Electronic Supplementary Information

X-ray photoelectron spectroscopy of morpholinium ionic liquids: Impact of the long alkyl side substituent on the cation-anion interactions

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Synthesis of ionic liquids

[C_2C_1Mor]Br

Into a three-neck round-bottomed flask, 1-methylmorpholine was placed. The system was fitted with an air condenser topped with a blue silica tube aiming to avoid introducing of moisture. 1.2 Equivalent of 1-bromoethane was added into the reaction system by dropping 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-methylmorpholine. The desired product, [C_2C_1Mor]Br, was firstly dried using a rotary evaporator and then under high vacuum at 60 ^{o}C for 12 h to yield a white solid.[1, 2]

^{1}H NMR δ_H (500Hz, DMSO-d_6) 1.25 (t, J = 7.3 Hz, 3H), 3.11 (s, 3H), 3.40 (m, 4H), 3.53 (m, 2H), 3.91 (br.s, 4H).

[C_4C_1Mor]Br

A similar procedure to that outlined for [C_2C_1Mor]Br excpet that the reaction temperature was set to 70 ^{o}C, was used to yield [C_4C_1Mor]Br as a white solid.

^{1}H NMR δ_H (500Hz, DMSO-d_6) 0.94 (t, J = 7.3 Hz, 3H), 1.32 (m, 2H), 1.67 (m, 2H), 3.12 (s, 3H), 3.40 (m, 6H), 3.91 (m, 4H).

[C_8C_1Mor]Br

A similar procedure to that outlined for [C_4C_1Mor]Br was used to yield [C_8C_1Mor]Br as a pale yellow solid.

^{1}H NMR δ_H (500Hz, DMSO-d_6) 0.87 (t, J = 7.3 Hz, 3H), 1.29 (m, 10H), 1.69 (m, 2H), 3.15 (s, 3H), 3.45 (m, 6H), 3.91 (m, 4H).

[$C_{12}C_1$Mor]Br

A similar procedure to that outlined for [C_4C_1Mor]Br was used to yield [$C_{12}C_1$Mor]Br as a white solid.

^{1}H NMR δ_H (500Hz, DMSO-d_6) 0.87 (t, J = 7.3 Hz, 3H), 1.28 (m, 18H), 1.68 (m, 2H), 3.15 (s, 3H), 3.44 (m, 6H), 3.91 (m, 4H).

[C_2C_1Mor][Tf_2N]

[C_2C_1Mor]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_1Mor][Tf_2N] was then dried firstly under rotary evaporator and then under high vacuum at 60 ^{o}C for 12 h to yield a colourless liquid.[1, 3]

^{1}H NMR δ_H (500Hz, $CDCl_3$) 1.35 (t, J = 7.3 Hz, 3H), 3.06 (s, 3H), 3.34 (m, 4H), 3.45 (m, 2H), 3.92 (m, 4H).

[C_4C_1Mor][Tf_2N]

A similar procedure to that outlined for [C_2C_1Mor][Tf_2N] was used to yield [C_4C_1Mor][Tf_2N] as a colourless liquid.

^{1}H NMR δ_H (500Hz, DMSO-d_6) 0.93 (t, J = 7.3 Hz, 3H), 1.30 (m, 2H), 1.64 (m, 2H), 3.09 (s, 3H), 3.38 (m, 6H), 3.89 (br.s, 4H).

[C_8C_1Mor][Tf_2N]

A similar procedure to that outlined for [C_2C_1Mor][Tf_2N] was used to yield [C_8C_1Mor][Tf_2N] as a colourless liquid.

^{1}H NMR δ_H (500Hz, $CDCl_3$) 0.87 (t, J = 7.3 Hz, 3H), 1.31 (m, 10H), 1.72 (m, 2H), 3.15 (s, 3H), 3.34 (m, 2H), 3.41 (m, 4H), 3.96 (m, 4H).

[$C_{12}C_1$Mor][Tf_2N]

A similar procedure to that outlined for [C_2C_1Mor][Tf_2N] was used to yield [$C_{12}C_1$Mor][Tf_2N] as a colourless liquid.

^{1}H NMR δ_H (500Hz, DMSO-d_6) 0.86 (t, J = 7.3 Hz, 3H), 1.25 (m, 18H), 1.68 (m, 2H), 3.11 (s, 3H), 3.39 (m, 6H), 3.91 (m, 4H).

[C_8C_1Mor][PF_6]

[C_8C_1Mor]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_1Mor][PF_6] was firstly dried under rotary evaporator and then under high vacuum at 60 ^{o}C for 12 h to yield a yellow solid.[1, 4]

^{1}H NMR δ_H (600Hz, DMSO-d_6) 0.87 (t, J = 7.3 Hz, 3H), 1.30 (m, 10H), 1.67 (m, 2H), 3.10 (s, 3H), 3.38 (m, 6H), 3.90 (m, 4H).

XP spectra

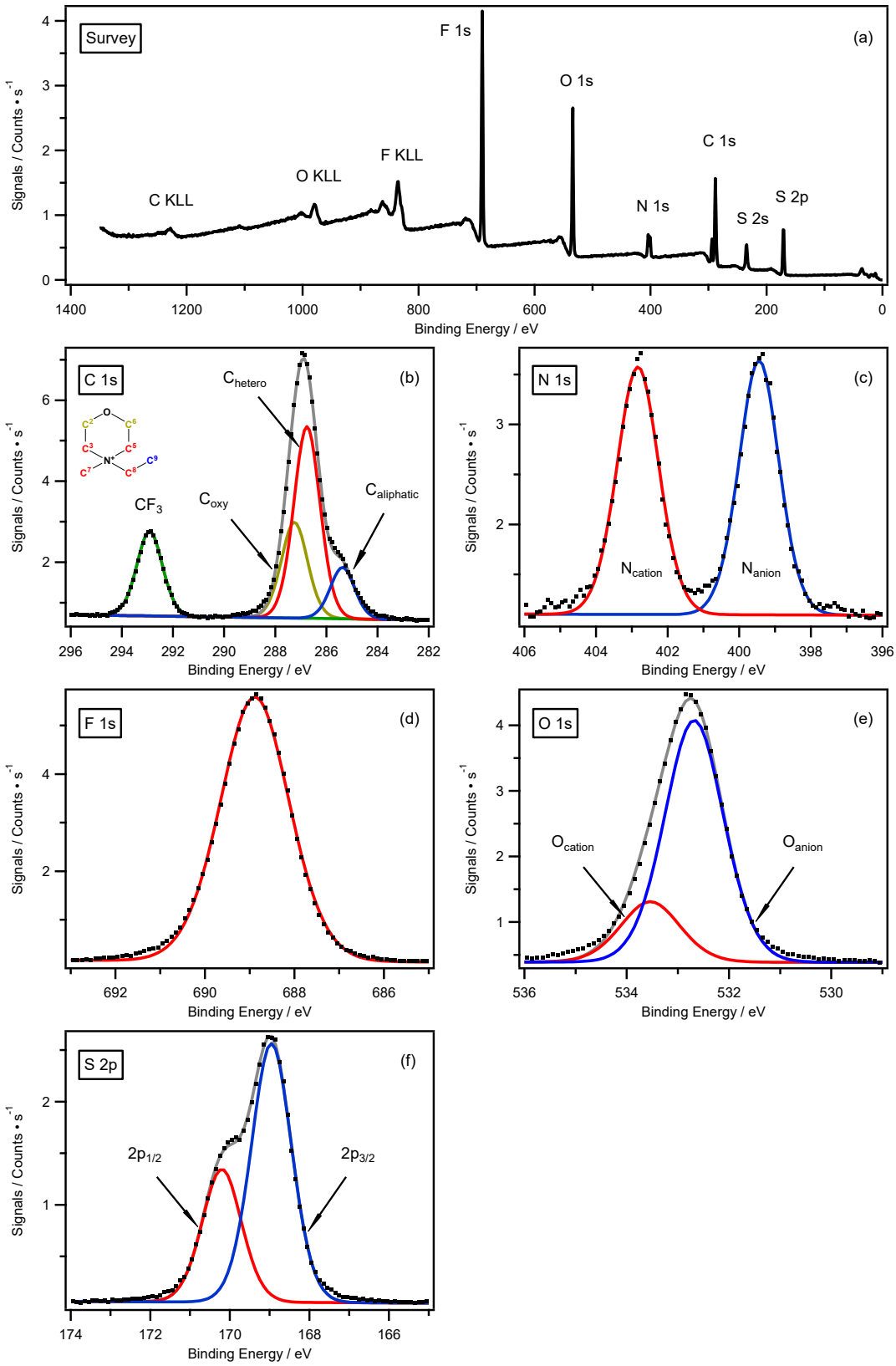

Figure S1 XP spectra of all elements for $[C_2C_1Mor][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

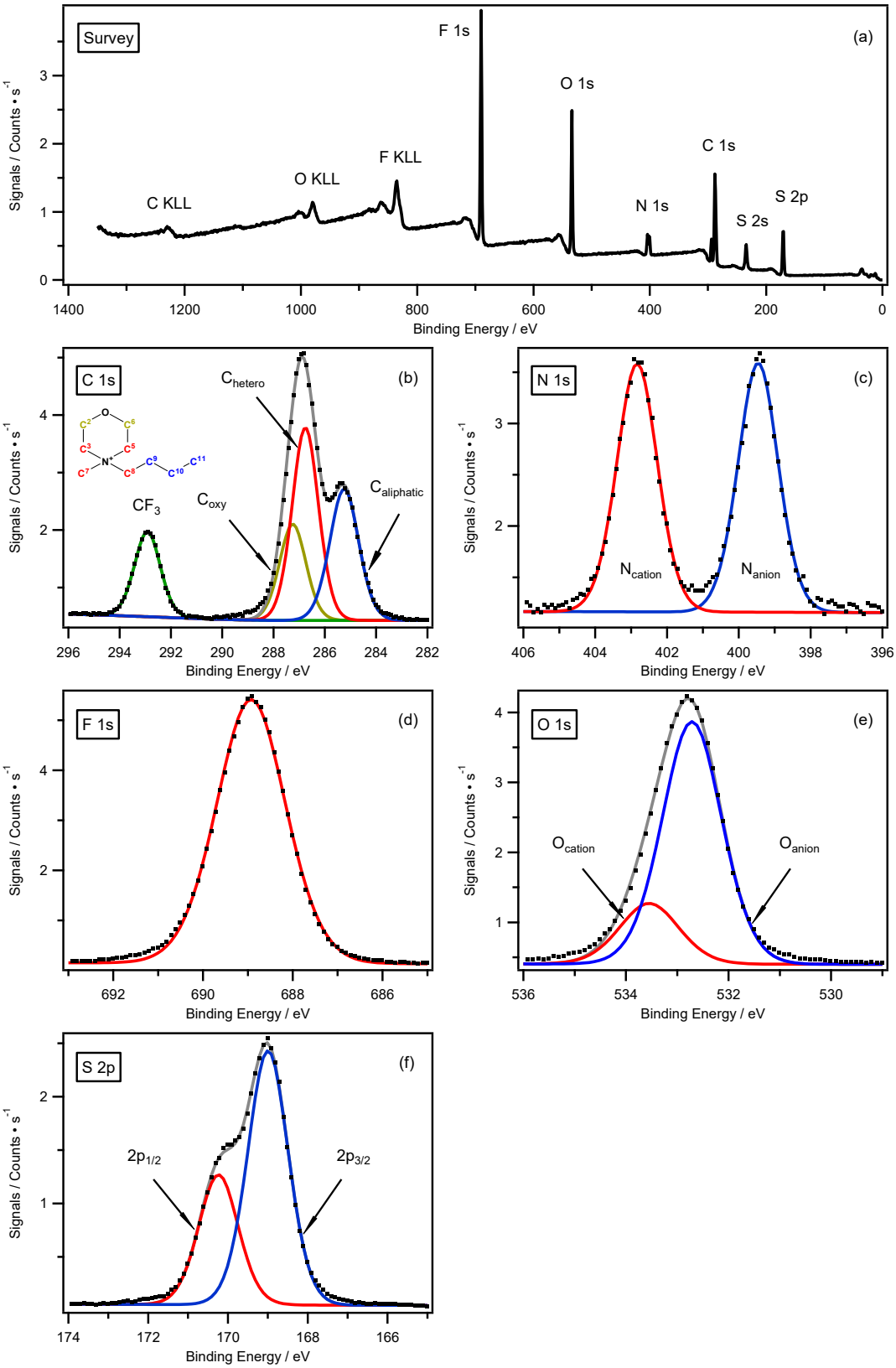

Figure S2 XP spectra of all elements for $[C_4C_1Mor][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

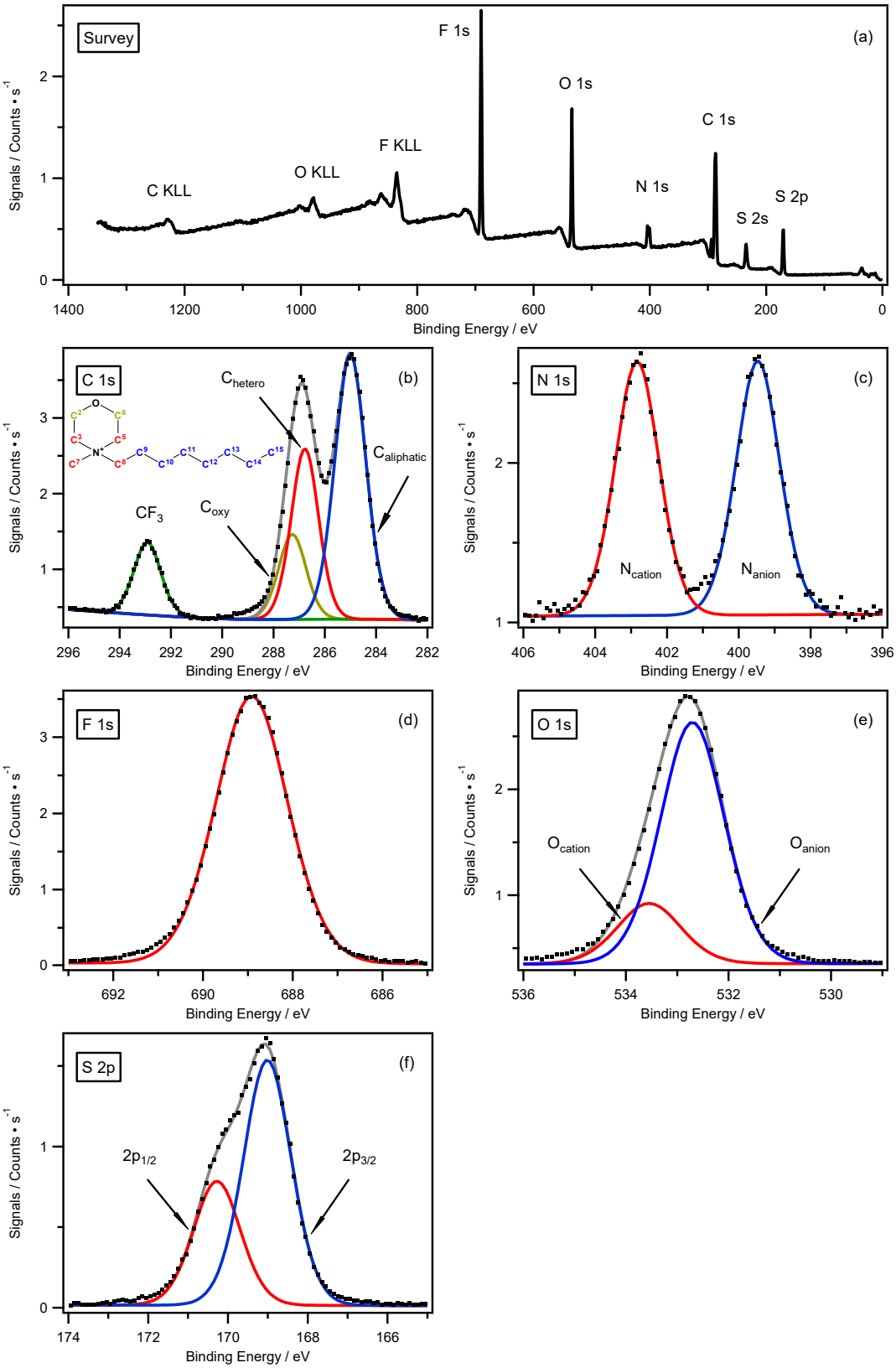

Figure S3 XP spectra of all elements for $[C_8C_1Mor][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

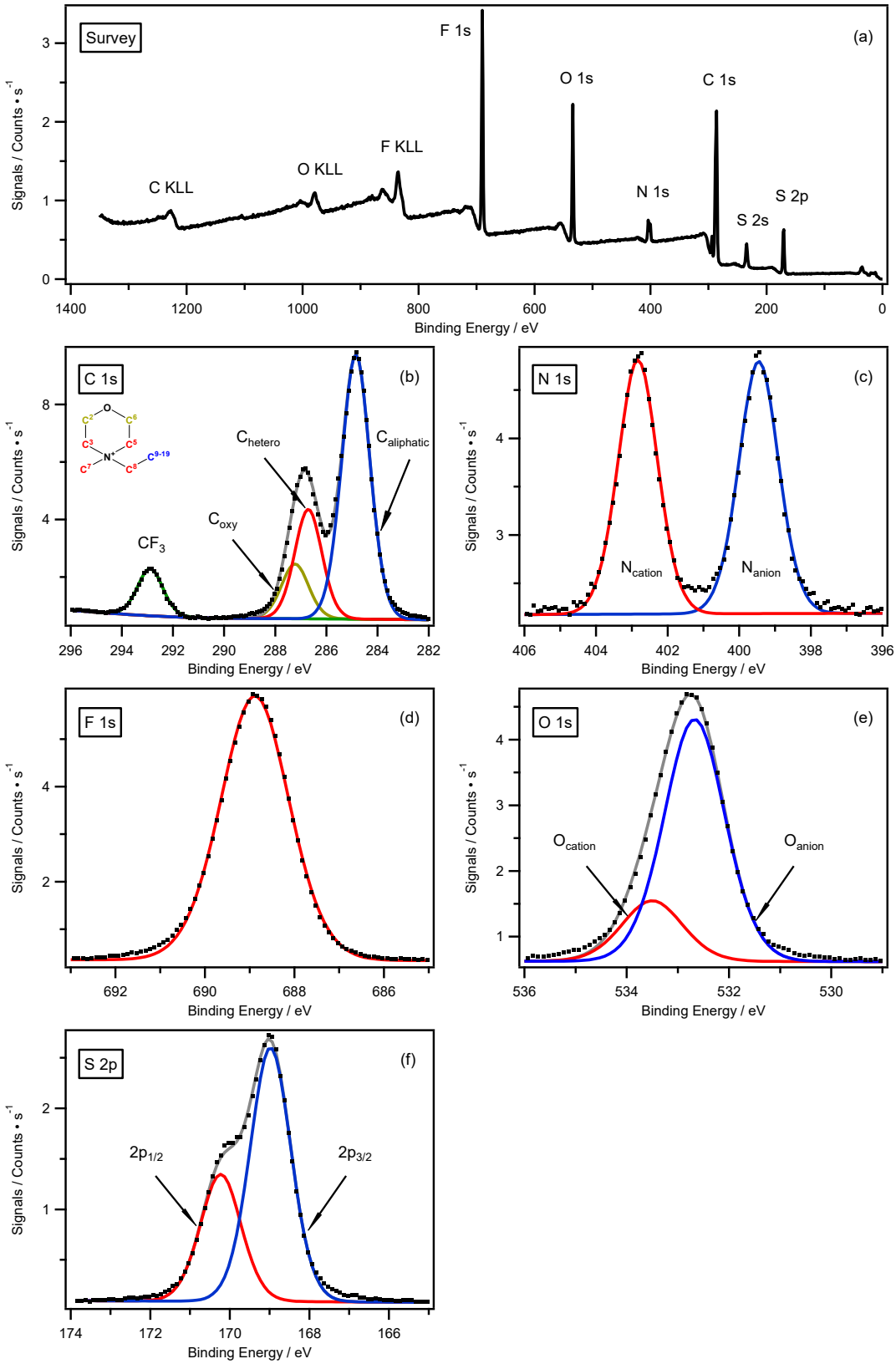

Figure S4 XP spectra of all elements for $[C_{12}C_1Mor][Tf_2N]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) O 1s and (f) S 2p.

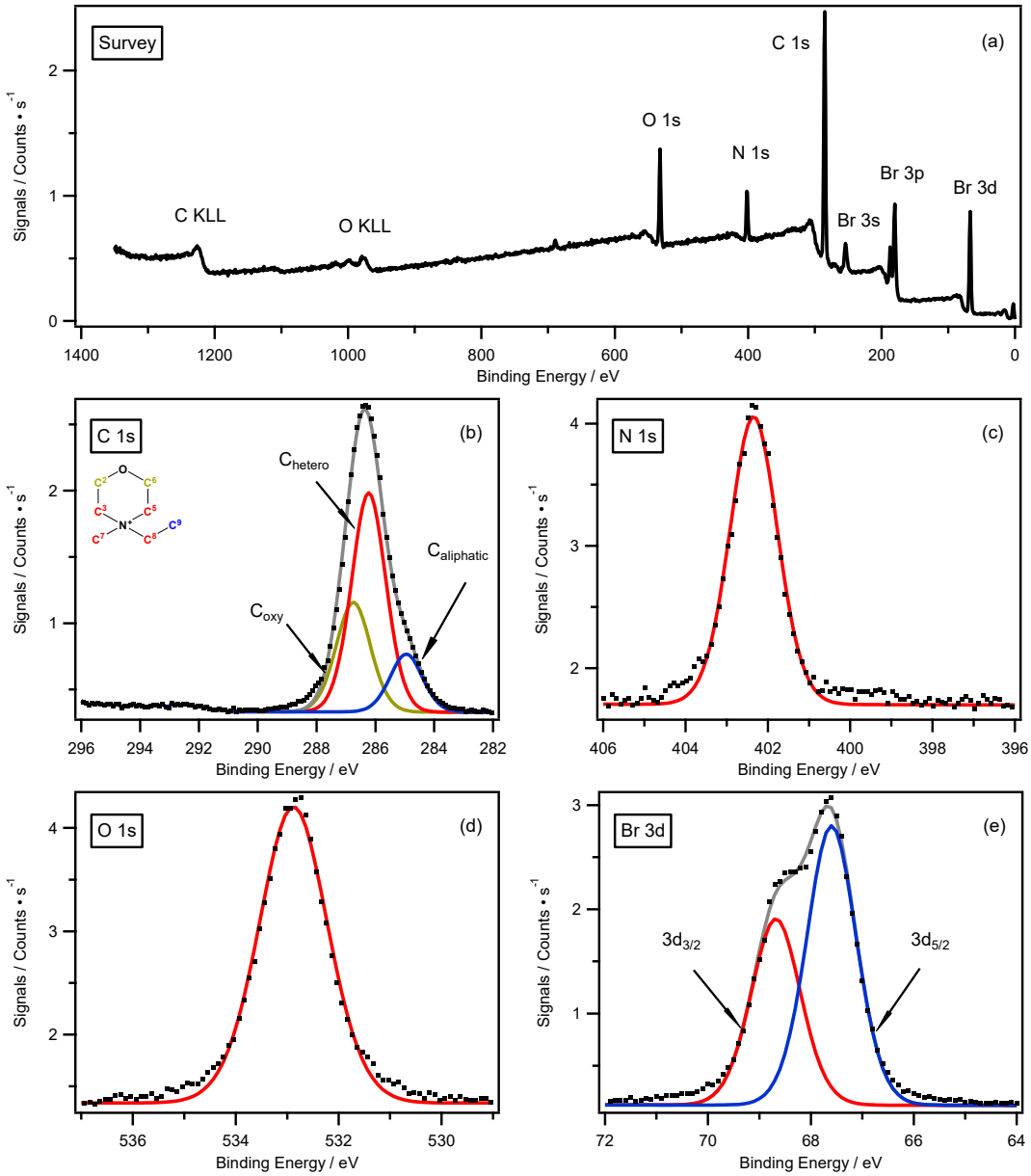

Figure S5 XP spectra of all elements for $[C_2C_1Mor]Br$: (a) Survey, (b) C 1s, (c) N 1s, (d) O 1s and (e) Br 3d.

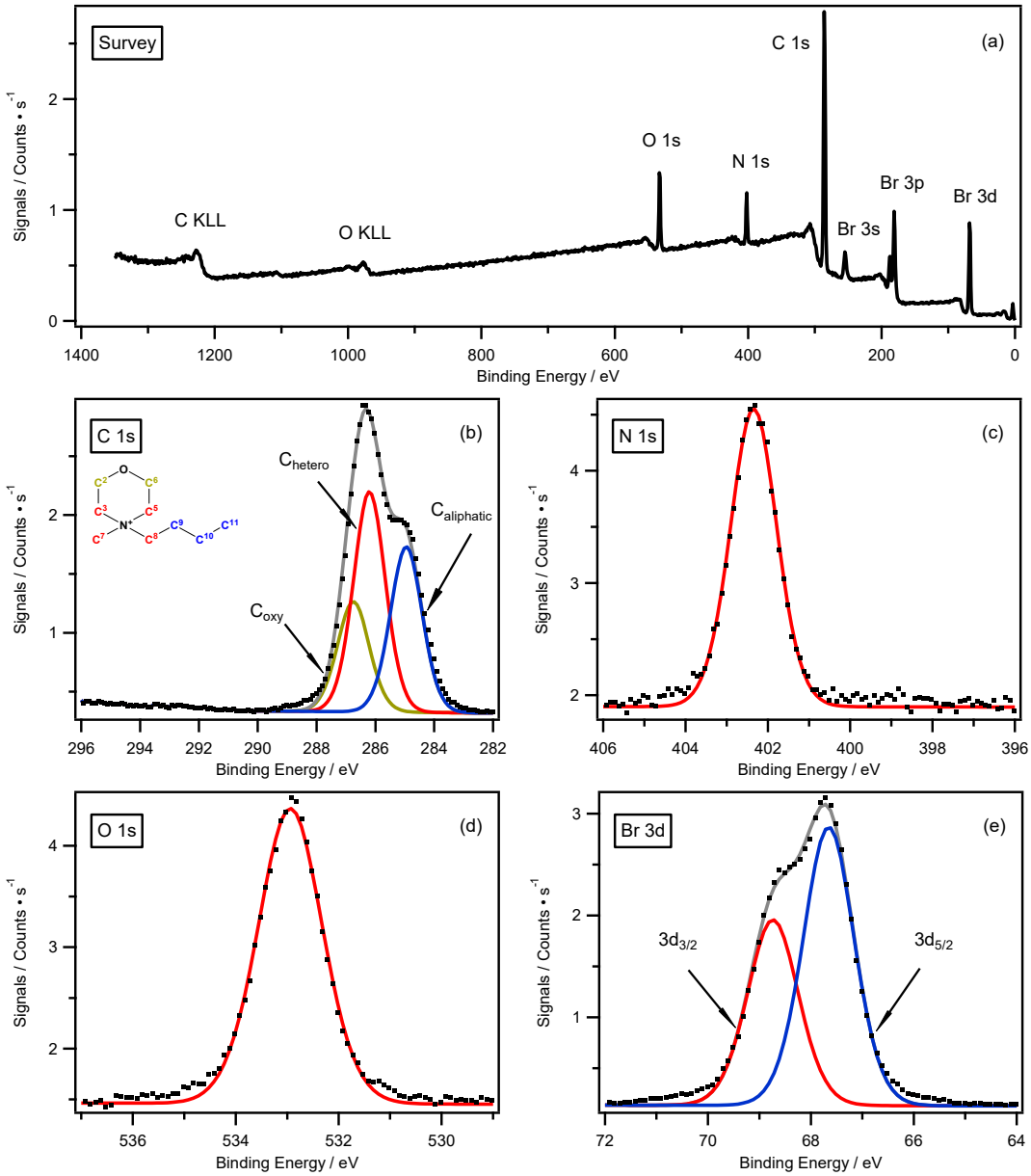

Figure S6 XP spectra of all elements for [C_4C_1Mor]Br: (a) Survey, (b) C 1s, (c) N 1s, (d) O 1s and (e) Br 3d.

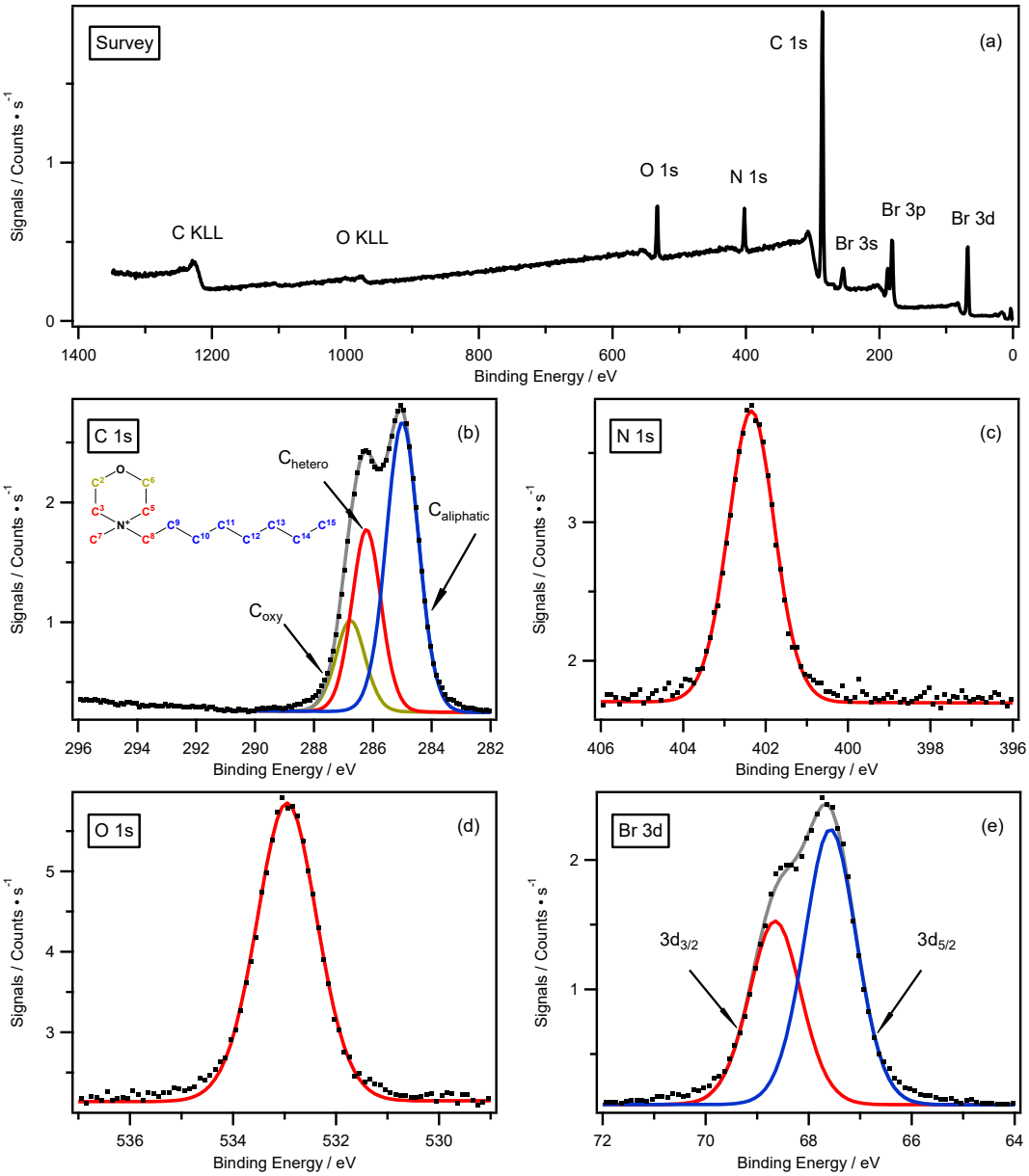

Figure S7 XP spectra of all elements for $[C_8C_1Mor]Br$: (a) Survey, (b) C 1s, (c) N 1s, (d) O 1s and (e) Br 3d.

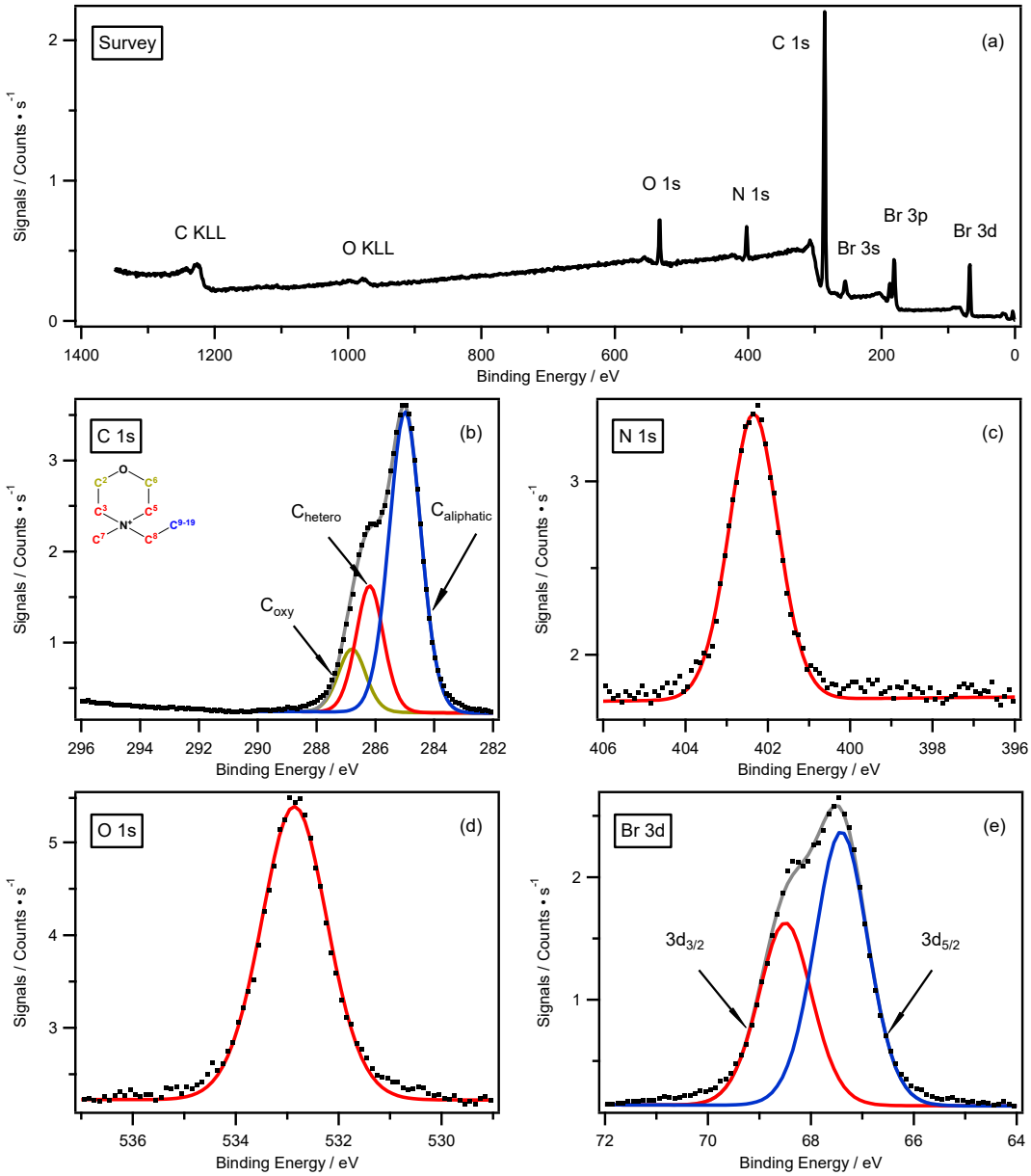

Figure S8 XP spectra of all elements for $[C_{12}C_1Mor]Br$: (a) Survey, (b) C 1s, (c) N 1s, (d) O 1s and (e) Br 3d.

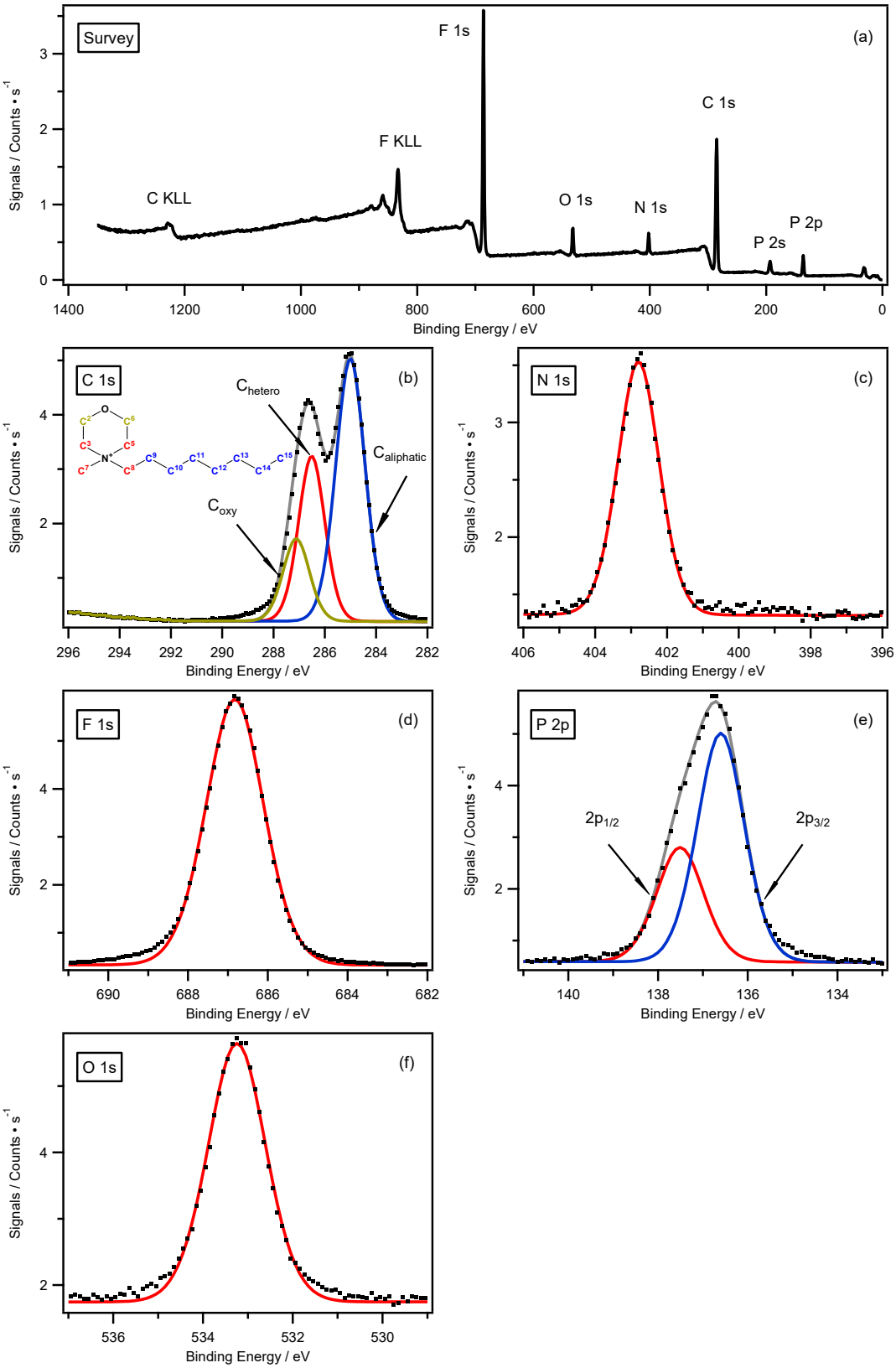

Figure S9 XP spectra of all elements for $[C_8C_1Mor][PF_6]$: (a) Survey, (b) C 1s, (c) N 1s, (d) F 1s, (e) P 2p and (f) O 1s.

References

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