

Supporting Information For

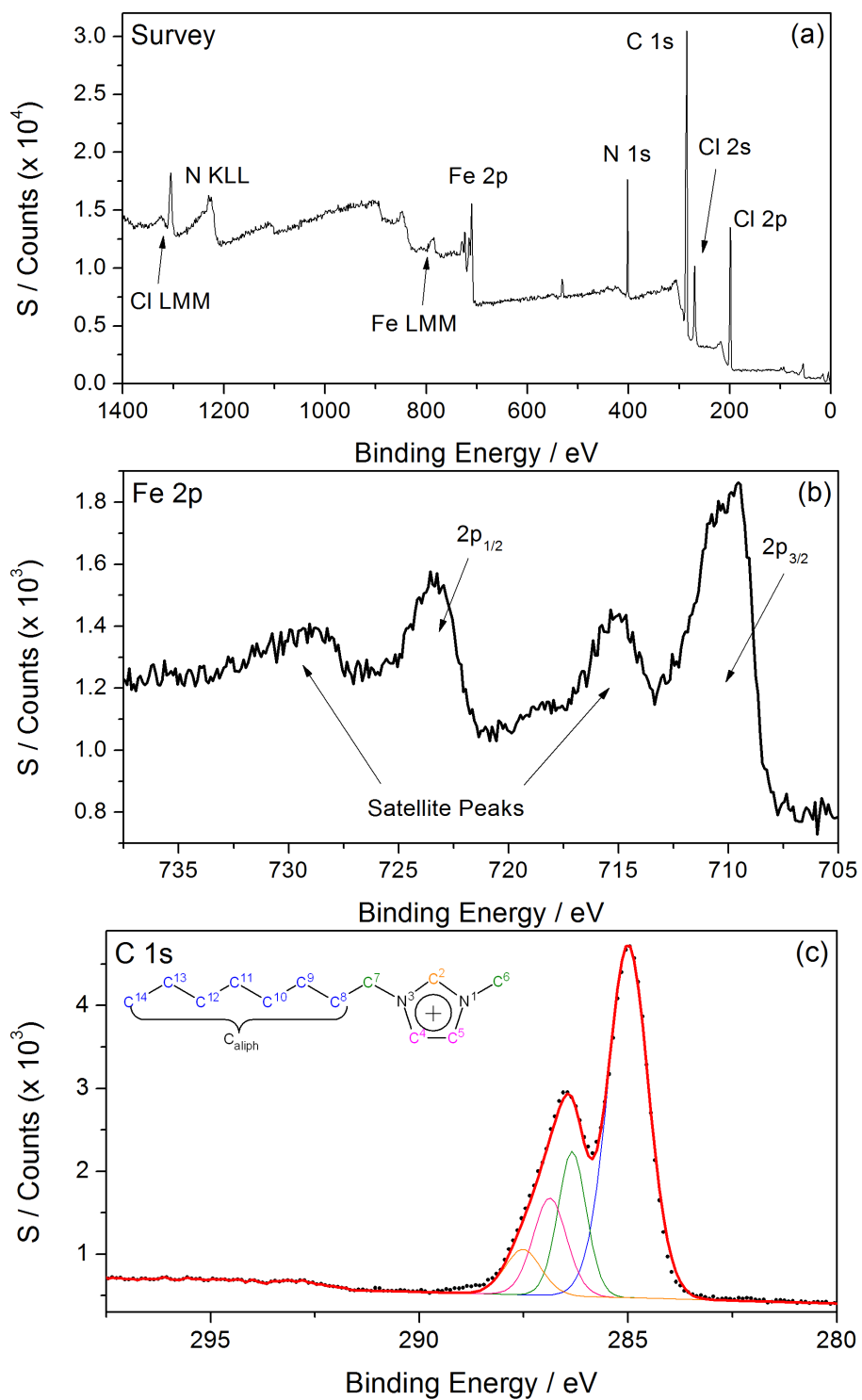
X-Ray Photoelectron Spectroscopy of Metal Ionic Liquids

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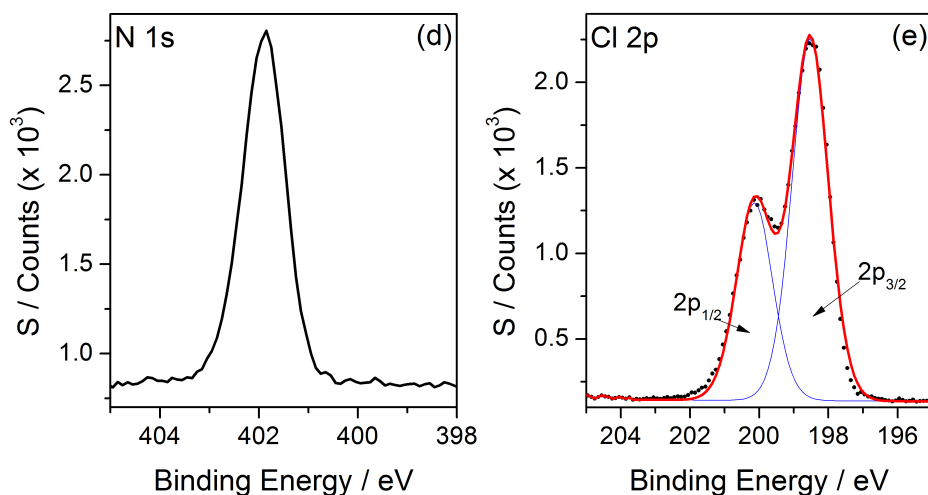
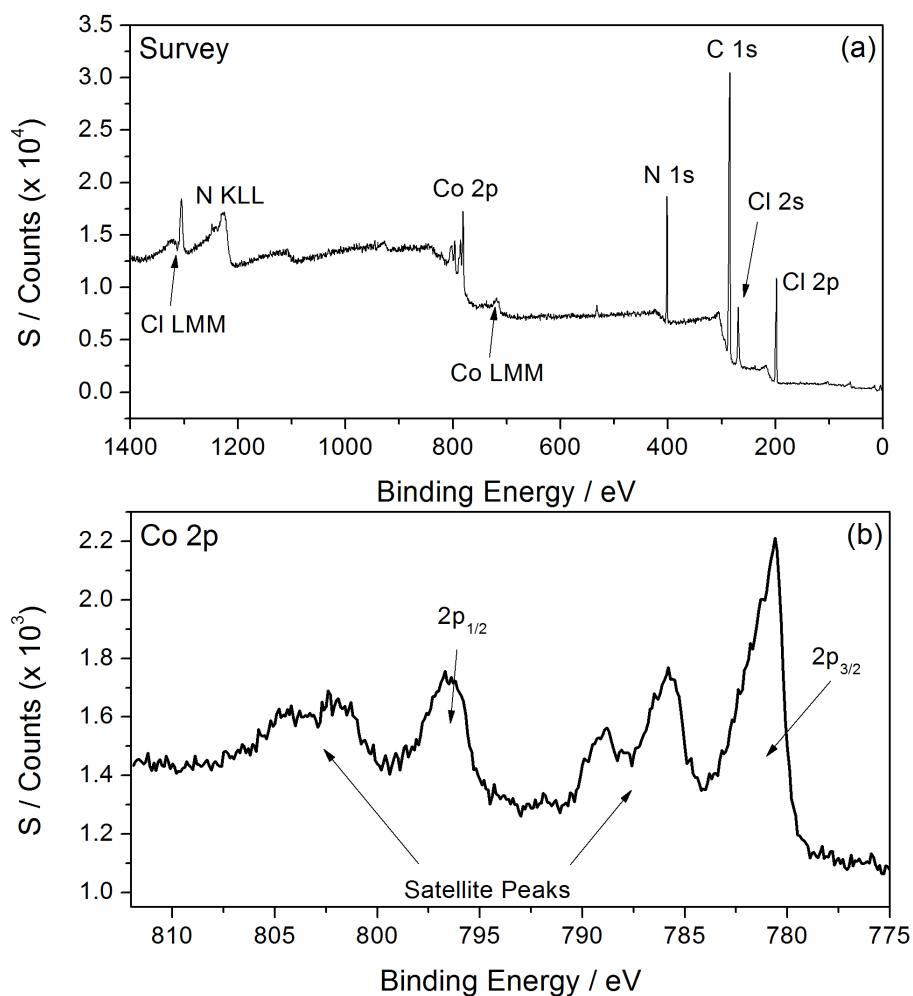


Figure S1 (a) Survey scan and high resolution XPS spectra of the (b) Fe 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of $[C_8C_1Im]Cl-Fe^{II}Cl_2$ ($\chi_{FeCl_2} = 0.33$). The components used to fit the C 1s XPS spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to $C_{aliph} 1s = 285.0$ eV.



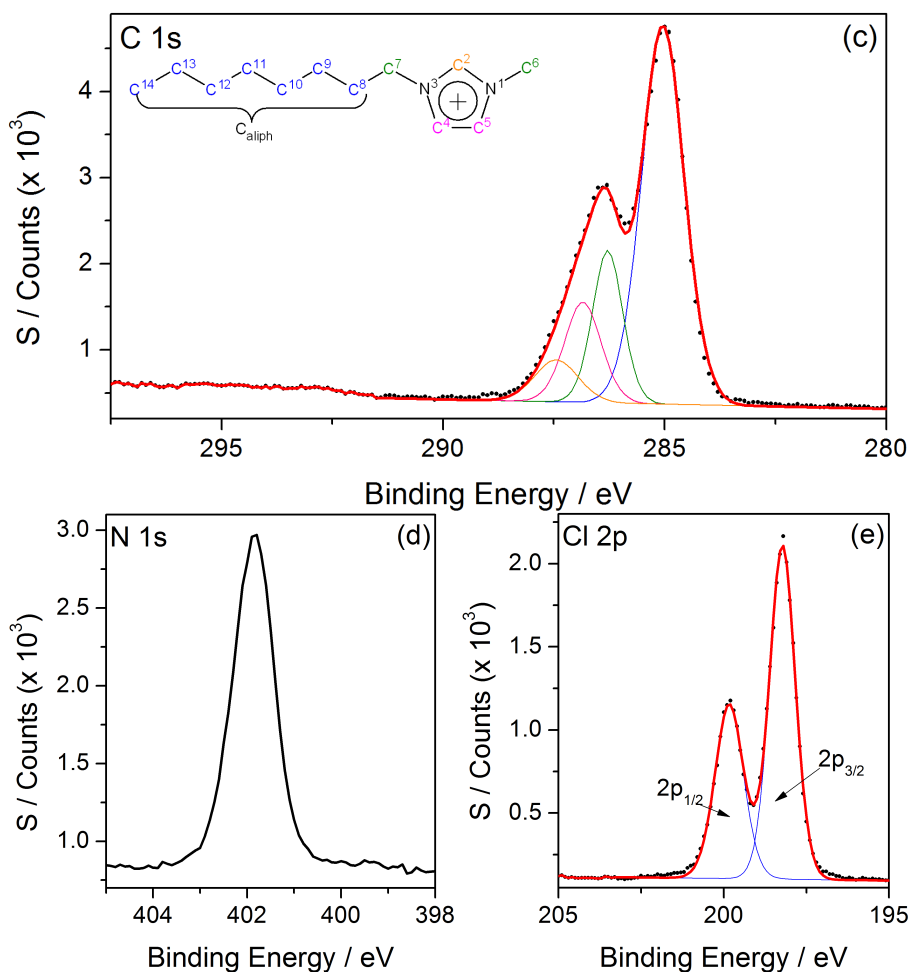
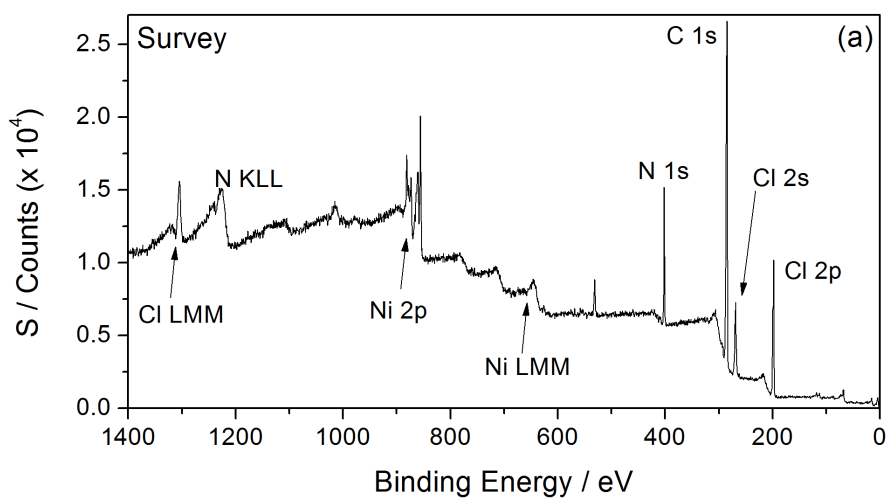


Figure S2 (a) Survey scan and high resolution XPS spectra of the (b) Co 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of [C₈C₁Im]Cl-Co^{II}Cl₂ ($\chi_{\text{CoCl}_2} = 0.33$). The components used to fit the C 1s XPS spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to C_{aliph} 1s = 285.0 eV.



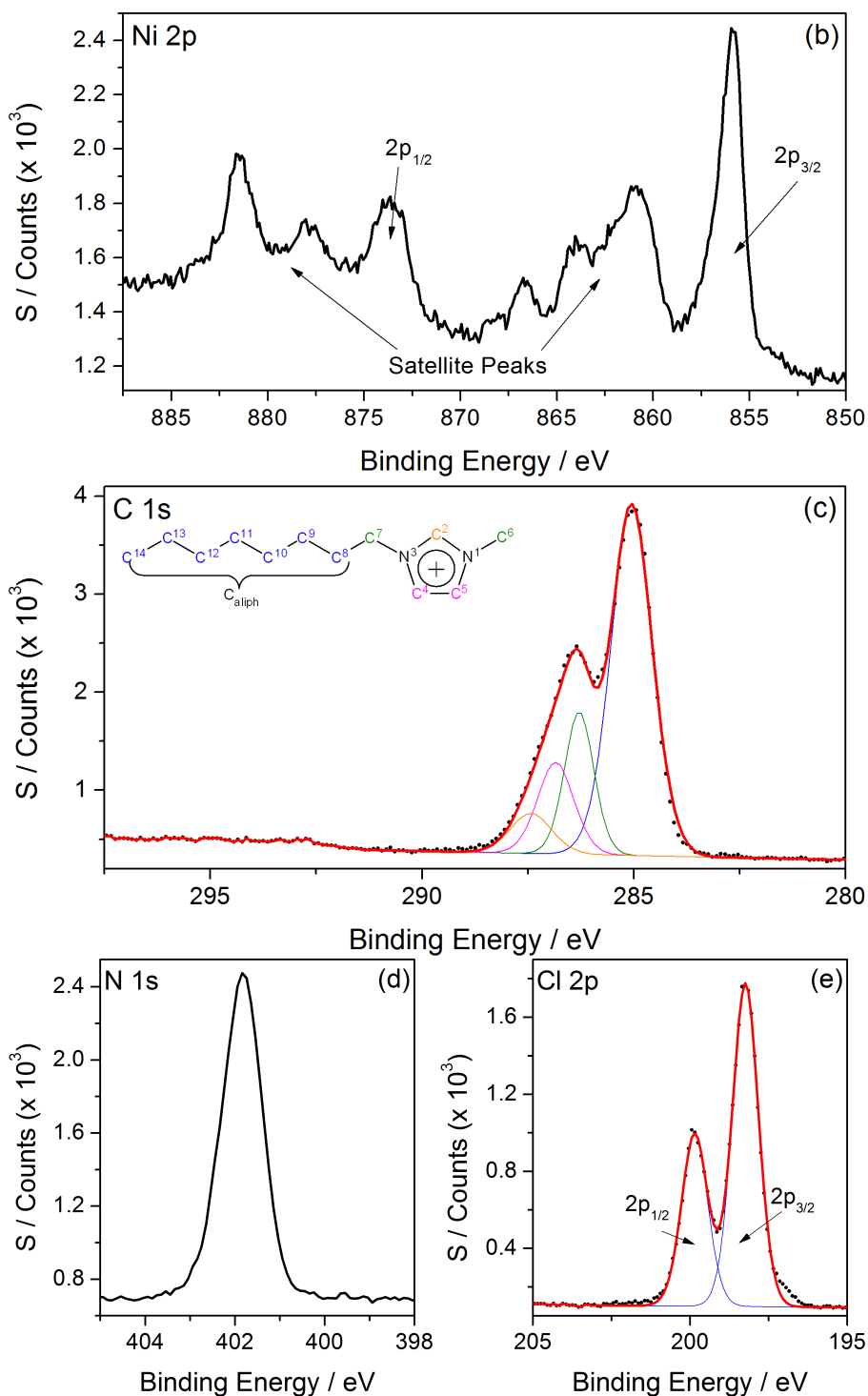
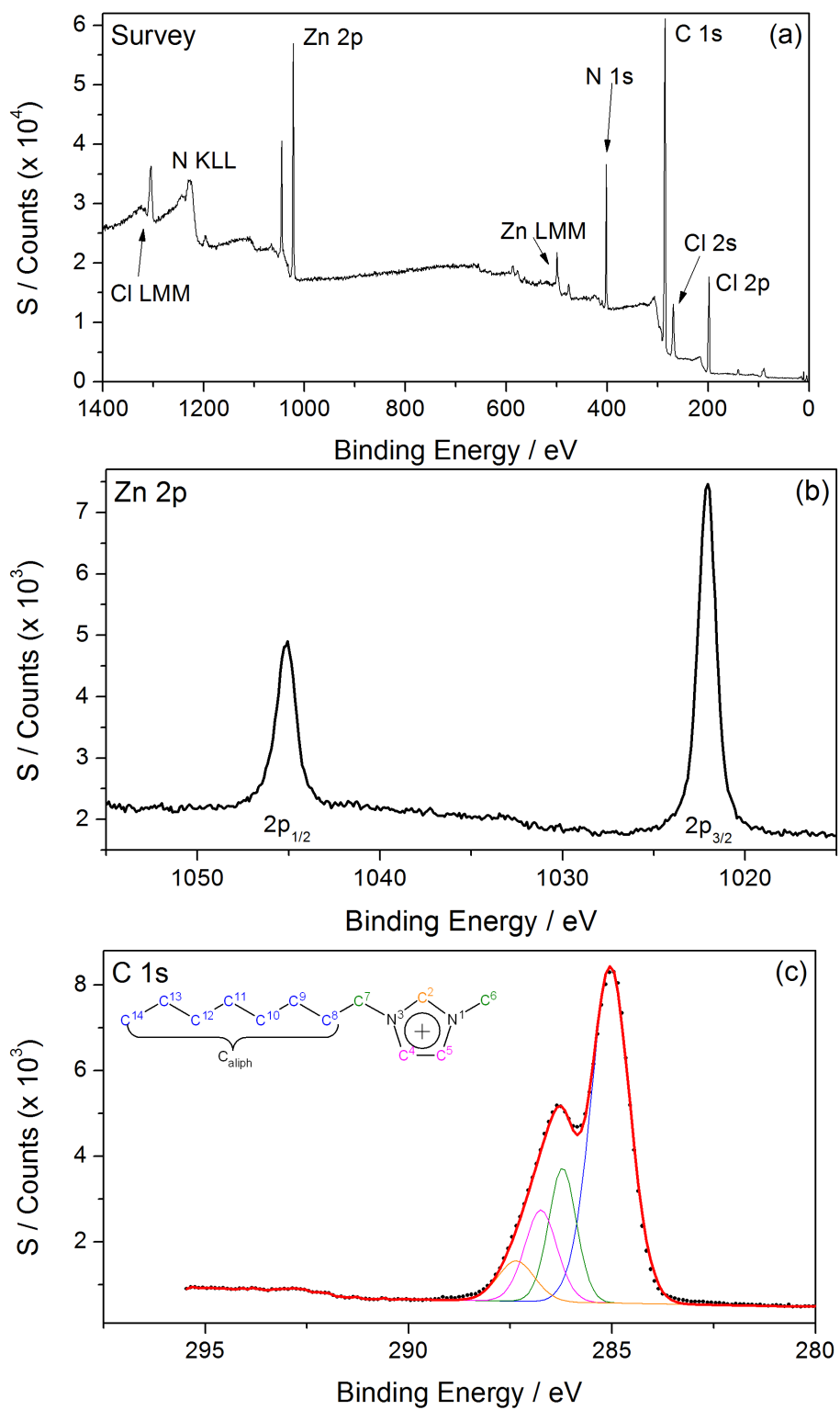


Figure S3 (a) Survey scan and high resolution XP spectra of the (b) Ni 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of $[C_8C_1Im]Cl-Co^{II}Cl_2$ ($\chi_{NiCl_2} = 0.33$). The components used to fit the C 1s XP spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to $C_{aliph} 1s = 285.0$ eV.



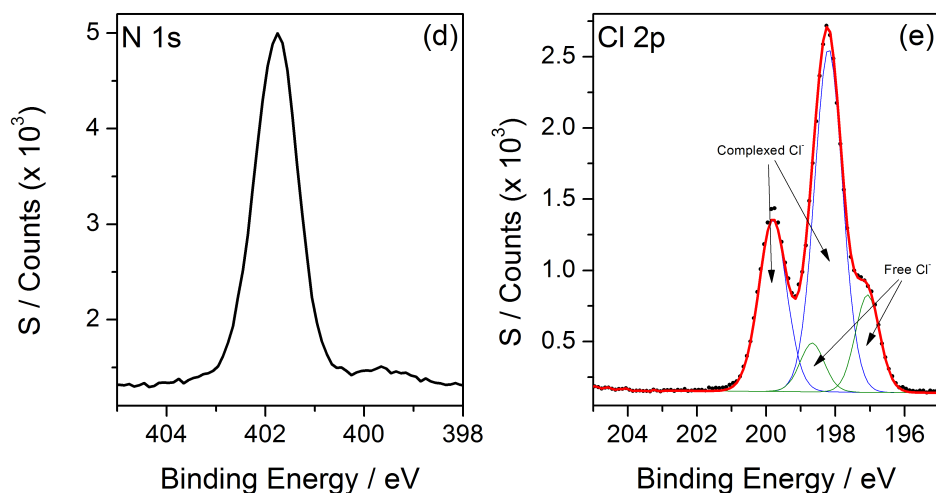
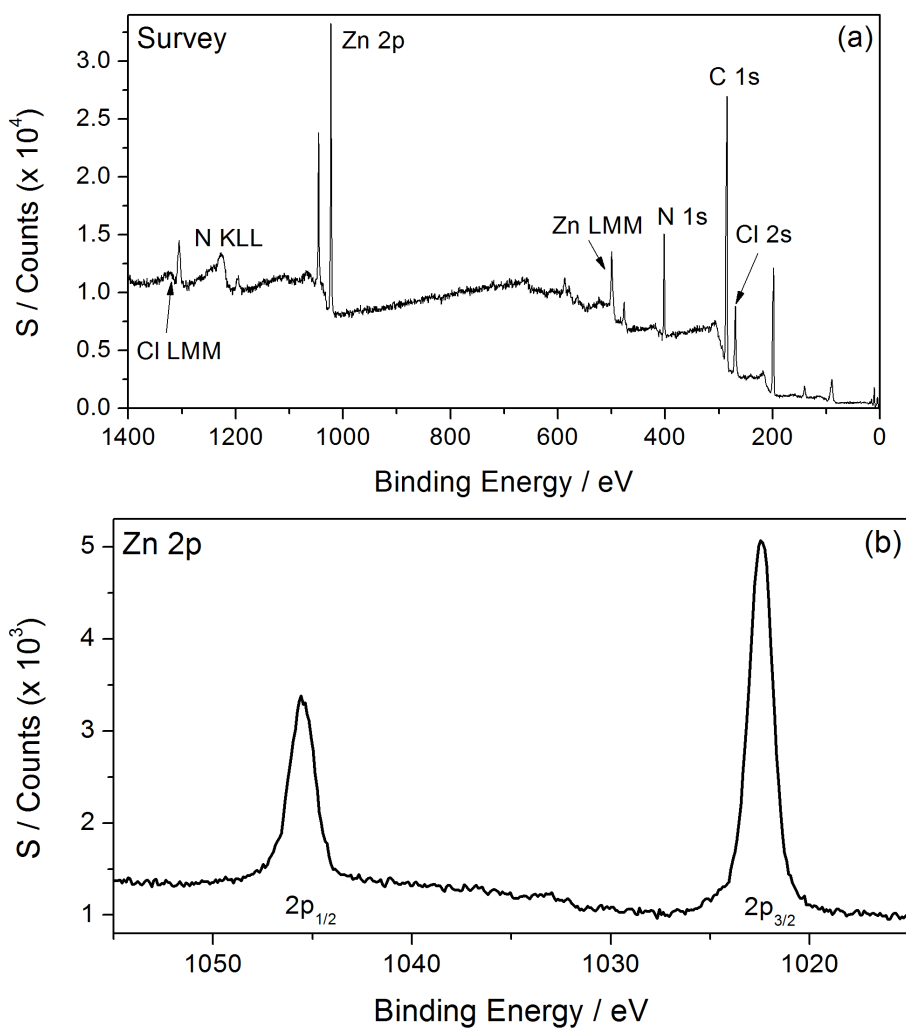


Figure S4 (a) Survey scan and high resolution XP spectra of the (b) Zn 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of $[C_8C_1Im]Cl-Zn^{II}Cl_2$ ($\chi_{ZnCl_2} = 0.25$). The components used to fit the C 1s XP spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to $Ca_{10} 1s = 285.0$ eV.



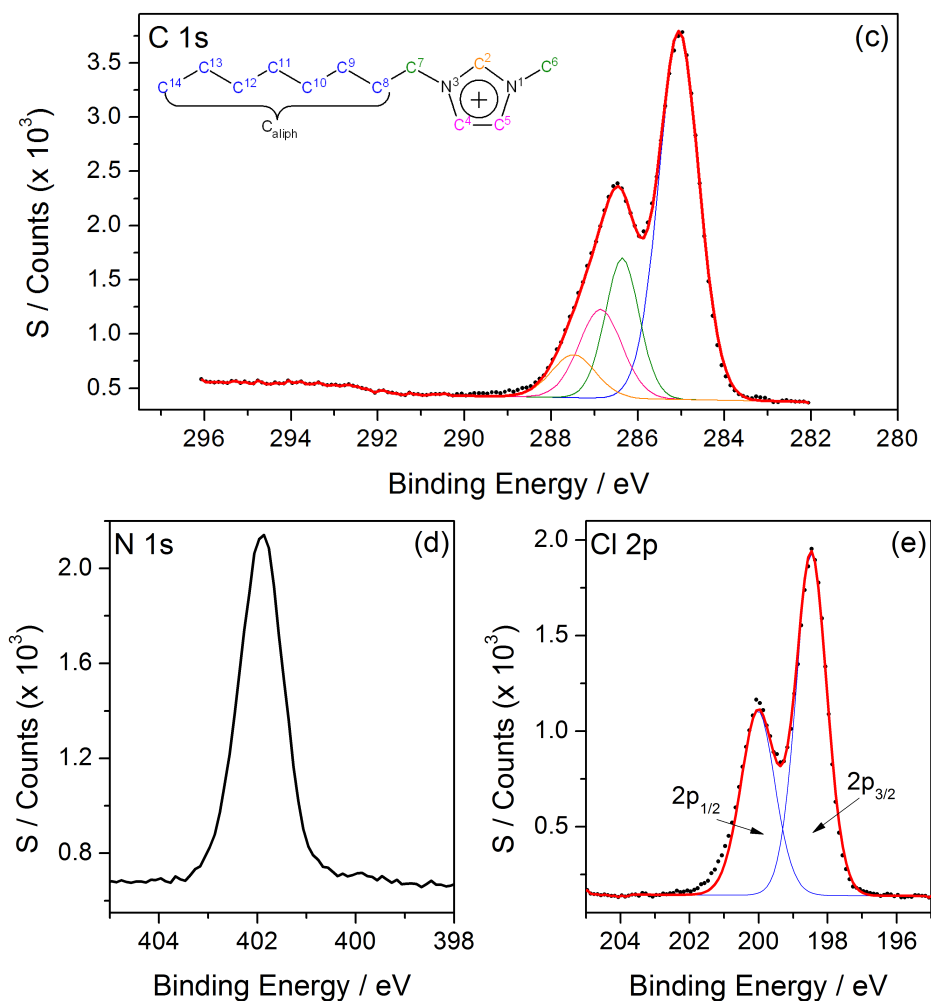
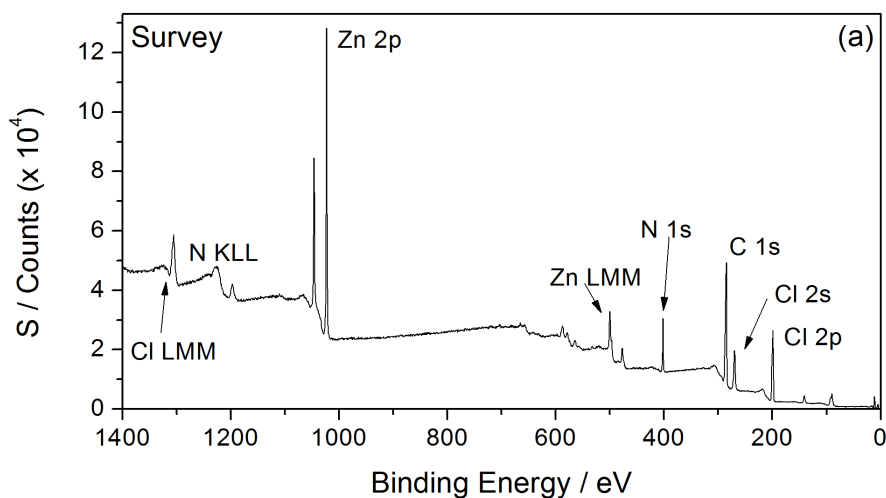


Figure S5 (a) Survey scan and high resolution XP spectra of the (b) Zn 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of [C₈C₁Im]Cl-Zn^{II}Cl₂ ($\chi_{\text{ZnCl}_2} = 0.33$). The components used to fit the C 1s XP spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to C_{aliph} 1s = 285.0 eV.



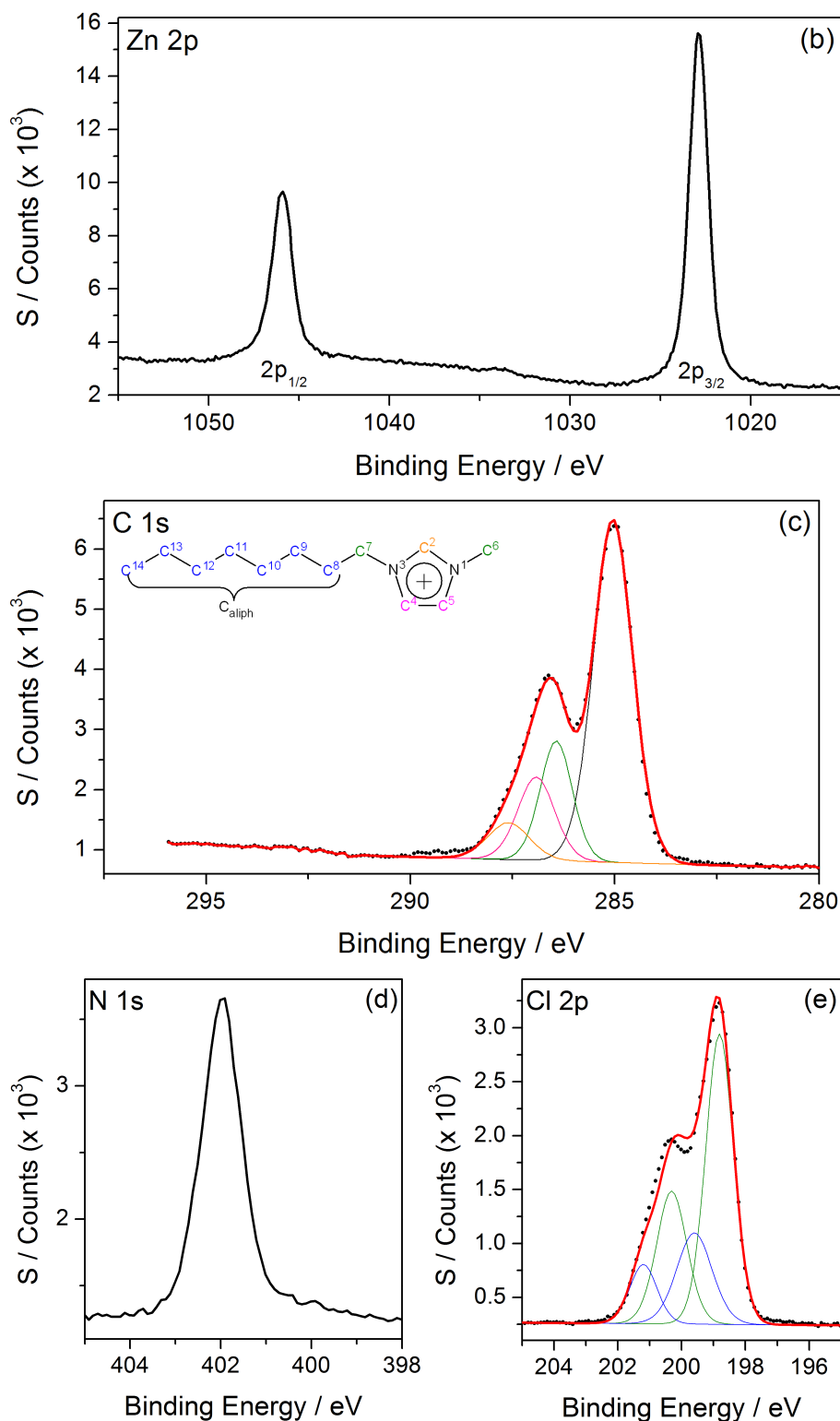
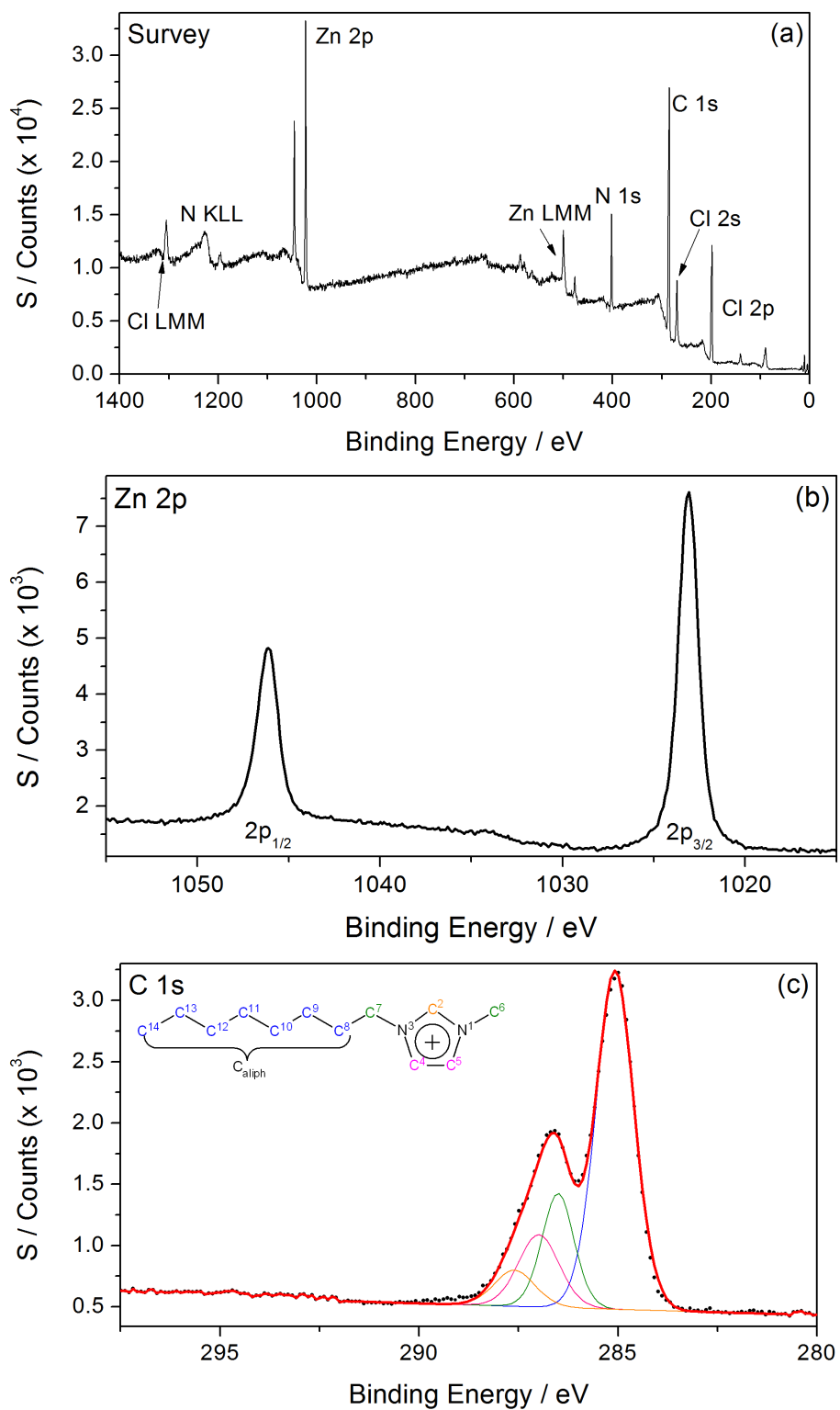


Figure S6 (a) Survey scan and high resolution XP spectra of the (b) Zn 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of [C₈C₁Im]Cl-Zn^{II}Cl₂ ($\chi_{\text{ZnCl}_2} = 0.5$). The components used to fit the C 1s XP spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to C_{aliph} 1s = 285.0 eV.



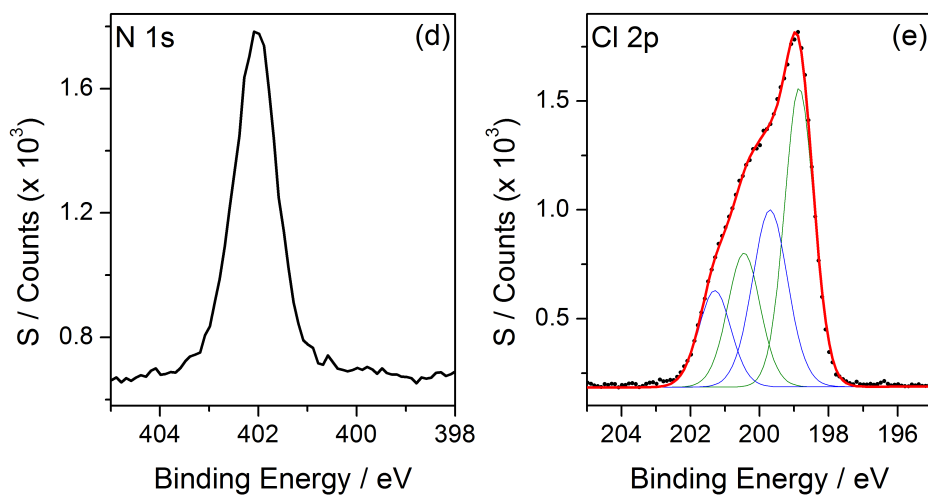


Figure S7 (a) Survey scan and high resolution XP spectra of the (b) Zn 2p, (c) C 1s, (d) N 1s and (e) Cl 2p regions of $[C_8C_{1Im}]Cl-Zn^{II}Cl_2$ ($\chi_{ZnCl_2} = 0.6$). The components used to fit the C 1s XP spectrum are shown in (c), allowing the simulated envelope to be compared with the experimental spectrum (black dots). Absolute binding energies are given in Table 1; all spectra were charge corrected to $C_{aliph} 1s = 285.0$ eV.

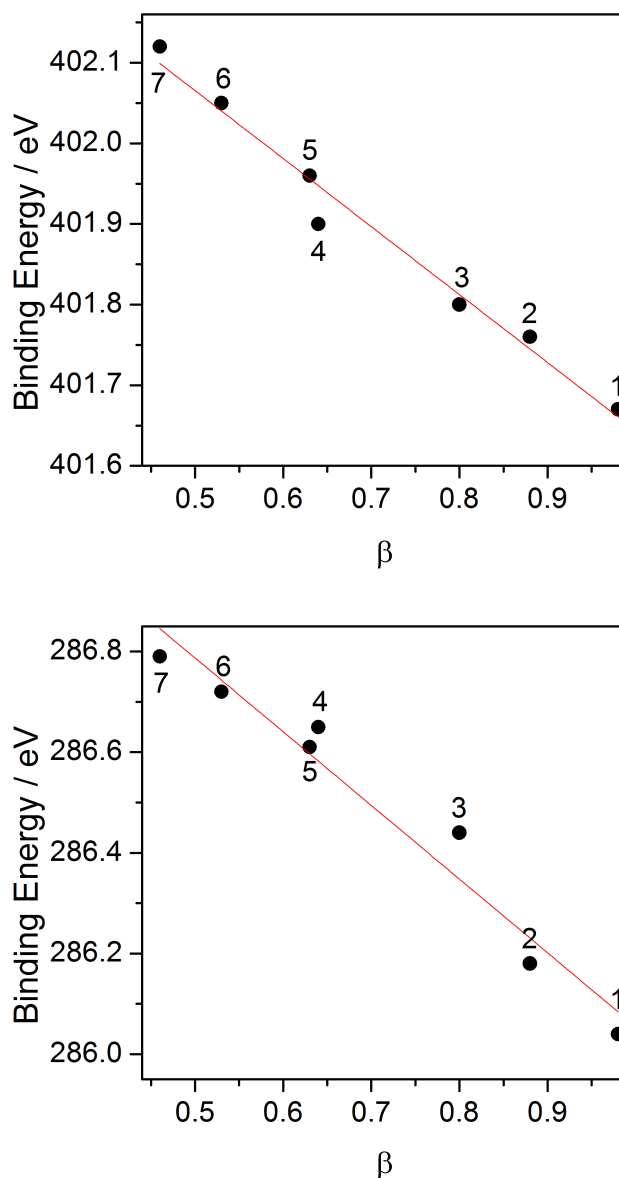


Figure S8 (a) N 1s and (b) C_{hetero} 1s binding energies taken from the XP spectra of 7 common [C₈C₁Im][X] ionic liquids plotted against β .^{1,2} The anions, X, are 1 = Cl⁻; 2 = Br⁻; 3 = I⁻; 4 = [TfO]⁻; 5 = [BF₄]⁻; 6 = [PF₆]⁻; 7 = [Tf₂N]⁻.

References

1. I. J. Villar-Garcia, E. F. Smith, A. W. Taylor, F. Qiu, K. R. J. Lovelock, R. G. Jones and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2797-2808.
2. R. Lungwitz and S. Spange, *New J. Chem.*, 2008, **32**, 392-394.