# Electronic Supplementary Information

## X-ray photoelectron spectroscopy of piperidinium ionic liquids: A comparison to the charge delocalised pyridinium analogues

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**Synthesis of ionic liquids**

**[$C_2C_1$Pip]Br**

1-Methylpiperidine was placed in a three necked round-bottomed flask fitted with an air condenser topped with a blue silica tube to avoid introducing of moisture. 1.2 Equivalent of 1-bromoethane was added into the system drop wise with stirring at room temperature. The reaction was allowed to proceed for 48-72 hours. The mixture was then washed with ethyl acetate three times to remove unreacted 1-methylpiperidine. The desired product, [$C_2C_1$Pip]Br, was firstly dried using a rotary evaporator and then under high vacuum at 60 $^oC$ for 12 h to yield a white solid.[1]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 1.20 (m, 3H), 1.52 (m, 2H), 1.75 (m, 4H), 3.02 (s, 3H), 3.35 (m, 4H), 3.46 (m, 2H).

**[$C_4C_1$Pip]Br**

A similar procedure to that outlined for [$C_2C_1$Pip]Br excpet that the reaction temperature was set to 70 $^oC$, was used to yield [$C_4C_1$Pip]Br as a white solid.[1]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.92 (t, $J$ = 7.3 Hz, 3H), 1.29 (m, 2H), 1.53 (m, 2H), 1.63 (m, 2H), 1.77 (m, 4H), 3.02 (s, 3H), 3.34 (m, 6H).

**[$C_8C_1$Pip]Br**

A similar procedure to that outlined for [$C_4C_1$Pip]Br was used to yield [$C_8C_1$Pip]Br as a white solid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.87 (t, $J$ = 7.3 Hz, 3H), 1.29 (m, 10H), 1.53 (m, 2H), 1.64 (m, 2H), 1.77 (m, 4H), 2.97 (s, 3H), 3.29 (m, 6H).

**[$C_{12}C_1$Pip]Br**

A similar procedure to that outlined for [$C_4C_1$Pip]Br was used to yield [$C_{12}C_1$Pip]Br as a white solid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.85 (m, 3H), 1.23 (m, 18H), 1.54 (m, 2H), 1.64 (m, 2H), 1.80 (m, 4H), 3.00 (s, 3H), 3.33 (m, 6H).

**[$C_2C_1$Pip][$Tf_2N$]**

[$C_2C_1$Pip]Br was dissolved in deionised water and then transferred to a three necked round-bottomed flask fitted with a water condenser topped with a blue silica tube. 1.2 Equivalent of lithium bis(trifluoromethanesulfonyl)imide was dissolved in deionised water firstly and then added drop wise into the system. The reaction mixture was then stirred at room temperature for 12 h. After separated completely, the lower phase was collected and washed with deionised water by at least five times. To aid fully separation, dichloromethane was added into the system. The desired [$C_2C_1$Pip][$Tf_2N$] was then dried firstly under rotary evaporator and then under high vacuum at 60 $^oC$ for 12 h to yield a white solid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 1.22 (m, 3H), 1.53 (m, 2H), 1.76 (m, 4H), 2.94 (s, 3H), 3.36 (m, 6H).

**[$C_4C_1$Pip][$Tf_2N$]**

A similar procedure to that outlined for [$C_2C_1$Pip][$Tf_2N$] was used to yield [$C_4C_1$Pip][$Tf_2N$] as a colourless liquid.[3]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.93 (t, $J$ = 7.3 Hz, 3H), 1.33 (m, 2H), 1.55 (m, 2H), 1.64 (m, 2H), 1.78 (m, 4H), 2.97 (s, 3H), 3.28 (m, 6H).

### [$C_8C_1$Pip][$Tf_2N$]

A similar procedure to that outlined for [$C_2C_1$Pip][$Tf_2N$] was used to yield [$C_8C_1$Pip][$Tf_2N$] as a colourless liquid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.87 (t, $J$ = 7.3 Hz, 3H), 1.29 (m, 10H), 1.54 (m, 2H), 1.65 (m, 2H), 1.77 (m, 4H), 2.98 (s, 3H), 3.29 (m, 6H).

### [$C_{12}C_1$Pip][$Tf_2N$]

A similar procedure to that outlined for [$C_2C_1$Pip][$Tf_2N$] was used to yield [$C_{12}C_1$Pip][$Tf_2N$] as a colourless liquid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.84 (m, 3H), 1.24 (m, 18H), 1.53 (m, 2H), 1.64 (m, 2H), 1.77 (m, 4H), 2.96 (s, 3H), 3.27 (m, 6H).

### [$C_8C_1$Pip][$PF_6$]

[$C_8C_1$Pip]Br was dissolved in deionised water firstly and then placed into a three-neck round bottomed flask. Potassium hexafluorophosphate (1.2 molar equivalents) was dissolved in deionised water and then added into the reaction system by dropping wise. The reaction was conducted under iced bath for 24 h with stirring. Dichloromethane was added into the mixture to aid the collection of the lower phase. After separation, the lower phase was washed with deionised water by at least five times (the solubility of potassium hexafluorophosphate in water is low). The desired [$C_8C_1$Pip][$PF_6$] was firstly dried under rotary evaporator and then under high vacuum at 60 $^oC$ for 12 h to yield a yellow solid.[2]

$^1$H NMR $\delta_H$ (400Hz, DMSO-$d_6$) 0.87 (t, $J$ = 7.3 Hz, 3H), 1.30 (m, 10H), 1.53 (m, 2H), 1.64 (m, 2H), 1.77 (m, 4H), 2.97 (s, 3H), 3.28 (m, 6H).

### Development of C 1s fitting model

Initially, C 1s spectra of 1-alkyl-1-methylpiperidinium ionic liquids were fitted with an established model according to the one developed for 1-alkyl-1-methylpyrrolidinium ionic liquids reported in literature.[4] Figure S1 shows the fitting of C 1s spectrum for [$C_8C_1$Pip][$Tf_2N$], wherein three components are used: $C_{hetero}$ represents carbon atoms bonded directly to the positive charged nitrogen centre; $C_{inter}$ represents carbon atoms which are β to the cationic nitrogen; $C_{aliphatic}$ represents the remaining carbon atoms locating further enough from the cationic nitrogen and bonded to carbon and hydrogen atoms only. This model allows a satisfactory fitting of the C 1s region for [$C_8C_1$Pip][$Tf_2N$].

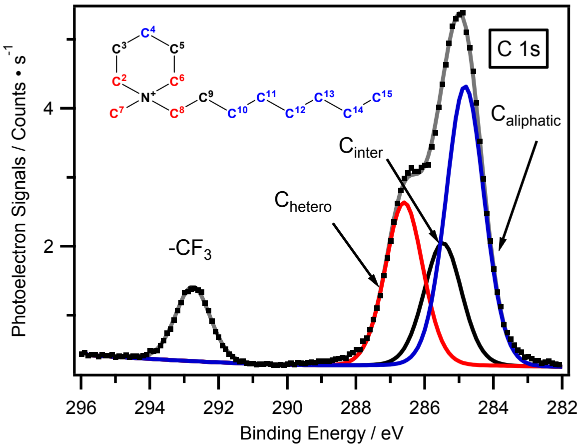

**Figure S1** C 1s XP spectrum with fittings for [$C_8C_1$Pip][$Tf_2N$]. A three-component model is used for the fitting: $C_{hetero}$ 1s ($C^2$, $C^6$, $C^7$ and $C^8$), $C_{inter}$ ($C^3$, $C^5$ and $C^9$) and $C_{aliphatic}$ 1s ($C^4$ and $C^{10}$ onwards).

However, when switching the anion from the less basic one to a moderate basic and even a more basic one, since the cation-anion interactions become more and more intense, the binding energy difference between $C_{inter}$ 1s and $C_{aliphatic}$ 1s is found smaller and smaller. Consequently, the above model is applicable for neither [$C_8C_1$Pip][$PF_6$] nor [$C_8C_1$Pip]Br. As shown in Figure S2, by using the three-component model, it is found that the binding energies for $C_{inter}$ 1s and $C_{aliphatic}$ 1s are electronic identical.

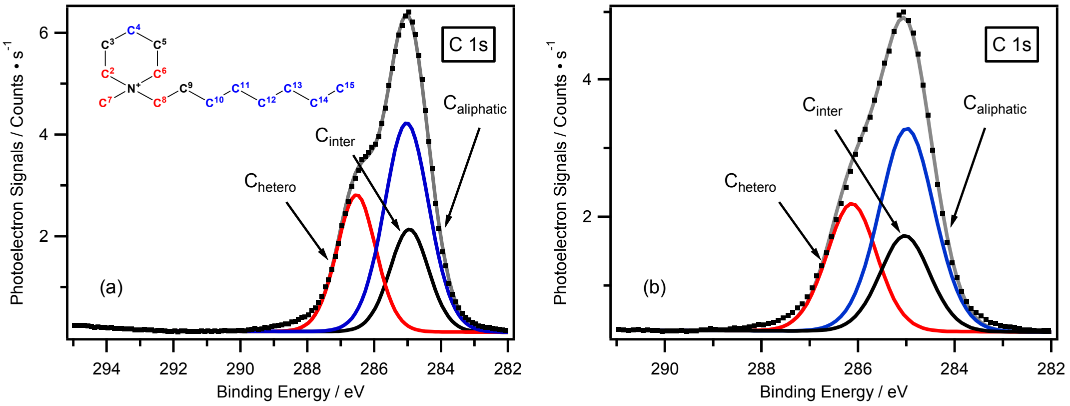

**Figure S2** C 1s XP spectra with fittings for (a) [$C_8C_1$Pip][$PF_6$] and (b) [$C_8C_1$Pip]Br. A three-component model is used for the fitting: $C_{hetero}$ 1s ($C^2$, $C^6$, $C^7$ and $C^8$), $C_{inter}$ ($C^3$, $C^5$ and $C^9$) and $C_{aliphatic}$ 1s ($C^4$ and $C^{10}$ onwards).

It concludes that the three-component model is not always reliable for the C 1s spectra fitting of 1-alkyl-1-methylpiperidinium ionic liquids. Consequently, it is decided that the two-component model which is demonstrated in Figure 1 in the manuscript should be used for the purpose of C 1s spectra fitting.

## XP spectra

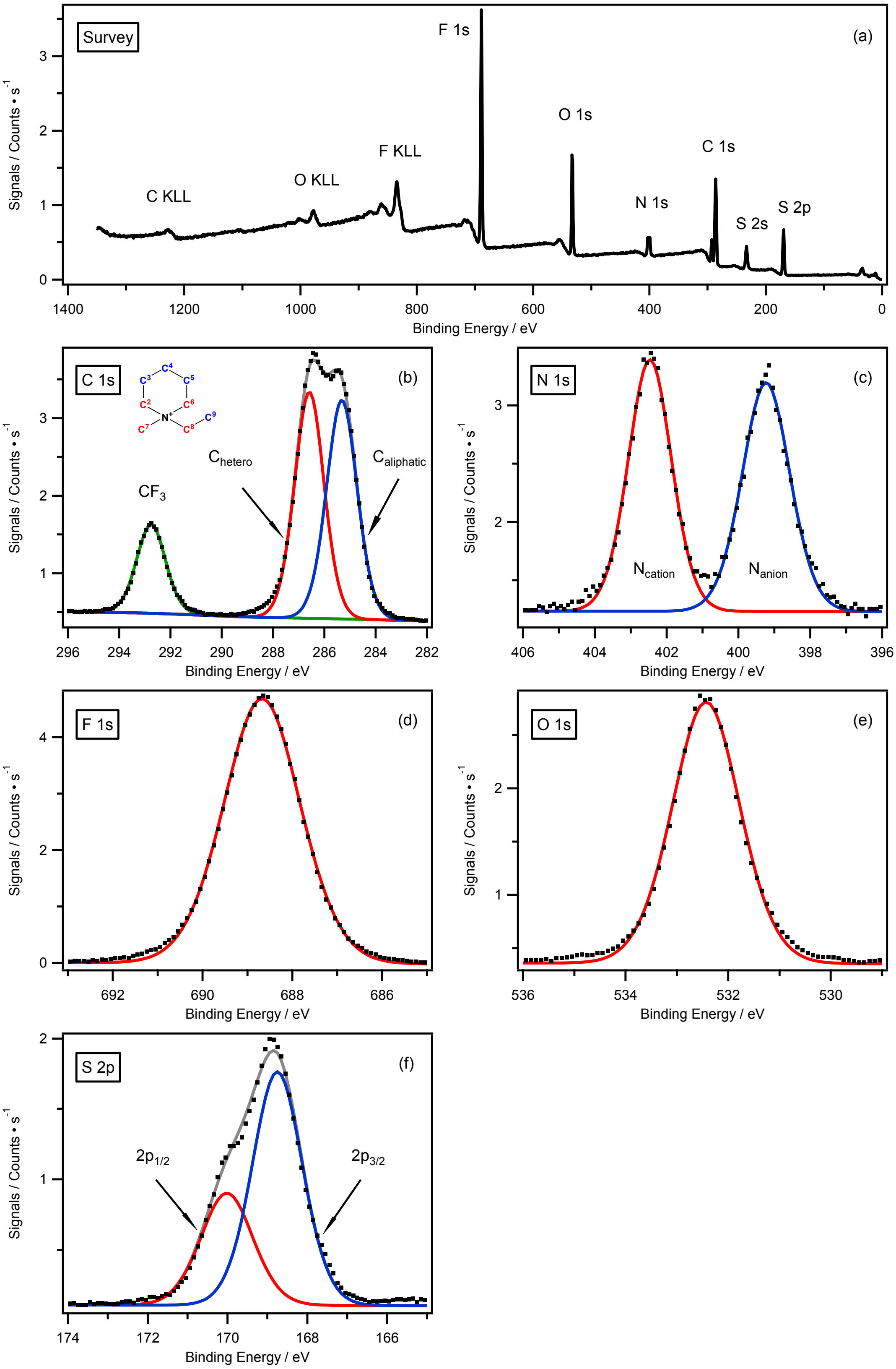

**Figure S3** XP spectra of all elements for [$C_2C_1$Pip][$Tf_2$N]: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

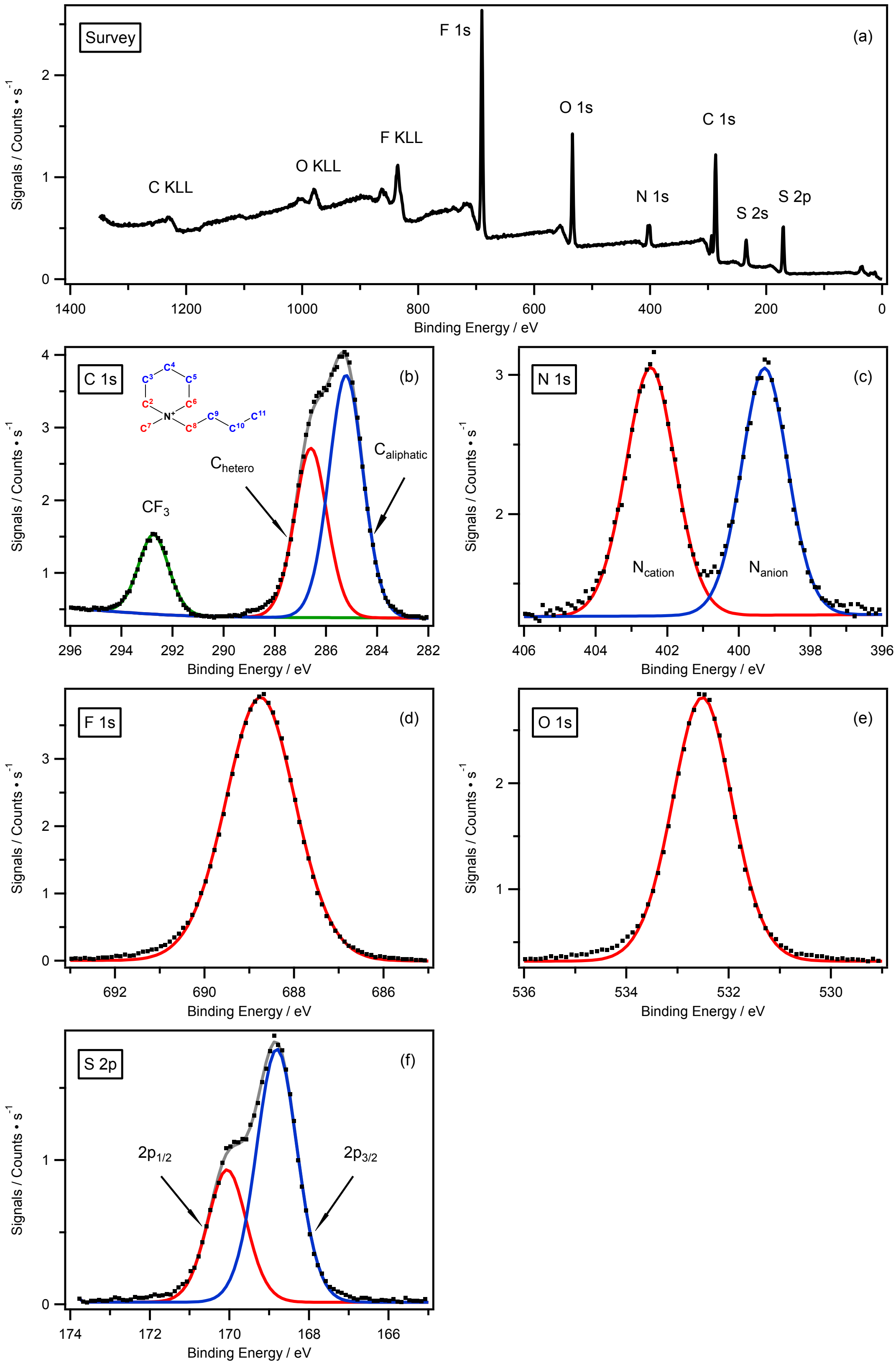

**Figure S4** XP spectra of all elements for $[C_4C_1Pip][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

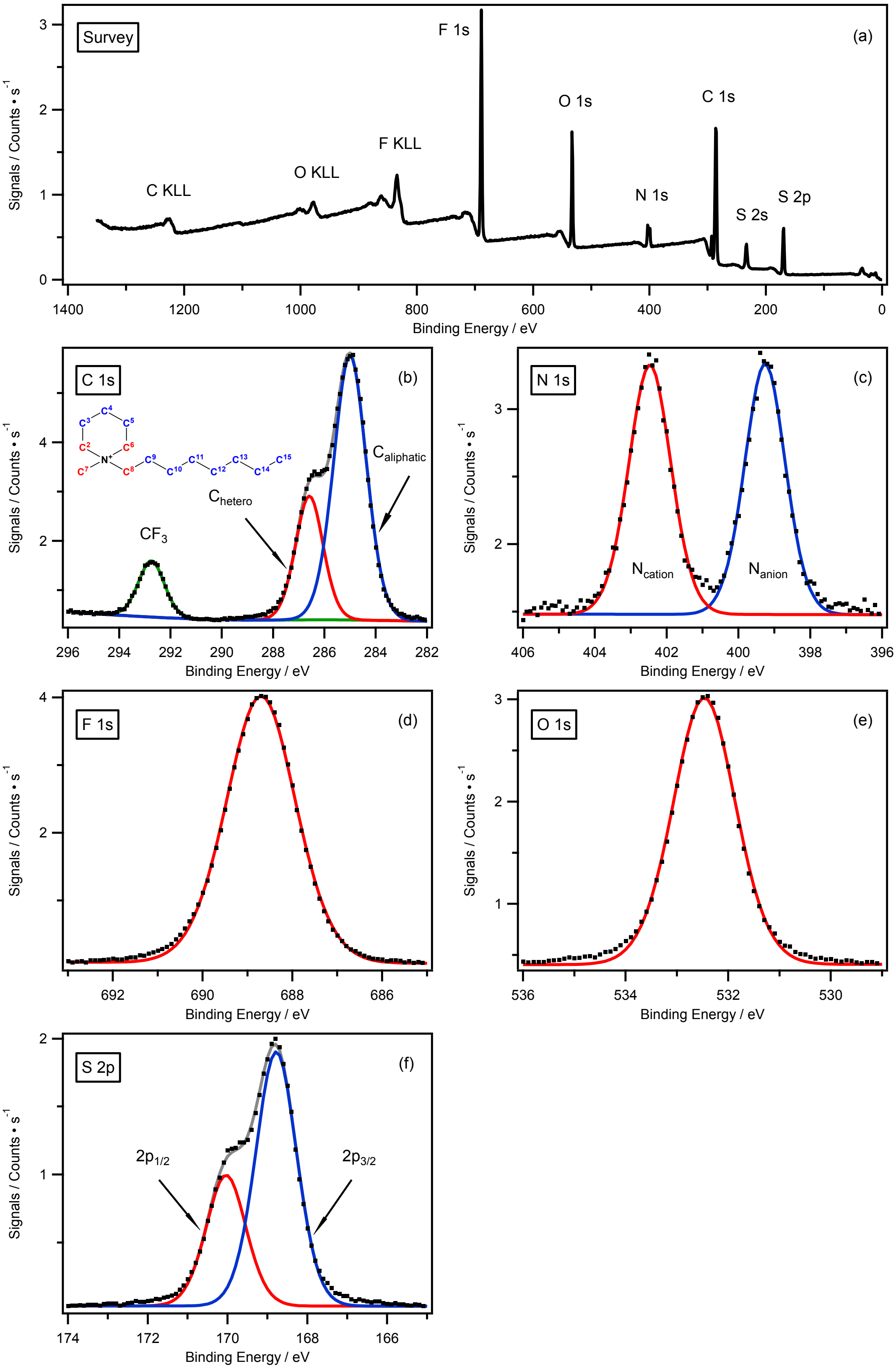

**Figure S5** XP spectra of all elements for [$C_8C_1$Pip][$Tf_2$N]: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

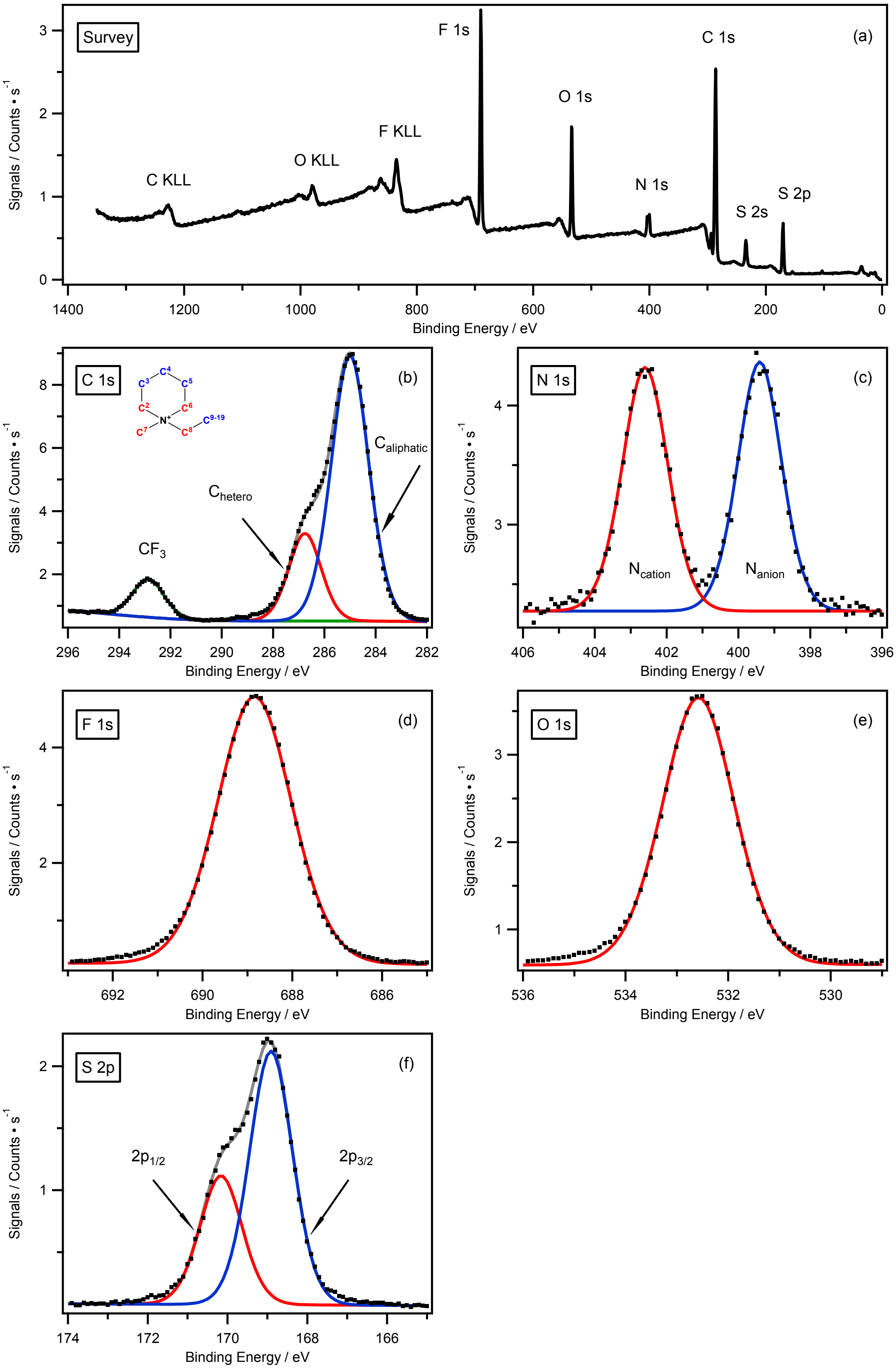

**Figure S6** XP spectra of all elements for $[C_{12}C_1Pip][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

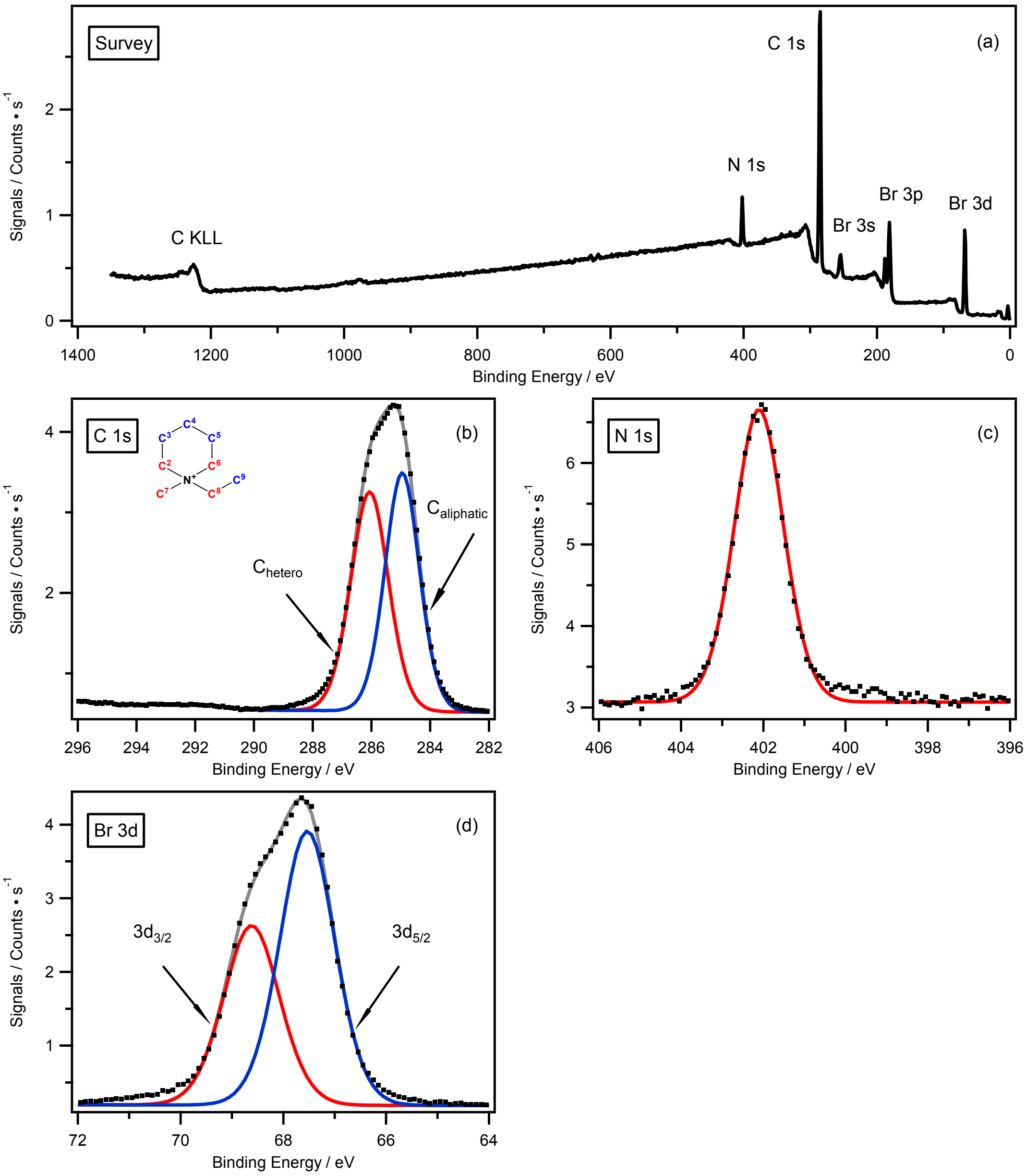

**Figure S7** XP spectra of all elements for [C$_2$C$_1$Pip]Br: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

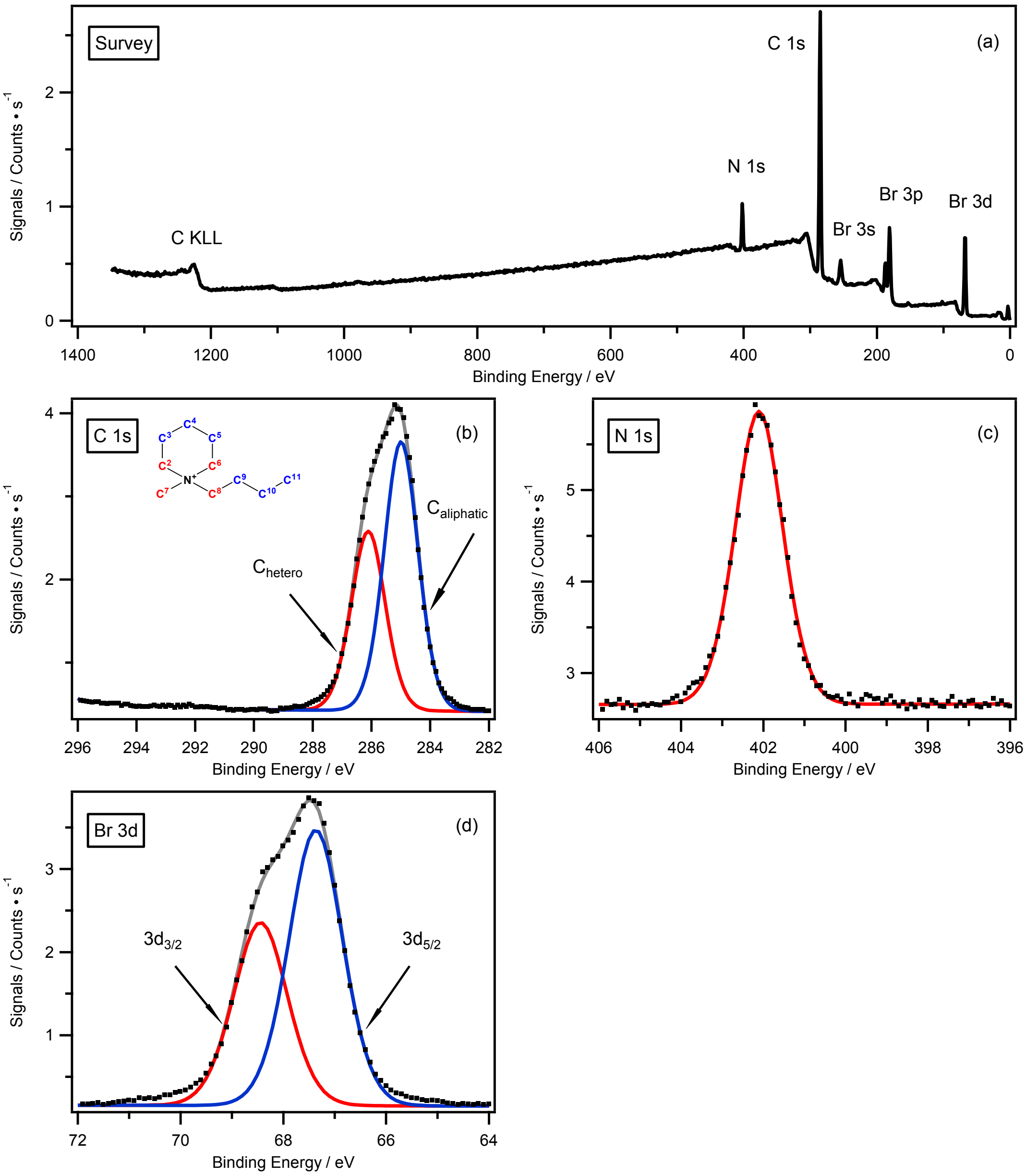

**Figure S8** XP spectra of all elements for [$C_4C_1$Pip]Br: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

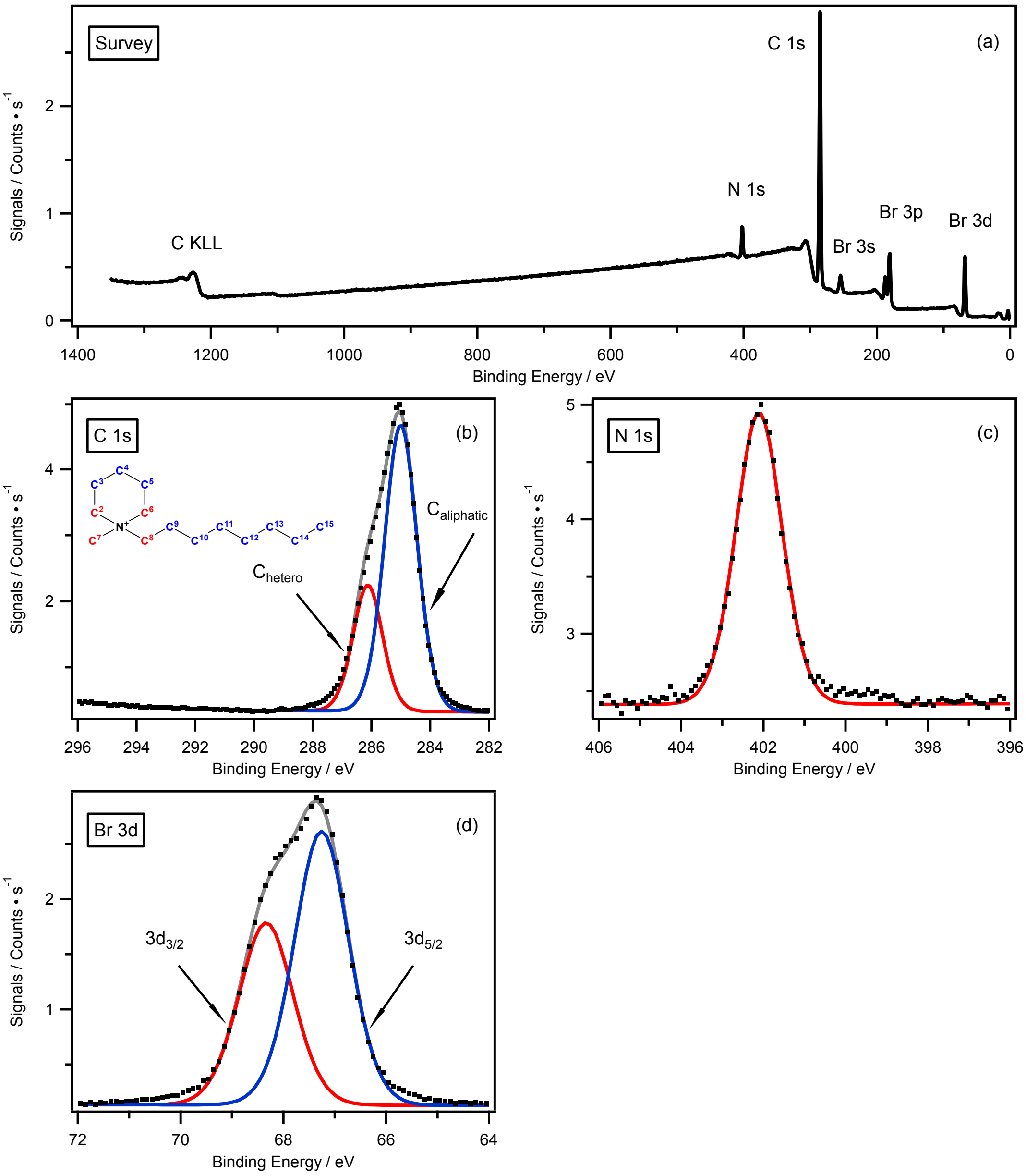

**Figure S9** XP spectra of all elements for [C$_8$C$_1$Pip]Br: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

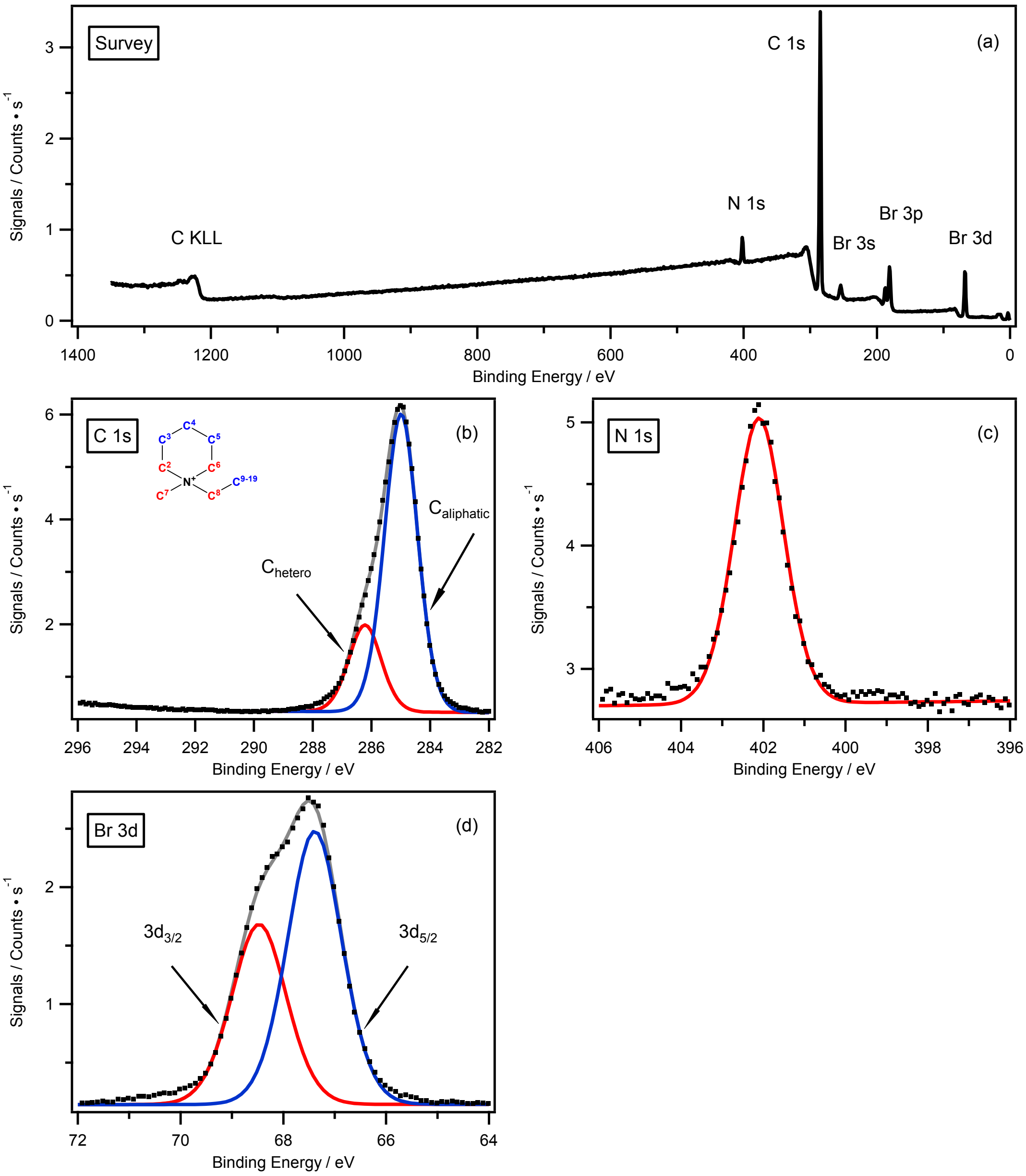

**Figure S10** XP spectra of all elements for $[C_{12}C_1Pip]Br$: (a) Survey, (b) C 1s, (c) N 1s and (d) Br 3d.

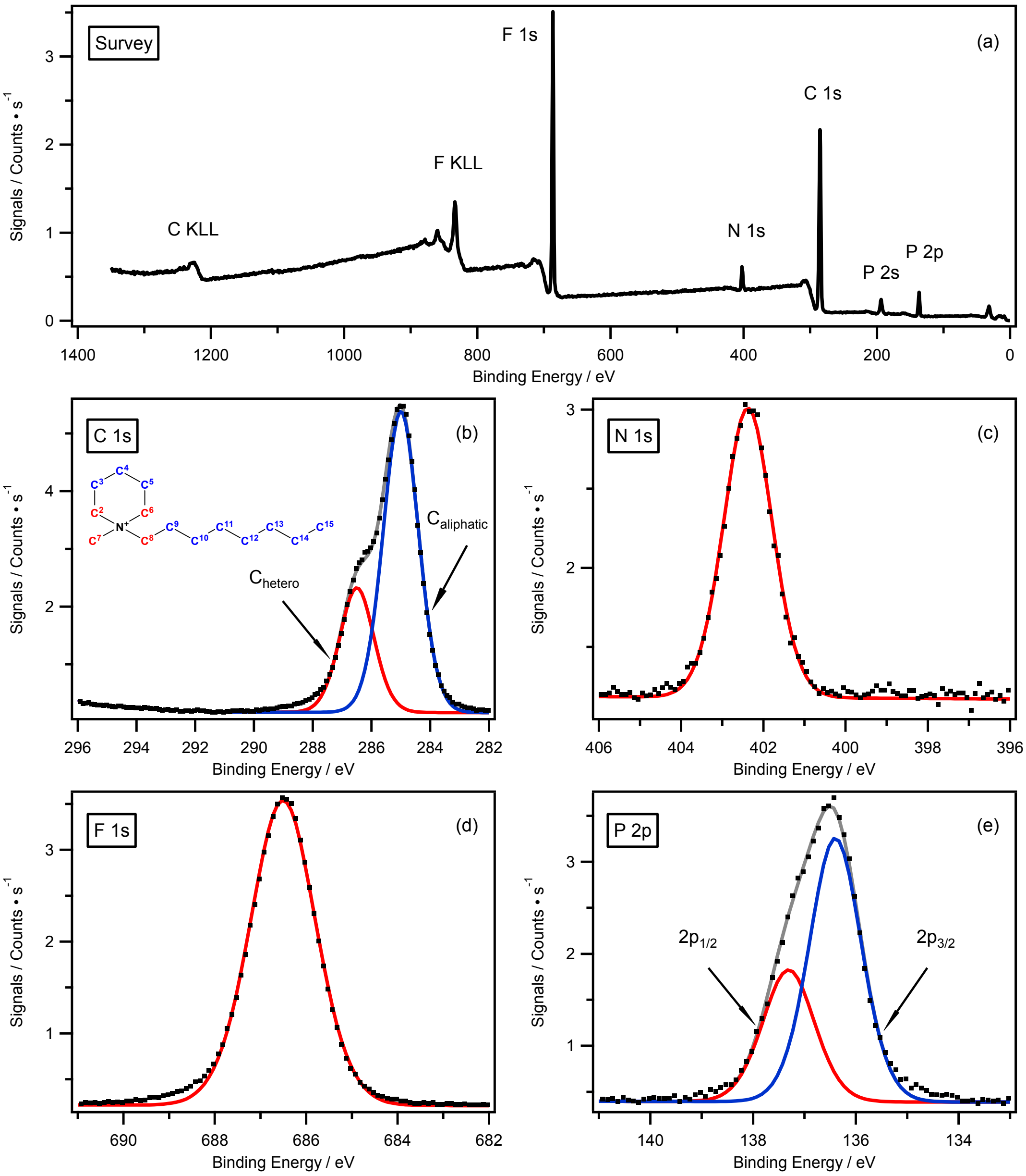

**Figure S11** XP spectra of all elements for $[C_8C_1Pip][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s and (e) P 2p.

## References

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