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X-ray photoelectron spectroscopy of pyrrolidinium-based ionic liquids: cation-anion interactions and a comparison to imidazolium-based analogues

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1. Synthesis of Ionic Liquids

All ionic liquids studied during this work were prepared in our laboratories using synthetic procedures that are published elsewhere.[1-3] All ionic liquids were dried *in vacuo* ($p \leq 10^{-3}$ mbar) before being fully characterised by ^{1}H NMR, ^{13}C NMR, ESI-MS and Karl Fischer titration, in all cases the concentration of residual water was < 200 ppm. When ion exchange was one of the synthetic steps, ion chromatographic analysis (both anion and cation) showed that residual ion concentrations (Cl^-, Br^-, Li^+) were all below accepted threshold concentrations, *i.e.,* < 10 ppm. In all cases, no residual signals of either halide, or lithium were observed during XPS analysis*, i.e.*, the concentration was below the limit of detection. Full data, including full XPS data sets with peak deconstruction models, for all of the materials studied in this work appears in the supplementary information.

All analytical data for these materials was consistent with those published, for ease of reference we include a copy of the NMR. The 1:1 mixture of $[C_8C_1Pyrr][Tf_2N]$:$[C_8C_1Pyrr]I$ was prepared by mixing 1:1 moles of pure $[C_8C_1Pyrr][Tf_2N]$ and $[C_8C_1Pyrr]I$.

$[C_2C_1Pyrr][Tf_2N]$: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.62-3.53 (m, 4 H), 3.52-3.43 (m, 2 H), 3.09 (s, 3 H), 2.32 (br. s., 4 H), 1.48 (t, J=7.3Hz, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 8.82, 21.37, 47.60, 59.70, 63.92, 117.67, 121.93. ESI-MS negative: 279.92. ESI-MS positive: 508.17 (2 cation plus 1 anion).
Mpt. 361.9 K.

$[C_4C_1Pyrr][Tf_2N]$: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.65-3.43 (m, 4 H), 3.40-3.24 (m, 2 H), 3.06 (s, 3H), 2.28 (br. s., 4 H), 1.85-1.67 (m, 2 H), 1.52-1.34 (m, 2 H), 1.01 (t, J=7.3Hz, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 13.39, 19.53, 21.55, 25.75, 48.55, 64.60, 64.65, 117.70, 121.96. ESI-MS negative: 279.92. ESI-MS positive: 564.23 (2 cation plus 1 anion). Mpt. 253.7 K.

$[C_6C_1Pyrr][Tf_2N]$: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.69-3.42 (m, 4 H), 3.39-3.22 (m, 2 H), 3.05 (s, 3 H), 2.45-2.13 (m, 4 H), 1.89-1.65 (m, 2 H), 1.50-1.21 (m, 6 H), 1.03-0.80 (m, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 13.73, 21.47, 22.26, 23.73, 25.76, 31.00, 48.36, 64.51, 64.81, 117.70, 121.95. ESI-MS negative: 279.92. ESI-MS positive: 620.30 (2 cation plus 1 anion). Mpt. 254.5 K.

$[C_8C_1Pyrr][Tf_2N]$: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.68-3.42 (m, 4 H), 3.40-3.22 (m, 2 H), 3.06 (s, 3 H), 2.42-2.15 (m, 4 H), 1.89-1.65 (m, 2 H), 1.48-1.14 (m, 10H), 0.90 (t, J=7.0 Hz, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 13.98, 21.49, 22.51, 23.81, 26.13, 28.90, 31.55, 48.38, 64.54, 64.83, 117.70, 121.96. ESI-MS negative: 279.92. ESI-MS positive: 198.22. Mpt 258.5 K.

$[C_{10}C_1Pyrr][Tf_2N]$: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.54 (br. s., 4 H), 3.41-3.23 (m, 2 H), 3.07 (s, 3 H), 2.29 (br. s., 4H), 1.78 (m, 2H), 1.50-1.13 (m, 14 H), 0.91 (t, J=7.0 Hz, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 14.06, 21.49, 22.62, 23.83, 26.15, 28.96, 29.18, 29.26, 29.34, 31.80, 48.38, 64.54, 64.84, 117.70, 121.96. ESI-MS negative: 279.92. ESI-MS positive: 226.25. Mpt 262.0 K.

[C_8C_1Pyrr]I: ^{1}H NMR δ_H (300MHz, $CDCl_3$), 3.70-4.05 (m, 4H), 3.65 (m, 2H), 3.33 (s, 3H), 2.31 (br. s., 4H), 1.62-1.92 (m, 2H), 1.11-1.54 (m, 10H), 0.90 (t, J=6.9 Hz, 3H). ^{13}C NMR δ_C (75MHz, $CDCl_3$), 13.89, 21.56, 22.37, 23.96, 26.14, 28.83, 28.96, 31.44, 49.10, 64.27, 64.63. ESI-MS negative: 452.03(1 cation plus 2 anion). ESI-MS positive: 198.22. Mpt 344.0 K.

[C_8C_1Pyrr][PF_6]: ^{1}H NMR δ_H (300MHz, DMSO-d_6), 3.39-3.63 (m, 4 H), 3.42-3.34 (m, 2H), 3.05 (s, 3 H), 2.22 (br. s., 4 H), 1.67-1.92 (m, 2 H), 1.19-1.53 (m, 10 H), 0.87 (t, J=6.9 Hz, 3H). ^{13}C NMR δ_C (75MHz, DMSO-d_6), 13.93, 21.05, 22.03, 22.89, 25.90, 28.44, 28.50, 31.16, 47.45, 63.08, 63.38. ESI-MS negative: 488.15(1 cation plus 2 anion). ESI-MS positive: 198.22. Mpt 314.6 K.

2. Peak fitting procedure for 1-alkyl-3-methylimidazolium-based [C_nC_1Im][X] ionic liquids

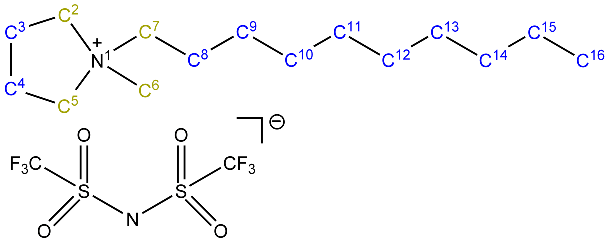
A robust and reliable fitting model for the C 1s region of imidazolium-based cations has been developed by our group.[4, 5] Four components are used to fit imidazolium-based C 1s spectra. The peak at lowest binding energy is labelled as $C_{aliphatic}$, carbon atoms bonded only to carbon and hydrogen atoms. The $C_{aliphatic}$ component can also be labelled as C_{C*-C-C}. Three other components are fitted, all of which are due to carbon atoms bonded to heteroatoms; for non-functionalised imidazolium-based cations the only heteroatoms are nitrogen atoms. These three components can collectively be labelled as C_{hetero}.

3. Details of an attempted two-component fitting model initially used for fitting the C 1s region of [C_nC_1Pyrr][X]

To begin with, the focus will be upon [C_2C_1Pyrr][Tf_2N]. The nominal stoichiometry for C_{hetero}:$C_{aliphatic}$ is 4:3 for [C_2C_1Pyrr][Tf_2N]. C_{hetero} are the four carbon atoms bonded directly to nitrogen and the $C_{aliphatic}$ represents the other three carbon atoms, bonded directly to carbon and hydrogen only. When fitting this region with two components and fixing the component intensity to 4:3, a very satisfactory fit was achieved. The full width half maxima for the two components were very similar, 1.18 eV for C_{hetero} and 1.21 eV for $C_{aliphatic}$ (a ratio of 1:1.03). It must be noted that the FWH maxima for all components for [C_2C_1Pyrr][Tf_2N] are ~10 % larger than those for n = 4 - 10. This difference is because [C_2C_1Pyrr][Tf_2N] is a solid under the XPS conditions whereas the other four ionic liquids are liquid. Therefore, it is likely that a relatively small amount of sample charging occurred for this solid ionic liquid.

For [C_4C_1Pyrr][Tf_2N] for the two-component model, the nominal stoichiometry assumed was C_{hetero}:$C_{aliphatic}$ as 4:5. Such a two-component fit gave FWH maxima as 1.03 eV for C_{hetero} and 1.22 eV for $C_{aliphatic}$ (a ratio of 1.18:1). The FWHM for C_{hetero} remains effectively constant as n increases from 4 to 10 (1.02 ± 0.03 eV), whereas for $C_{aliphatic}$ the FWHM increases as n increases. Therefore, the FWHM ratio for $C_{aliphatic}$:C_{hetero} increases with increasing n. This trend shows that as more carbon atoms are added to the chain, *i.e.*, as n increases, the variation in the electronic environment of the aliphatic carbons increases also. Generally, the carbon atoms located further away from the positively charged nitrogen atom are expected to be less positively charged, and therefore more like "normal" aliphatic carbons, *i.e.*, like carbons in simple molecules such as hexane. Therefore, for the ionic liquids with smaller n, it appeared that the component fitted as $C_{aliphatic}$ gave rise to a binding energy that did not match that of aliphatic carbon atoms. Therefore, it was decided that a two component fitting model for C 1s would not produce accurate binding energies for $C_{aliphatic}$. Therefore, satisfactory internal referencing could not be carried out using the $C_{aliphatic}$ component. Consequently, reliable and reproducible binding energies could not be obtained for pyrrolidinium-based ionic liquids using the two component fitting model for the C 1s region.

[C_2C_1Pyrr][Tf_2N] contains no $C_{aliphatic}$ atoms. Hence, there are only two electronic environments present in [C_2C_1Pyrr]$^+$. Therefore, the two-component fitting model gave a satisfactory fit for [C_2C_1Pyrr][Tf_2N]. For $n \geq 4$, the two-component model produced good agreement between experimental and fitted envelopes, but the model did not produce a reliable value for the binding energy of $C_{aliphatic}$.



Scheme 1. $[C_{10}C_1Pyrr][Tf_2N]$ labelled structure for the proposed two-component fitting model (not used in the fittings): ($C^2 + C^5 + C^6 + C^7$) = C_{hetero} and ($C^3 + C^4 + C^8$ to C^{16}) = $C_{aliphatic}$.

Table S1. Full width half maxima (FWHM) for C_{hetero} and $C_{aliphatic}$ for $[C_nC_1Pyrr][Tf_2N]$ for the C 1s two-component fitting model.

	FWHM		
n for $[C_nC_1Pyrr][Tf_2N]$	C_{hetero} 1s / eV	$C_{aliphatic}$ 1s / eV	($C_{aliphatic}$ 1s):(C_{hetero} 1s)
2	1.18	1.21	1.03
4	1.03	1.22	1.18
6	1.04	1.30	1.25
8	1.01	1.35	1.33
10	0.99	1.32	1.34

Table S2. Full width half maxima (FWHM) for all regions for $[C_nC_1Pyrr][X]$ for a C 1s three component fitting model (note: a two component fitting model was used for $[C_2C_1Pyrr][Tf_2N]$). The FWH maxima for C_{hetero} 1s and C_{inter} 1s were constrained to be equal. The FWH maxima for S $2p_{3/2}$ and S $2p_{1/2}$ were constrained to be equal. The FWH maxima for P $2p_{3/2}$ and P $2p_{1/2}$ were constrained to be equal. The FWH maxima for I $3d_{5/2}$ and I $3d_{3/2}$ were constrained to be equal.

		Cation				Anion							
Anion for $[C_nC_1Pyrr][X]$	*n* for $[C_nC_1Pyrr][X]$	$C_{aliphatic}$ 1s	C_{hetero} 1s	C_{inter}1s	N_{cation} 1s	C_{CF3} 1s	N_{anion} 1s	O 1s	F 1s	S 2p	P 2p	I 3d	($C_{aliphatic}$ 1s):(C_{hetero} 1s)
$[Tf_2N]^-$	2		1.19	1.19	1.23	1.09	1.30	1.36	1.73	1.12			
$[Tf_2N]^-$	4	1.19	1.10	1.10	1.08	1.01	1.06	1.18	1.66	0.93			1.08
$[Tf_2N]^-$	6	1.25	1.07	1.07	1.07	0.98	1.04	1.15	1.64	0.93			1.17
$[Tf_2N]^-$	8	1.18	1.09	1.09	1.09	1.02	1.11	1.18	1.64	0.96			1.09
$[Tf_2N]^-$	10	1.12	1.10	1.10	1.07	0.98	1.08	1.16	1.63	0.92			1.03
I^-	8	1.18	1.07	1.05	1.14							1.24	1.10
$[PF_6]^-$	8	1.14	1.03	1.03	1.09				1.46		0.86		1.10
I^- and $[Tf_2N]^-$	8	1.19	1.08	1.08	1.07	0.99	1.12	1.15	1.63	0.90		1.12	1.10

4. XP spectra at θ = 0° for pure [C_nC_1Pyrr][X]

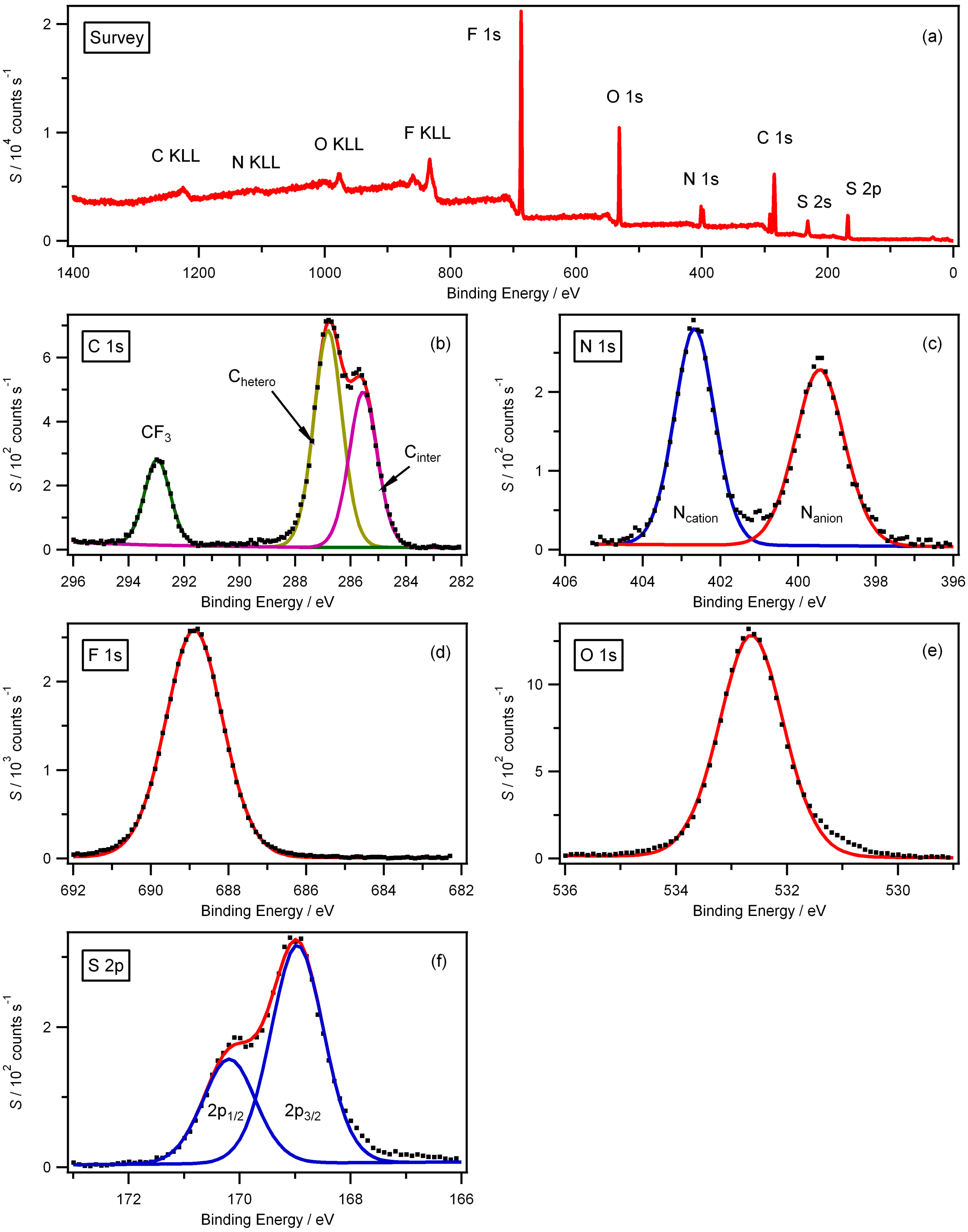


Figure S1. XP spectra with component fittings of [C_2C_1Pyrr][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p. Note this sample was cast as a melt and then cooled to form a flat glass during pumping, C 1s was deconstructed using the 3-component model outlined in the main paper.

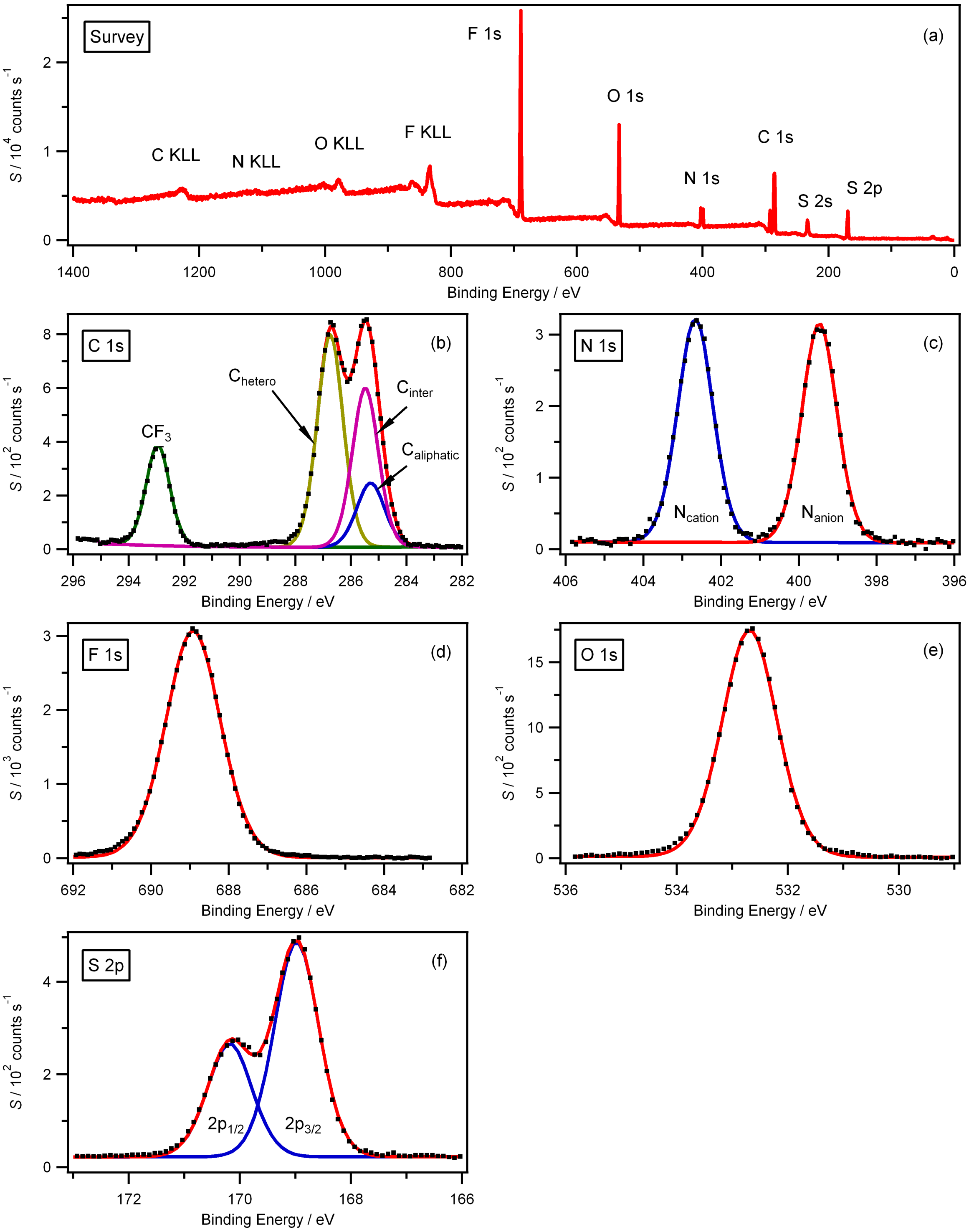


Figure S2. XP spectra with component fittings of [C_4C_1Pyrr][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p. C 1s was deconstructed using the 3-component model outlined in the main paper.

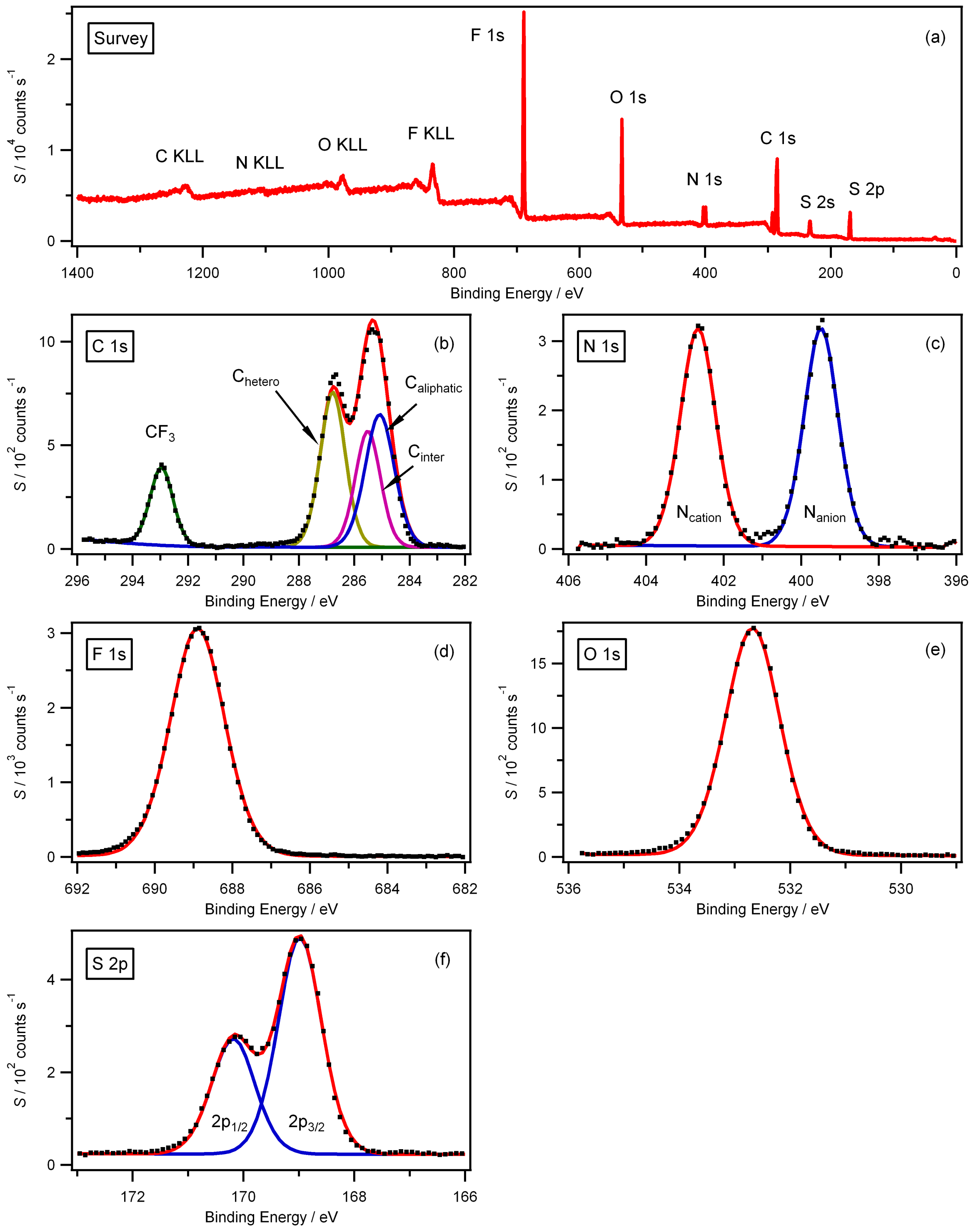


Figure S3. XP spectra with component fittings of [C_6C_1Pyrr][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p. C 1s was deconstructed using the 3-component model outlined in the main paper.

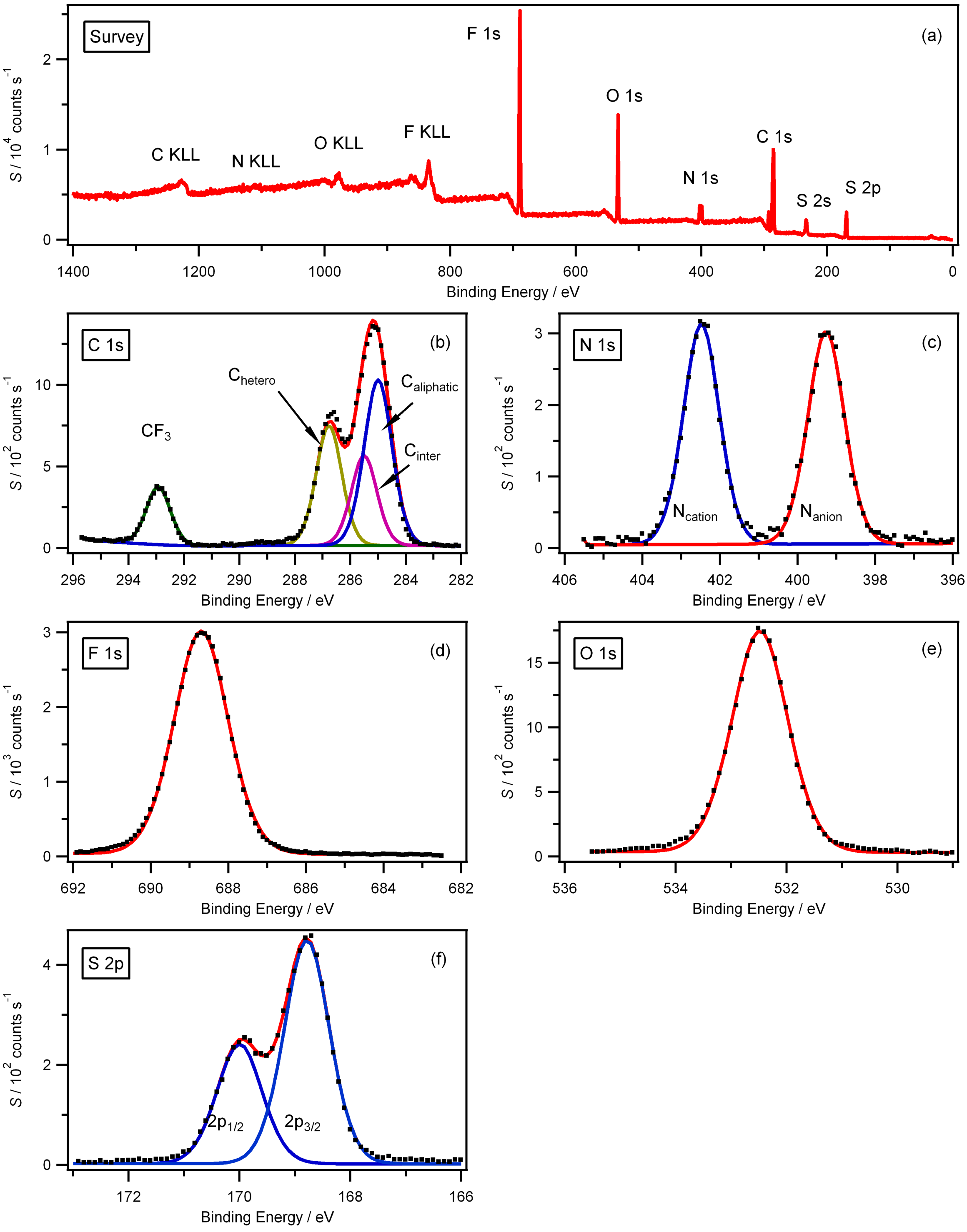


Figure S4. XP spectra with component fittings of [C_8C_1Pyrr][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p. C 1s was deconstructed using the 3-component model outlined in the main paper.

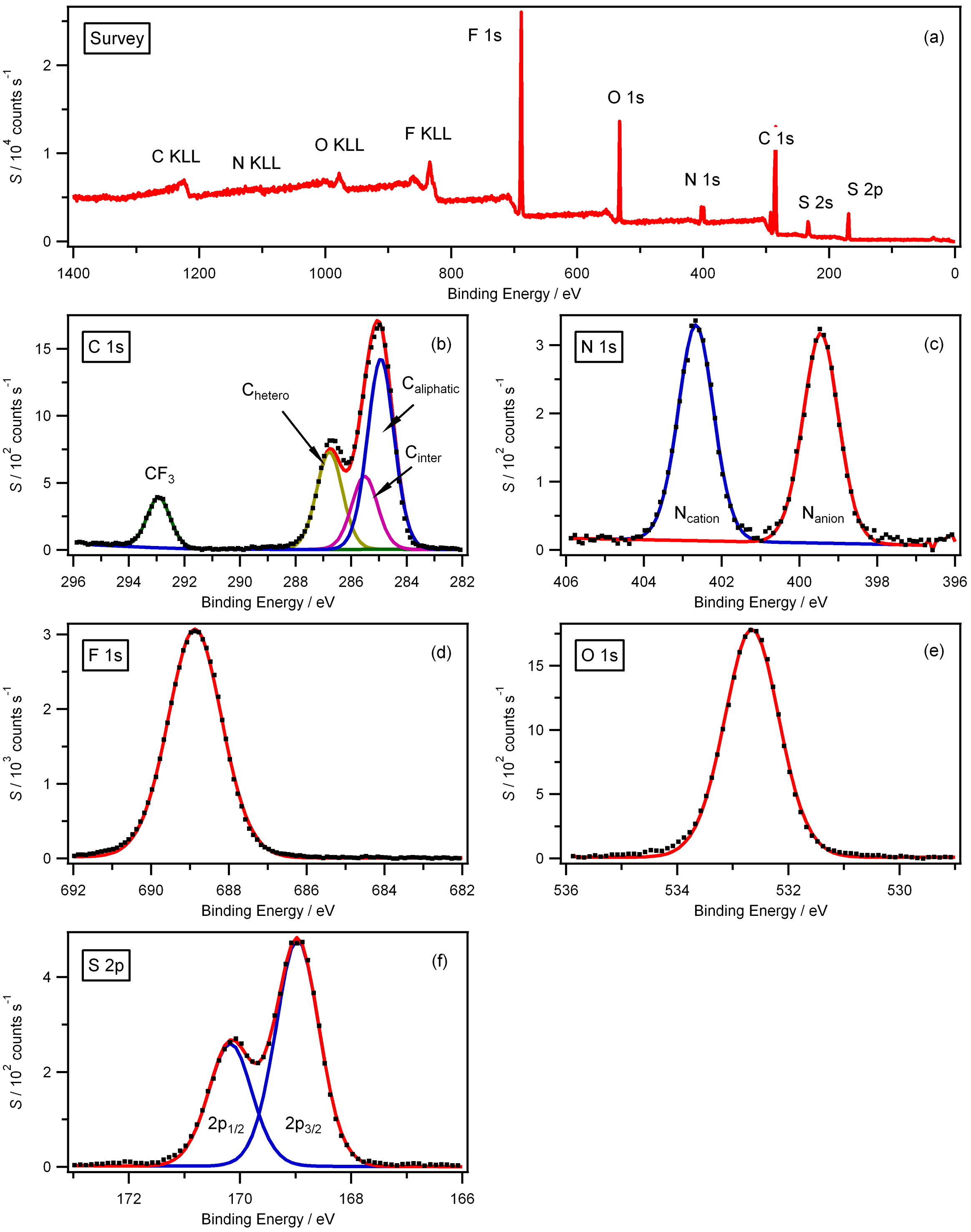


Figure S5. XP spectra with component fittings of [$C_{10}C_1$Pyrr][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p. C 1s was deconstructed using the 3-component model outlined in the main paper.

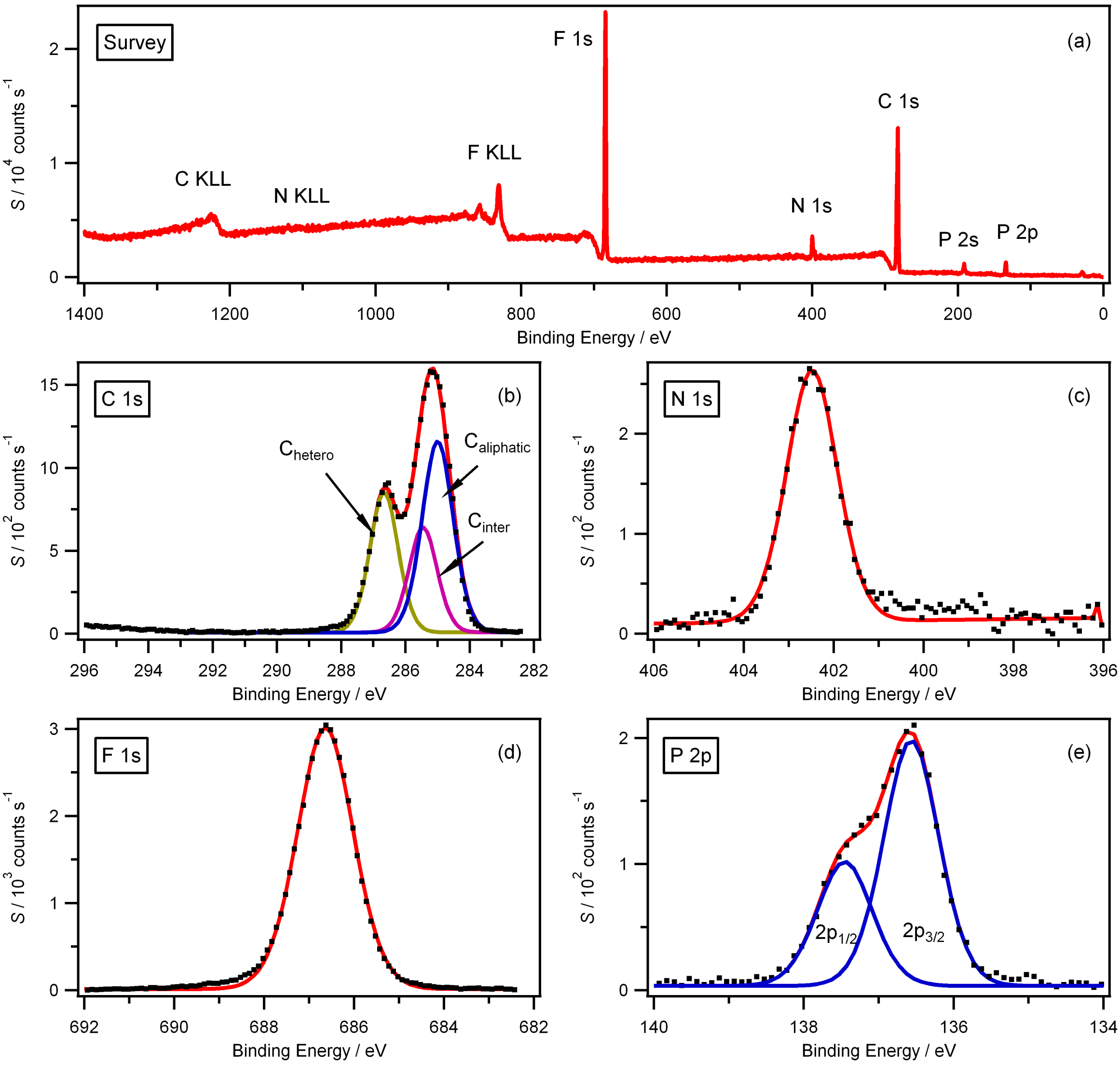


Figure S6. XP spectra with component fittings of [C_8C_1Pyrr][PF_6] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) P 2p. C 1s was deconstructed using the 3-component model outlined in the main paper.

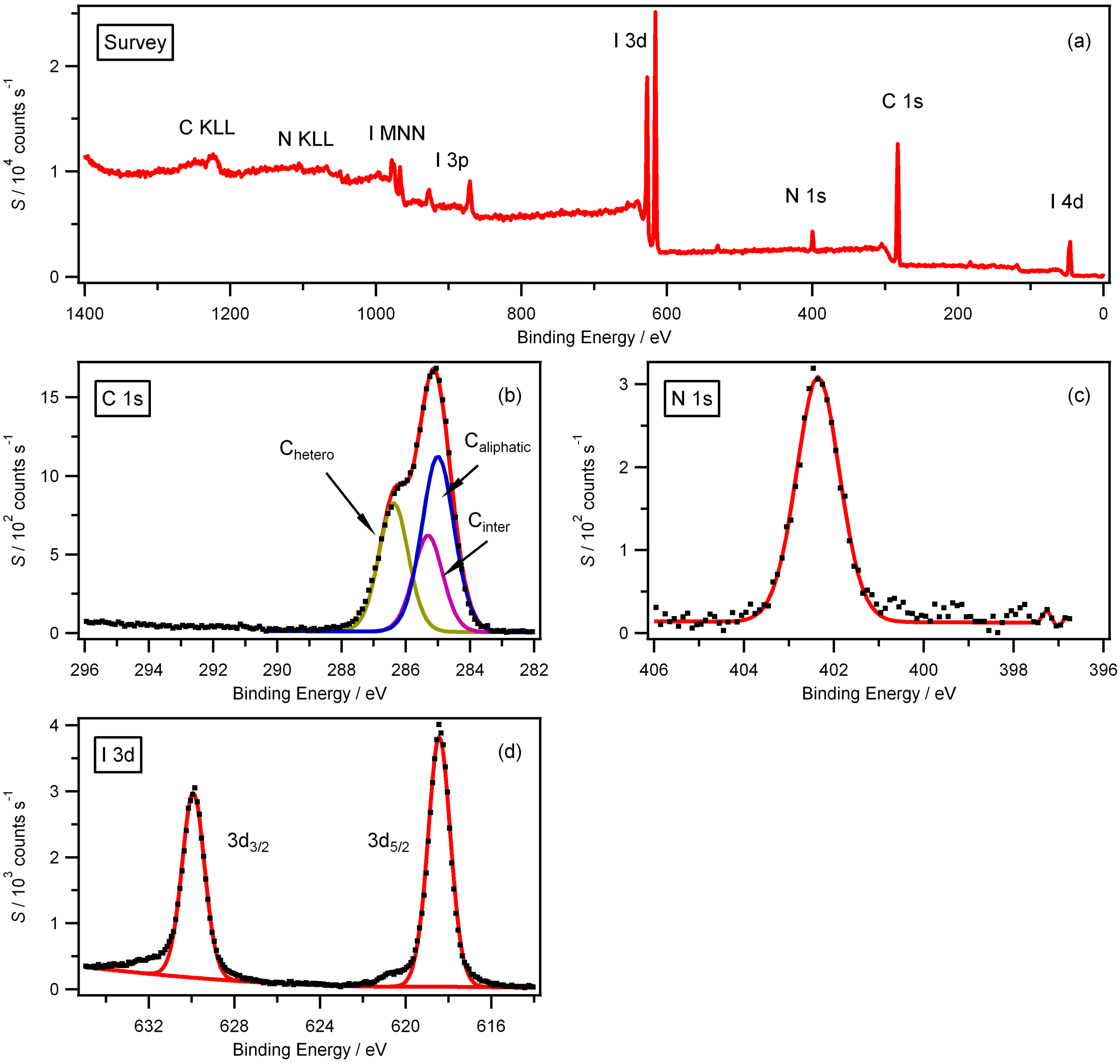


Figure S7. XP spectra with component fittings of [C_8C_1Pyrr]I for: (a) survey, (b) C 1s, (c) N 1s, (d) I 3d. C 1s was deconstructed using the 3-component model outlined in the main paper.

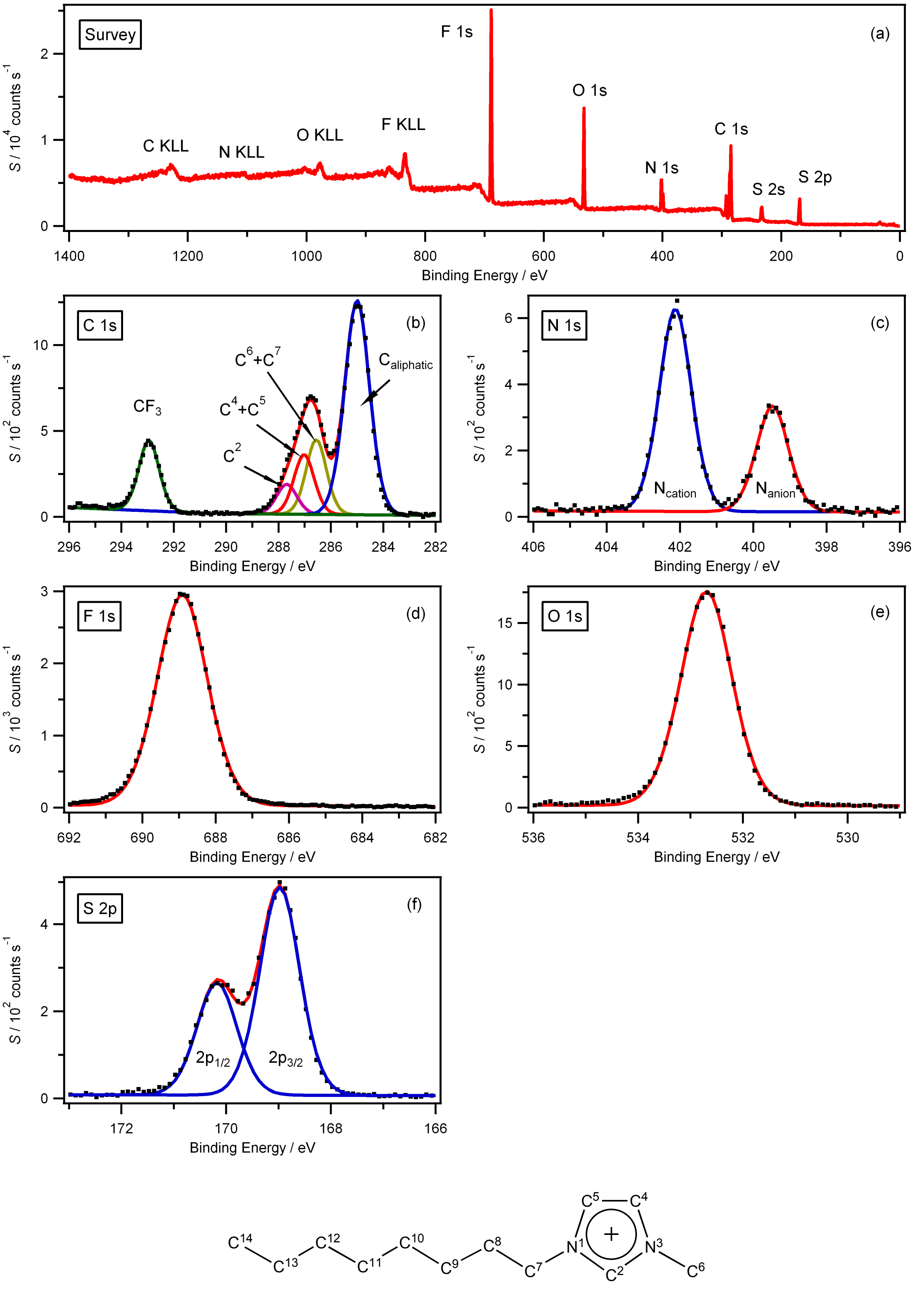


Figure S8. XP spectra with component fittings of $[C_8C_1Im][Tf_2N]$ for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p, C 1s peak components numbers with reference to structure.

5. XP spectra and binding energies at θ = 0° for a 1:1 mixture of $[C_8C_1Pyrr][Tf_2N]:[C_8C_1Pyrr]I$

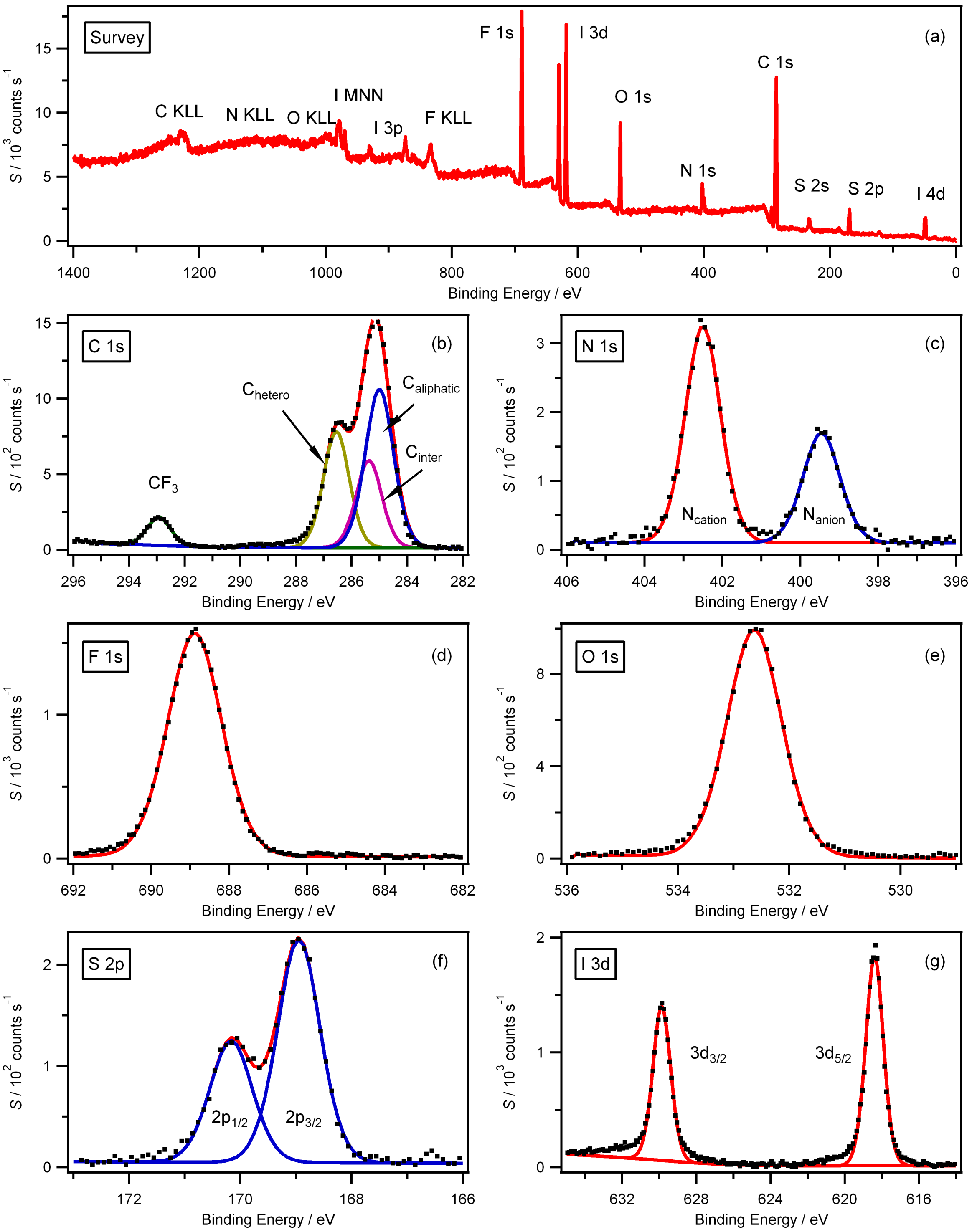


Figure S9. XP spectra with component fittings of 1:1 mixture of $[C_8C_1Pyrr][Tf_2N]:[C_8C_1Pyrr]I$ for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s, (f) S 2p, (g) I 3d.

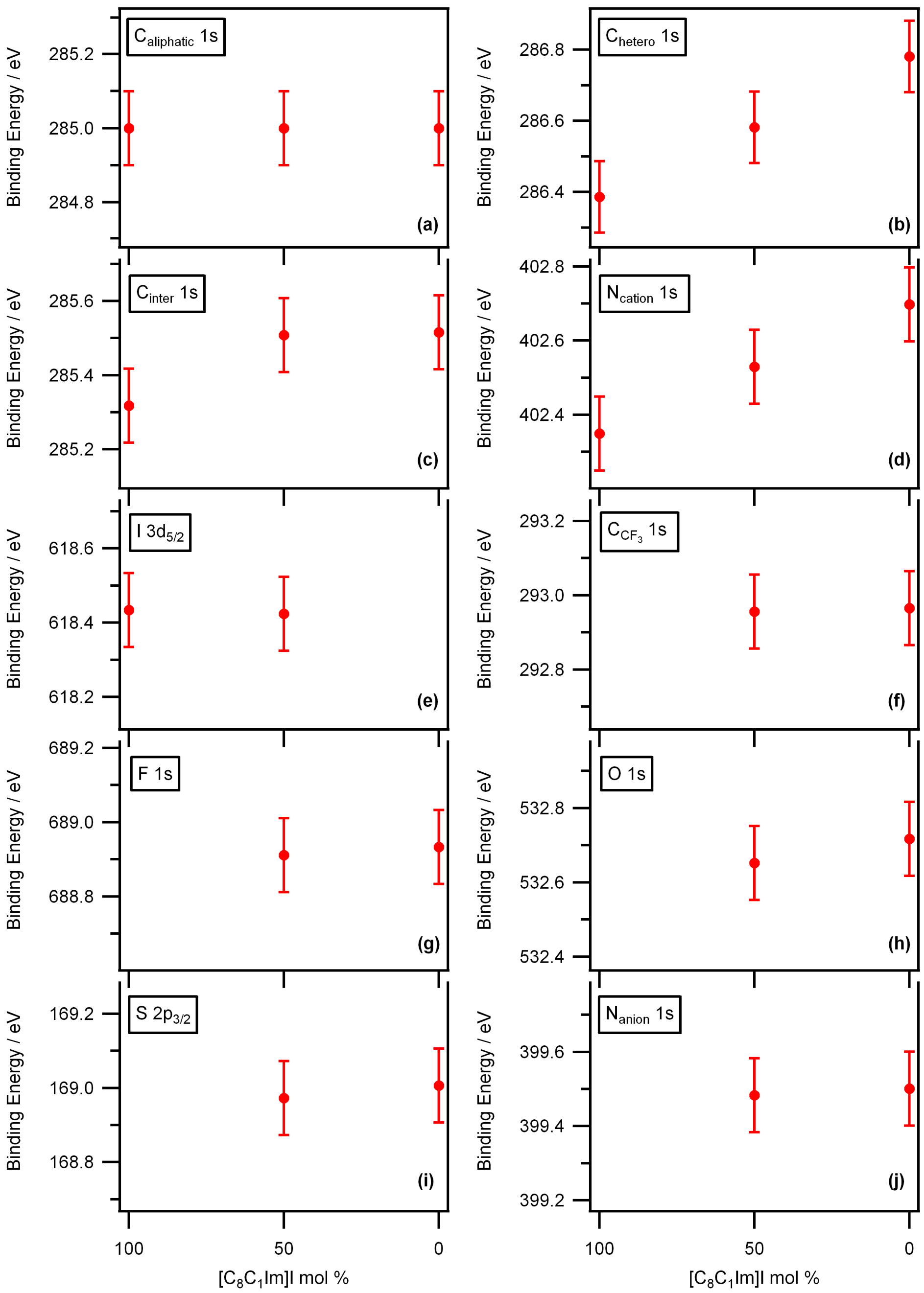


Figure S10. Binding energy shifts for a 1:1 mixture of $[C_8C_1Pyrr][Tf_2N]$ and $[C_8C_1Pyrr]I$ and pure ionic liquids: (a) $C_{aliphatic}$ 1s, (b) C_{hetero} 1s, (c) C_{inter} 1s, (d) N_{cation} 1s, (e) I $3d_{5/2}$, (f) C_{CF3} 1s, (g) F 1s, (h) O 1s, (i) S $2p_{3/2}$ and (j) N_{anion} 1s.

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