

The impact of sulfur functionalisation on nitrogen-based ionic liquid cations

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It has been demonstrated that bonding and interactions within ionic liquids (ILs) can be elegantly tuned by manipulation of structure and the introduction of functional groups. Here we use XPS to investigate the impact of sulfur containing substituents on the electronic structure of a series N-based cations, all with a common anion, [NTf₂]. The experiments reveal complexity and perturbation of delocalised systems which cannot be easily interpreted by NMR and XPS alone, DFT provides critical insight into bonding and underpins the assignment of spectra and development of deconstruction models for each system studied.

Ionic Liquids (ILs) have the potential to provide a family of uniquely tunable solvents that offer endless opportunity to optimise reaction conditions such that real advantages in terms of selectivity or productivity can be realised.¹ This is clearly a powerful factor that has driven the rapid uptake of ionic liquids in applications spanning catalysis, advanced materials processing, and separation science.^{2,3} On a more fundamental level, the diversity of structural changes that can be realised ensures that ILs can provide a palette of idealised structures that can be deployed to probe subtle variations in ion-ion interactions and consequently solvent-solute interactions.^{4,5}

Over the past 10 years we have systematically applied X-ray photoelectron spectroscopy (XPS) to probe IL based systems, particularly focusing on the impacts of structural variation on the electronic environment within the liquid. We have developed a range of deconstruction models that allows information about each atom in a polyatomic charge carrier group, *i.e.* imidazolium, pyridinium, or pyrrolidinium, to be extracted and their relative experimental charge densities compared with those predicted by calculation, or indeed derived from other experimental probes including nuclear magnetic resonance (NMR) experiments.⁶⁻⁸ We recently reported XPS data for a range of functionalised guanidinium based systems,⁹ the measured

binding energies (BEs) for the N_{cation} 1s component in guanidinium ILs showed a large shift to lower values when compared to other families of ILs. These results suggest a weaker anion/cation interaction which could impact upon the ability of anions to interact with solutes or indeed boost the potency of disruption towards hydrogen bonded systems hence promoting dissolution. In a similar vein, Cremer *et al.* observed a notable shift in the ¹³C NMR signal assigned to the C₂ component of more simple imidazolium-based ILs. However, Cremer noted no significant differences in the C_{hetero} environments of their non-monochromatised XPS. Furthermore, this structural disruption, of the ability to form hydrogen bonds to the C₂ position, was accompanied by a modest shift in N_{cation} BE to lower energy.¹⁰ When placed in the context of our results on more complex nitrogen containing cations, this observation suggests that structural complexity and functionalisation in the cation, may also be used to manipulate anion/cation interactions and hence the solvation properties of the ionic liquid itself, a property which is largely dominated by the influence of the anion.

To explore this assumption, we replaced one of the nitrogen atoms in the guanidinium moiety with sulfur, the resulting thiourea is abundant in nature, biodegradable and used widely in organocatalysis.¹¹⁻¹³ When compared to nitrogen, sulfur is larger and softer, consequently we might anticipate a significant difference in bonding which should be evident in measured BEs. Substitution of the C_{core} position (C_{core} = analogous to imidazole C₂) of the imidazole, thiazole and thiazoline structures with sulfur was carried out (**Fig 1. ILs 5, 6 and 7** respectively) and relevant comparisons made.

XP spectra were recorded using a Kratos Axis Ultra Spectrometer employing a monochromated Al K_α source (1486.6 eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD). Samples were prepared by placing a small amount (≈ 10 mg) of IL onto a stainless steel or gold-coated stub. All samples were pre-pumped in a preparative chamber to pressures lower than 10⁻⁶ mbar before transfer into the main analytical chamber to ensure removal of any volatile material. Charge referencing was achieved post-data collection by setting the F 1s component to 688.8 eV, a full description of this procedure has been described elsewhere.⁸

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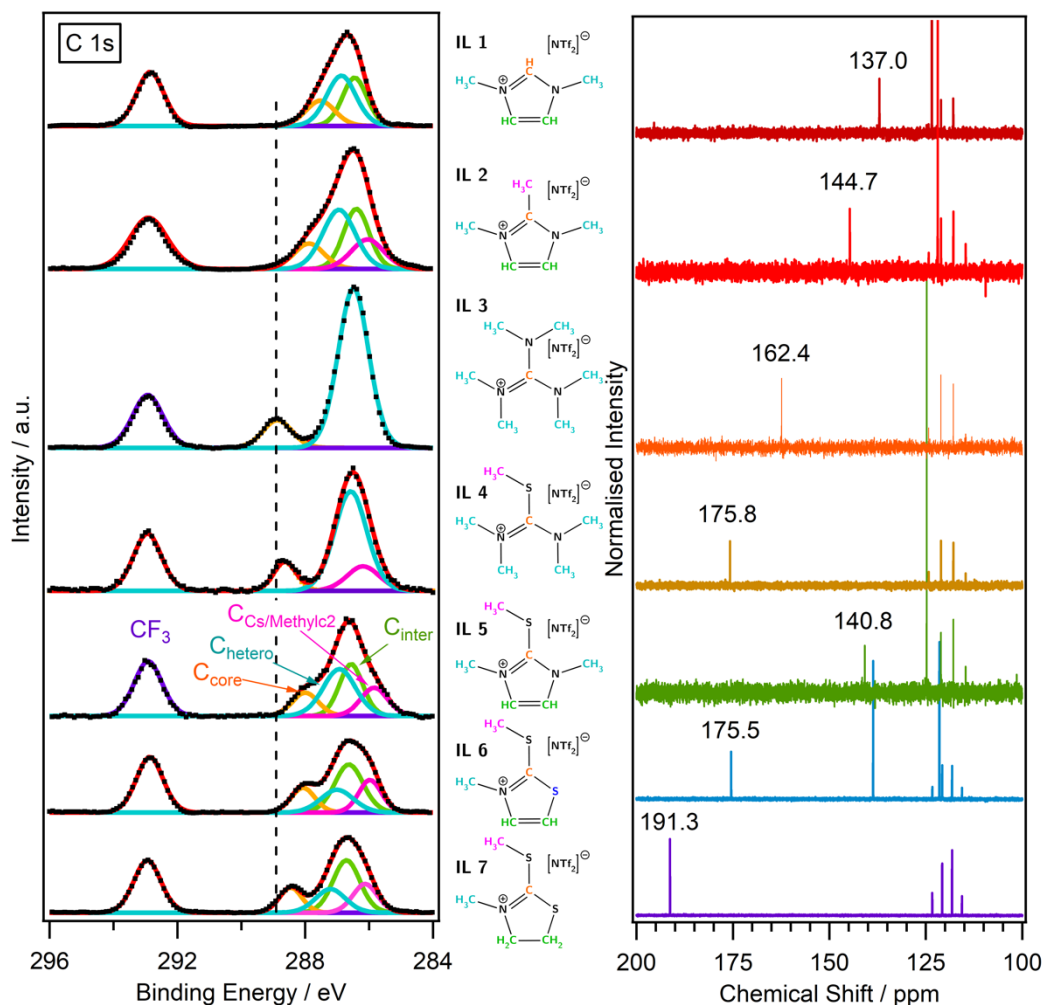


Fig. 1 C 1s XP spectra (left) of all ILs studied. Intensities are normalised to the anion-based C_{CF_3} 1s peak of **IL 4**. XP spectra were charge corrected by referencing the F 1s photoemission peak to 688.8 eV. ^{13}C NMR (right) are compared (signals originating from the $[NTf_2]^-$ ion lay between 125–114 ppm). The chemical ppm values at C_{core} are highlighted and spectra truncated between 200–100 ppm. Full spectra available on the ESI[†].

ILs investigated were prepared using established synthetic methods^{14–16} all 1H (400 MHz), ^{13}C (100 MHz) and ^{19}F (376 MHz) NMR spectra were recorded at room temperature on a Bruker AV3-400HD. Density functional theory (DFT) simulations of NMR and core ionization properties were calculated using the Q-Chem software package. Structures were optimised at the PBE0/6-31+G(d) level of theory and properties calculated at the PBE0/IGLO-II level with an implicit solvent model. Further details are available in the ESI[†].

To provide a better understanding on the specific interactions within structurally-related ILs, we present here XPS and NMR analysis to study the core carbon environment. All ILs incorporating these structural changes were synthesised in high purity in our laboratory (for experimental procedures, see ESI[†]), *i.e.* the alkyl imidazolium (**IL 1**) and (**IL 2**), the guanidinium (**IL 3**) along with its acyclic analogue, thiuronium cation (**IL 4**), and finally the cyclic ILs with thioimidazolium (**IL 5**), thiazolium (**IL 6**) and thiazolinium (**IL 7**) moieties. As the cations investigated in this study did not contain long alkyl substituents (eight carbons or more), charge referencing was accomplished by setting the measured F 1s photoemission peak associated with the $[NTf_2]^-$ equal to 688.8 eV. ^{13}C NMR analyses were

performed in $DMSO-d_6$, which has been demonstrated to provide robust chemical shift data that is directly comparable to that recorded in solvent-free (liquid) and solid state spectra,¹⁷ a reliable internal reference was provided by the CF_3 group of the anion, $[NTf_2]^-$.

The analysis of the C 1s photoemission can reveal interesting information on the C_{core} electronic environment (**Fig. 1** left). Upon close inspection, the C_{core} of the guanidinium (**IL 3**) and thiuronium (**IL 4**) have BEs of 288.9 eV and 288.6 eV respectively, (see **Table 3** in ESI[†]). This shift to lower BE can be attributed to expected differences in the size and charge density of the sulfur in **IL 4**, and the nitrogen in **IL 3**, leading to a more electron rich C_{core} in **IL 4** (288.6 eV) and a more electron deficient C_{core} environment in **IL 3** (288.9 eV). Interestingly, the findings for C_{core} chemical shifts on the ^{13}C NMR spectra (**Fig. 1** right) do not directly correlate to the XPS measurements, which suggest increased shielding in the guanidinium system (**IL 3**) compared to the thiuronium (**IL 4**), with measured δ values of 162.4 and 175.8 ppm respectively.

Turning to the cyclic thioimidazolium (**IL 5**), which is a hybrid structure which includes structural motifs drawn from both the thiuronium (**IL 4**) and the methylated imidazolium (**IL 2**), from

inspection of the relevant XP and NMR data, it is clear that the situation is quite different. ^{13}C NMR analysis shows only a small variation for C_{core} chemical shifts in **IL 2** and **IL 5** (i.e. 144.7 and 140.8 ppm, respectively), while the BE values for C_{core} in **IL 2** and **IL 5** are 287.9 and 288.0 eV respectively. Interestingly, Cremer *et al.*,¹⁰ reported that the methylated imidazolium cation (**IL 2**) does not exhibit a similar high BE shift when compared to its imidazolium counterpart (287.6 eV for **IL 1**) as seen for the ^{13}C NMR chemical shift. However, the BEs presented in this work provide further evidence that the methylation in **IL 2** has the same effect on the imidazolium ring as the sulfur atom in **IL 5**. Upon comparison of the thioimidazolium (**IL 5**) with thiouronium (**IL 4**), a striking chemical shift of 35 ppm to higher fields on the ^{13}C NMR spectra is noticed, whilst just a 0.6 eV difference to lower BEs for C_{core} is observed in the high-resolution spectra for **IL 5** (288.0 eV) and **IL 4** (288.6 eV). Although the difference in BEs is clearly less pronounced than the difference in ^{13}C NMR chemical shifts, these findings support the assumption that C_{core} on the thioimidazolium (**IL 5**) has a more electron rich environment than the C_{core} on the thiouronium cation (**IL 4**). This may be a reflection of the extra electron enrichment coming from electrons that are delocalised throughout the ring. For that reason, it is not surprising that the C_{core} position on the thioimidazolium (**IL 5**) has a similar ^{13}C NMR chemical shift and BE when compared to the methylated imidazolium counterpart (**IL 2**). These observations provide interesting insight into the impact that modest structural variation can impact upon the electronic structure and bonding in cyclic/acyclic IIs.

The impact of inserting sulphur directly into the cyclic cation was also investigated. Thus, the XPS binding energies for the C_{core} in the thioimidazolium (**IL 5**), its thiazolium counterpart (**IL 6**), and the non-aromatic thiazolinium (**IL 7**), were measured and observed at, 288.0, 288.1 and 288.4 eV, respectively. It is noteworthy that **IL 7** bears a positive charge localised on the S- C_{core} -N bonds, while **IL 5** and **IL 6** are both aromatic compounds, resulting in a more electron deficient C_{core} environment. When compared to the thioimidazolium (**IL 5**), a shift downfield on the ^{13}C NMR spectra was observed for both the thiazolium (**IL 6**) and thiazolinium (**IL 7**). Although the shift in NMR signals follows the same trend in XPS (towards higher BEs), it is more pronounced in the ^{13}C NMR spectra, suggesting that this phenomenon cannot be solely explained by aromaticity effects.¹⁰ Another interesting region to consider in this analysis is the S 2p photoemission envelope, **Fig. 2**. Although the S 2p peak for the $S_{\text{cation exocyclic}}$ in **IL 5** (164.8 eV), **IL 6** (164.9 eV), and the equivalent S atoms present in **IL 7** (165.1 eV), have roughly the same electronic environment, the BE for the $S_{\text{cation cyclic}}$ in **IL 6** is observed at a slightly higher BE (165.9 eV). As a general comment, it can be concluded that the sulfur atom positioned within the heterocycle ($S_{\text{cation cyclic}}$) is observed to be more electron deficient when compared to exocyclic sulfur containing substituents ($S_{\text{cation exocyclic}}$) this is also reflected in similarly attenuated binding energies for C_{core} in thiazolium (**IL 6**) and thiazolinium cation (**IL 7**). These experimental trends again support the thesis that the electronic environment of the relative C_{core} components in methylated imidazolium-based systems is very similar to thio-methylated analogues, although it is recognised that solvent solute interactions of these materials, particularly with respect to active co-ordination chemistry associated with the S- CH_3 functionality, could well be very much different.

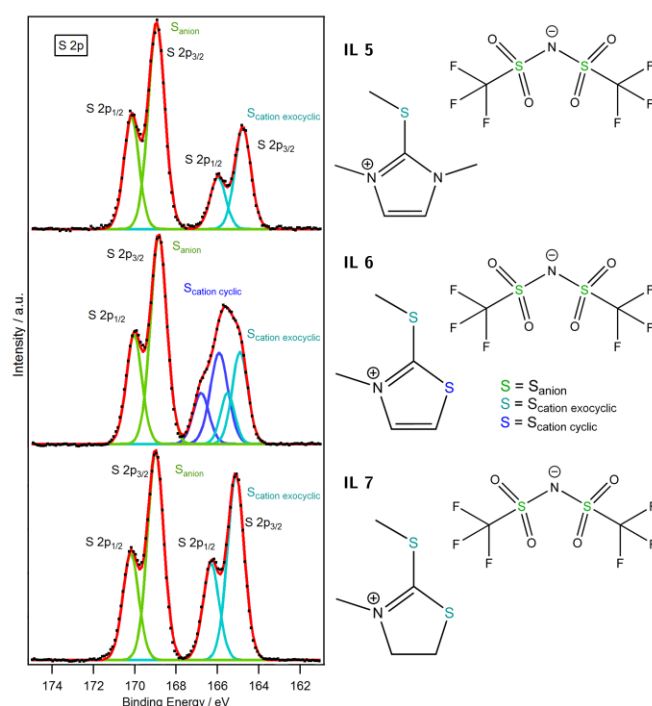


Fig. 2 High-resolution XP spectra of the S 2p region with component fittings for **IL 5**, **IL 6** and **IL 7**. All XP spectra charge corrected to F 1s = 688.8 eV. Intensities are normalised to the S_{anion} 2p photoemission peak for **IL 5**.

Analysis of the C 1s and S 2p photoemission envelopes reveal significant perturbation of the electronic structure within the cation itself, we now investigate the impact that this can have on interactions with the anion which can be probed by considering shifts in the N_{cation} 1s photoemission. The N_{cation} 1s BEs of all IIs investigated are presented in **Table 3** (see ESI[†]), the data demonstrates an opposing trend to that observed for the respective C_{core} 1s contributions. This observation suggests that charge transfer between cation and anion is weakened, especially in the case of the guanidinium core, as a result of its increased delocalisation. The N 1s peak of the thiouronium cation has a higher BE, 401.1 eV, when compared to the guanidinium, 400.8 eV. This could suggest that the delocalisation on the guanidinium system is indeed more effective and the presence of the extra nitrogen provides a more electron rich environment around these three equivalent atoms. The suggestion that the orbital of the sulfur disrupts somewhat the delocalisation on this structure is also consistent with this result. It should reflect the loss of a pair of electrons from the extra nitrogen and therefore the two nitrogen atoms on the thiouronium cation are in a more electron poor environment than the three nitrogen atoms in the guanidinium cation. In contrast, the N 1s peak of the thioimidazolium cation displays a higher BE, 402.0 eV, and when compared to its imidazolium counterparts, no noticeable difference is observed (402.1 eV for **IL 1** and 401.8 eV for **IL 2**). Nevertheless, when compared to the thiouronium, a significant shift of 0.9 eV on the N_{cation} can be noted to higher BEs for the thioimidazolium cation. This shift suggests that the nitrogen atoms are in a more electron poor environment, which leads us to assume that although more electrons are present in the ring structure, the electrons are delocalised throughout the five elements of the ring. For the thiouronium cation,

however, as a result of the poor orbital overlap of the sulfur with C_{core} and conformational restraints, the electrons would only delocalise around three elements of the cation, $N-C_{\text{core}}-S$. This would then result in a more electron rich $N_{\text{cation}} 1s$ environment and therefore a shift to lower BE.

Table 1 XPS binding energies (BE), ^{13}C NMR chemical shifts (δ) and DFT calculations for the C_{core} for guanidinium, sulfur and imidazolium based ILs studied in this work.

XPS, ^{13}C NMR and DFT calculations for C_{core}				
Compound	XPS (eV)	CEBE – DFT (eV)	^{13}C NMR (ppm)	^{13}C NMR – DFT (ppm)
IL 1 [$C_1C_1\text{Im}$][NTf ₂]	287.6	290.27	137.0	143.93
IL 2 [$C_1C_1C_1\text{Im}$][NTf ₂]	287.9	290.48	144.7	144.53
IL 3 [(C_1C_1) ₂ dmg][NTf ₂]	288.9	291.52	162.4	169.83
IL 4 [(C_1) ₅ TU][NTf ₂]	288.6	291.45	175.8	181.11
IL 5 [$C_1(C_1)_2\text{ThioIm}$][NTf ₂]	288.0	290.78	140.8	138.59
IL 6 [(C_1) ₂ Thio][NTf ₂]	288.1	290.97	175.5	176.24
IL 7 [(C_1) ₂ Thiz][NTf ₂]	288.4	291.33	191.3	204.79

The DFT calculations of both the BEs and ^{13}C NMR shifts in **Table 1**, are in good agreement with the experimental data, and predict the same trends in variation between the experimental techniques. In particular, the calculations confirm that the C_{core} for the guanidinium cation displays the higher BE, and that the thiazolinium cation shows the higher chemical shift toward lower field.

These data show that ^{13}C NMR is more sensitive than XPS to functionalisation at the cation core. Structural changes seem to have a clear impact upon the C_{core} chemical shift, whereas by XPS this effect is less apparent, and in some cases within the experimental error. Although there seems to be an apparent correlation between the C_{core} 1s BE and ^{13}C NMR C_{core} shifts for most ILs studied in this work, however in the case of acyclic ILs this relationship is not observed. Consequently, there seems to be a notable impact upon the ^{13}C NMR of C_{core} upon functionalisation, which could be used to probe specific interactions within ILs, potentially informing the choice of IL for a specific application. It is noted that the correlation appears to be structure dependent suggesting that additional effects also influence the measurement of data. Most significantly the role of solvents and variation in solvent-solute interactions which could induce a more pronounced perturbation in solution based techniques including NMR. Interestingly, a similar series of observations that display a similar effect have been attributed to additive contributions of substituents in α , β , γ and δ positions.^{18, 19} As such, ^{13}C NMR does not seem to provide a reliable indicator of nuances within the chemistry of these materials; ^1H NMR, however, is much less influenced by these effects and provides a better description of the chemical environment. Furthermore, NMR is undeniably a bulk sensitive analytical tool whereas XPS is often thought of as a surface sensitive technique, under normal operation conditions, the XPS information depth in a typical IL experiment is of the order 7–9 nm, which corresponds to multiple molecules in thickness; pseudo-bulk in nature. Of course, application of angle resolved XPS (AR-XPS), particularly at extended grazing angles can provide much more surface specific data, which may exhibit differences to that observed in the bulk. However in the case of powdered solid samples, the sample is presented to the incident X-ray as an ensemble of small particles with no preferred orientation

or significant longer range order, as a result AR-XPS data will simply be an average of many aggregates and will hence also be reflective of the bulk. In the work presented here, we have demonstrated the complementary nature of XPS and ^{13}C NMR, we also demonstrate how computational methods can provide critical insight that allows the full interpretation of complex experimental datasets. XPS data of functionalised ILs provides new significant insight into bonding and electronic structure that may not be anticipated, or observed in NMR based techniques alone. These data highlight subtle differences in the electronic structure and behaviour of cyclic versus acyclic ILs which could provide an additional factor to underpin future IL selection.

Conflicts of interest

There are no conflicts to declare.

Notes and references

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