Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplementary Information

The impact of cation acidity and alkyl substituent on the cation-anion interactions of 1-alkyl-2,3-dimethylimidazolium ionic liquids

Yanhui Liu[1], Xianze Chen[1], Shuang Men[1*], Peter Licence[2*], Feng Xi[1], Zhen Ren[1] and Weiwei Zhu[1]

1 School of Material Science and Engineering
Shenyang Ligong University
Shenyang, P. R. China
110159

2 School of Chemistry
The University of Nottingham
Nottingham, United Kingdom
NG7 2RD

*To whom correspondence should be addressed:
menshuang@hotmail.com
Tel: +86 18240150162
pete.licence@nottingham.ac.uk

Synthesis of ionic liquids

Synthesis of $[C_4C_1C_1Im]Cl$: 1,2-Dimethylimidazole was placed in a two necked round-bottomed flask fitted with a water condenser topped with a blue silica tube. 1-Chlorobutane (1.2 molar equivalents) was added drop wise into the flask with stirring at 70 °C. The reaction was allowed to proceed for 48-72 hours. The unreacted 1,2-Dimethylimidazole was then removed by washing the mixture with ethyl acetate three times. The desired product, $[C_4C_1C_1Im]Cl$, was firstly dried using a rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a white solid.[1]

^{1}H NMR, δ_H (300 MHz, $CDCl_3$): 0.97 (3H, t, *J* = 7.3 Hz), 1.38 (2H, m), 1.80 (2H, m), 2.82 (3H, s), 4.01 (3H, s), 4.21(2H, t, *J* = 7.4 Hz), 7.56 (1H, d, J = 2.0 Hz), 7.83 (1H, d, J = 2.0 Hz).

Synthesis of $[C_4C_1C_1Im][PF_6]$: $[C_4C_1C_1Im]Cl$ was transferred to a round-bottomed flask and dissolved in deionised water. KPF_6 (1.2 molar equivalents) was dissolved in deionised water firstly and then added drop wise into the flask. The mixture was stirred for 24 h under ice bath. The upper phase was removed and the lower phase was washed with deionised water five times. Finally, the desired $[C_4C_1C_1Im][PF_6]$ was dried firstly under rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a white solid.[1]

^{1}H NMR, δ_H (300 MHz, D_2O), 0.85 (3H, t, *J* = 7.4 Hz), 1.29 (2H, m), 1.79 (2H, q, J = 7.4 Hz), 3.83 (3H, s), 4.09 (2H, t, *J* = 7.4 Hz), 7.28 (1H, s), 7.31 (1H, s).

Synthesis of $[C_8C_1C_1Im]Cl$: A similar procedure to that outlined for $[C_4C_1C_1Im]Cl$ was used to yield $[C_8C_1C_1Im]Cl$ as a pale yellow wax.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 0.76 (3H, t, *J* = 7.4 Hz), 1.12 (10H, m), 1.70 (2H, m), 2.48 (3H, s), 3.66 (3H, s), 4.00 (2H, t, *J* = 7.4 Hz), 7.21 (1H, s), 7.24 (1H, s).

Synthesis of $[C_8C_1C_1Im]Br$: A similar procedure to that outlined for $[C_4C_1C_1Im]Cl$ was used to yield $[C_8C_1C_1Im]Br$ as a white solid.[2, 3]

^{1}H NMR, δ_H (300 MHz, D_2O), 0.74 (3H, t, *J* = 7.4 Hz), 1.13 (10H, m), 1.70 (2H, m), 2.50 (3H, s), 3.67 (3H, s), 4.01 (2H, t, *J* = 7.4 Hz), 7.21 (1H, s), 7.24 (1H, s).

Synthesis of $[C_8C_1C_1Im][PF_6]$: A similar procedure to that outlined for $[C_4C_1C_1Im][PF_6]$ was used to yield $[C_8C_1C_1Im][PF_6]$ as a white wax.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 0.77 (3H, t, *J* = 7.4 Hz), 1.16 (10H, m), 1.78 (2H, m), 2.51 (3H, s), 3.70 (3H, s), 4.12 (2H, t, *J* = 7.4 Hz), 7.23 (1H, s), 7.27 (1H, s).

Synthesis of $[C_8C_1C_1Im][Tf_2N]$: $[C_8C_1C_1Im]Cl$ was transferred to a round bottomed flask and dissolved in 50 ml of deionised water. 1.2 molar equivalents of lithium bis[(trifluoromethane)sulfonyl)]imide was dissolved in deionised water firstly and then added drop wise while stirring the aqueous solution at room temperature. After reacted for 12 h, the upper phase was removed and the lower phase was washed with deionised water three times. Finally, the desired $[C_8C_1C_1Im][Tf_2N]$ was dried firstly under rotary evaporator and then under high vacuum at 60 °C for 12 h to yield a pale yellow liquid.[3, 4]

^{1}H NMR, δ_H (300 MHz, CD_3OD): 0.96 (3H, t, *J* = 6.8 Hz), 1.21 (10H, m), 1.86 (2H, m), 2.89

(3H, s), 3.85 (3H, s), 4.16 (2H, t, *J* = 7.4 Hz), 7.52 (1H, t, *J* = 1.7 Hz), 7.60 (1H, t, *J* = 1.7 Hz).

Synthesis of [$C_{12}C_1C_1Im$]Cl: A similar procedure to that outlined for [$C_4C_1C_1Im$]Cl was used to yield [$C_{12}C_1C_1Im$]Cl as a white solid.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 0.81 (3H, t, *J* = 6.1 Hz), 1.19 (18H, m), 1.75 (2H, t, J = 6.9 Hz), 2.77 (3H, s), 4.01 (3H, s), 4.17 (2H, t, *J* = 7.4 Hz), 7.49 (1H, d, J = 1.9 Hz), 7.86 (1H, d, J = 1.9 Hz).

Synthesis of [$C_{12}C_1C_1Im$][PF_6]: A similar procedure to that outlined for [$C_4C_1C_1Im$][PF_6] was used to yield [$C_{12}C_1C_1Im$][PF_6] as a white solid.

^{1}H NMR, δ_H (300 MHz, $CDCl_3$), 0.85 (3H, t, *J* = 7.4 Hz), 1.17 (18H, m), 1.77 (2H, m), 2.81 (3H, s), 4.07 (3H, s), 4.22 (2H, t, *J* = 7.4 Hz), 7.53 (1H, s), 7.87 (1H, s).

Survey XP spectrum

Ionic liquids prepared in this study were characterised by XPS. Survey XP spectra indicate that no silicon or oxygen impurities were detected, as has been observed previously for ionic liquids using XPS.[5, 6] In addition, no additional hydrocarbon signal was observed, indicating that the samples were of high purity, as shown in Figure S1(a) the survey spectrum for a representative example in this paper, [$C_4C_1C_1Im$]Cl. The elements present [$C_4C_1C_1Im$]Cl are chlorine, nitrogen and carbon. Therefore, N 1s, C 1s, Cl 2p are the most probable ionization orbitals. In addition, 2s signal for chlorine is also found in the spectrum. Apart from the photoelectron emissions, KLL carbon and LMM chlorine auger lines are also paralleled observed.

XP spectra

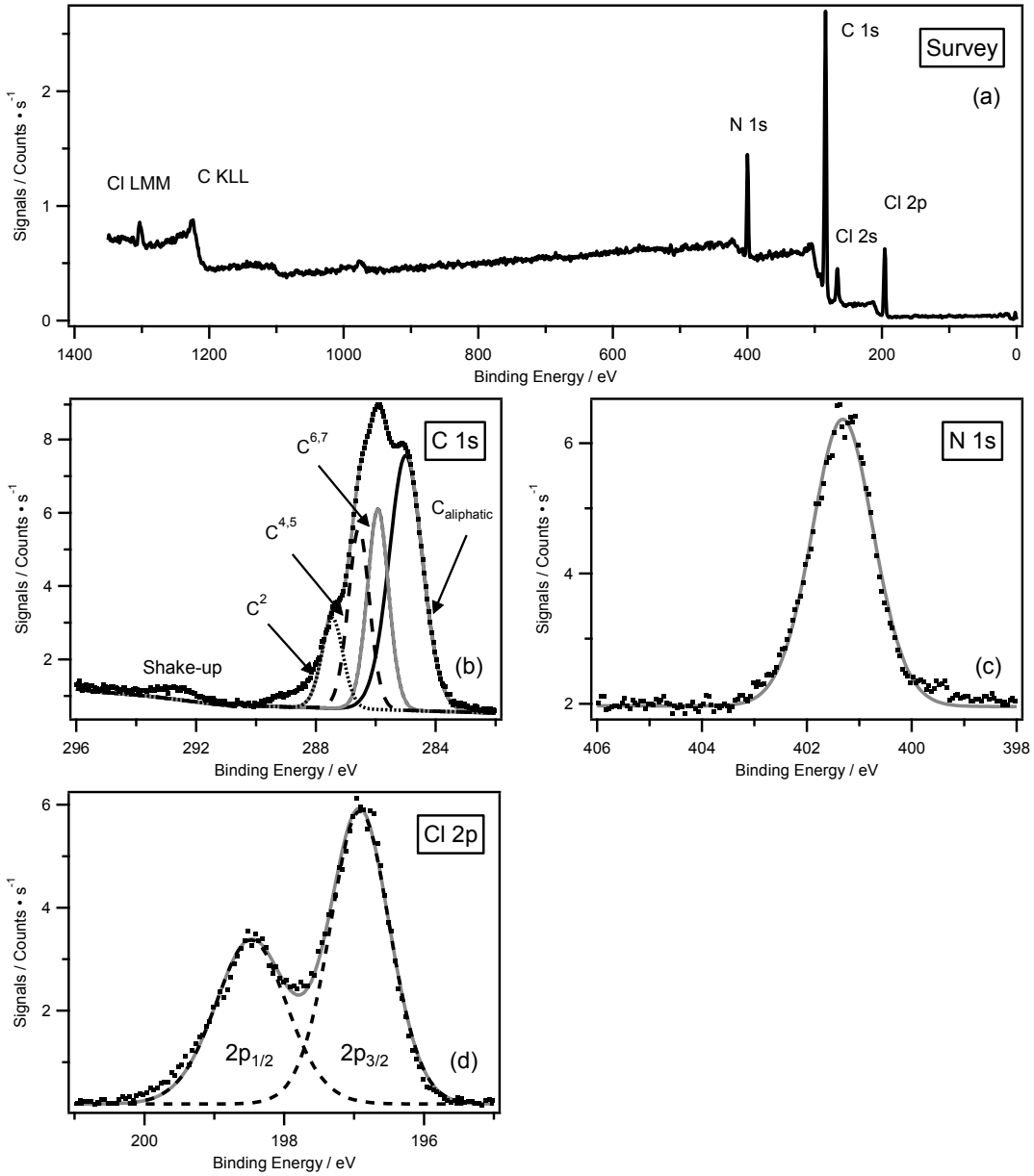

Figure S1 XP spectra for $[C_4C_1C_1Im]Cl$: (a) Survey, (b) C 1s, (c) N 1s and (d) Cl 2p.

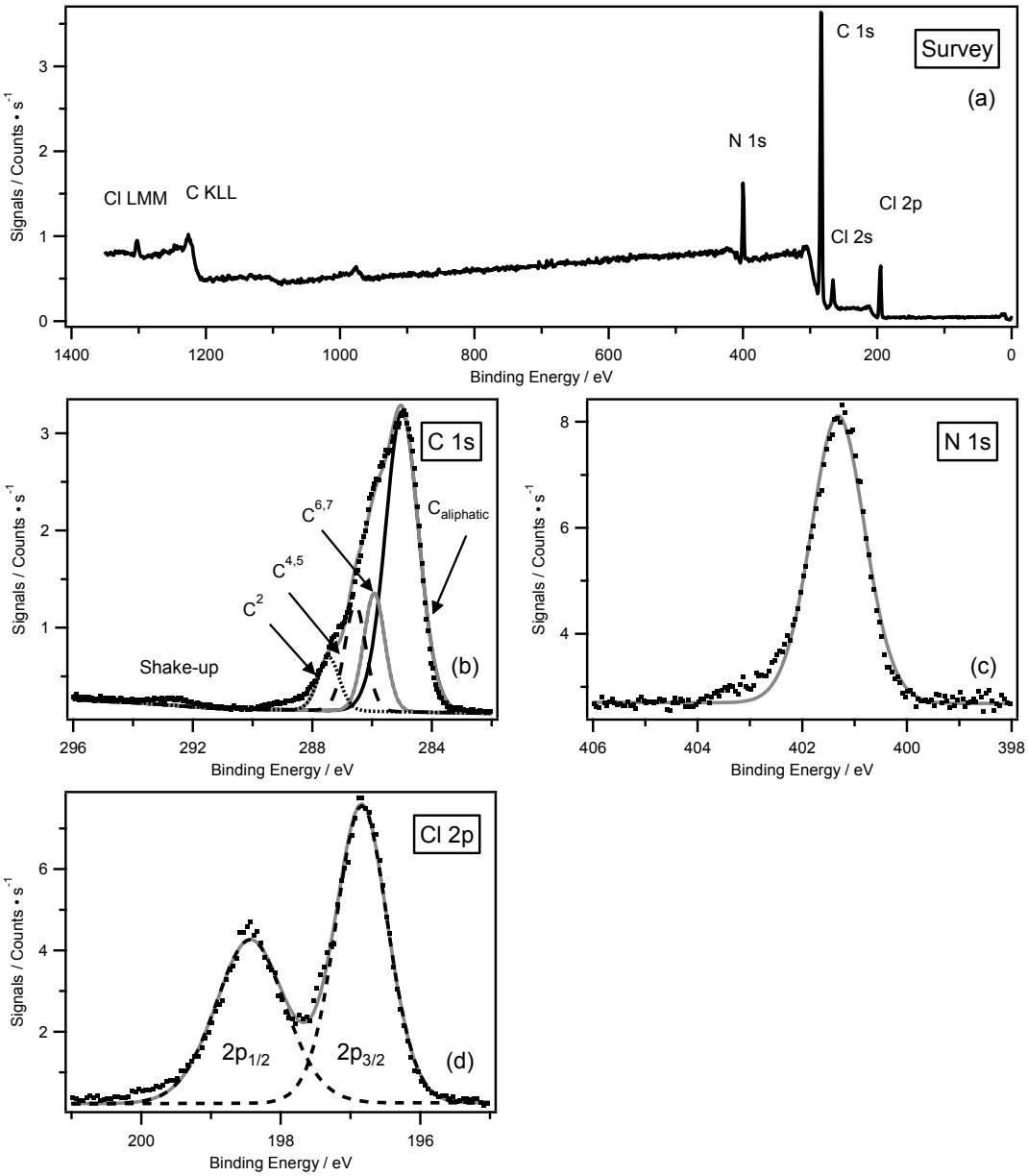

Figure S2 XP spectra for $[C_8C_1C_1Im]Cl$: (a) Survey, (b) C 1s, (c) N 1s and (d) Cl 2p.

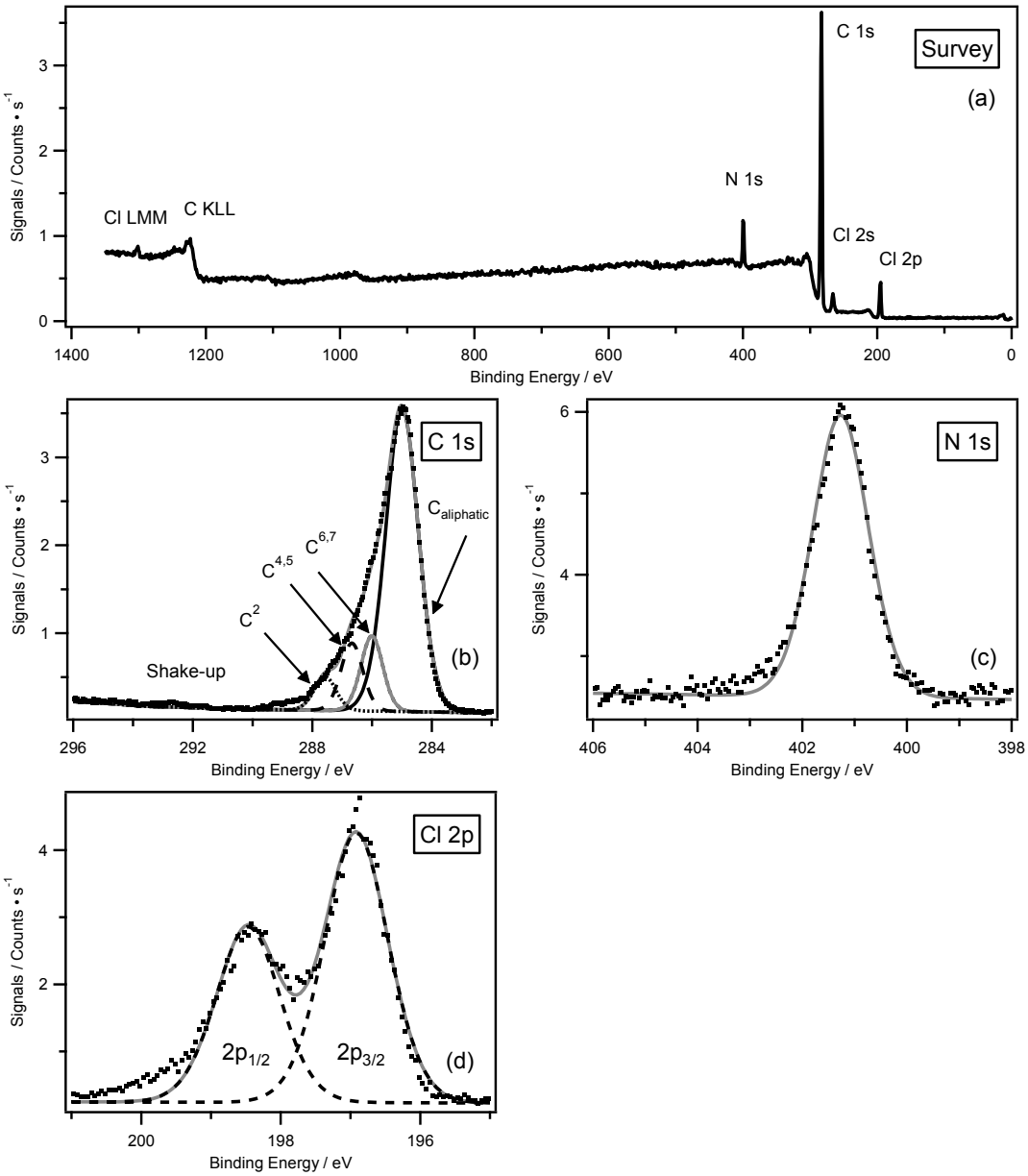

Figure S3 XP spectra for $[C_{12}C_1C_1Im]Cl$: (a) Survey, (b) C 1s, (c) N 1s and (d) Cl 2p.

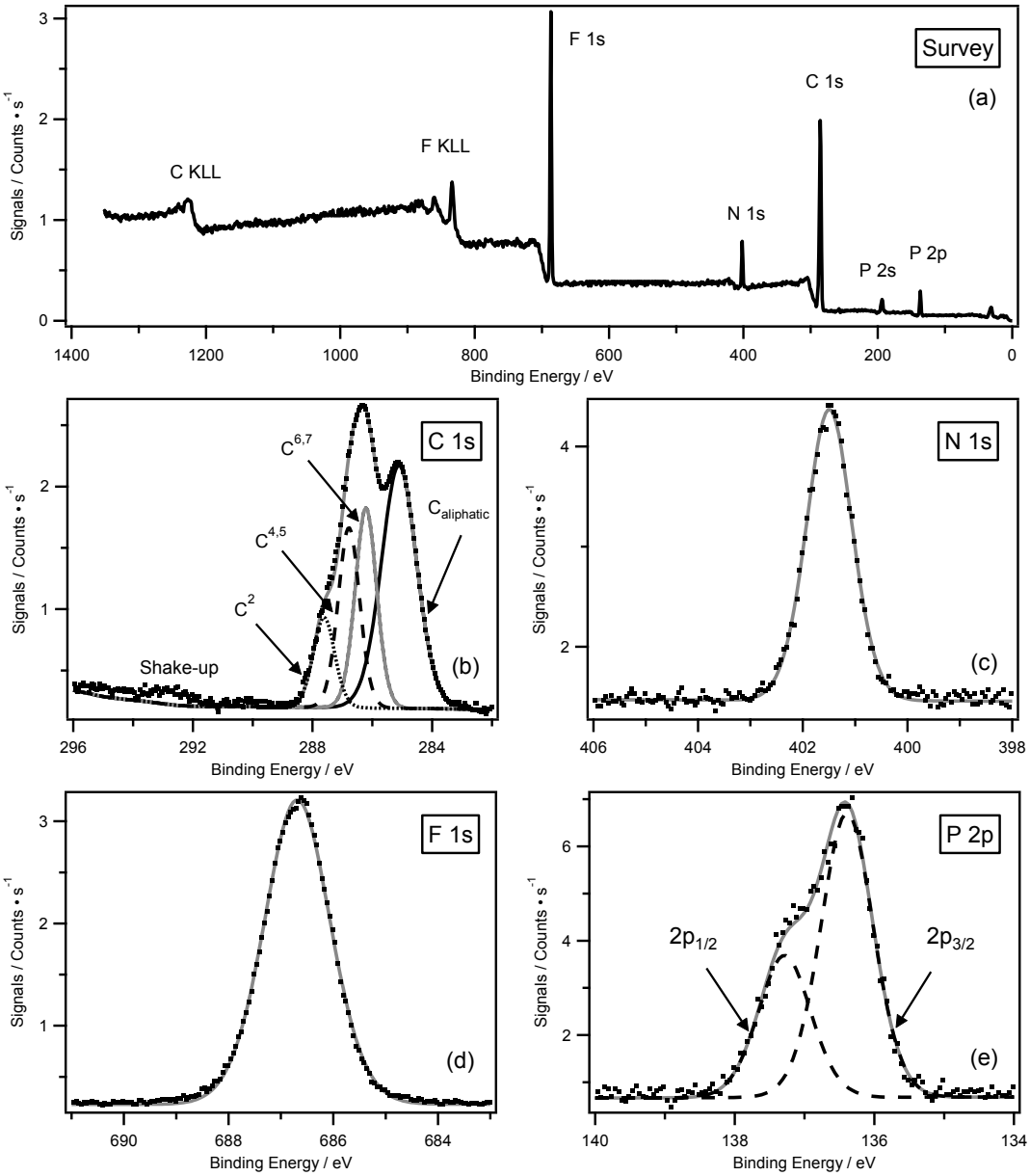

Figure S4 XP spectra for $[C_4C_1C_1Im][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) P 2p.

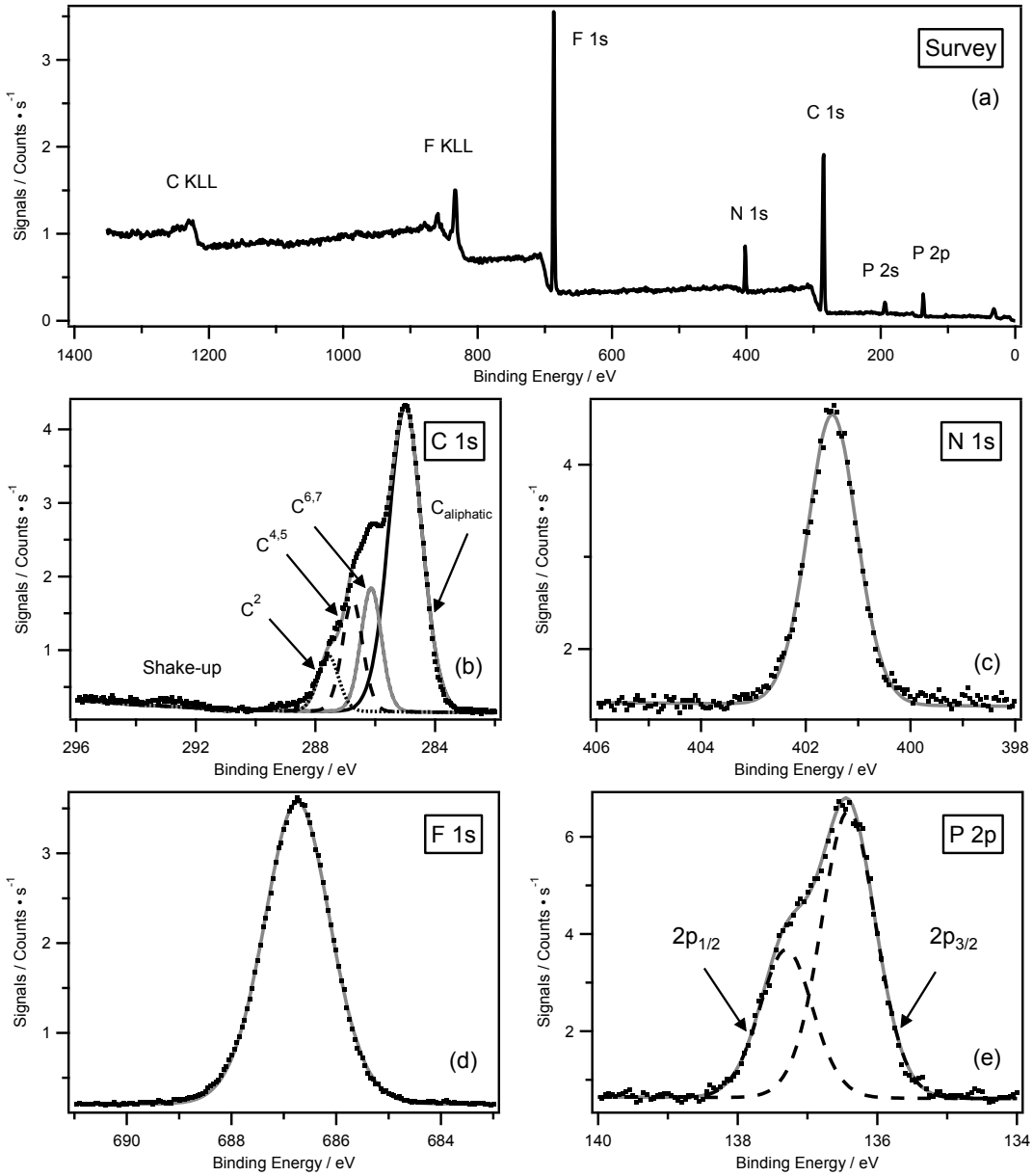

Figure S5 XP spectra for $[C_8C_1C_1Im][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) P 2p.

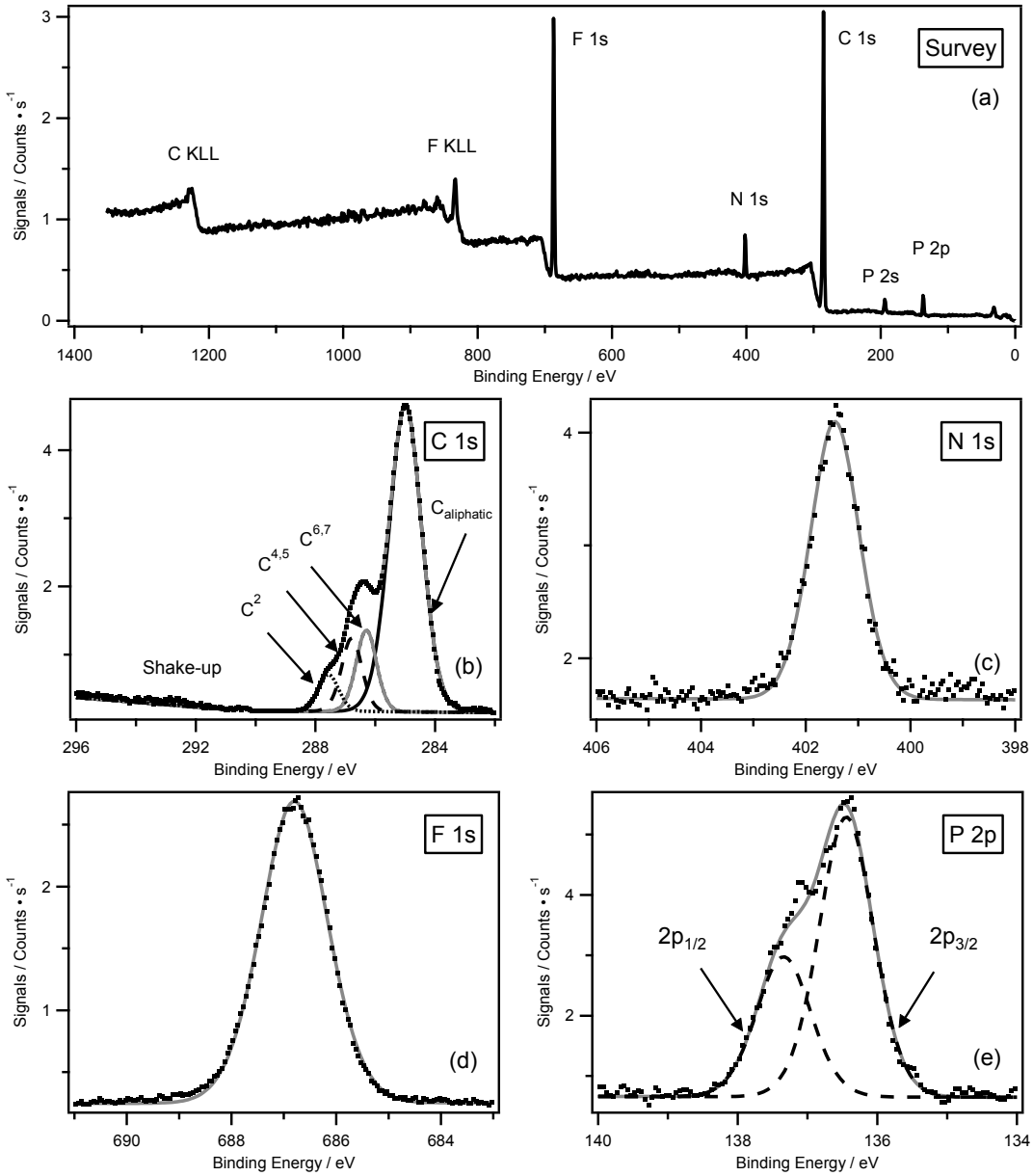

Figure S6 XP spectra for $[C_{12}C_1C_1Im][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) P 2p.

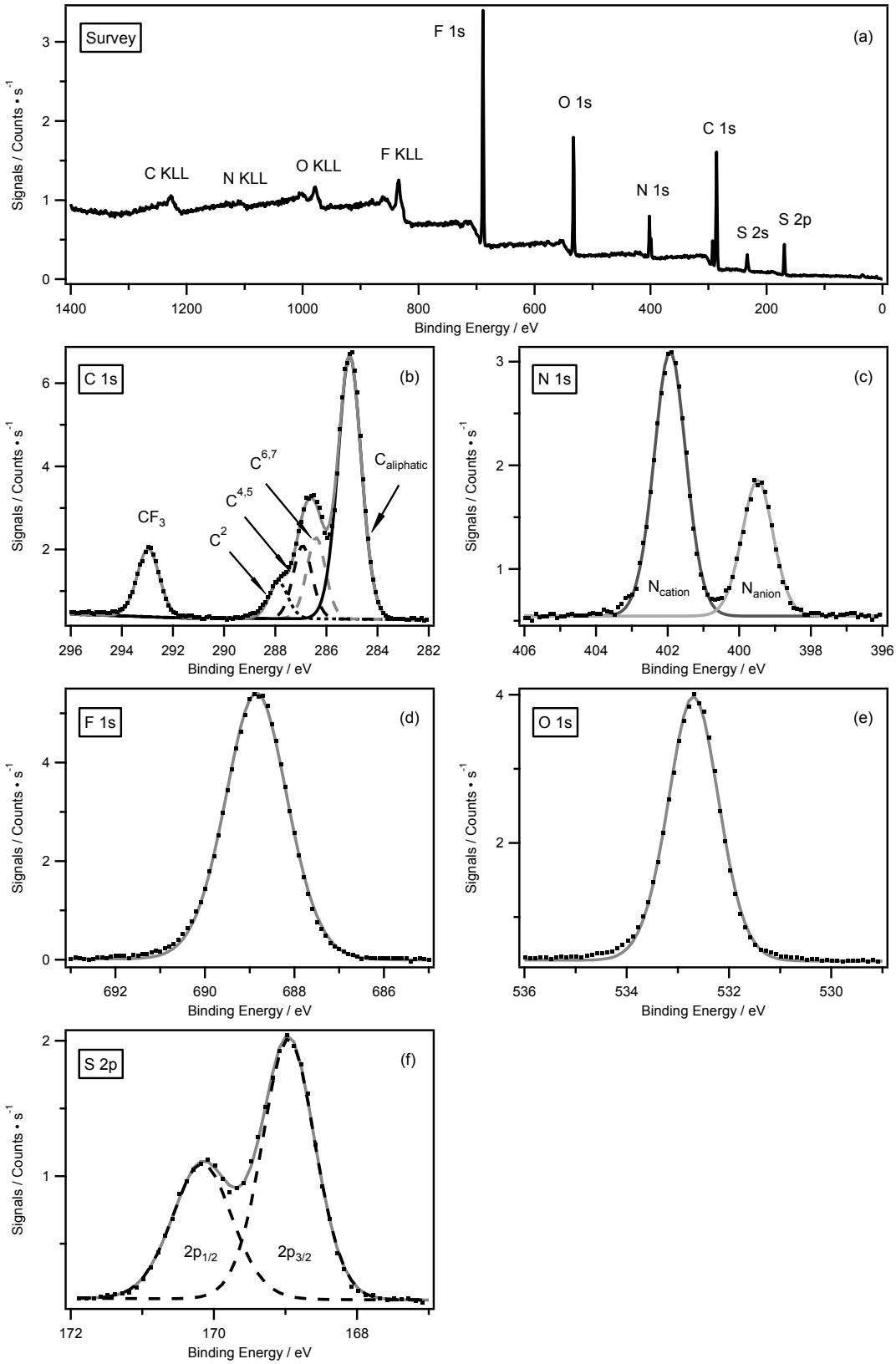

Figure S8 XP spectra for $[C_8C_1C_1Im][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

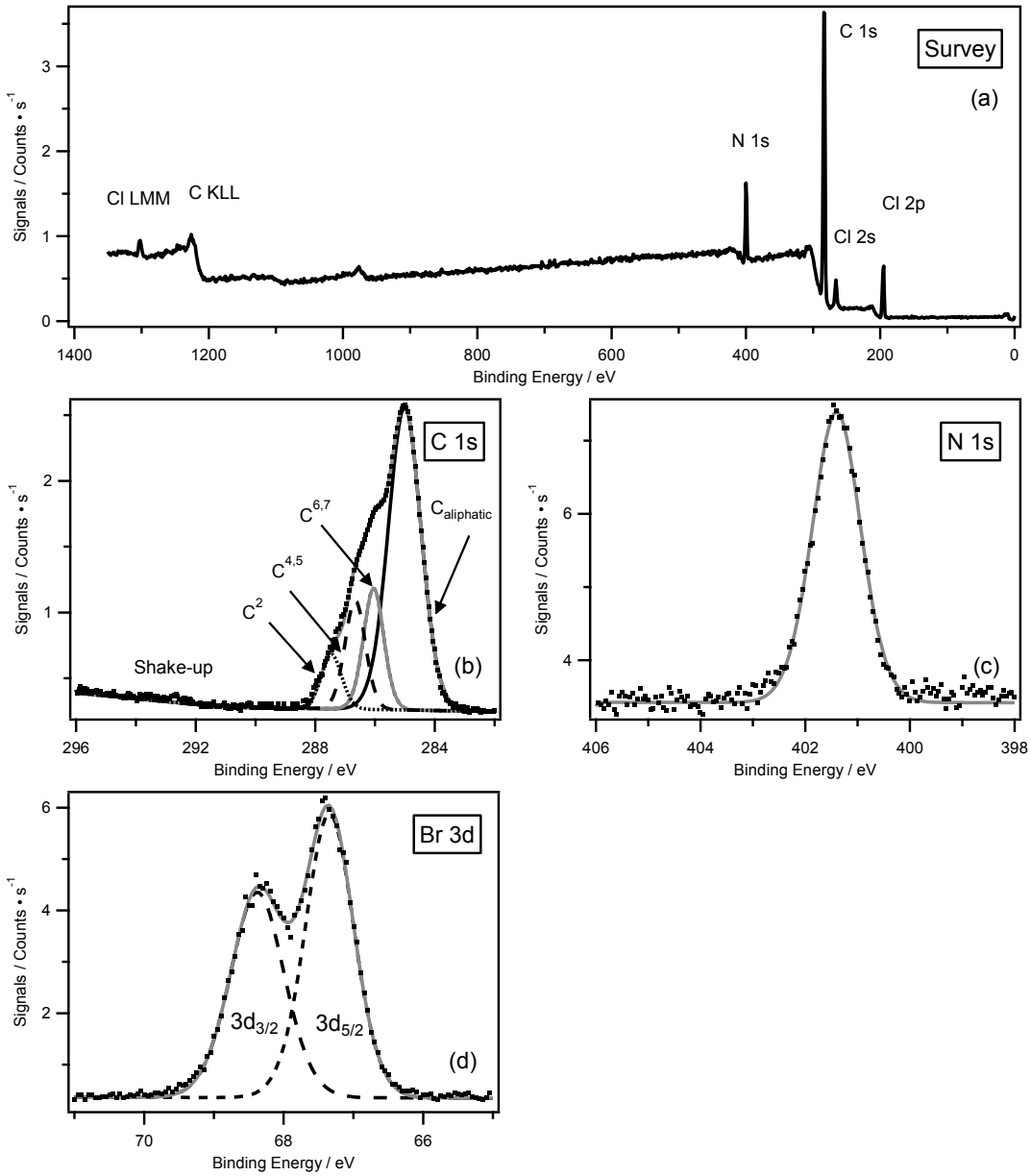

Figure S8 XP spectra for $[C_8C_1C_1Im]Br$: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

References

1. J. G. Huddleston, A. E. Visser, W. M. Reichert, H. D. Willauer, G. A. Broker and R. D. Rogers, *Green Chem.*, 2001, **3**, 156-164.
2. P. Bonhôte, A. P. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
3. P. Bonhôte, A. P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1998, **37**, 166-166.
4. B. D. Fitchett, T. N. Knepp and J. C. Conboy, *J. Electrochem. Soc.*, 2004, **151**, E219-E225.
5. J. M. Gottfried, F. Maier, J. Rossa, D. Gerhard, P. S. Schulz, P. Wasserscheid and H. P. Steinrück, *Z. Phys. Chemie-Int. J. Res. Phys. Chem. Chem. Phys.*, 2006, **220**,

1439-1453.

6. H. Hashimoto, A. Ohno, K. Nakajima, M. Suzuki, H. Tsuji and K. Kimura, *Surf. Sci.*, 2010, **604**, 464-469.