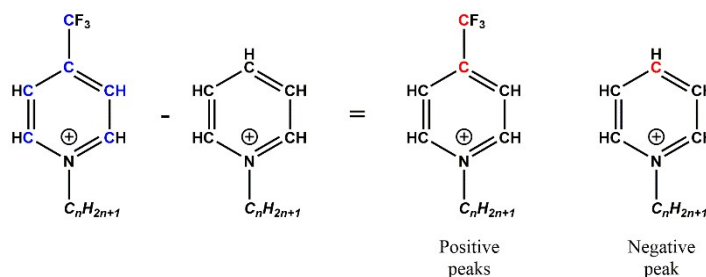


Figure S4 Structural representation of the C 1s difference spectra 6, showing the positive and negative carbon peak identities (red).

- Difference 7 = [C₈Py-4-(CF₃)][NTf₂] F 1s - [C₈Py][NTf₂] F 1s

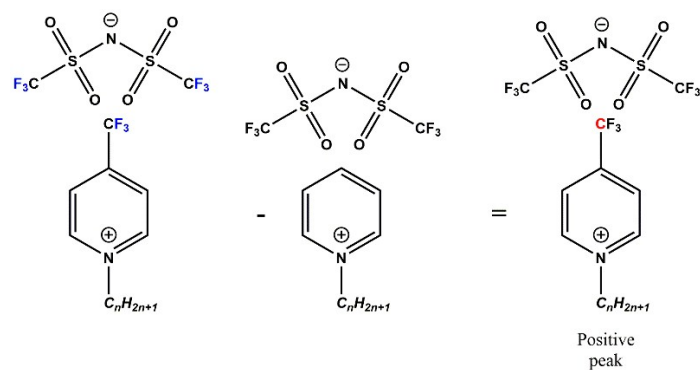


Figure S5 Structural representation of the F 1s difference spectra 7, showing the positive fluorine identity (red).

- Difference 8 = $[\text{C}_4\text{C}_1\text{Im-4-Cl}][\text{NTf}_2] \text{ C } 1\text{s} - [\text{C}_4\text{C}_1\text{Im}][\text{NTf}_2] \text{ C } 1\text{s}$
- Difference 9 = $[\text{C}_8\text{C}_1\text{Im-4-Cl}][\text{NTf}_2] \text{ C } 1\text{s} - [\text{C}_8\text{C}_1\text{Im}][\text{NTf}_2] \text{ C } 1\text{s}$

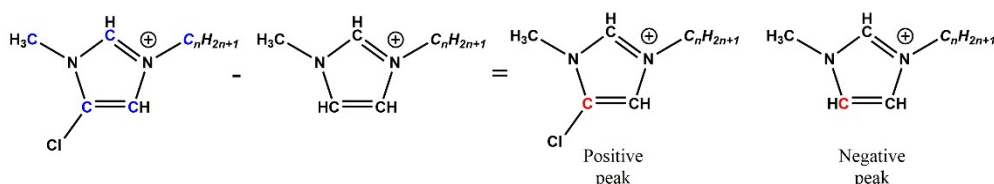


Figure S6 Structural representation of the C 1s difference spectra 8 and 9, showing the positive and negative carbon identity (red).

4. Additional Data

Table S1 The experimental elemental compositions and nominal (brackets) stoichiometries for the ionic liquids presented in this work.

Cation	Anion	C	N	O	F	B	S	Cl
RSF		0.278	0.477	0.780	1.000	0.159	0.668	0.891
$[\text{C}_4\text{Py-2-Cl}]$	$[\text{NTf}_2]$	46.6 (42.3)	7.1 (7.7)	13.6 (15.4)	21.4 (23.1)		7.5 (7.7)	3.8 (3.8)
$[\text{C}_8\text{Py-2-Cl}]$	$[\text{NTf}_2]$	54.5 (50.0)	6.0 (6.7)	11.7 (13.3)	18.6 (20.0)		6.2 (6.7)	3.0 (3.3)
$[\text{C}_4\text{Py-3-Cl}]$	$[\text{NTf}_2]$	45.5 (42.3)	7 (7.7)	13.8 (15.4)	21.7 (23.1)		8.1 (7.7)	3.9 (3.8)
$[\text{C}_8\text{Py-3-Cl}]$	$[\text{NTf}_2]$	54.5 (50.0)	6.1 (6.7)	11.5 (13.3)	18.1 (20.0)		6.6 (6.7)	3.2 (3.3)
$[\text{C}_8\text{Py-3-Cl}]$	$[\text{BF}_4]$	67.4 (65.0)	4.6 (5.0)		18.1 (20.0)	5.35 (5.0)		4.59 (5.0)
$[\text{C}_8\text{Py-4-(CF}_3)]$	$[\text{NTf}_2]$	49.0(48.5)	6.1(6.0)	11.1(12.1)	28.0(27.3)		5.79(6.1)	
$[\text{C}_4\text{C}_1\text{Im-4-Cl}]$	$[\text{NTf}_2]$	46.6 (42.3)	7.1 (7.7)	13.8 (15.4)	21.3 (23.1)		7.5 (7.7)	3.7 (3.8)
$[\text{C}_8\text{C}_1\text{Im-4-Cl}]$	$[\text{NTf}_2]$	54.5 (50.0)	6.0 (6.7)	11.7 (13.3)	18.6 (20.0)		6.2 (6.7)	3.0 (3.3)

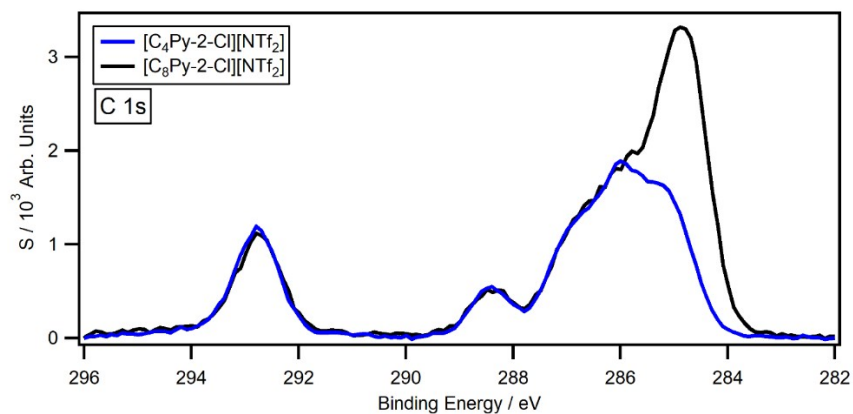


Figure S7 The normalised and overlaid C 1s photoemissions of [C_nPy-2-Cl][NTf₂] (n = 2 or 8).

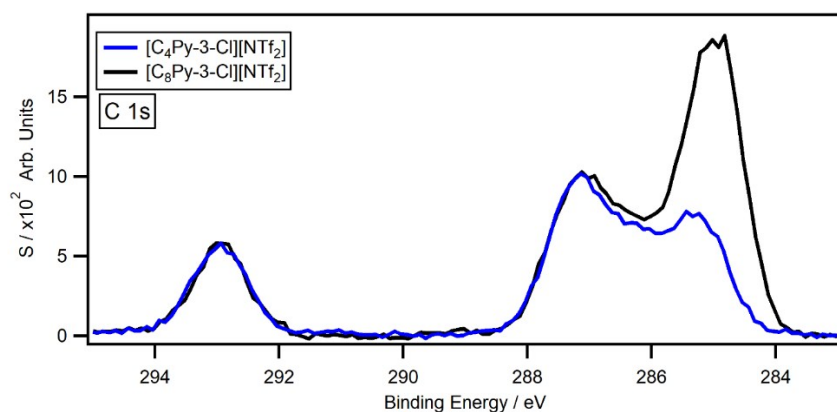


Figure S8 The normalised and overlaid C 1s photoemissions of [C_nPy-3-Cl][NTf₂] (n = 2 or 8).

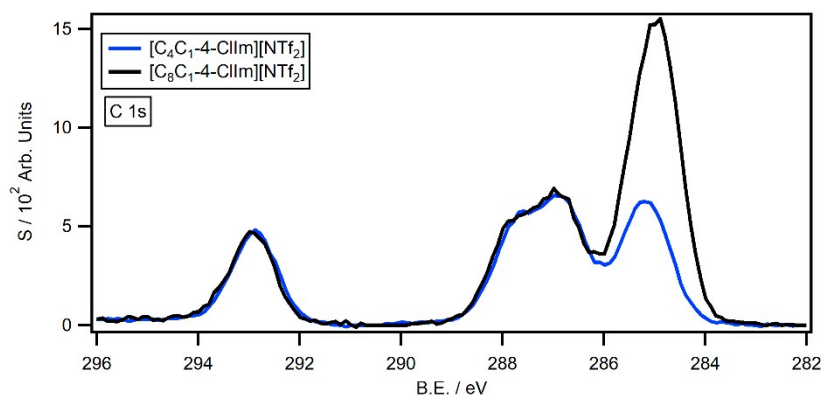


Figure S9 The overlaid C 1s high resolution photoemissions of [C₄C₁-4-Im][NTf₂] and [C₈C₁-4-Im][NTf₂].

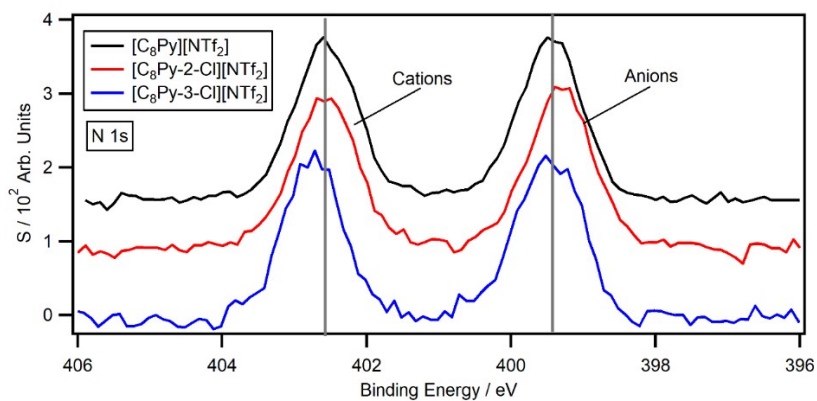


Figure S10 The overlaid and normalised N 1s high resolution regions of the $[\text{C}_8\text{Py}][\text{NTf}_2]$ IL (black), and the 2-chloro $[\text{C}_8\text{Py-2-Cl}][\text{NTf}_2]$ (red) and 3-chloro $[\text{C}_8\text{Py-3-Cl}][\text{NTf}_2]$ (blue) functionalised ILs.

5. Survey and High Resolution XP Spectra

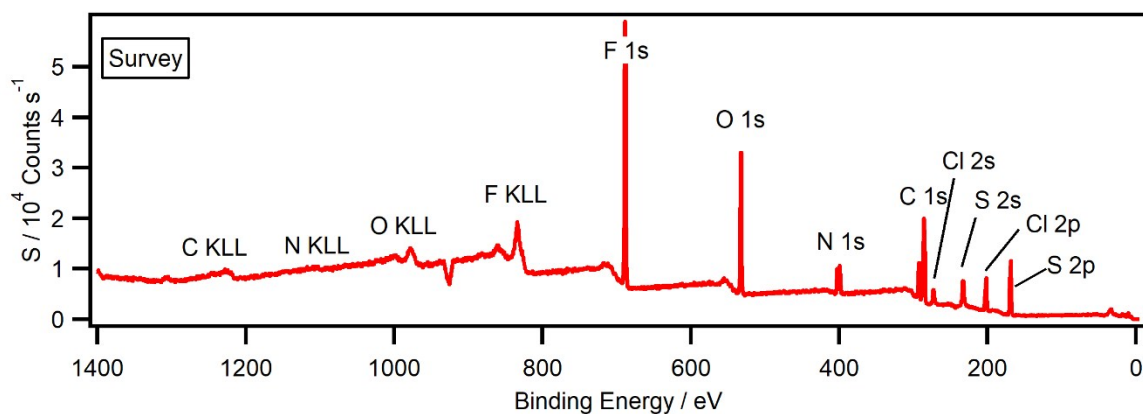


Figure S11 Survey scan of $[\text{C}_4\text{Py-2-Cl}][\text{NTf}_2]$.

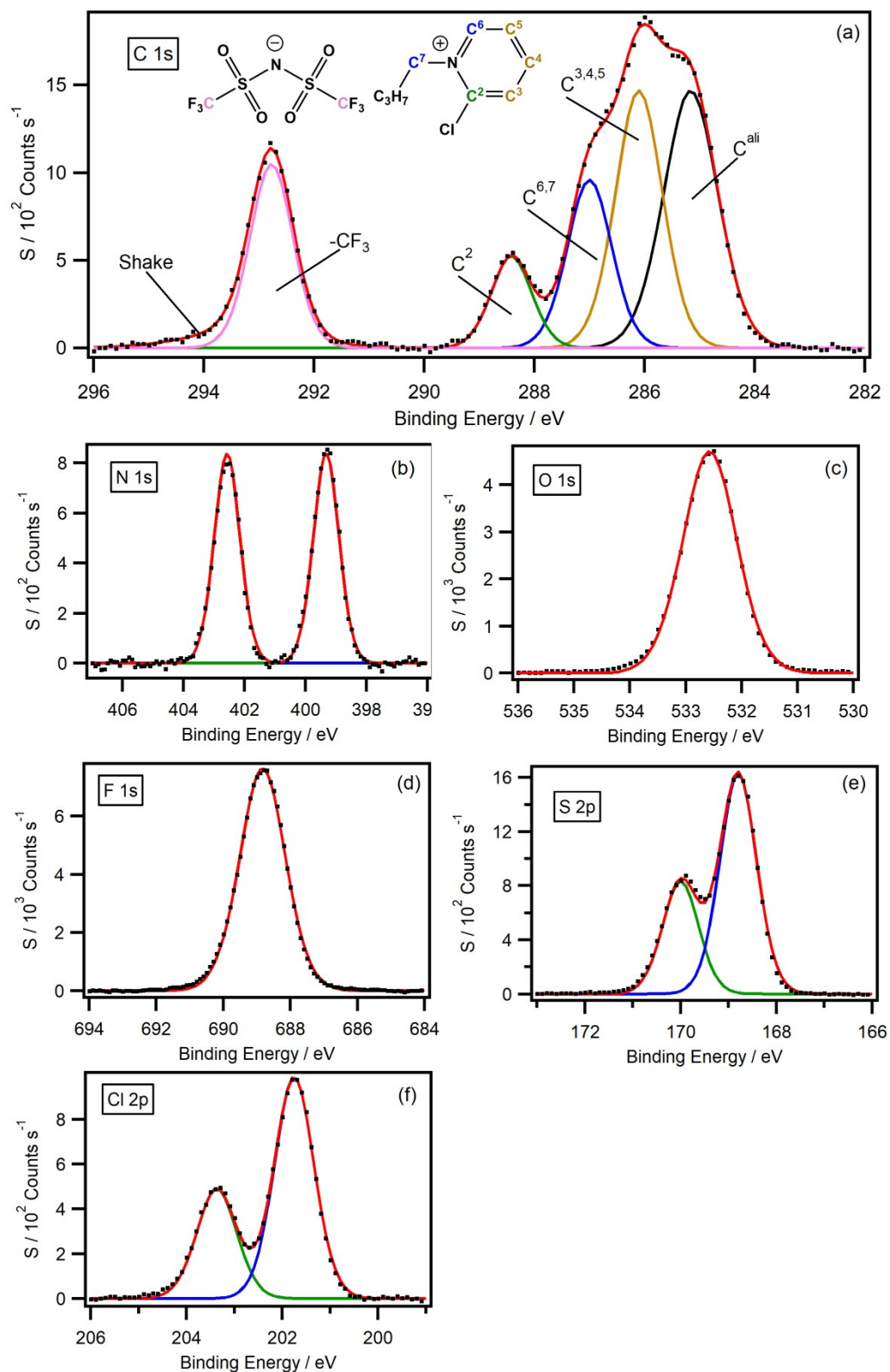


Figure S12 High resolution XPS spectra of [C₄Py-2-Cl][NTf₂] showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

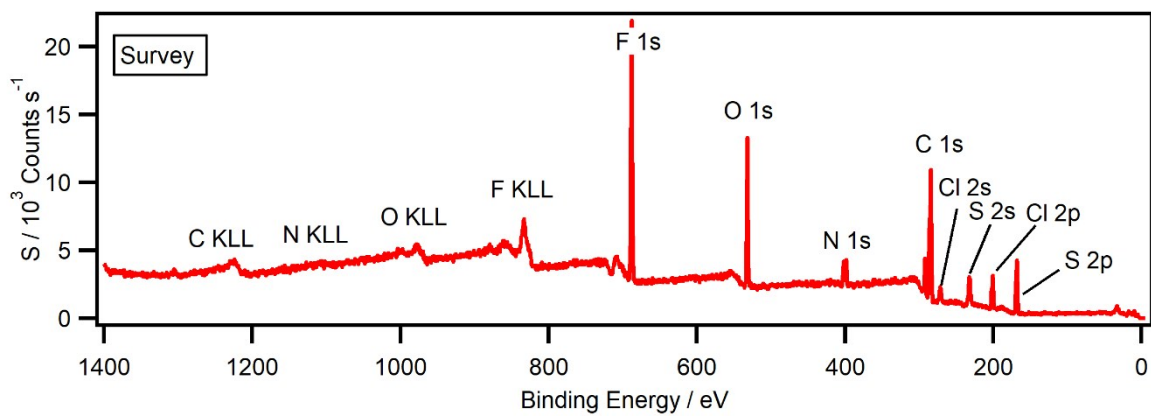


Figure S13 Survey scan of [C₈Py-2-Cl][NTf₂].

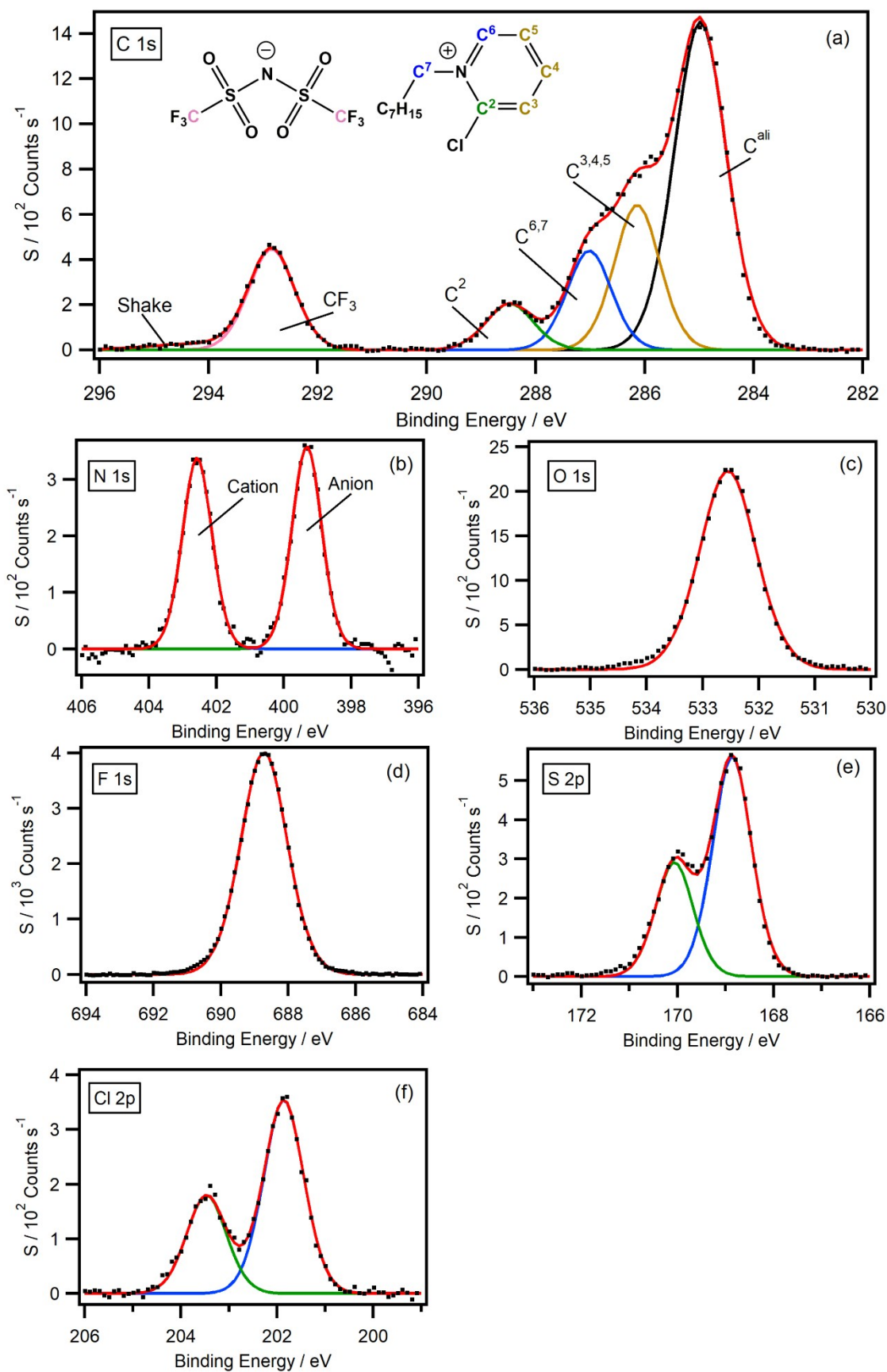


Figure S14 High resolution XP spectra of [C₈Py-2-Cl][NTf₂] showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

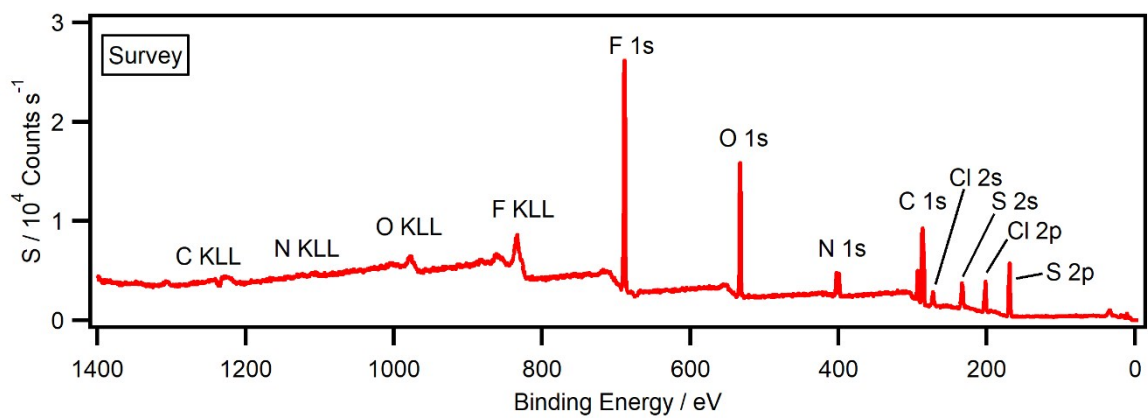


Figure S15 Survey scan of [C₄Py-3-Cl][NTf₂].

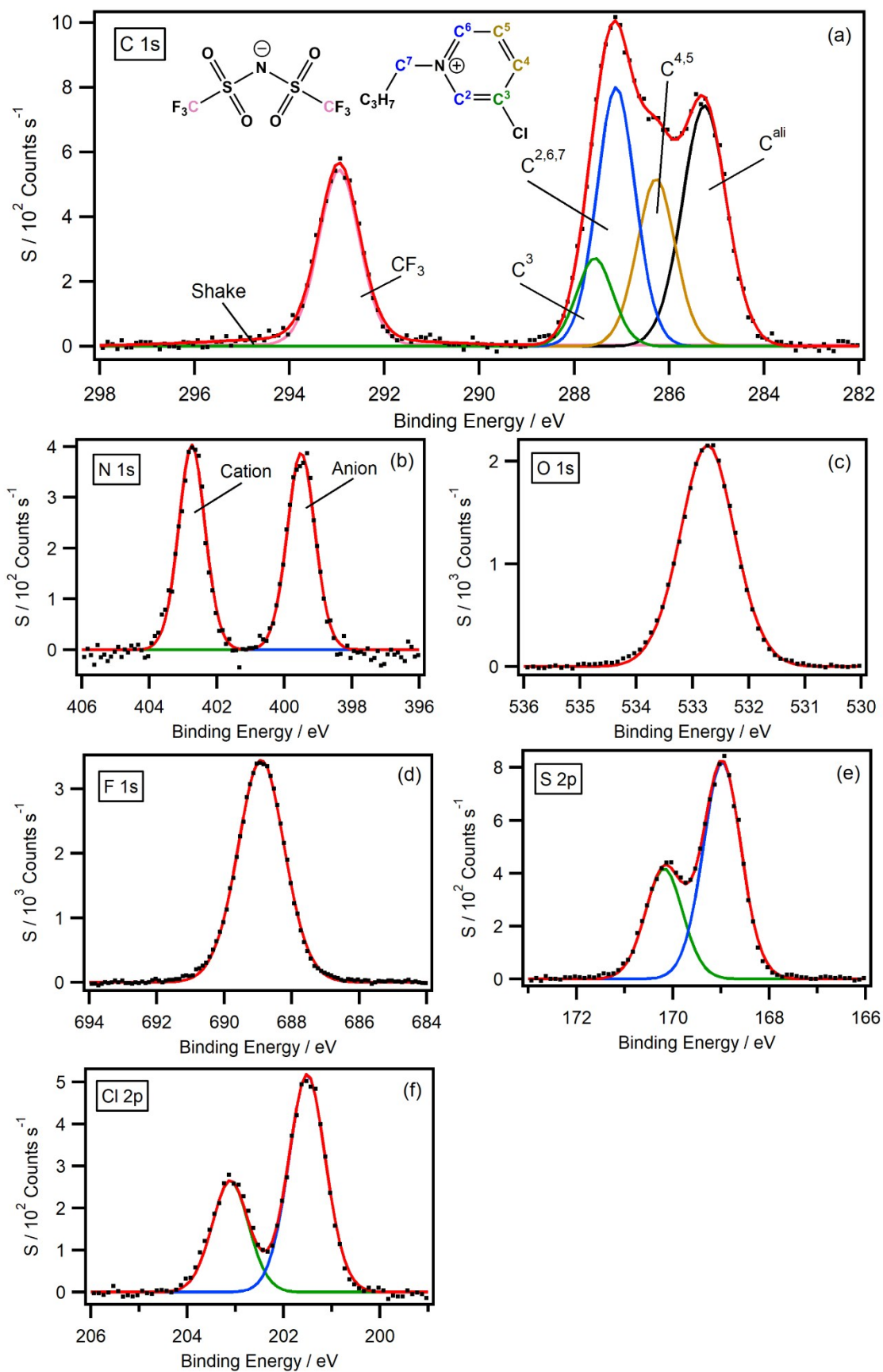


Figure S16 High resolution XP spectra of $[C_4Py-3-Cl][NTf_2]$ showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

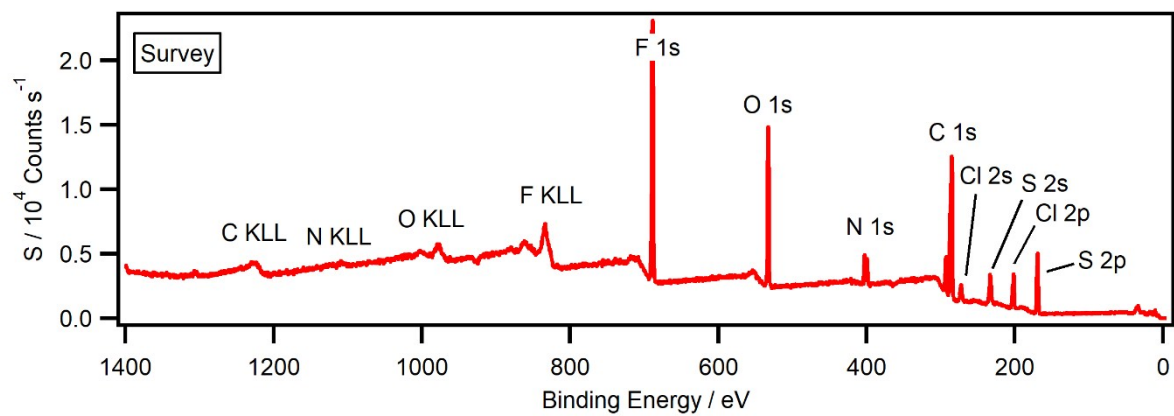


Figure S17 Survey scan of $[C_8Py-3-Cl][NTf_2]$.

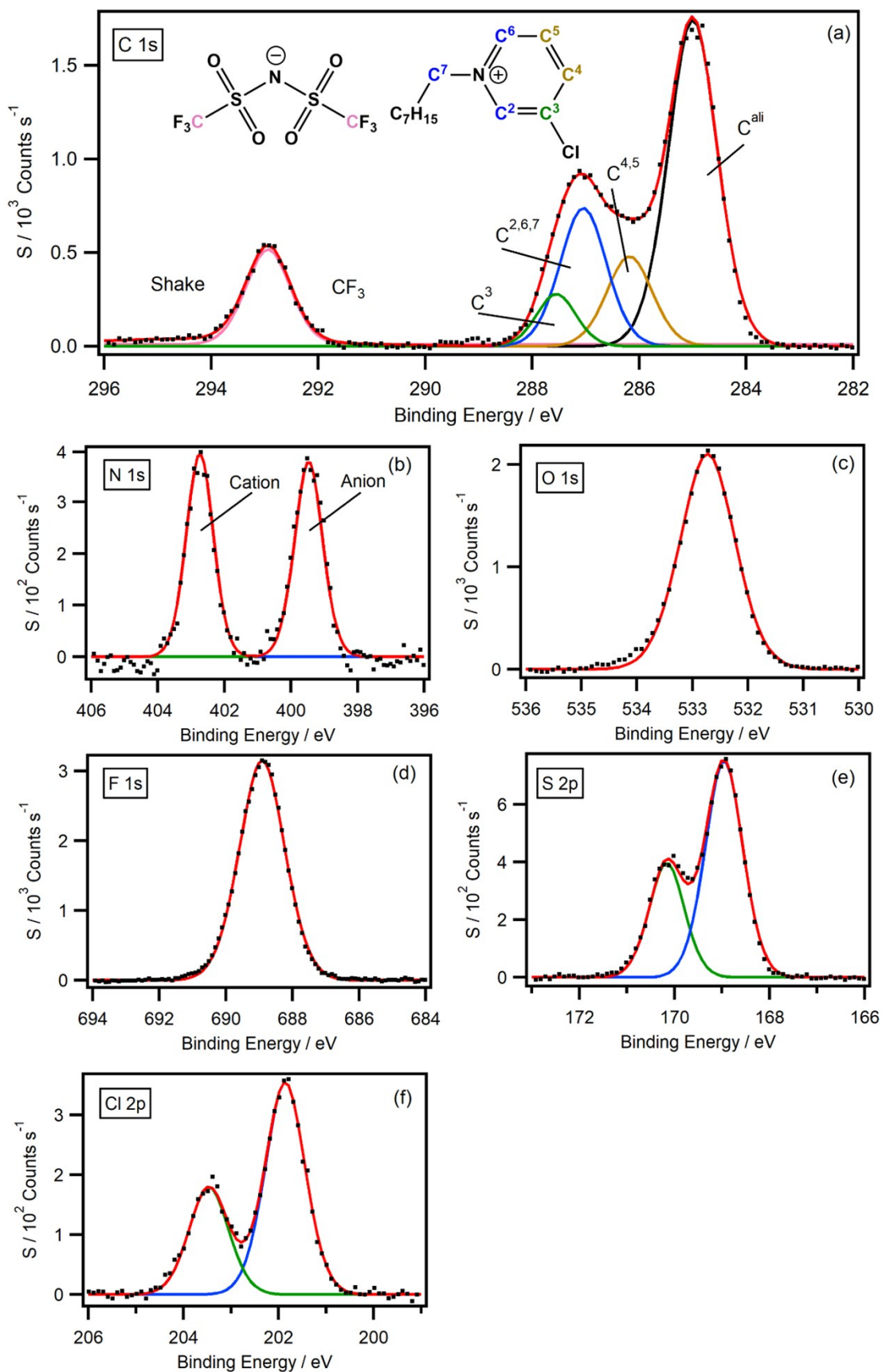


Figure S18 High resolution XPS spectra of [C₈Py-3-Cl][NTf₂] showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

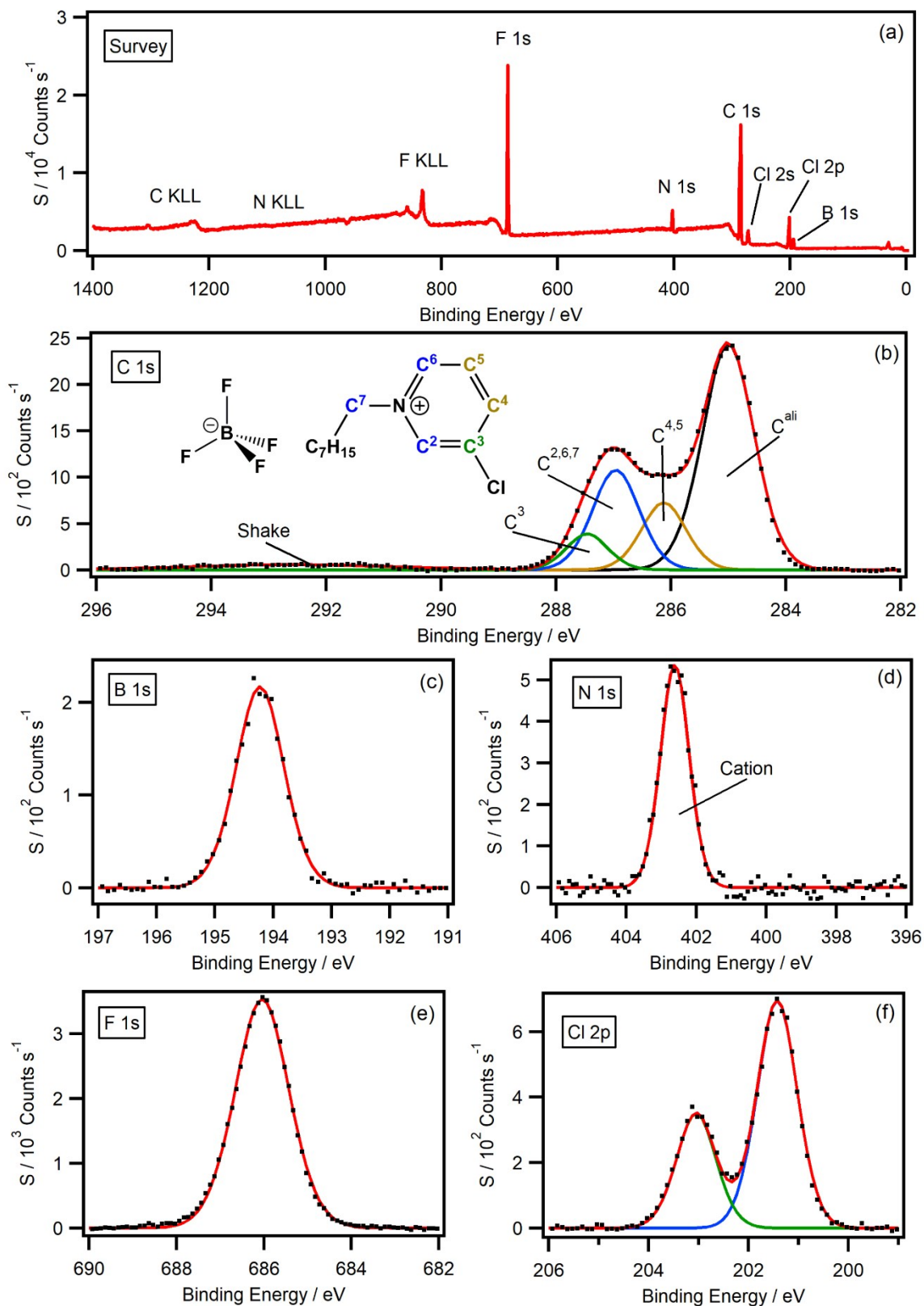


Figure S19 XPS spectra of $[C_8Py-3-Cl][BF_4]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

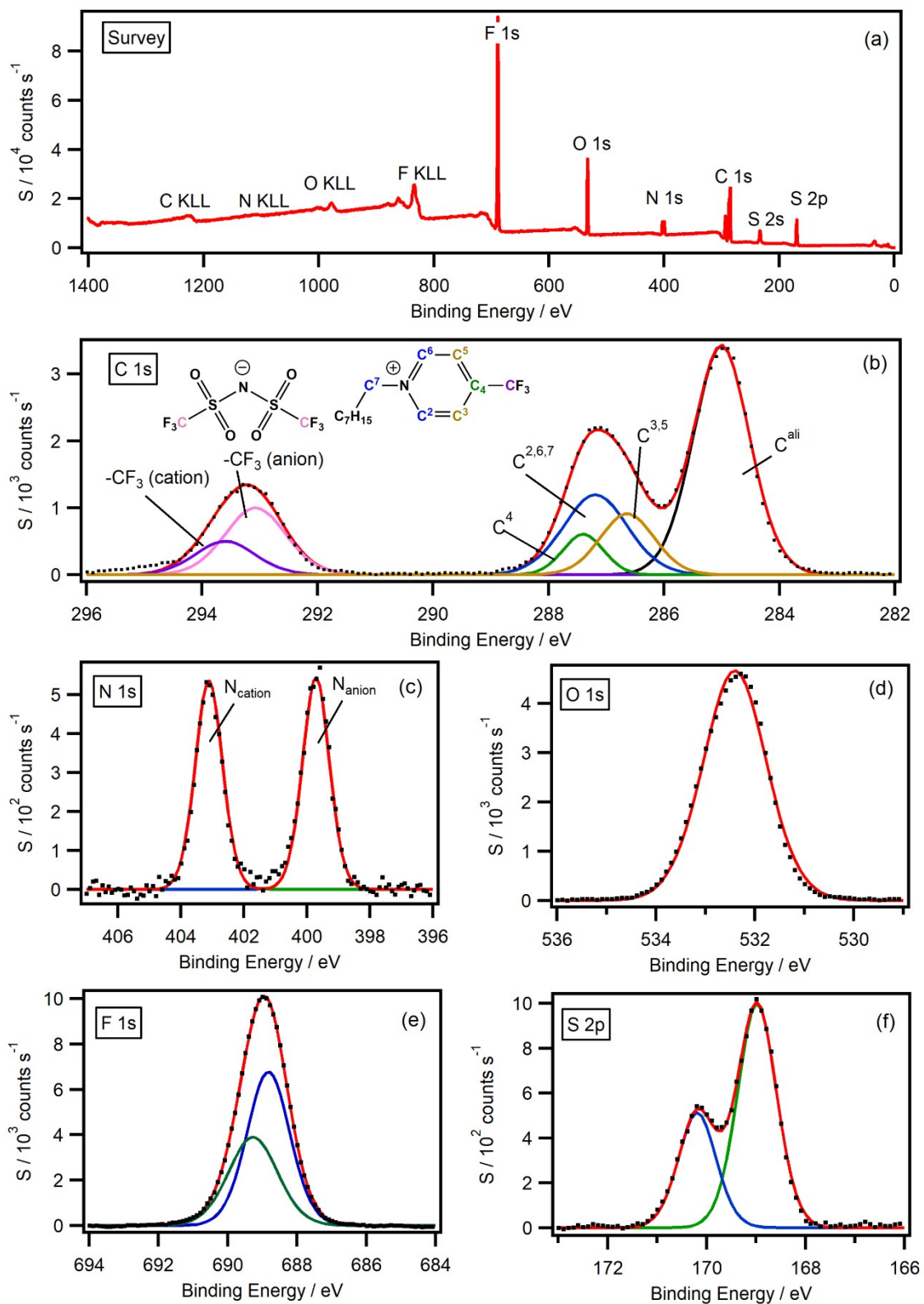


Figure S20 XPS spectra of $[C_8Py-4-(CF_3)][INTf_2]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

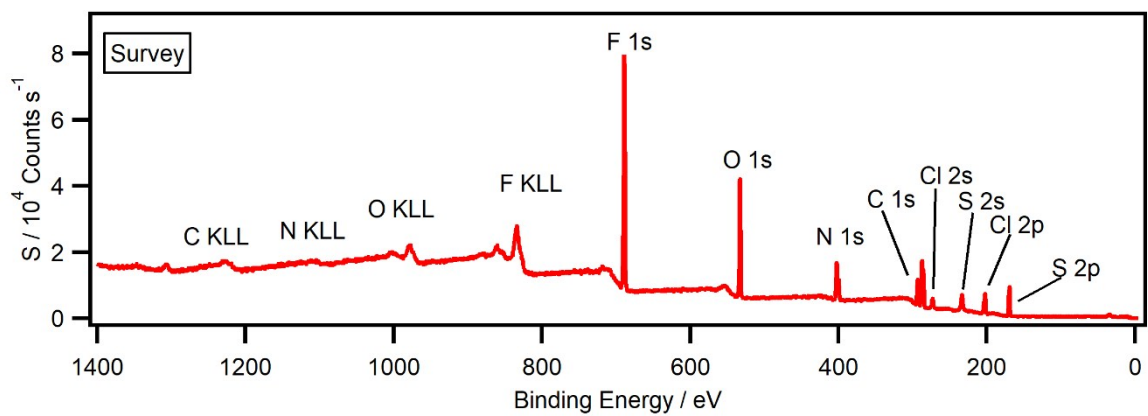


Figure S21 Survey scan of $[C_4C_1Im-4-Cl][NTf_2]$.

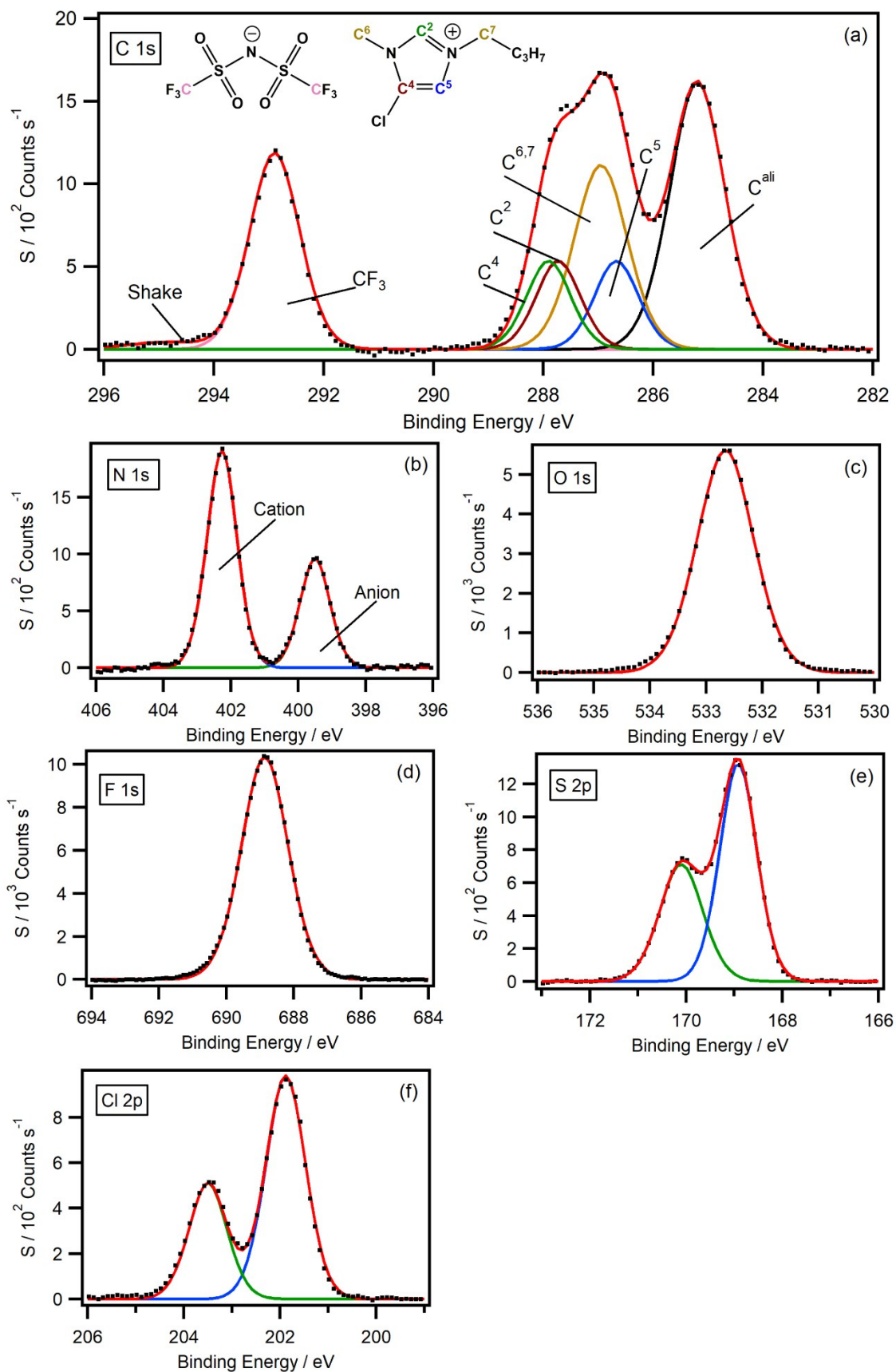


Figure S22 High resolution XPS spectra of $[\text{C}_4\text{C}_1\text{Im-4-Cl}][\text{NTf}_2]$ showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

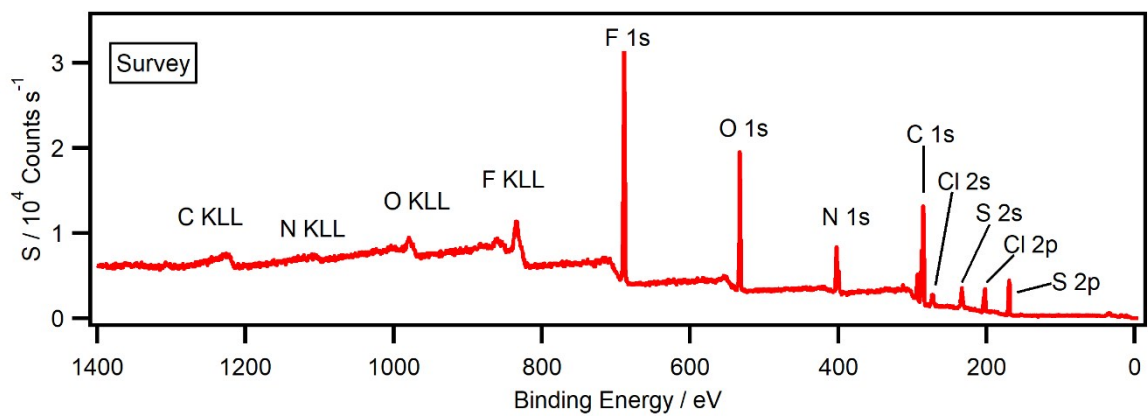


Figure S23 Survey scan of [C₈C1Im-4-Cl][NTf₂].

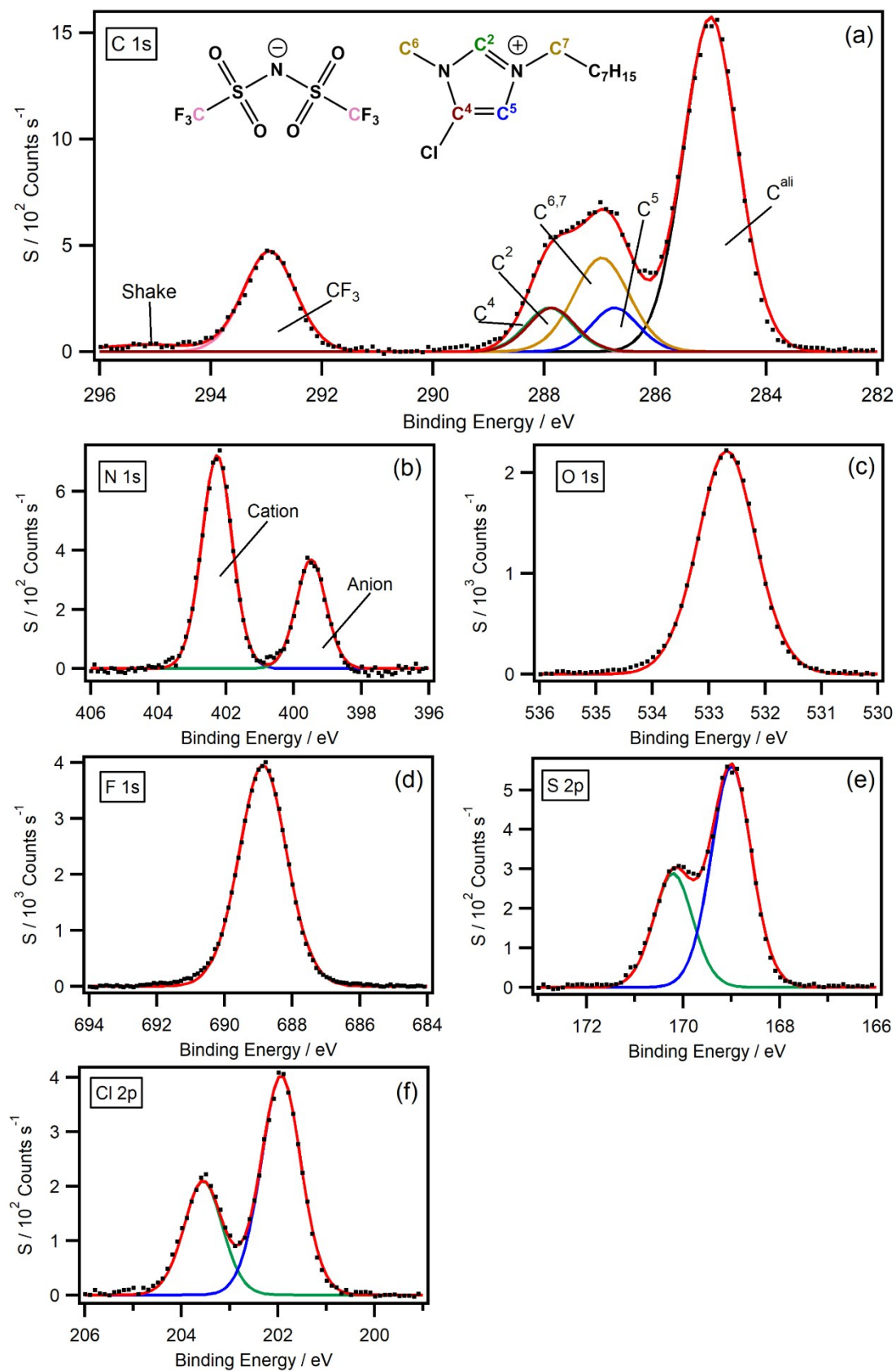


Figure S24 High resolution XPS spectra of $[\text{C}_8\text{C}_1\text{Im-4-Cl}][\text{NTf}_2]$ showing (a) peak fitted C 1s with structural assignment and (b-f) heteroatom high resolution scans.

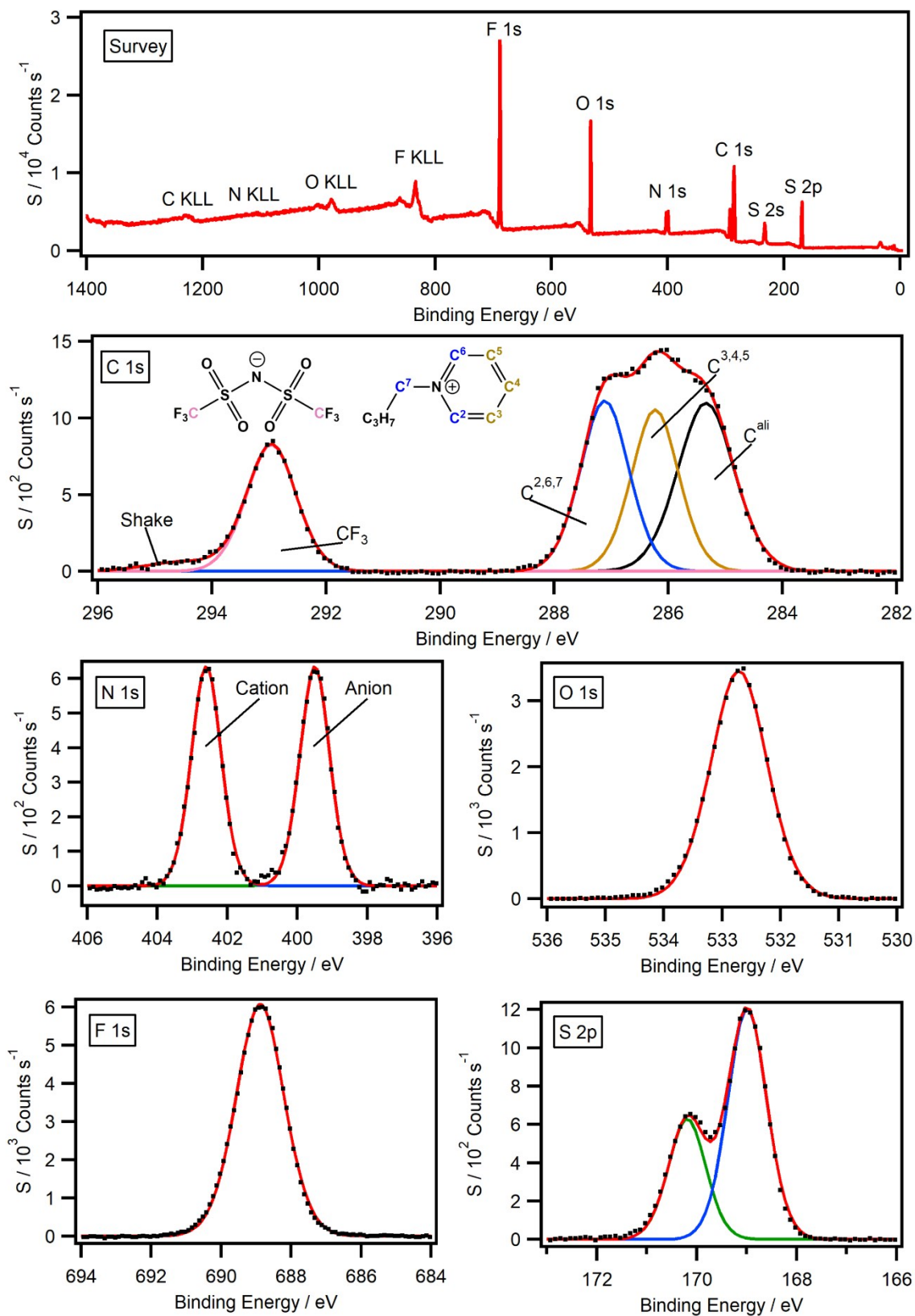


Figure S25 XPS spectra of $[C_4Py][NTf_2]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

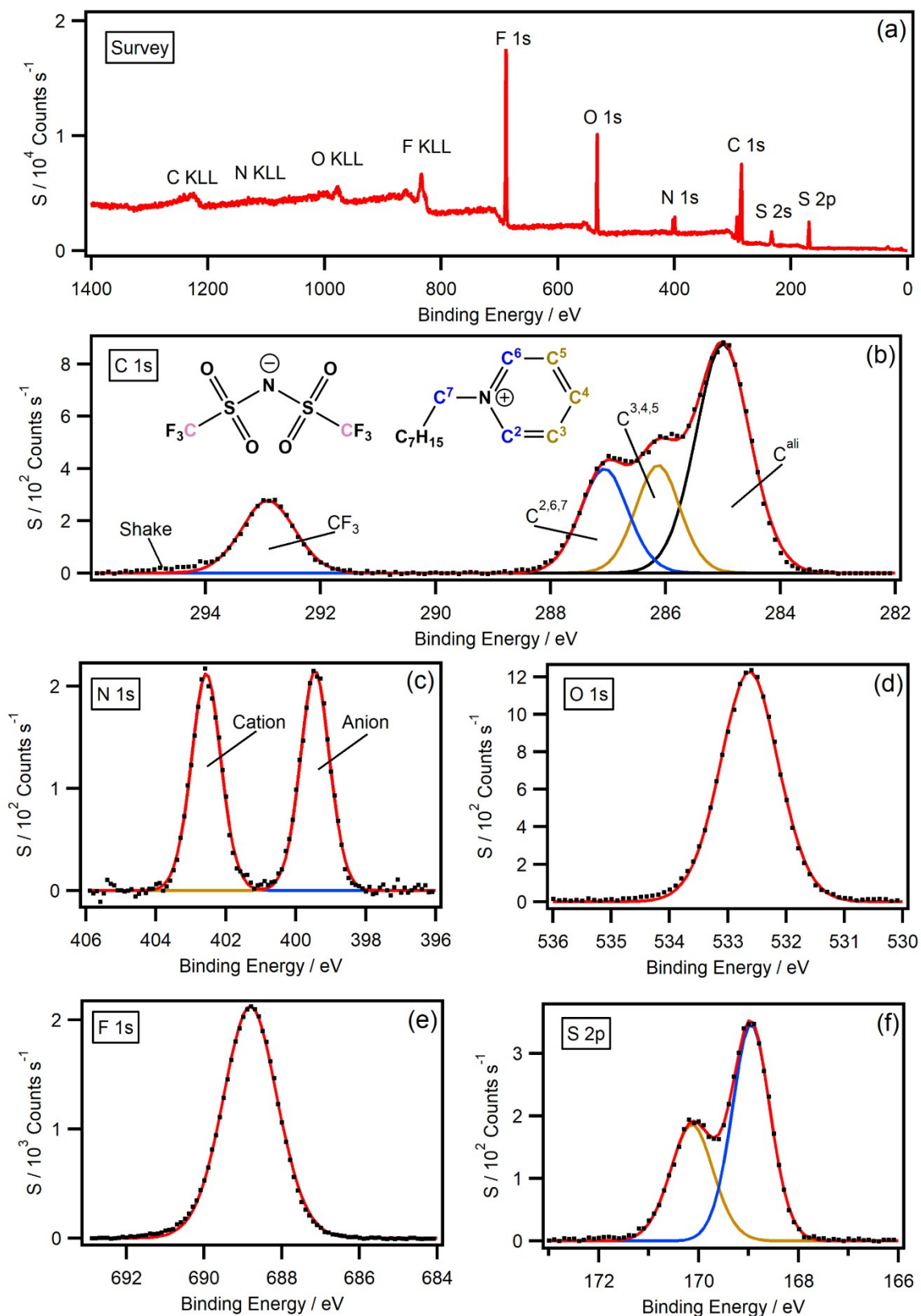


Figure S26 XPS spectra of $[C_8Py][NTf_2]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

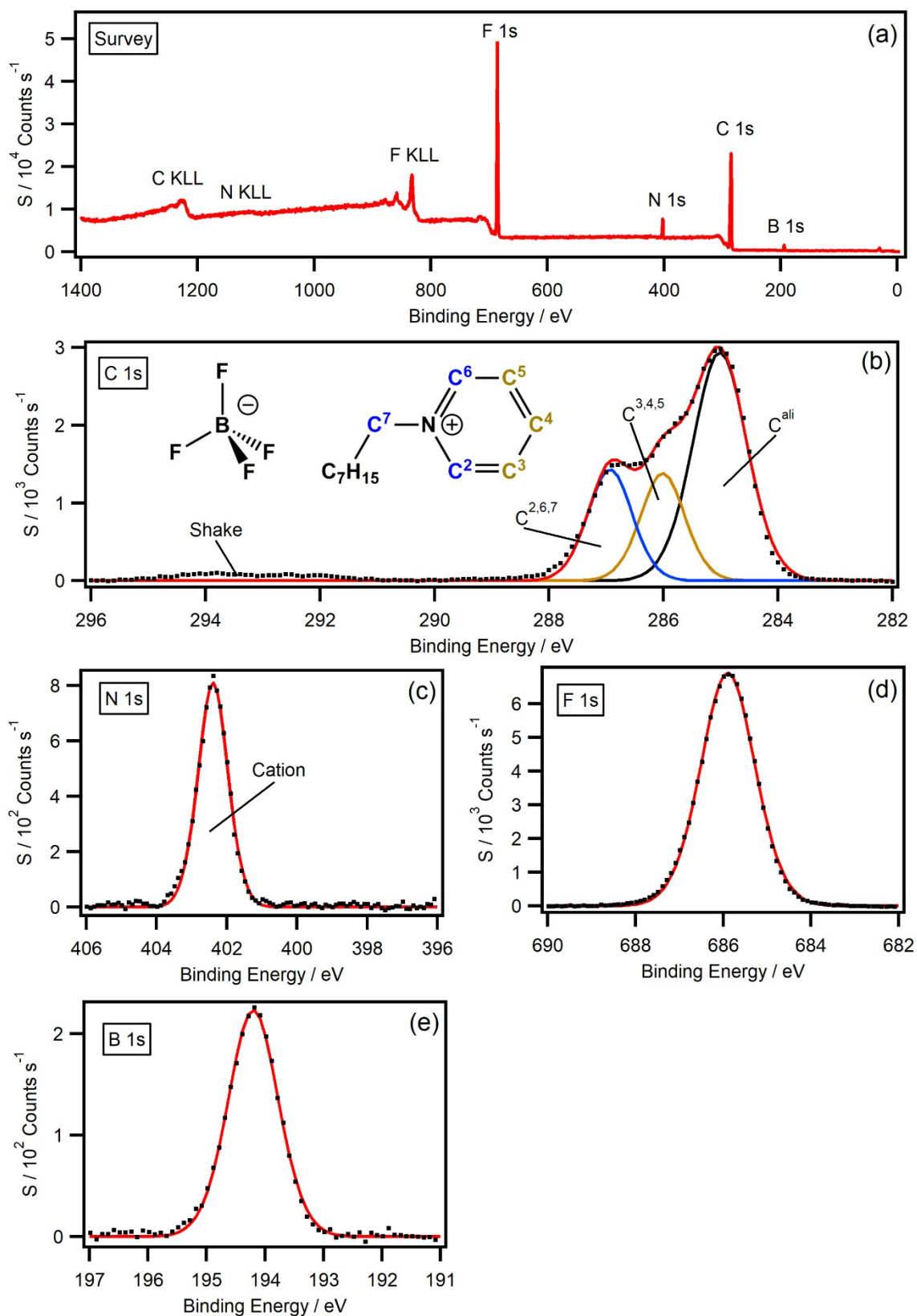


Figure S27 XPS spectra of $[C_8Py][BF_4]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-e) heteroatom high resolution scans.

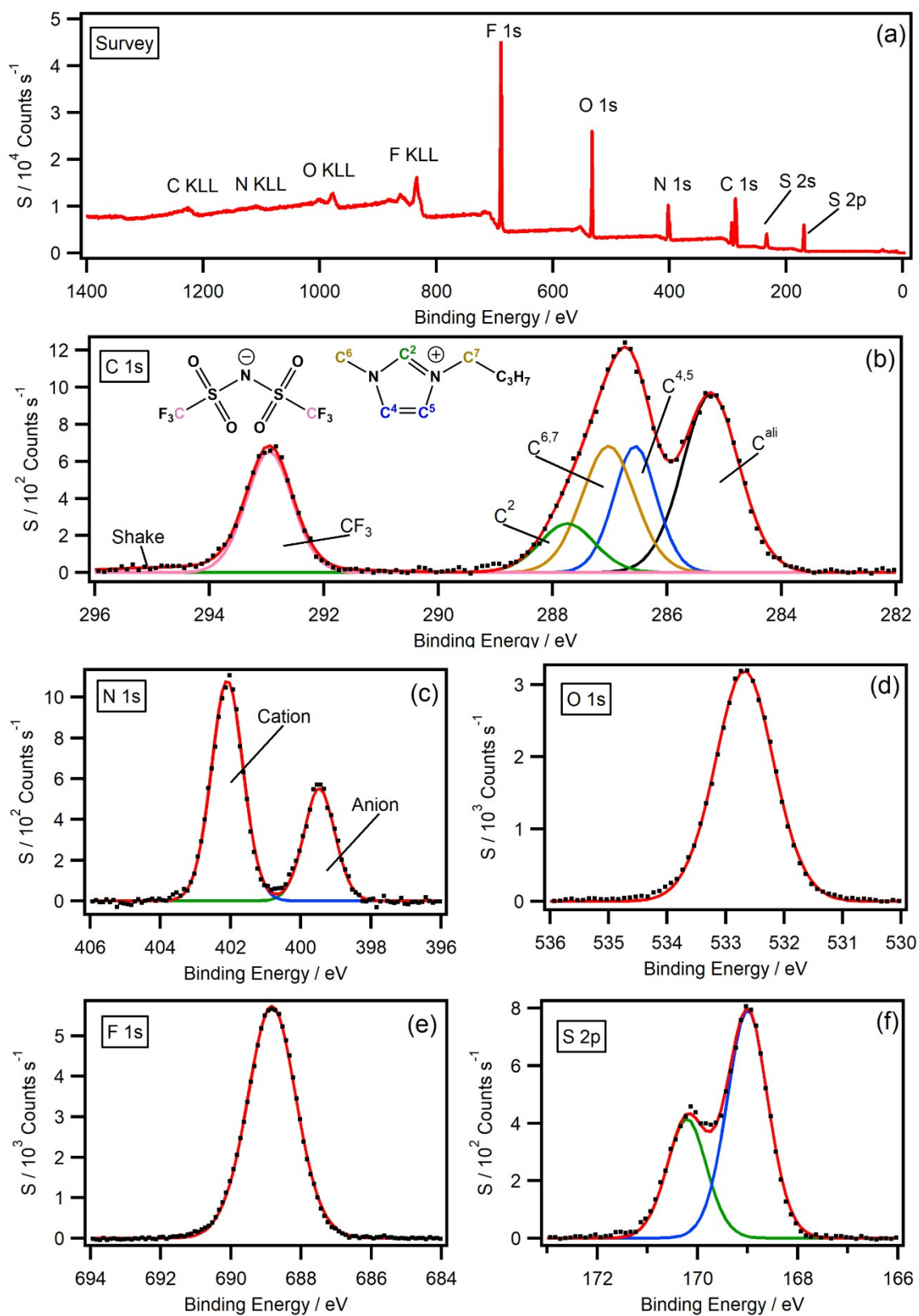


Figure S28 XPS spectra of $[C_4C_1Im][NTf_2]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

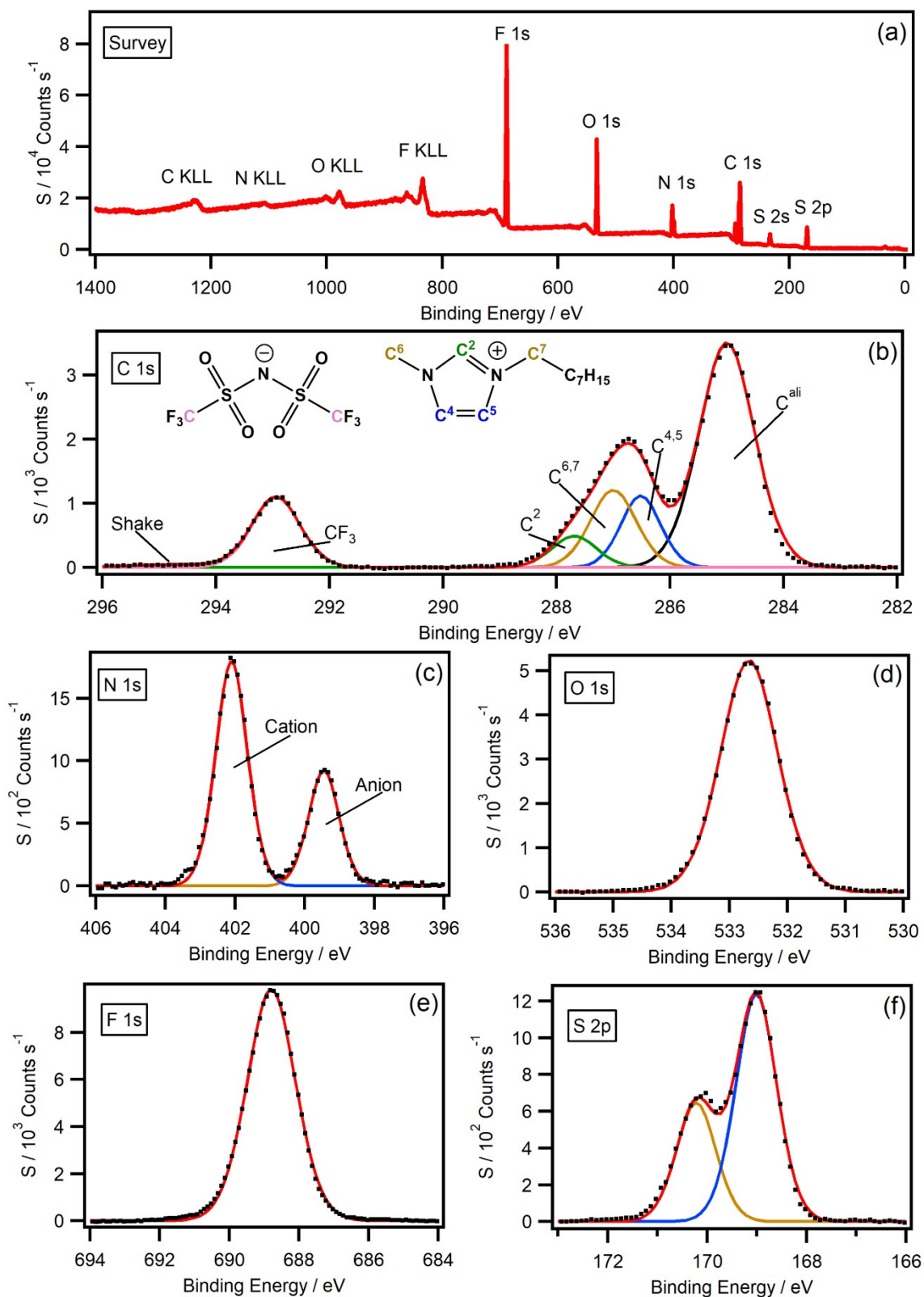


Figure S29 XPS spectra of $[C_8C_1Im][NTf_2]$ showing the (a) survey scan (b) C 1s high resolution scan with fitting, and (c-f) heteroatom high resolution scans.

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