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

An ARXPS and ERXPS Study of Quaternary Ammonium and Phosphonium Ionic Liquids: Utilising a High Energy Ag Lα' X-ray Source

Supplementary Information

*Rebecca K. Blundell, Astrid Delorme, Emily F. Smith and Peter Licence**

The GlaxoSmithKline Carbon Neutral Laboratory,
School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK

**To whom correspondence should be addressed:*

peter.licence@nottingham.ac.uk

Tel: +44 115 84661

Ionic Liquid	Binding Energy / eV									
	Cation					Anion				
	$C_{aliphatic}$ 1s	C_{inter} 1s	C_{hetero} 1s	N_{cation} 1s	P_{cation} $2p_{3/2}$	C_{anion} 1s	N_{anion} 1s	O 1s	F 1s	S $2p_{3/2}$
$[P_{4,4,4,1}][NTf_2]$[a]	285.1	-	285.6	-	132.7	292.7	399.2	532.4	688.6	168.8
$[P_{6,6,6,14}][NTf_2]$[a]	285.0	-	285.9	-	132.7	292.8	399.3	532.5	688.7	168.8
$[N_{4,4,4,1}][NTf_2]$[a]	285.1	285.4	286.6	402.5	-	292.8	399.3	532.5	688.7	168.8
$[N_{6,6,6,14}][NTf_2]$[a]	285.0	285.7	286.7	402.5	-	292.8	399.3	532.5	688.7	168.9
$[C_8C_1Pyrr][NTf_2]$[b]	285.0	285.6	286.8	402.7	-	292.9	399.5	532.7	688.8	169.0

Table S1. Experimental binding energies in eV for the ionic liquids studied in this work using the Al Kα x-ray source. The associated experimental error is ± 0.1 eV. $[N_{6,6,6,14}]^+$/ $[P_{6,6,6,14}]^+$/ $[C_8C_1Pyrr]^+$ compounds charge corrected by setting $C_{aliphatic}$ 1s to 285.0 eV. $[N_{4,4,4,1}]^+$/$[P_{4,4,4,1}]^+$ compounds charge corrected by setting N_{cation} 1s/P_{cation} 2p to the value obtained for the $[N_{6,6,6,14}]^+$/ $[P_{6,6,6,14}]^+$ analogue. [a] Taken from ref. 1. [b] Taken from ref.2.

Estimating S 2p and S 1s Attenuation Lengths for the Ag Lα' source

To estimate the attenuation length (λ_{AL}) for the five ionic liquids the NIST Effective-Attenuation-Length database was used to first calculate the inelastic mean free path (λ_{IMFP}) for each ionic liquid using the TPP-2M method. This calculation can only be carried out up to kinetic energies of 2000 eV. Consequently, extrapolation of the obtained data set up to 3000 eV is required to obtain an estimate for IMFP in the energy range 2000 – 3000 eV. The resultant plots of IMFP *versus* Kinetic Energy for each ionic liquid are presented in figure s1.

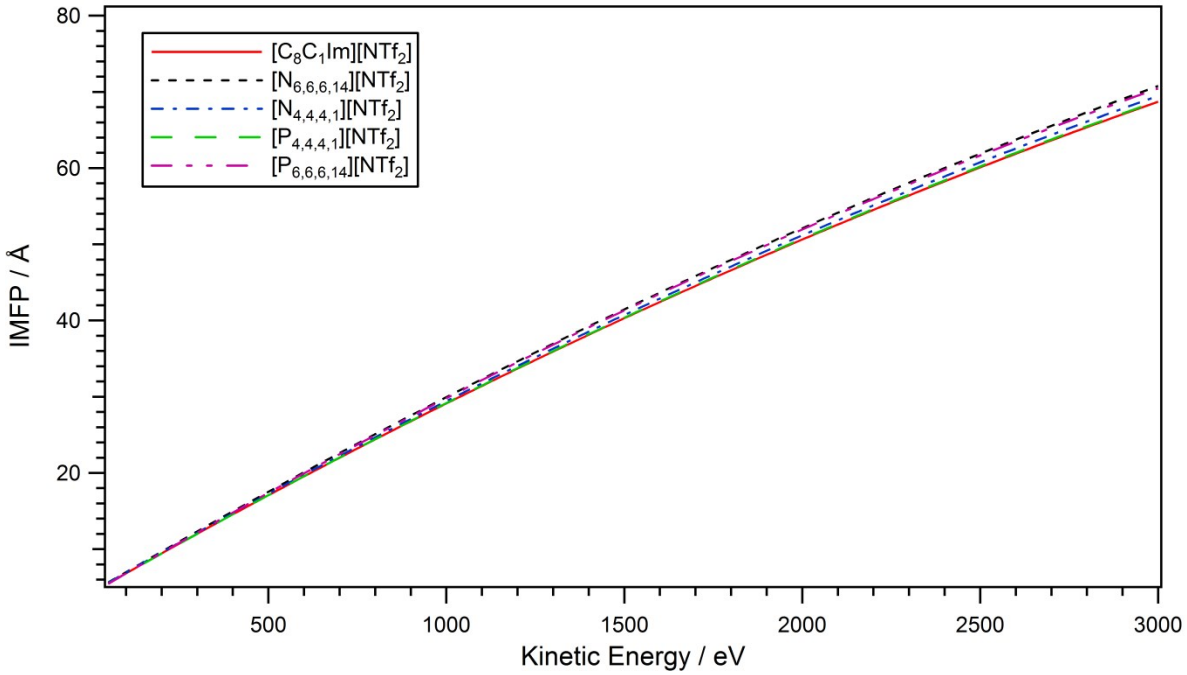


Figure S1. Calculated λ_{IMFP} values for the kinetic energy range 0 – 3000 eV for all five ionic liquids studied.

The λ_{AL} is typically 20 % smaller than the calculated λ_{IMFP} as it does not include elastic scattering events; subsequently, this has been accounted for to estimate λ_{AL} in this work. Figure S2 provides a representative example of this procedure for the ionic liquid $[N_{4,4,4,1}][NTf_2]$. This shows a plot of the calculated λ_{IMFP} in the energy range 0 – 3000 eV (solid line), and the estimated λ_{AL} (dashed line) - which is 80 % of λ_{IMFP}. The λ_{AL} values can then be determined for the required kinetic energies.

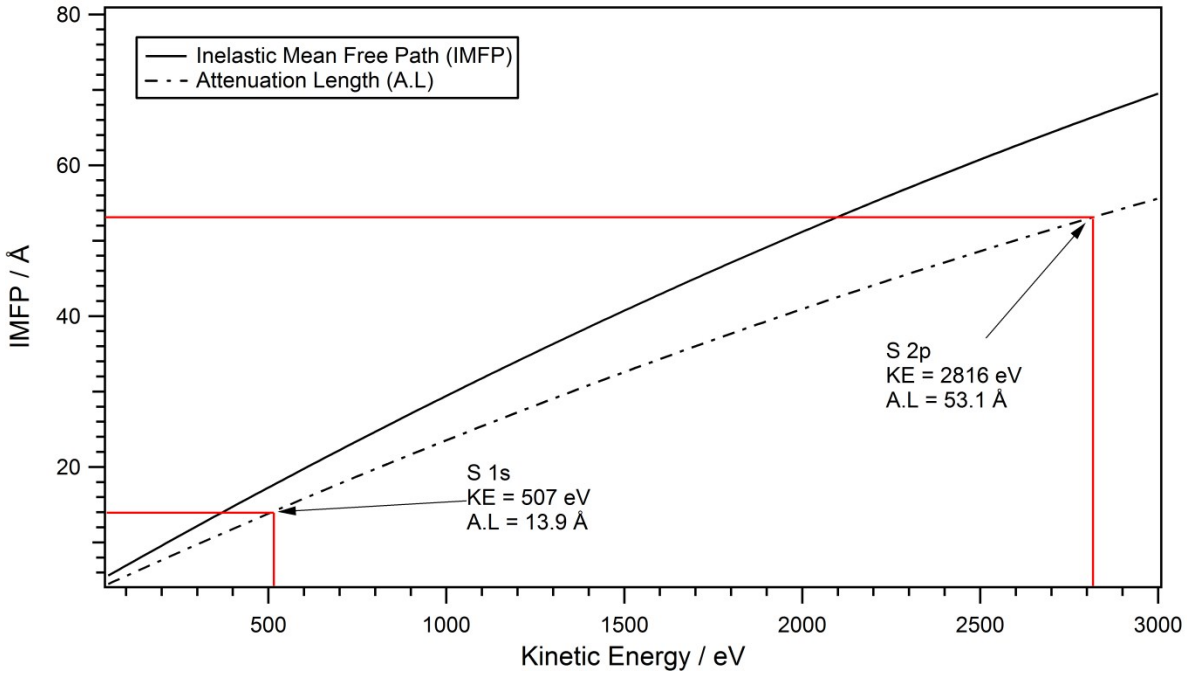


Figure S2. Plot describing the calculated λ_{IMFP} (solid black line) and estimated λ_{AL} (dashed line) for $[N_{4,4,4,1}][NTf_2]$. Highlighting the λ_{AL} values obtained for S 1s and S 2p photoelectrons.

The λ_{IMFP} and λ_{AL} values obtained for each ionic liquid for the S 1s and S 2p photoelectrons are presented in table S2. It can be seen that the values are consistent between samples and are therefore not sensitive to the ionic liquid.

	S 2p		S 1s	
	IMFP (nm)	A.L (nm)	IMFP (nm)	A.L (nm)
$[C_8C_1Im][NTf_2]$	6.6	**5.3**	1.7	**1.4**
$[N_{6,6,6,14}][NTf_2]$	6.8	**5.4**	1.8	**1.4**
$[N_{4,4,4,1}][NTf_2]$	6.6	**5.3**	1.7	**1.4**
$[P_{4,4,4,1}][NTf_2]$	6.6	**5.3**	1.7	**1.4**
$[P_{6,6,6,14}][NTf_2]$	6.7	**5.4**	1.8	**1.4**

Table S2. λ_{IMFP} and λ_{AL} values for the S 2p and S 1s photoelectrons for all five ionic liquids.

XP spectra at θ = 0° and 80° - Al Kα x-ray source

Figure S3. XP spectra for $[C_8C_1Pyrr][NTf_2]$ for both emission angles.

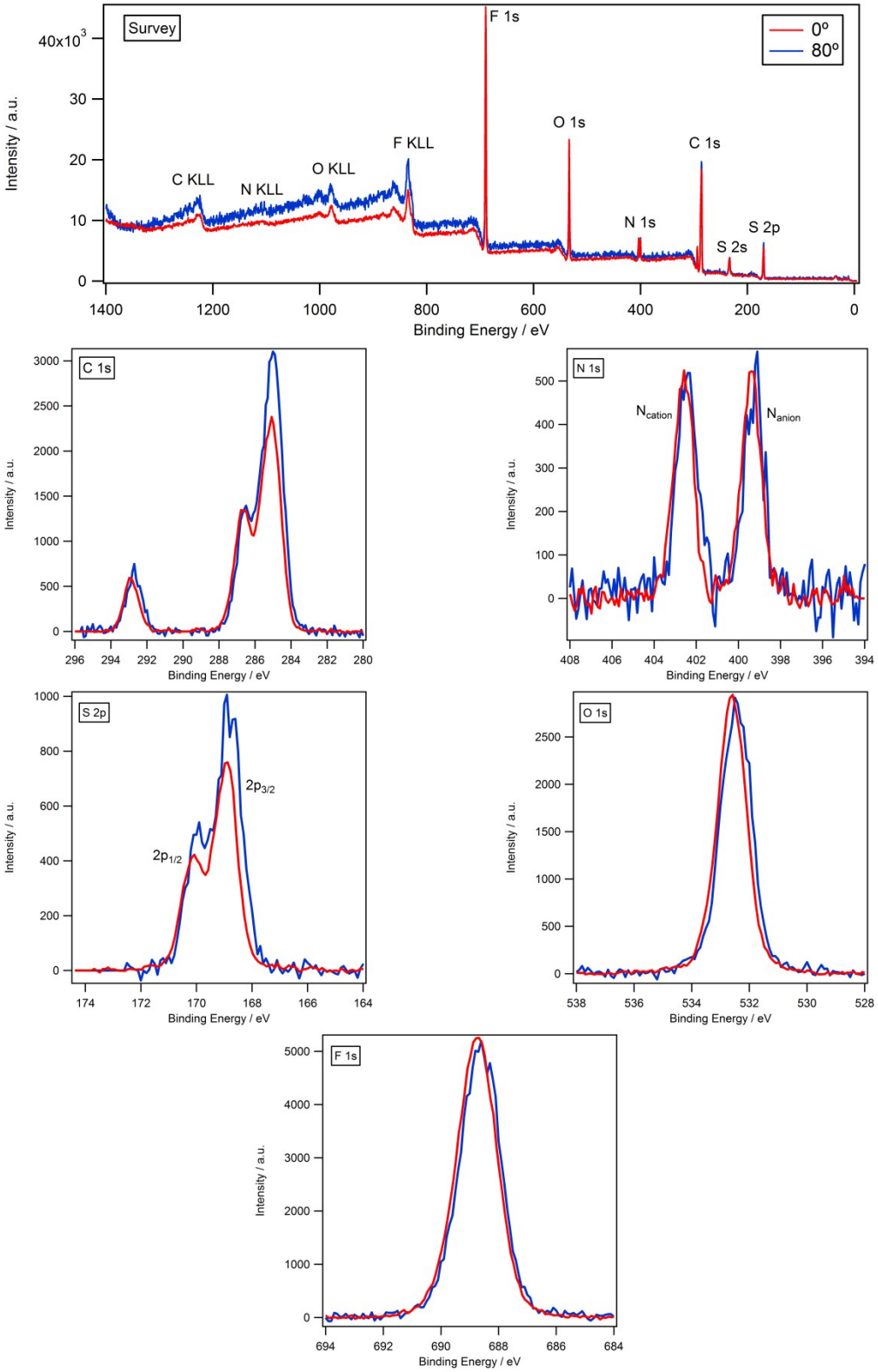


Figure S4. XP spectra for $[N_{4,4,4,1}][NTf_2]$ for both emission angles.

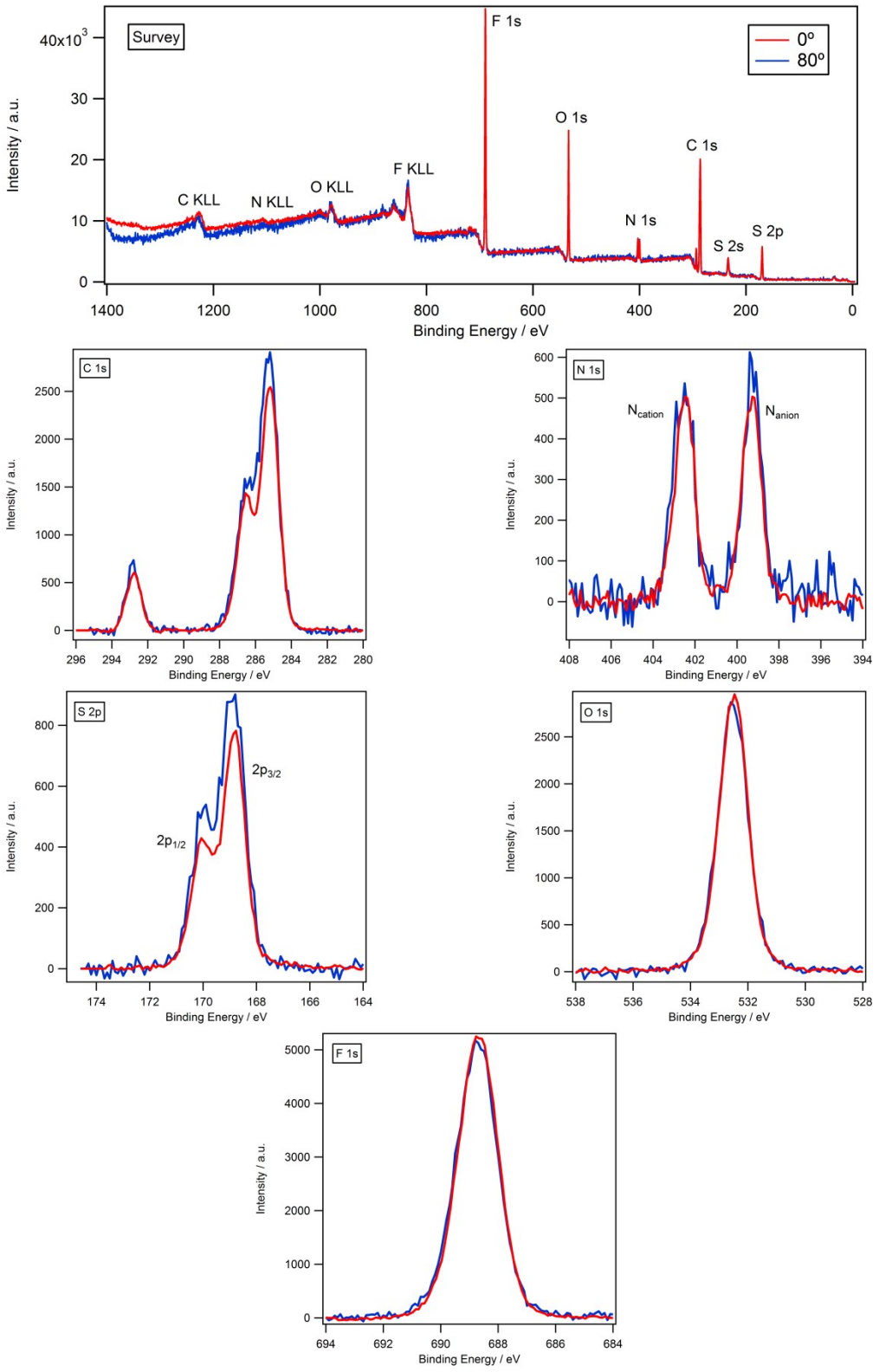


Figure S5. XP spectra for $[P_{4,4,4,1}][NTf_2]$ for both emission angles.

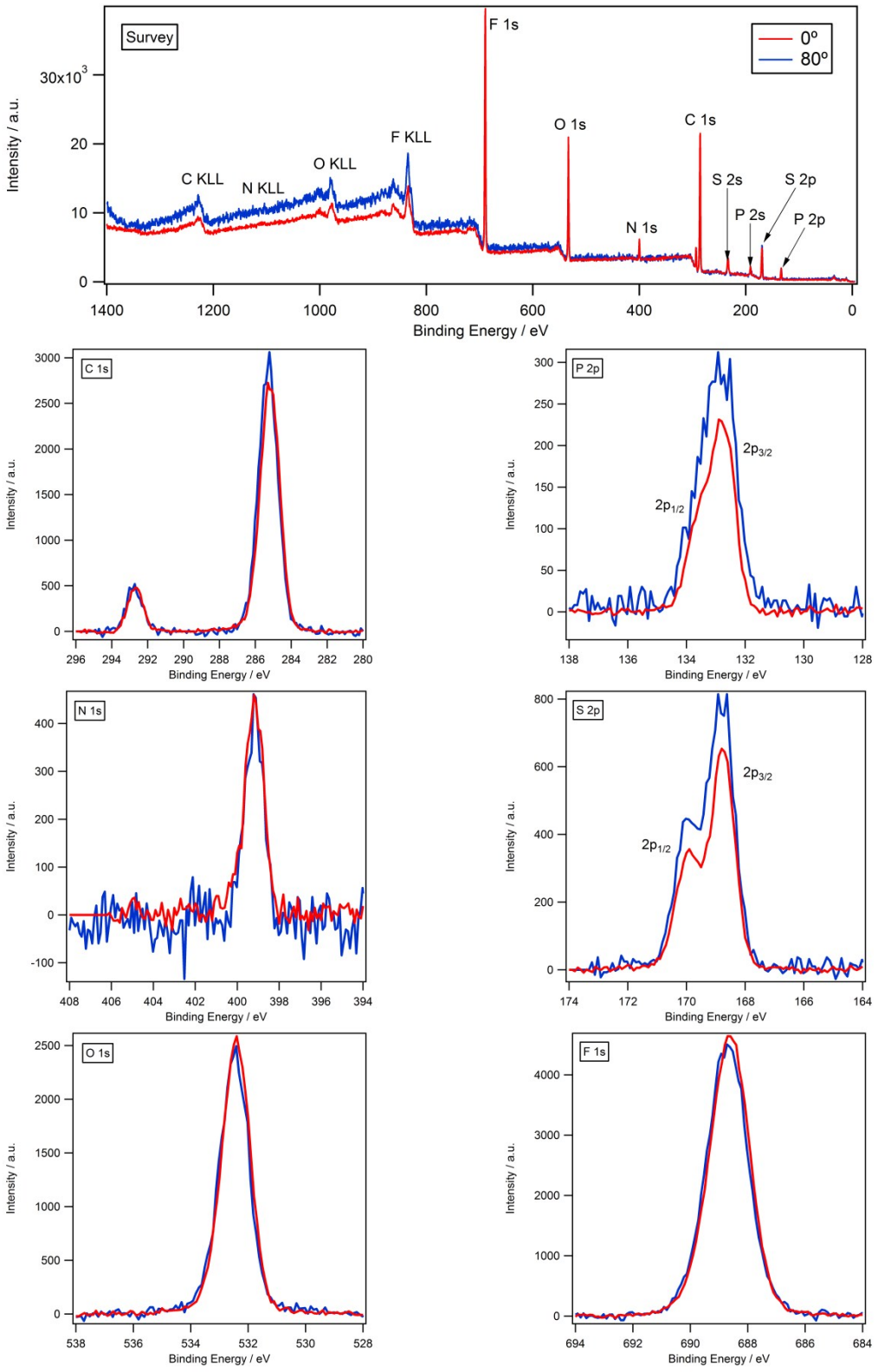


Figure S6. XP spectra for $[N_{6,6,6,14}][NTf_2]$ for both emission angles.

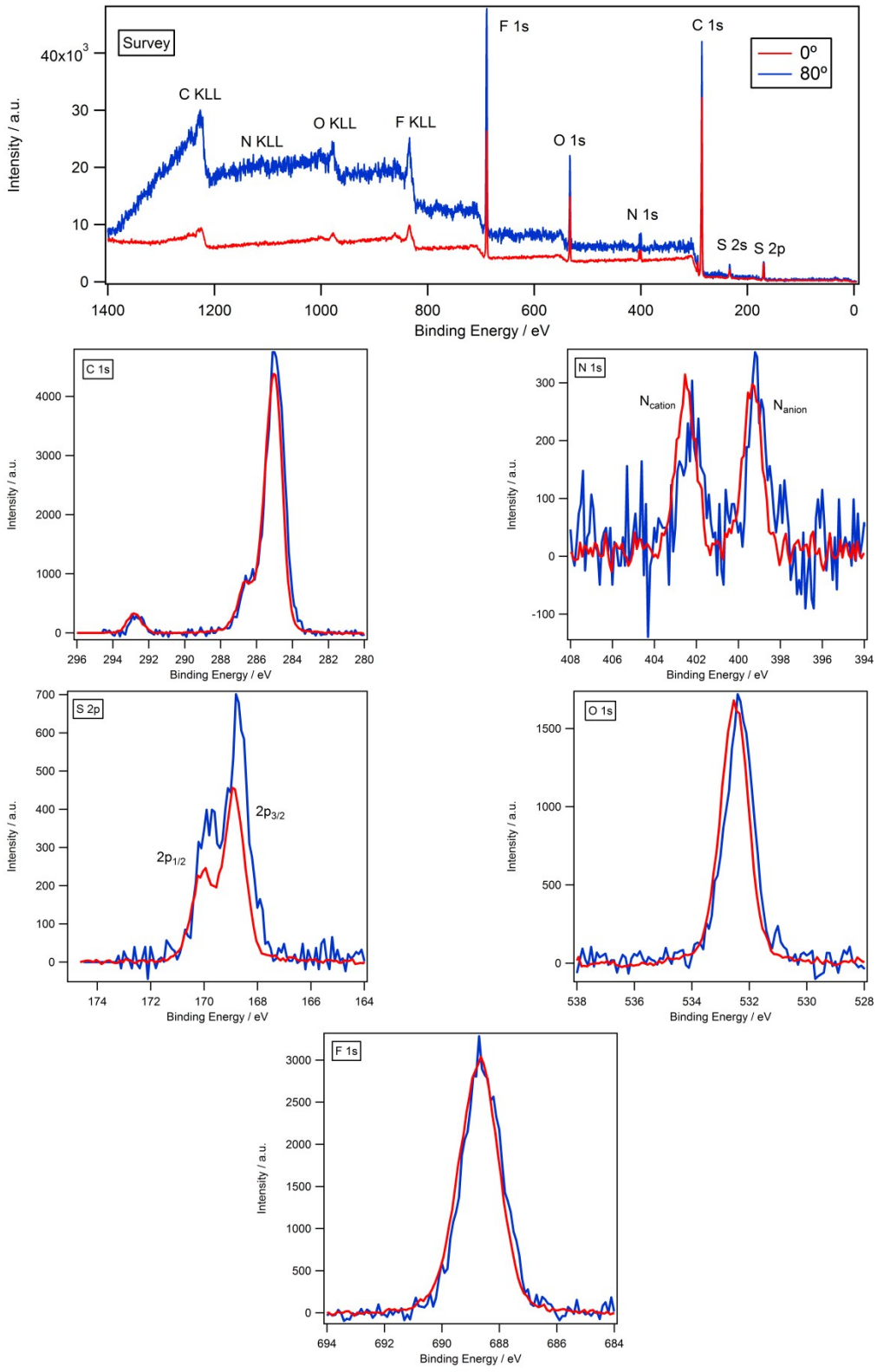
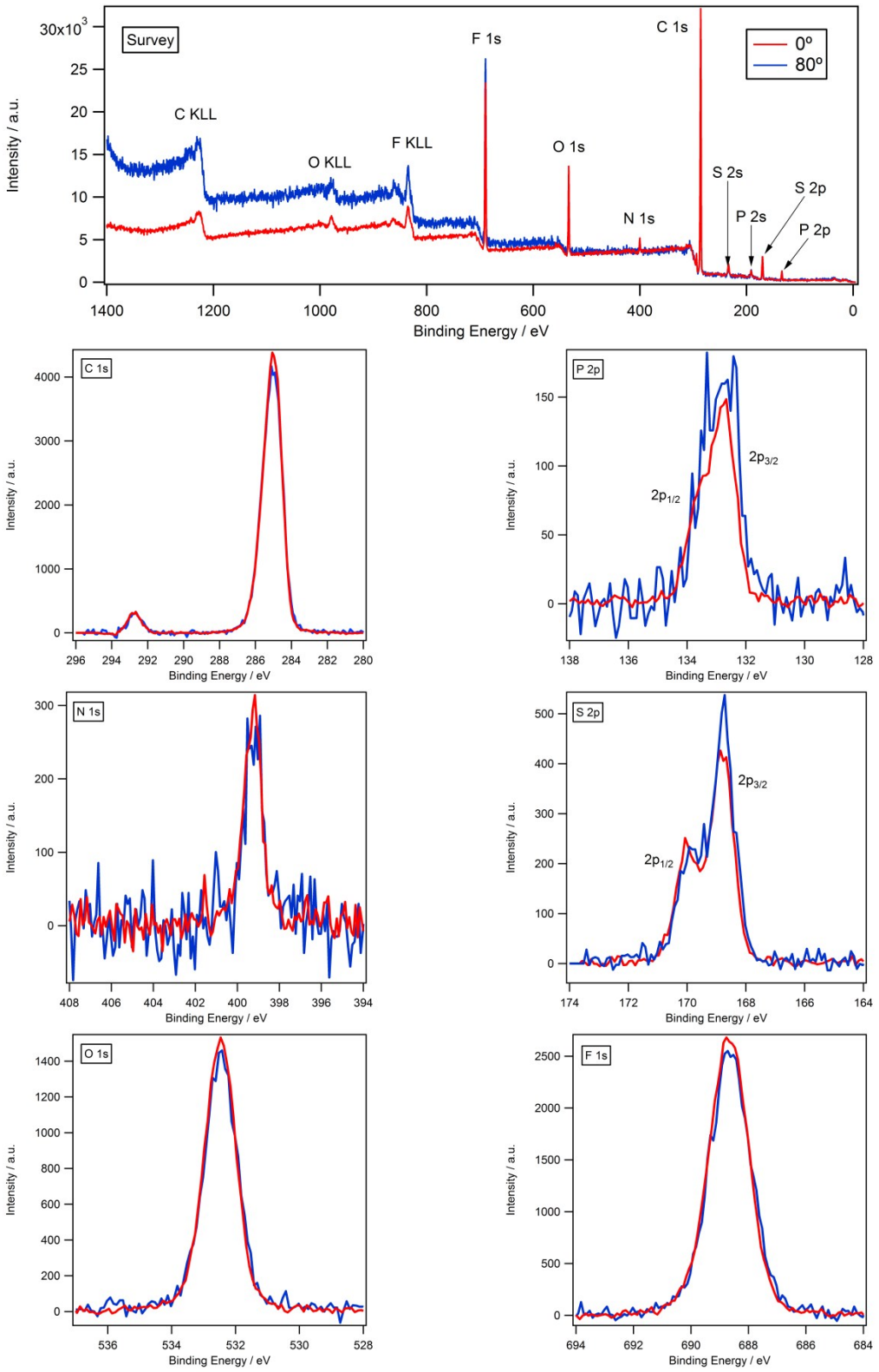


Figure S7. XP spectra for $[P_{6,6,6,14}][NTf_2]$ for both emission angles.



XP Spectra – Ag Lα' x-ray source

Figure S8. $[C_8C_1Pyrr][NTf_2]$ survey and high resolution spectra.

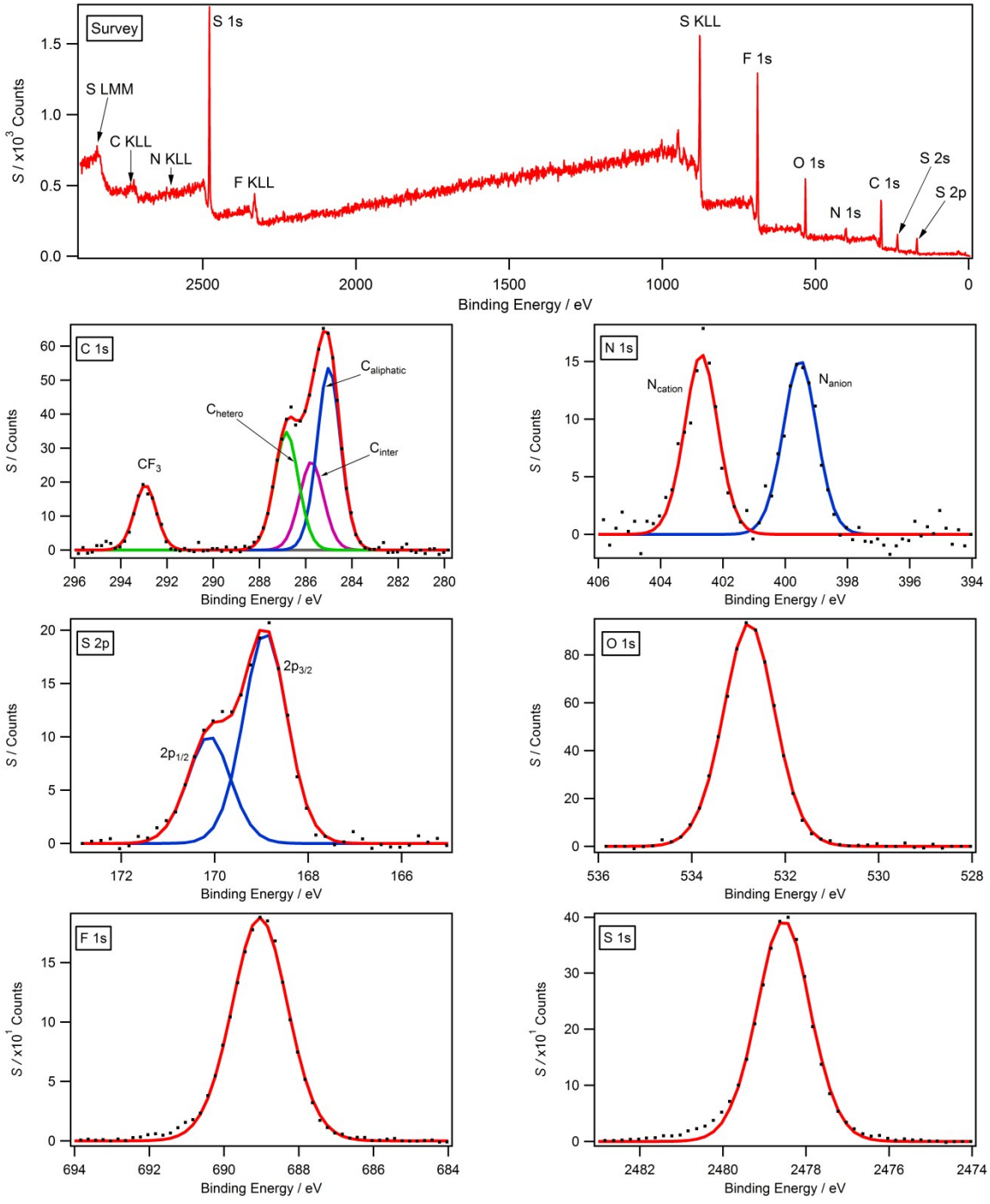


Figure S9. $[N_{4,4,4,1}][NTf_2]$ survey and high resolution spectra.

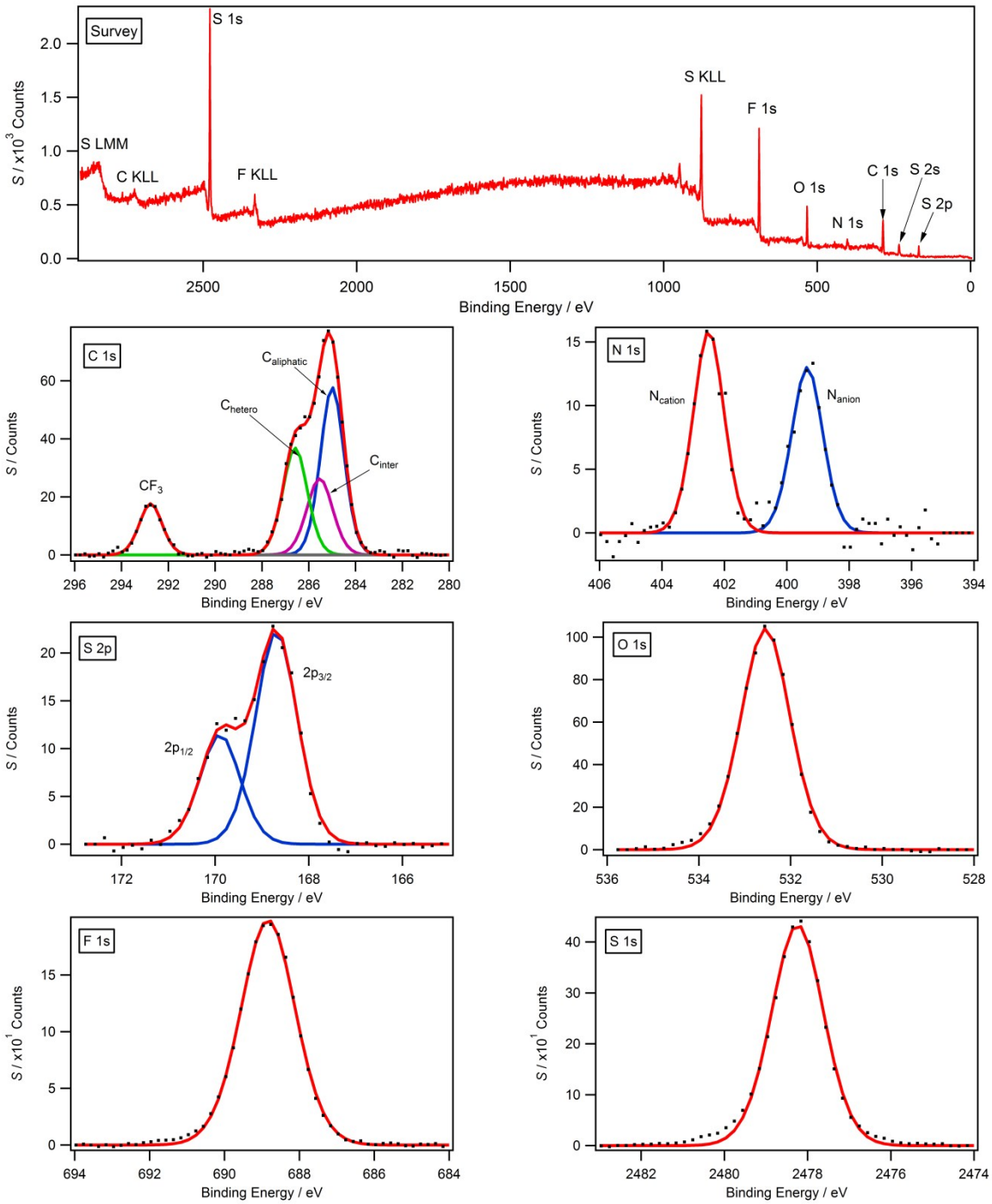


Figure S10. $[P_{4,4,4,1}][NTf_2]$ survey and high resolution spectra.

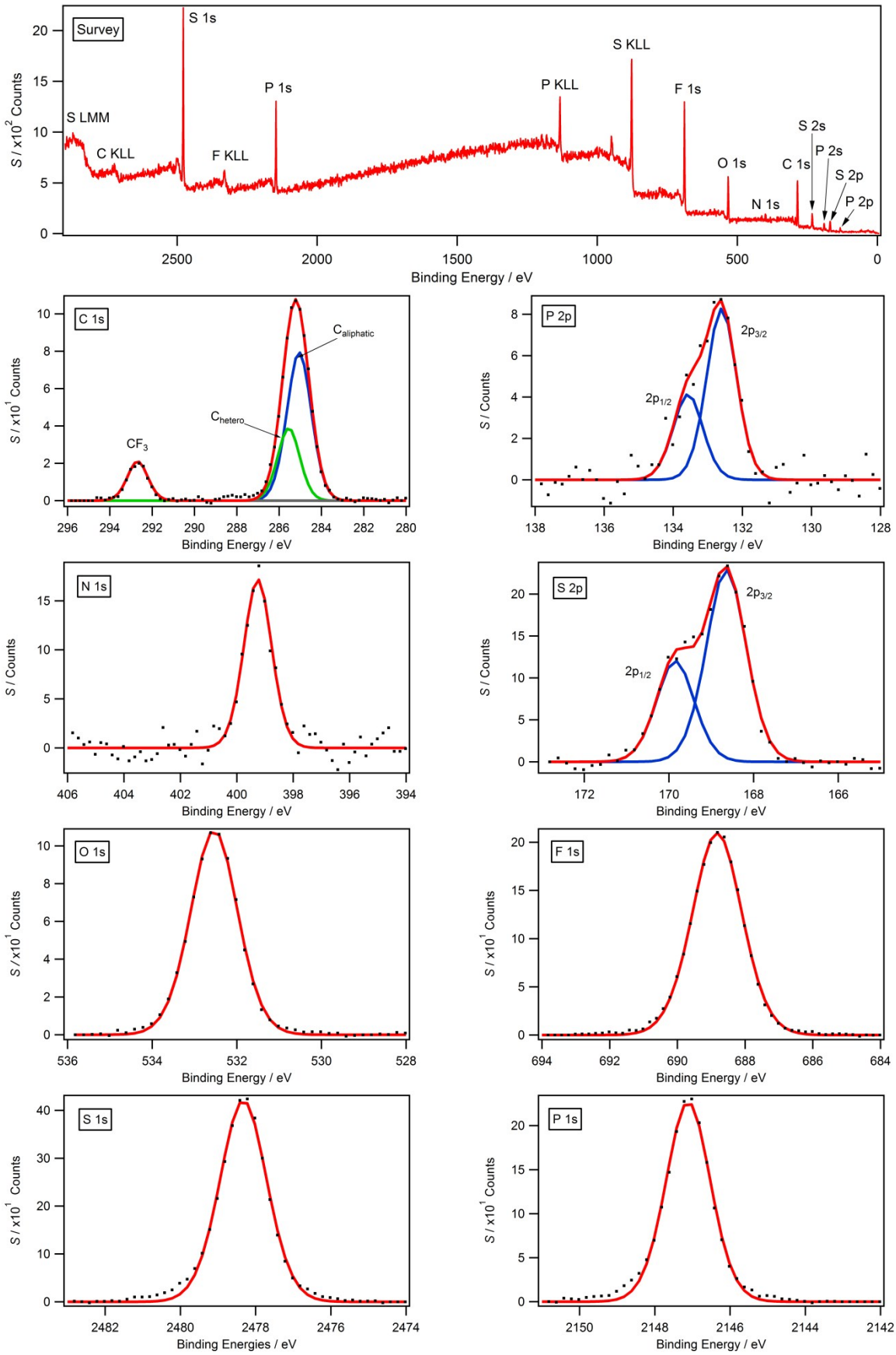


Figure S11. $[N_{6,6,6,14}][NTf_2]$ survey and high resolution spectra.

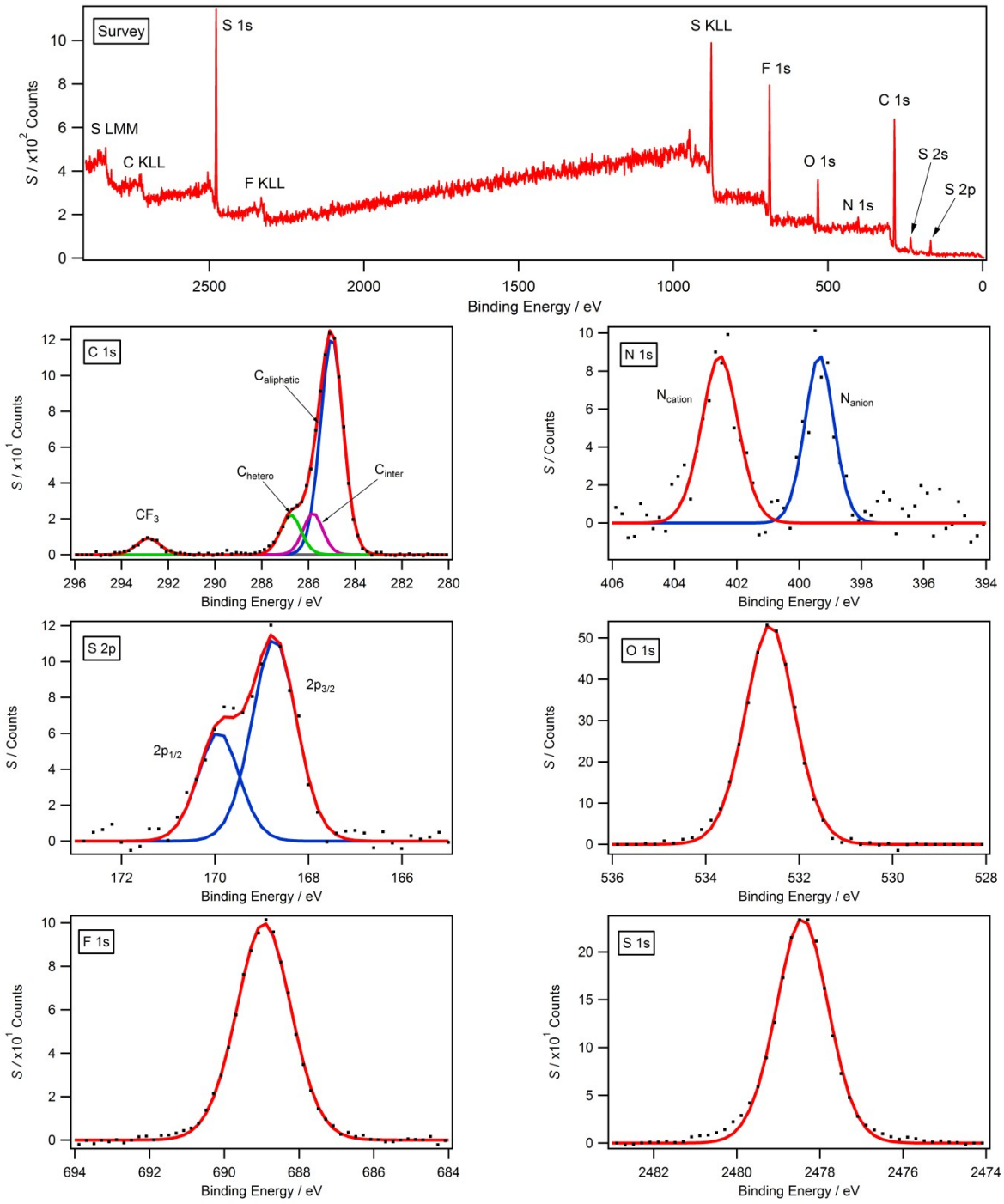
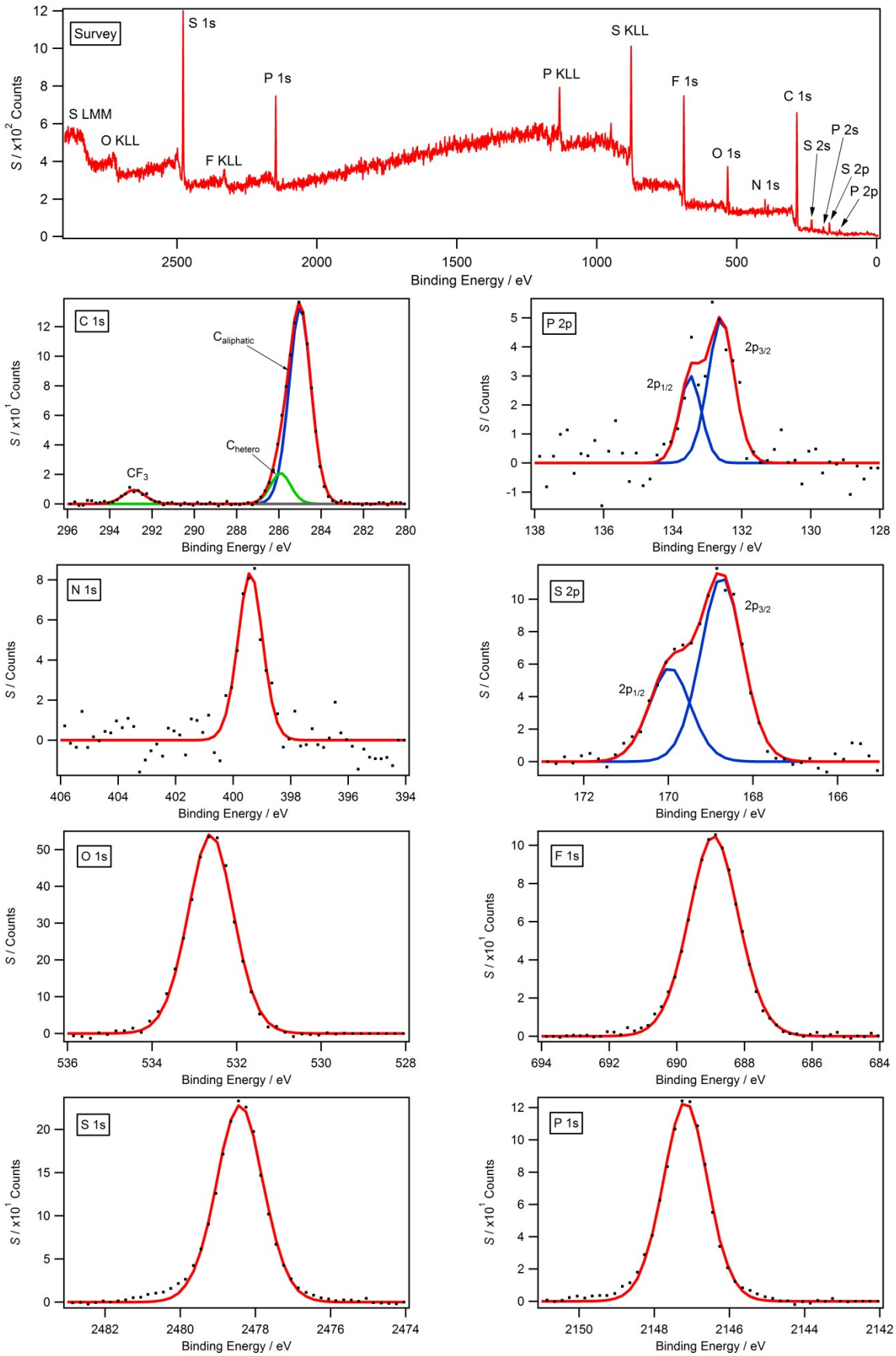


Figure S12. $[P_{6,6,6,14}][NTf_2]$ survey and high resolution spectra.



References

1. R. K. Blundell and P. Licence, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15278 - 15288

2. R. K. Blundell and P. Licence, *Chem. Commun.*, 2014, **50**, 12080 - 12083