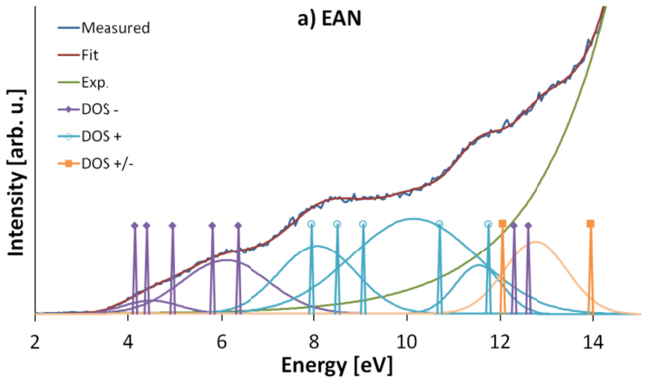
Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

The full-width-half-maximum (FWHM) of the functions used to describe the measured electron spectra are influenced by the line width of the molecular orbital (MO), the resolution of the spectrometer and the distribution of the excitation energy. In case a function represents more than a single MO, the range over which the binding energy of the covered MOs is distributed influences the FWHM as well. The respective functions have to be considered in that case as a sum of individual functions, where each individual functions is owing to a single MO. The FWHM of the final functions, as well as the intensities of the functions, are used as a fitting parameter for fitting the sum of the functions to the measured spectra. The constraints in this fitting procedure were that the relative positions of the functions as well as the FWHM were the same for both MIES and UPS, as neither the energies of the MOs or their FWHM are affected by the excitation technique.

It is important to note that the signal in the measured NICISS profiles can be seen at negative depth; this is due to the finite FWHM of the energy distribution in the backscattering process. A deconvolution procedure can be performed that takes into account the varying FWHM in the backscattering energy as a function of depth [1], but would not reveal any new details in the current study.



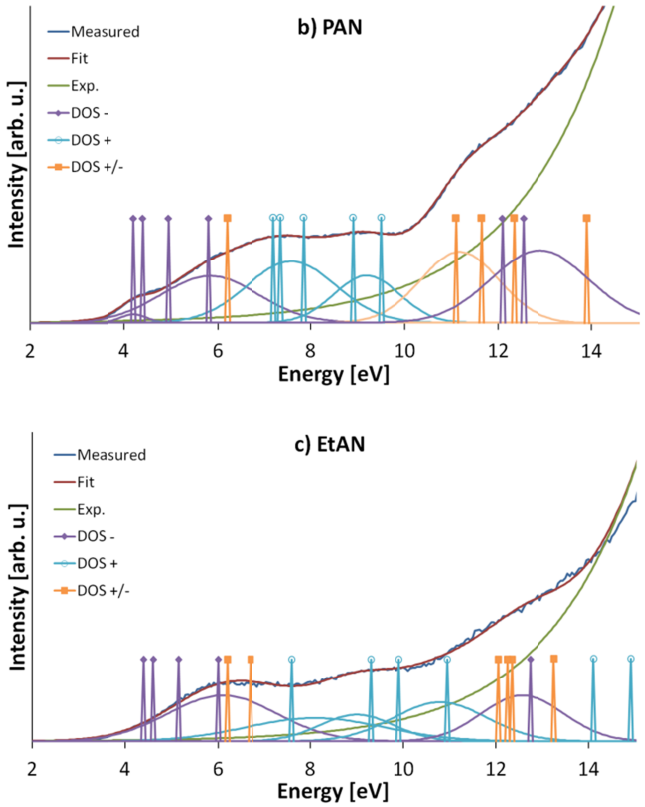


Figure S1 – Measured UP spectra of the three ILs along with the Gaussian functions used for MO fitting

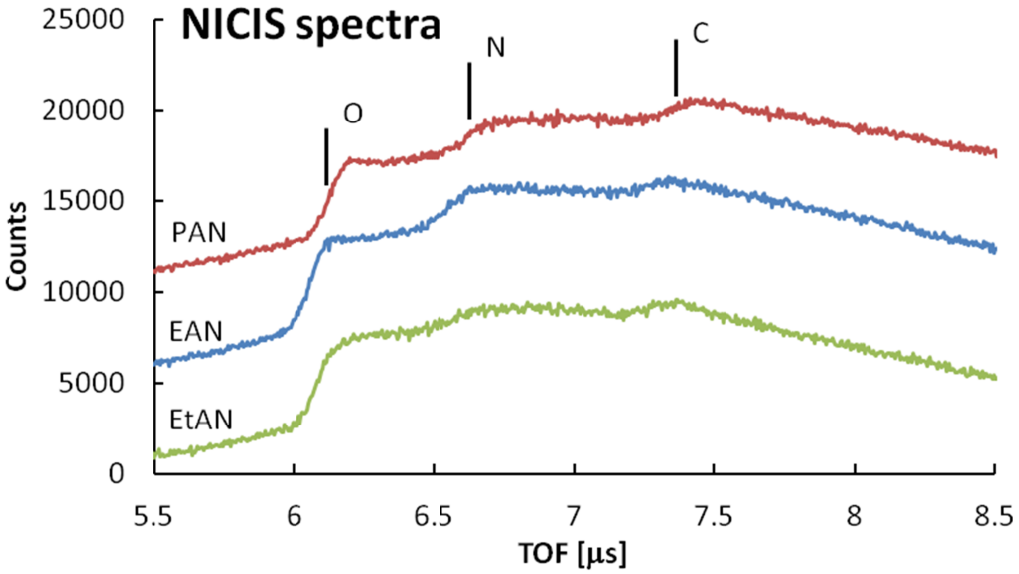


Figure S2 – Measured NICISS spectra of the three ILs investigated, with the onset of each element's step indicated. An offset is applied to the individual spectra for clarity.

1. G. Andersson, *Physical Review A*, 2007, **75**, 032901.