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Supporting Information

Proton Transfer on the Edge of the Salt/Co-Crystal Continuum: X-ray Photoelectron Spectroscopy (XPS) of Three Isonicotinamide Salts

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Survey Spectra for the calculation of elemental composition and adventitious carbon

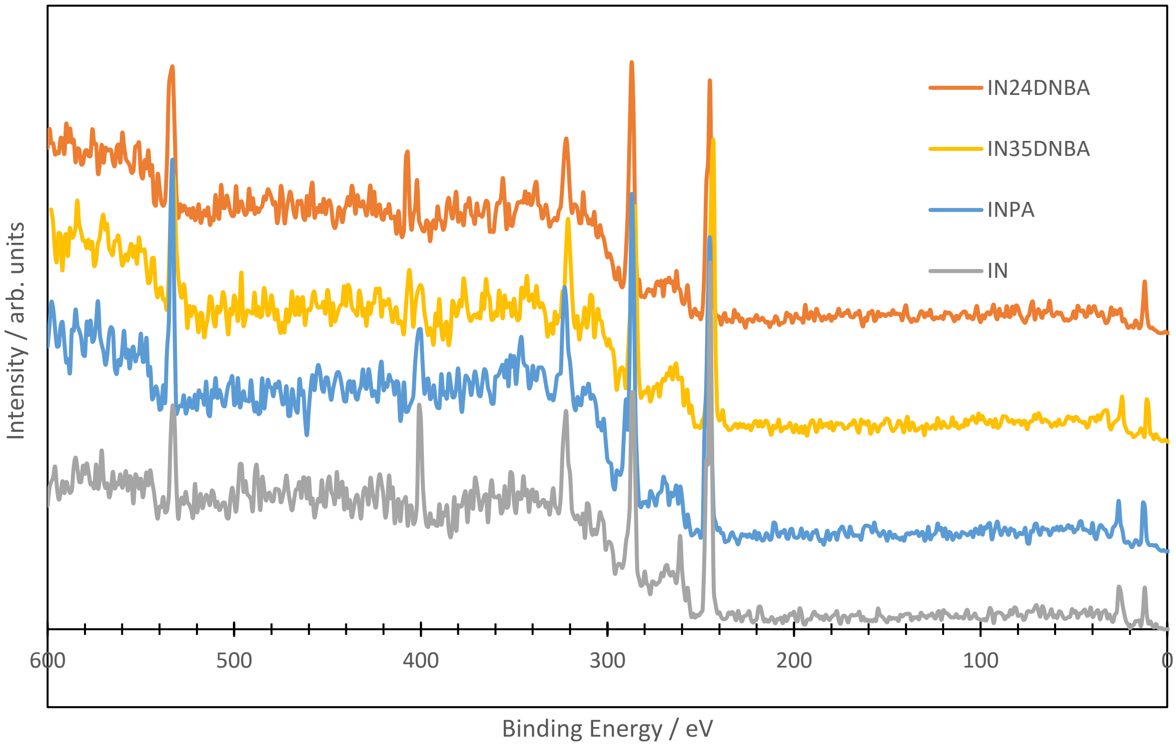

Figure S1: Survey Spectra for the four samples measured using the NAP-XPS instrument.

The four survey spectra shown in Figure S1 show those obtained when measuring the final data used in the paper. The C 1s, N 1s and O 1s emission lines are obviously present at roughly 290 eV, 400 eV and 530 eV as expected. The additional features at 245 eV and 320 eV are due to the Argon 2p and 2s emissions from the Argon in the chamber.

Table S1: Hydrogen bond interaction lengths and angles for the complexes from XRD. [1]

IN24DNBA	N–H / Å	H···O / Å	N···O / Å	N–H···O / °
N–H···O	1.046	1.572	2.600	166.2

IN35DNBA	N–H / Å	H···O / Å	N···O / Å	N–H···O / °
N–H···O	1.084	1.484	2.535	161.4

INPA	N–H/ N···H / Å	H–O/H···O / Å	N···O / Å	N–H···O / °
N–H···O	1.102	1.449	2.550	176.7
N···H–O	1.662	1.042	2.696	179.2

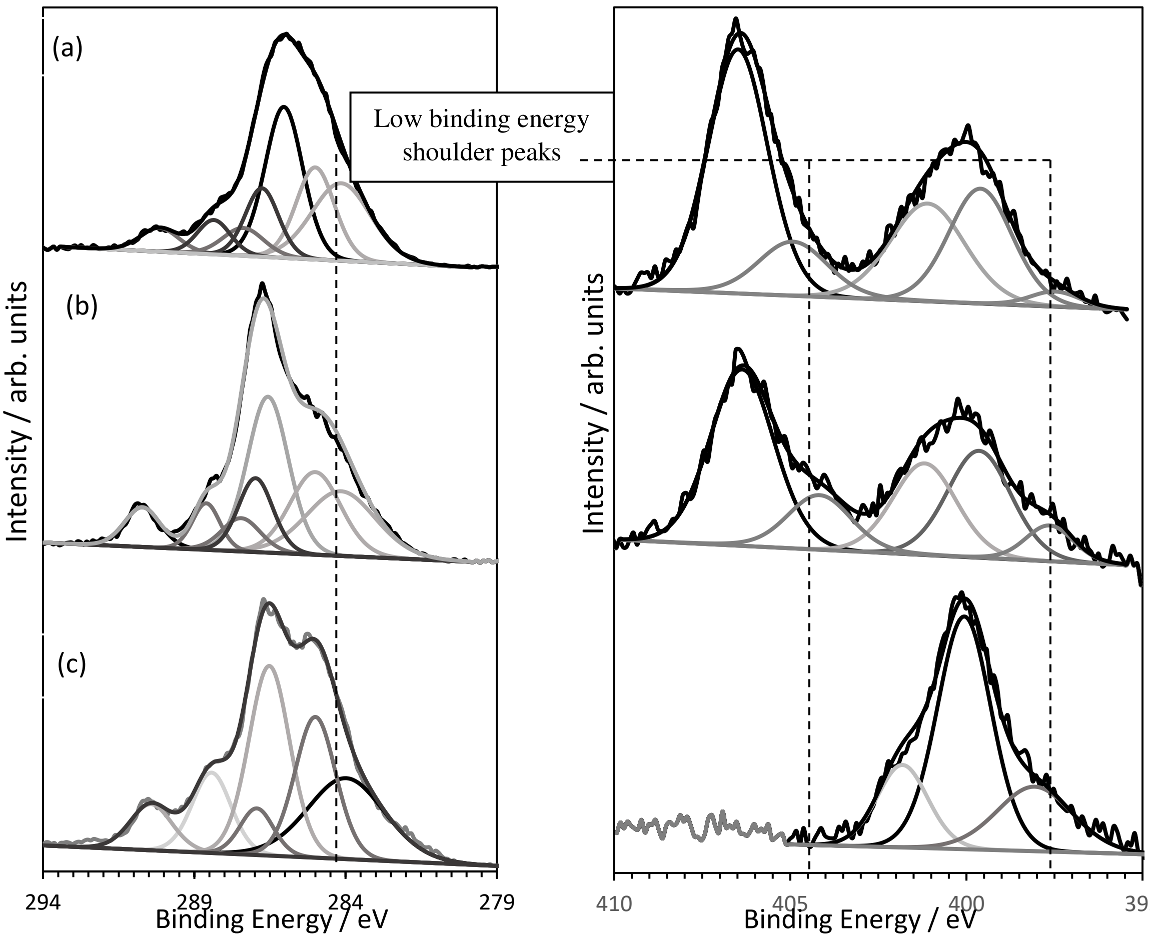

Figure S2: Measurements of (left) C 1s and (right) N 1s emission lines using ultra high vacuum XPS (UHV-XPS) for (a) IN24DNBA, (b) IN35DNBA and (c) INPA. In each case a low binding energy shoulder peak is present due to differential charging.

Initial XPS measurements showing radiation damage and charging effects

Early measurements shown in Figure S2 were taken using a UHV-XPS instrument which under the chosen measurement conditions produced spectra including a low binding energy component often associated with sample charging. Despite these challenges, the conclusions from the N 1s spectra remain the same as for the published data, with the difficulties in binding energy scale calibration and component peak fitting overcome by fitting all of the appropriate charging effects and using the same consistent method of binding energy scale calibration using the adventitious carbon.

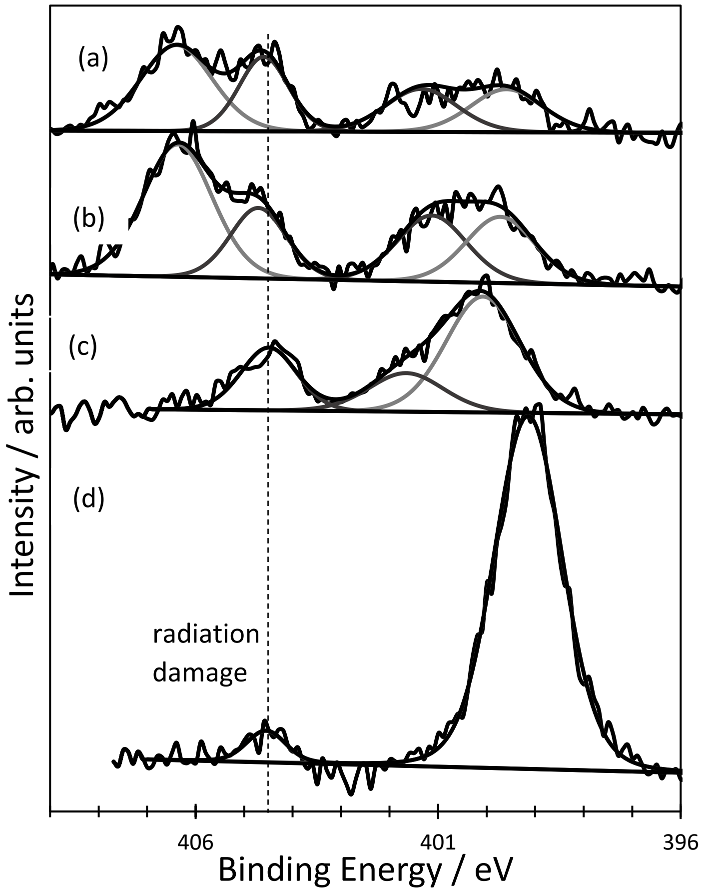

Figure S3: Measurements of N 1s emission lines of (a) IN24DNBA, (b) IN35DNBA, (c) INPA and (d) IN using NAP-XPS with radiation damage peaks identified by dashed line. All remaining peak locations are consistent with final results due to consistent method of binding energy scale calibration.

Figure S3 shows the initial measurements of the four samples using the NAP-XPS instrument, with an additional component evident at ~404.5 eV which is believed to be attributed to radiation damage and an uncontrolled amount of residual air in the analysis chamber. The exact chemical origins of this additional feature are uncertain but could be associated with the formation of azo or azido groups. However, the remaining peaks are unchanged compared to the published data. This implies that the method using XPS works even where spectral features not directly associated with sample chemistry are observed, so long as careful and consistent analysis identifies and accounts for these features, and the same self-consistent method of binding energy scale calibration is carried out.

References

[1] L. K. Saunders, H. Nowell, L. E. Hatcher, H. J. Shespherd, S. J. Teat, D. R. Allan, P. R. Raithby and C. C. Wilson, *Cryst. Eng. Comm.,* vol. 21, no. 35, pp. 5249-5260, 2019.