Amino Acid-Based Ionic Liquids: Using XPS to Probe the Electronic Environment via Binding Energies

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S 1. Characterisation of amino acid containing ionic liquids using standard analytical techniques (NMR, MS, DSC, TGA and Polarimetry).

S 1.1 1-octyl-3-methylimidazolium glycinate, $[C_8C_1Im][Gly]$

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.84 (t, J = 7.00 Hz, 3H), 1.18 - 1.30 (m, 10H), 1.76 (quin, J = 7.23 Hz, 2H), 2.67 (br. S, 2H), 3.86 (s, 3H), 4.16 (t, J = 7.23 Hz, 2H), 7.74 (s, 1H), 7.80 (s, 1H), 9.62 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.9, 22.0, 25.5, 28.4, 28.5, 29.4, 31.2, 35.6, 46.6, 48.7, 122.2, 123.5, 137.2, 174.8.

T_g = -52.3 °C , **T_{decom}** = 190.9 °C

$[\alpha]_D^{24}$ = 0 (c 3.7, MeOH)

S 1.2 1-octyl-3-methylimidazolium alaninate, $[C_8C_1Im][Ala]$

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.85 (t, J = 7.20 Hz, 3H), 1.00 (d, J = 6.78 Hz, 3H), 1.15 - 1.32 (m, 10H), 1.77 (quin, J = 7.25 Hz, 2H), 2.76 - 2.83 (bs, 1H), 3.87 (s, 3H), 4.17 (t, J = 7.22 Hz, 2H), 7.74 (s, 1H), 7.81 (s, 1H), 9.71 (s, 1H)

^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.9, 22.0, 23.0, 25.5, 28.3, 28.5, 29.4, 31.1, 35.6, 48.6, 51.8, 122.2, 123.5, 137.2, 177.8.

T_g = -64.7 °C, T_{decomp} = 202.5 °C

$[\alpha]_D^{24}$ = +1.3 (c 2.2, MeOH)

S 1.3 1-octyl-3-methylimidazolium valinate, $[C_8C_1Im][Val]$:

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.68 (d, J = 6.70 Hz, 3H), 0.81 (d, J = 6.70 Hz, 3H), 0.85 (t, J = 7.20 Hz, 3H), 1.16 - 1.33 (m, 10H), 1.77 (quin, J = 7.23 Hz, 2H), 1.85 - 1.97 (m, 1H), 2.68 (bs, 1H), 3.86 (s, 3H), 4.17 (t, J = 7.31 Hz, 2H), 7.73 (s, 1H), 7.80 (s, 1H), 9.63 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 14.0, 17.3, 20.5, 22.1, 25.6, 28.4, 28.5, 29.5, 31.2, 31.6, 35.7, 48.7, 61.5, 122.3, 123.6, 137.3, 182.5.

T_g= -56.3 °C, **T_{decom}** = 204.7 °C,

$[\alpha]_D^{24}$ = +5.4 (c 3.6, MeOH)

S 1.4 1-octyl-3-methylimidazolium isoleucinate, $[C_8C_1Im][Ile]$

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.69 - 0.80 (m, 6H), 0.85 (t, J = 7.30 Hz, 3H), 0.92 - 1.07 (m, 1H), 1.16 - 1.42 (m, 12H), 1.77 (quin, J = 7.23 Hz, 2H), 2.68 (bs, 1H), 3.86 (s, 3H), 4.17 (t, J = 7.31 Hz, 2H), 7.73 (s, 1H), 7.79 (s, 1H), 9.67 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 12.2, 13.9, 16.8, 22.1, 23.8, 25.6, 28.3, 28.4, 28.5, 29.5, 31.2, 35.6, 48.7, 61.2, 122.2, 123.5, 137.3, 176.4.

T_g = -56.8 °C , **T_{decom}** = 202.2 °C

$[\alpha]_D^{24}$ = +6.8 (c 3.6, MeOH)

S 1.5 1-octyl-3-methylimidazolium methionate, $[C_8C_1Im][Met]$

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.85 (t, J = 7.20 Hz, 3H), 1.24 (m, 10H), 1.38 - 1.54 (m, 1H), 1.68 - 1.85 (m, 3H), 1.99 (s, 3H), 2.46 (t, J = 7.90 Hz, 2H), 2.75 - 2.88 (m, 1H), 3.86 (s, 3H), 4.16 (t, J = 7.16 Hz, 2H), 7.73 (s, 1H), 7.80 (s, 1H), 9.56 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.9, 14.7, 22.0, 25.5, 28.3, 28.5, 29.4, 30.9, 31.1, 35.6, 35.9, 36.1, 48.7, 55.5, 122.2, 123.5, 137.1, 176.1.

T_g = -60.2 °C ,**T_{decom}** = 193.8 °C ,

$[\alpha]_D^{24}$ = -2.9 (c 3.7, MeOH)

S 1.6 1-octyl-3-methylimidazolium serinate, [C_8C_1Im][Ser]

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.85 (t, *J* = 7.00 Hz, 3 H), 1.14 - 1.33 (m, 10 H), 1.77 (quin, *J* = 7.30 Hz, 2 H), 3.18 - 3.32 (m, 3 H), 3.85 (s, 3 H), 4.15 (t, *J* = 7.22 Hz, 2 H), 7.71 (s, 1 H), 7.78 (s, 1 H), 9.32 (s, 1 H)

^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.9, 22.0, 25.5, 28.3, 28.5, 29.4, 31.1, 35.7, 35.9, 36.1, 48.7, 65.8, 115.6, 122.2, 123.6, 136.8, 175.3.

T_g = -51.3 °C , **T_{decom}** = 198.4 °C

$[\alpha]_D^{24}$ = -3.2 (c 3.0, MeOH)

S 1.7 1-octyl-3-methylimidazolium tyrosinate, [C_8C_1Im][Tyr]

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.84 (t, *J* = 7.00 Hz, 3H), 0.95 - 1.47 (m, 12H), 1.76 (quin, *J* = 7.27 Hz, 2H), 2.20 (dd, *J* = 13.30, 9.21 Hz, 1H), 2.78 - 2.96 (m, 1H), 3.82 (s, 3H), 4.14 (t, *J* = 7.23 Hz, 2H), 6.49 (d, *J* = 8.33 Hz, 2H), 6.79 (d, *J* = 8.48 Hz, 2H), 7.70 (d, *J* = 1.90 Hz, 1H), 7.77 (s, 1H), 9.54 (br. s., 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 13.9, 22.0, 25.5, 28.4, 28.5, 29.4, 31.2, 35.6, 42.1, 48.7, 58.4, 115.8, 122.2, 123.5, 127.1, 129.6, 137.2, 160.0, 176.9, 190.8, 190.9.

T_g= -23.9 °C ,**T_{decom}** = 200.8 °C

$[\alpha]_D^{24}$ = -2.2 (c 3.2, MeOH)

S 1.8 1-octyl-3-methylimidazolium asparaginate, [C_8C_1Im][Asn]

^{1}H NMR (400 MHz, DMSO-d_6) δ = 0.85 (t, *J* = 7.00 Hz, 3H), 1.06 - 1.45 (m, 10H), 1.77 (quin, *J* = 7.31 Hz, 2H), 1.90 - 2.03 (m, 1H), 2.40 (dd, *J* = 14.76, 4.53 Hz, 1H), 3.11 (br. S, 1H), 3.86 (s, 3H), 4.16 (t, *J* = 7.16 Hz, 2H), 6.58 (br. S, 1H), 7.73 (s, 1H), 7.79 (s, 1H), 8.10 (s, 1H), 9.45 (s, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ = 14.0, 22.1, 25.5, 28.4, 28.5, 29.4, 31.2, 35.7, 42.8, 48.7, 53.5, 122.2, 123.6, 137.0, 151.4, 174.7.

T_g = -35.4 °C ,**T_{decom}** = 196.1 °C

$[\alpha]_D^{24}$ = -15.4 (c 4.0, MeOH)

S2. Relative stability of AAILs under prolonged X-ray irradiation.

The surface composition of ionic liquids can be considered "chemically stable" if observed changes in the N 1s XP spectra are less than 5 % over the duration of an experiment. Recommended maximum exposure times ($t_{max,5\%}$) have been determined using a monochromated Al K_α source (power 100 W, emission current 10 mA and anode potential 10 kV). This data allows scan programmes to be developed, thus maintaining a stable surface throughout the analysis period.

AAIL sample	$t_{max,5\%}$ / min
$[C_8C_1Im][Gly]$	200
$[C_8C_1Im][Ala]$	350
$[C_8C_1Im][Val]$	320
$[C_8C_1Im][Ile]$	300
$[C_8C_1Im][Met]$	140
$[C_8C_1Im][Ser]$	60
$[C_8C_1Im][Tyr]$	100
$[C_8C_1Im][Asn]$	60

S 3. XP spectra, including fits, for all ionic liquids studied in this work. Note, the colours coding used in the C 1s deconstruction models is consistent with that used in Figure 2 of the main paper.

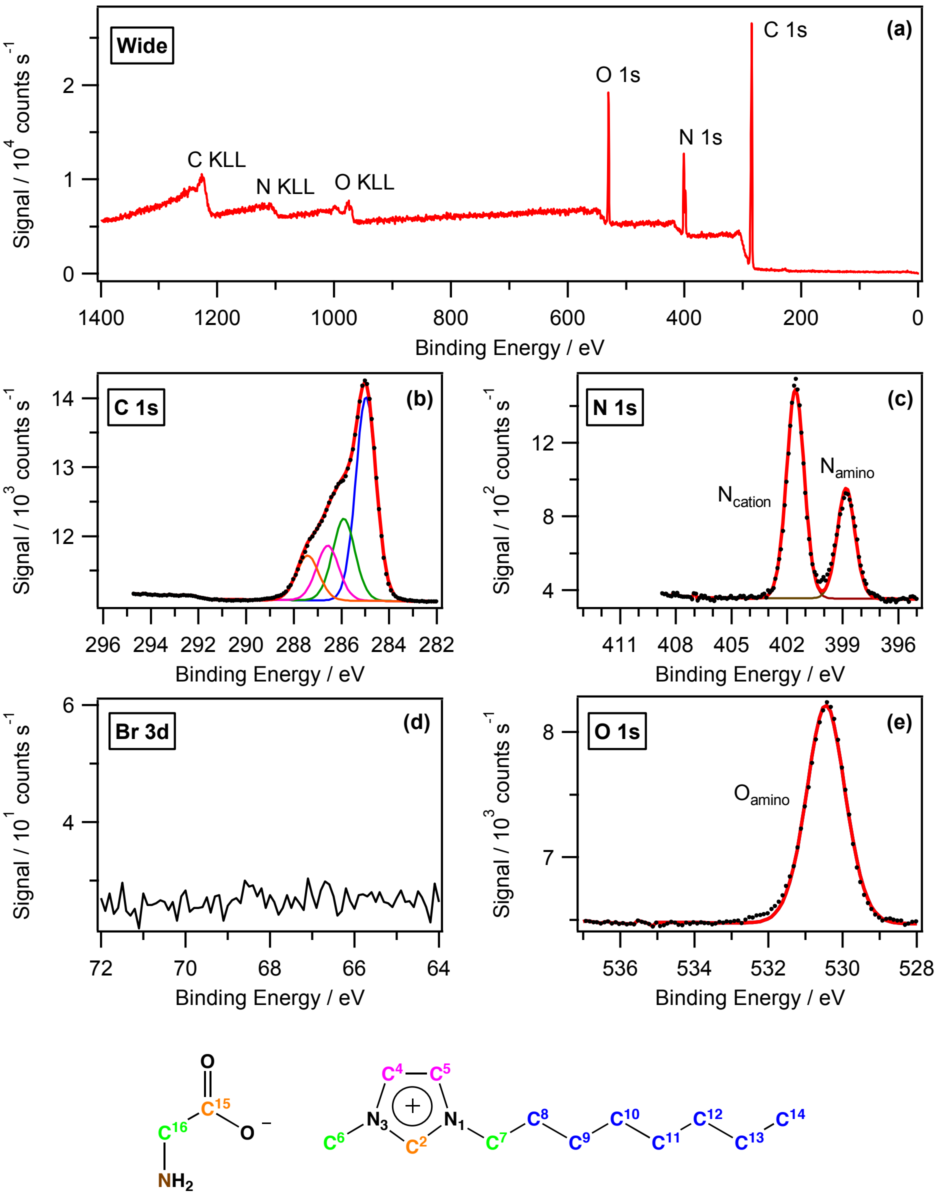

Figure S3.1 XP spectra with component fittings of [C_8C_1Im][Gly] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

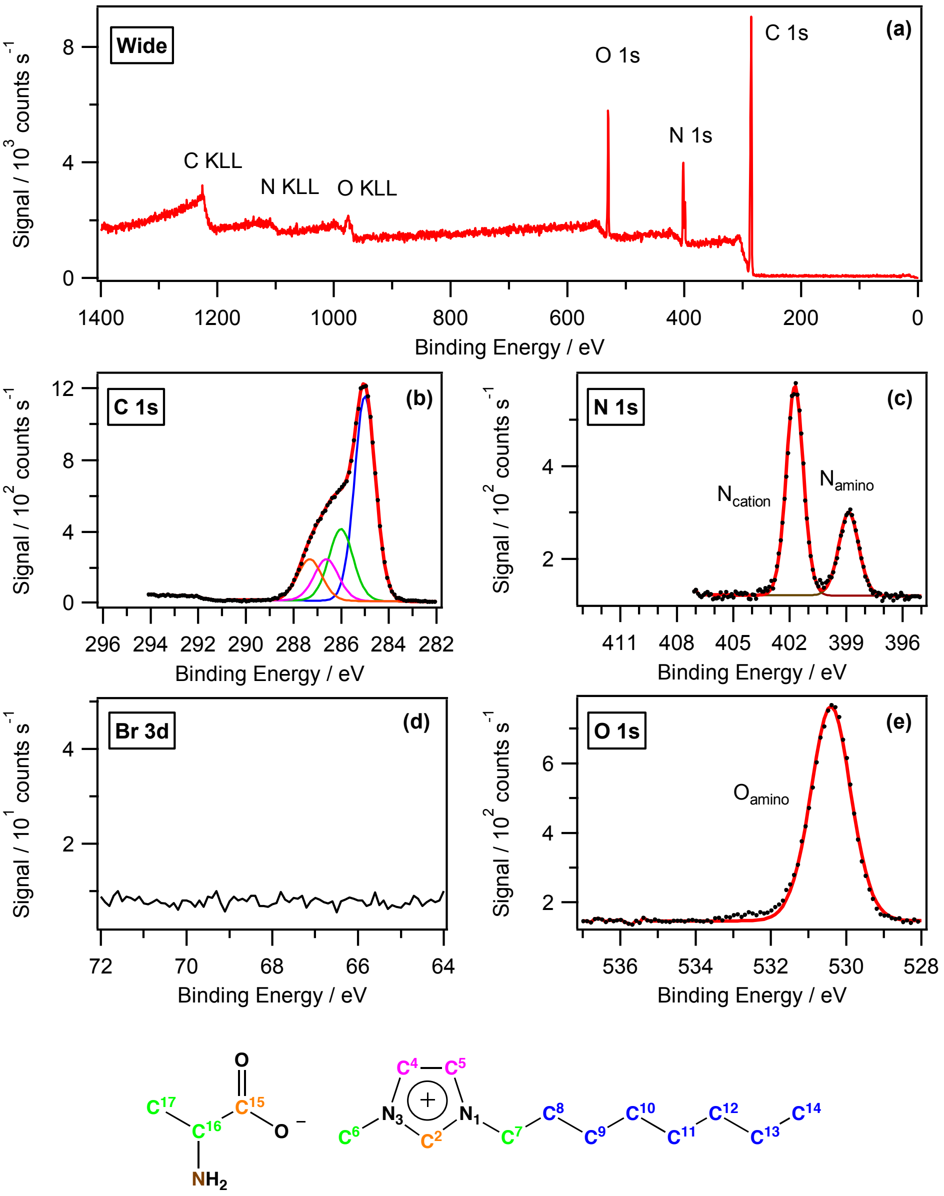

Figure S3.2 XP spectra with component fittings of [C_8C_1Im][Ala] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

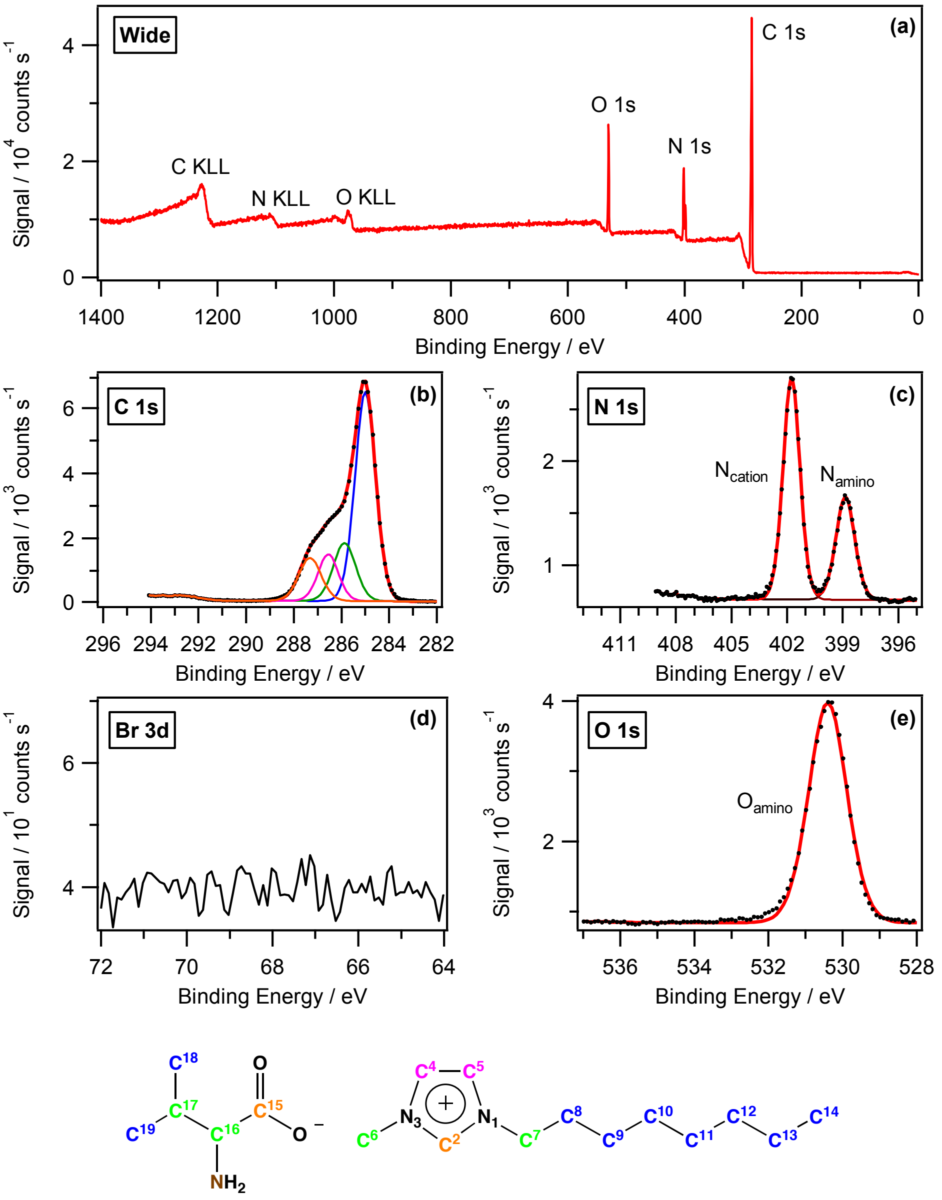

Figure S3.3 XP spectra with component fittings of [C_8C_1Im][Val] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

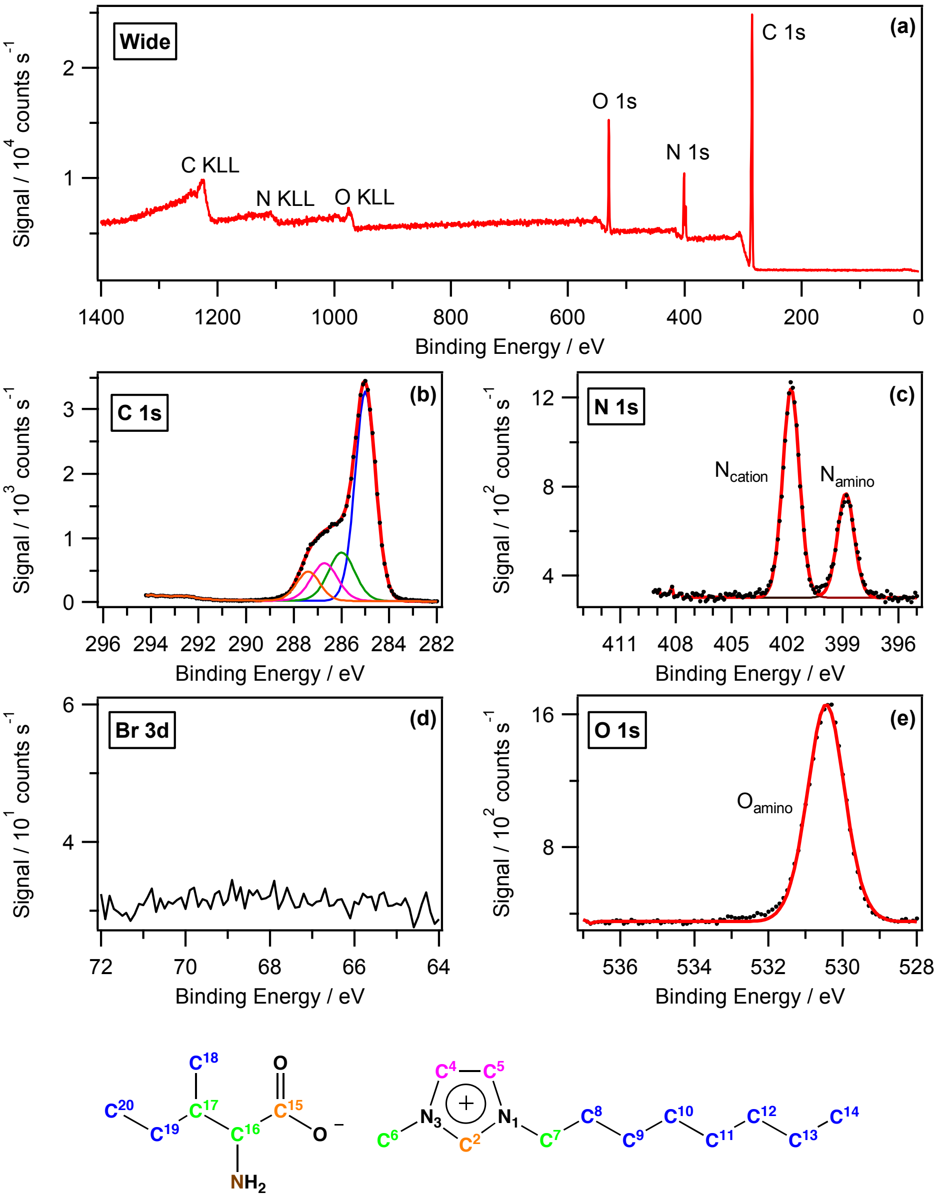

Figure S3.4 XP spectra with component fittings of [C_8C_1Im][Ile] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

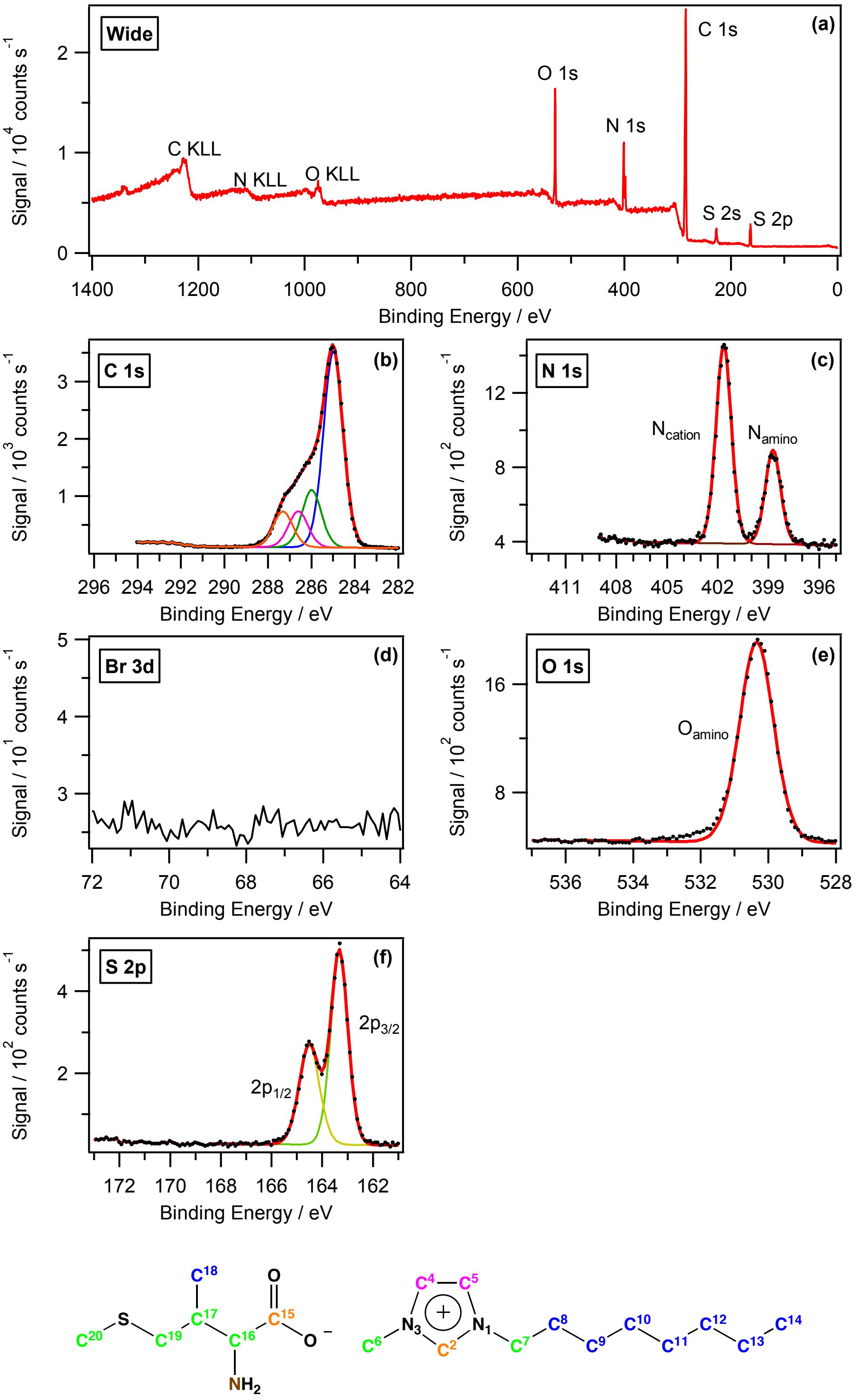

Figure S3.5 XP spectra with component fittings of [C_8C_1Im][Met] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d, (e) O 1s and (f) S 2p.

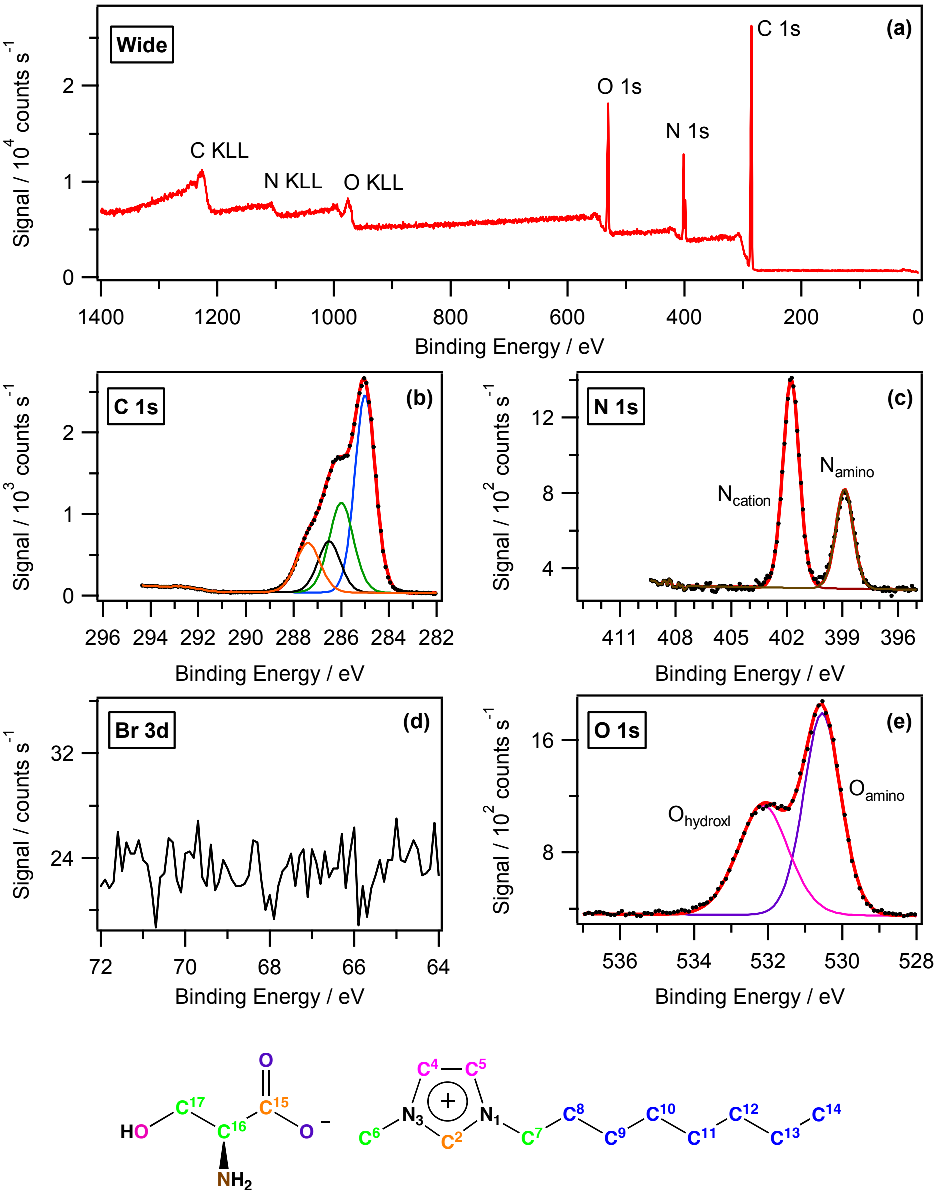

Figure S3.6 XP spectra with component fittings of $[C_8C_1Im][Ser]$ for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

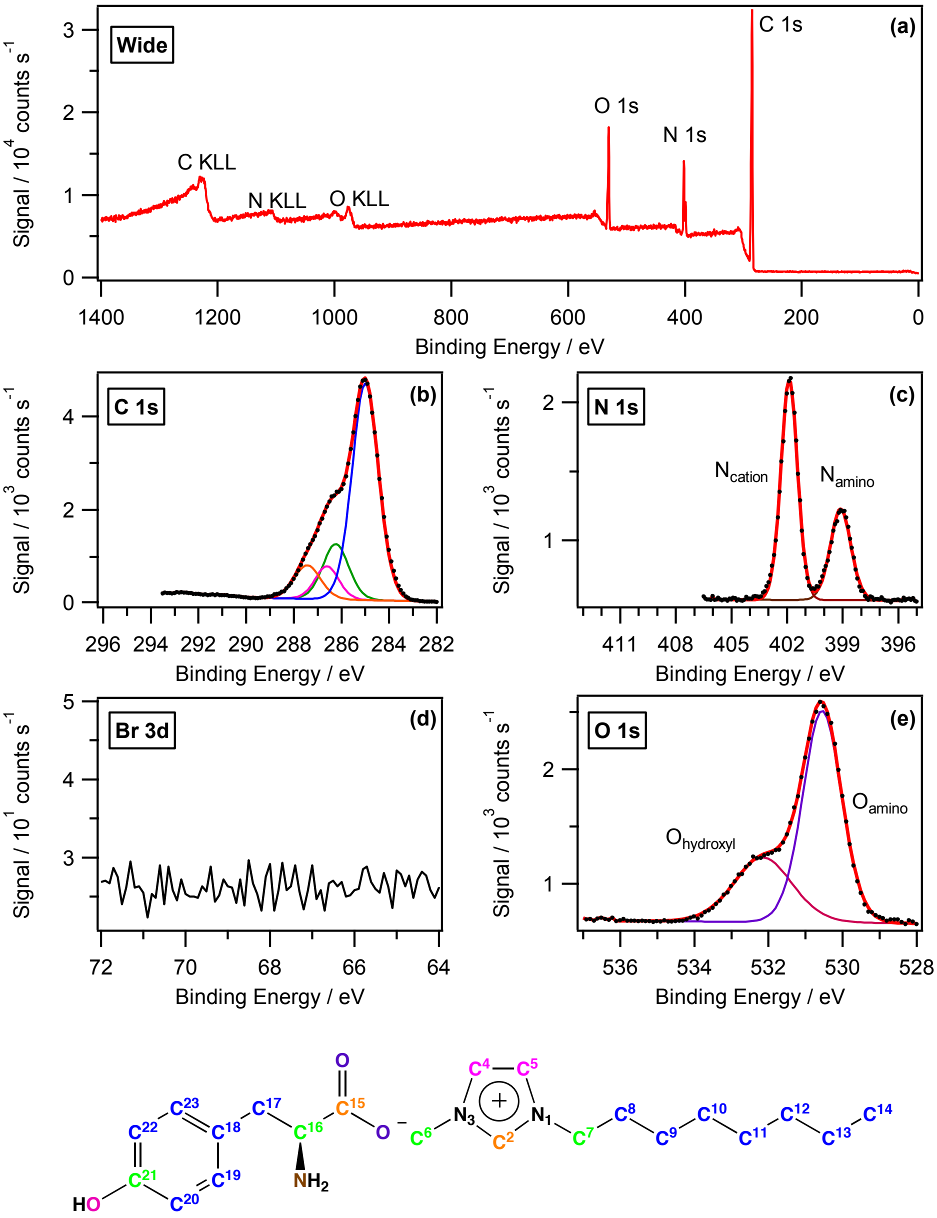

Figure S3.7 XP spectra with component fittings of [C_8C_1Im][Tyr] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

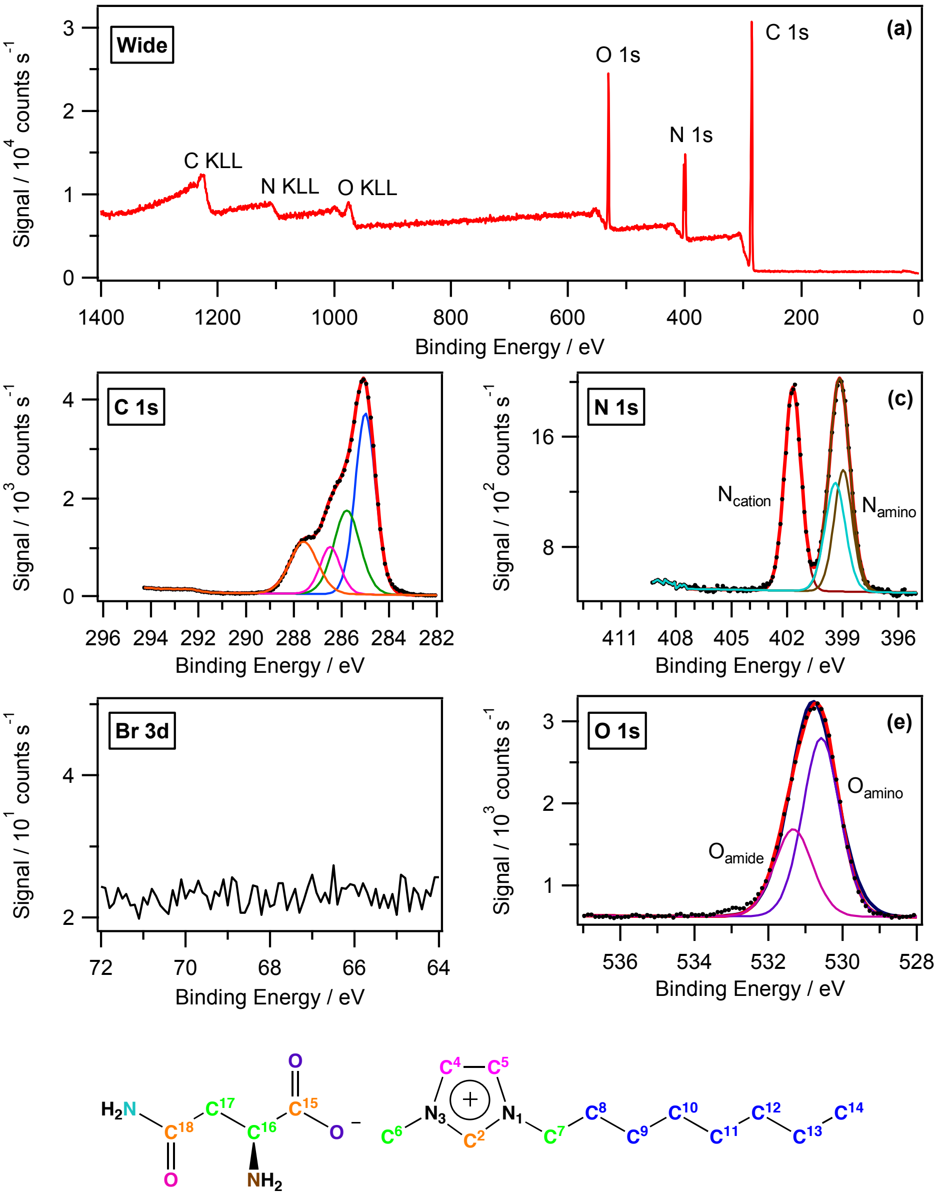

Figure S3.8 XP spectra with component fittings of [C_8C_1Im][Asn] for: (a) survey, (b) C 1s, (c) N 1s, (d) Br 3d and (e) O 1s.

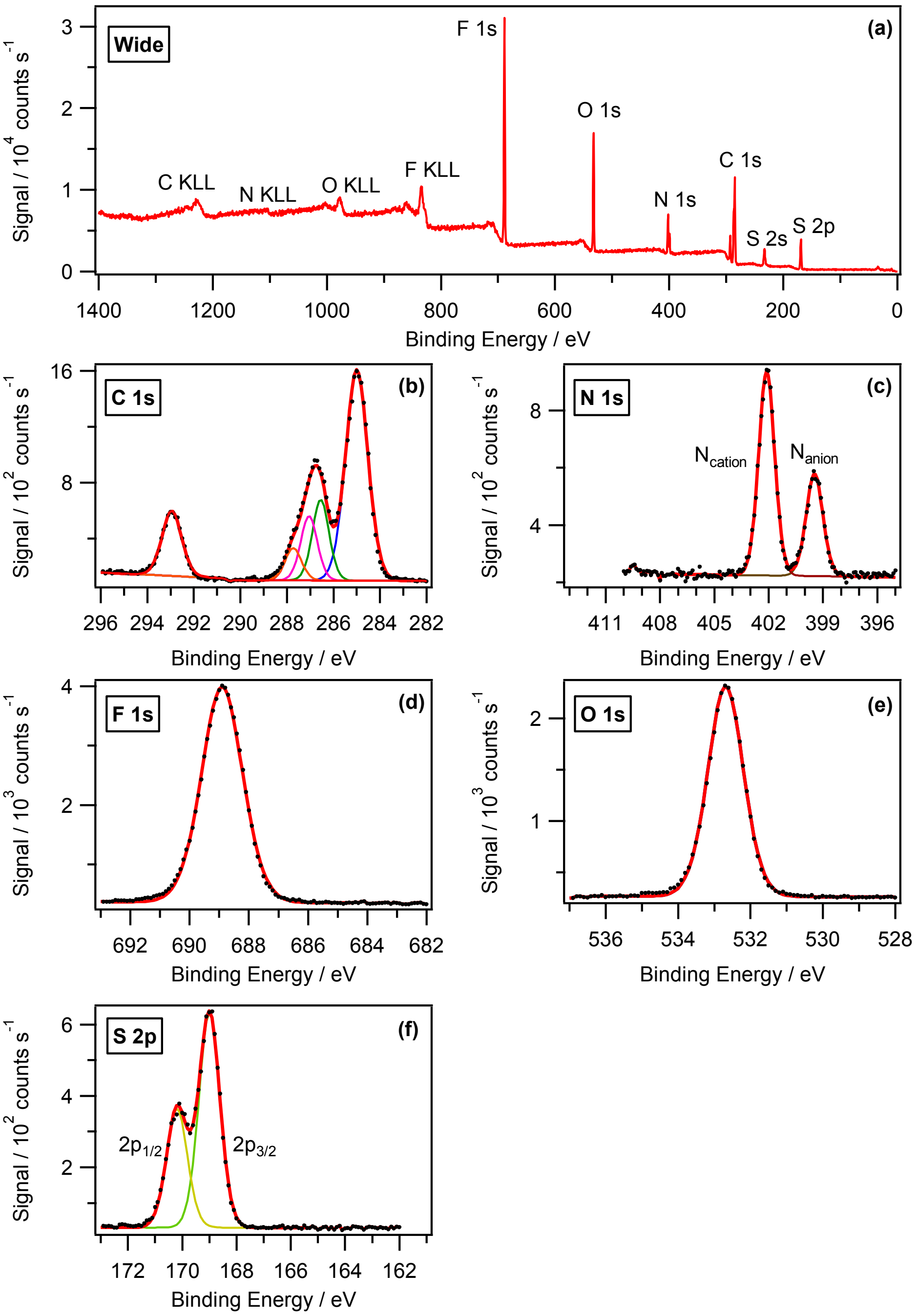

Figure S3.9 XP spectra with component fittings of [C_8C_1Im][Tf_2N] for: (a) survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

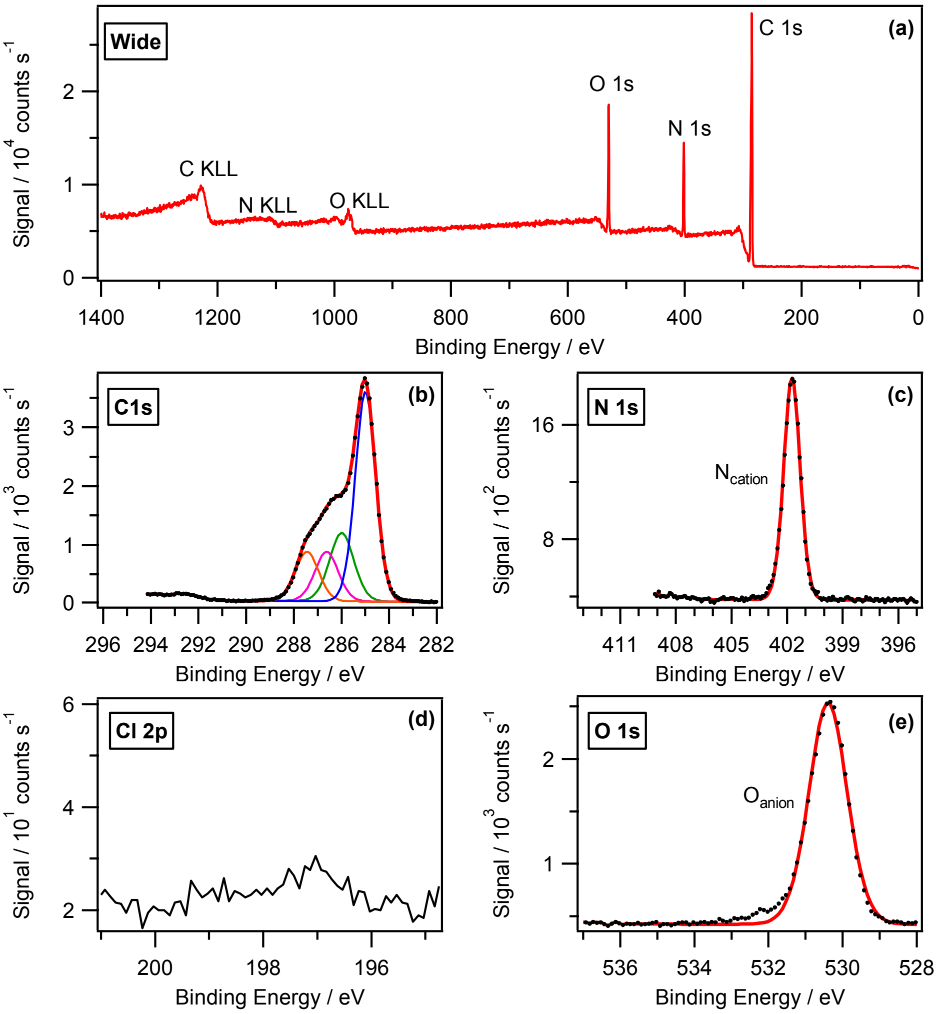

Figure S3.10 XP spectra with component fittings of [C_8C_1Im][OAc] for: (a) survey, (b) C 1s, (c) N 1s, (d) Cl 2p and (e) O 1s.

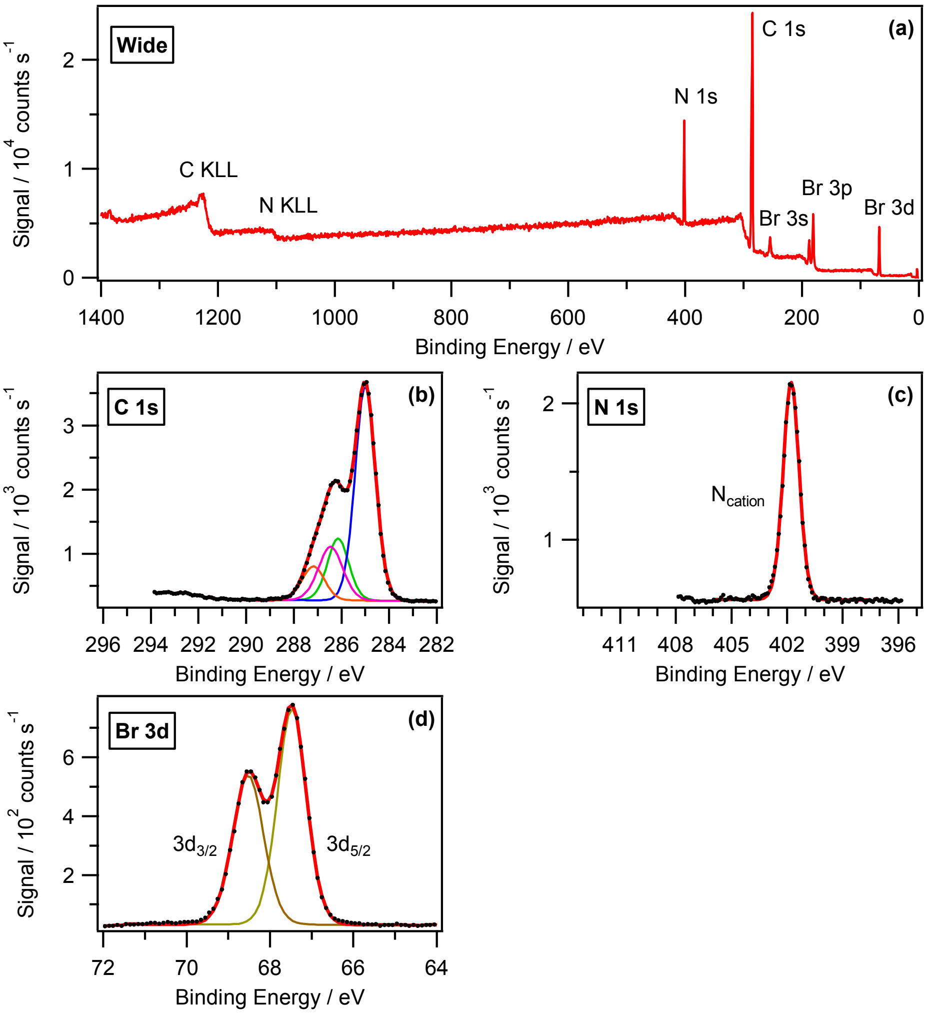

Figure S3.11 XP spectra with component fittings of $[C_8C_1Im]Br$ for: (a) survey, (b) C 1s, (c) N 1s and (d) Br 3d.

S 4 Table of molecular volumes of Amino Acid Ionic Liquids (AAILs), $[C_8C_1Im][AA]$.

The molecular volume of the amino acid anions were obtained by calculation using the theoretically calculated density of $[C_2C_1Im]^+$-based AAILs reported by Sirjoosingh *et al.*[1] The molecular volumes of $[C_2C_1Im]^+$ and $[C_8C_1Im]^+$ are 0.156 nm^3 and 0.288 nm^3 respectively obtained from the crystal structure data as reported by Priess *et al.*[2] The molecular volume of amino acid anions ($[AA]^-$) are obtained by subtracting the V_{mol} of $[C_2C_1Im]^+$ from $[C_2C_1Im][AA]$. Molecular volumes of $[C_8C_1Im][AA]$ were obtained by the summation of the cation and anion molecular volumes.

$[AA]^-$	gfm / g mol^{-1} $[C_2C_1Im][AA]$	ρ_{calc} $[C_2C_1Im][AA]$ / g cm^{-3}	V_{mol} $[C_2C_1Im][AA]$ / nm^3	V_{mol} $[AA]^-$ / nm^3	V_{mol} $[C_8C_1Im][AA]$ / nm^3
$[Gly]^-$	185.3	1.219	0.252	0.096	0.384
$[Ala]^-$	199.3	1.171	0.283	0.127	0.415
$[Val]^-$	227.3	1.101	0.343	0.187	0.475
$[Ile]^-$	241.4	1.067	0.376	0.220	0.508
$[Met]^-$	259.4	1.173	0.367	0.211	0.499
$[Ser]^-$	215.3	1.243	0.288	0.132	0.420
$[Tyr]^-$	291.4	1.144	0.423	0.267	0.555
$[Asn]^-$	242.3	1.250	0.322	0.166	0.454

1. A. Sirjoosingh, S. Alavi and T. K. Woo, *Journal of Physical Chemistry B*, 2009, **113**, 8103-8113.
2. U. P. R. M. Preiss, J. M. Slattery and I. Krossing, *Industrial & Engineering Chemistry Research*, 2009, **48**, 2290-2296.