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NEXAFS spectroscopy of ionic liquids: experiments versus calculations

Richard M. Fogarty,[1] Richard P. Matthews,[1] Matthew T. Clough,[1] Claire R. Ashworth,[1] Agnieszka Brandt,[2] Paul J. Corbett,[2] Robert G. Palgrave,[3] Richard A. Bourne,[4,5] Thomas W. Chamberlain,[5] Tom Vander Hoogerstraete,[6] Paul B. J. Thompson,[7] Patricia A. Hunt,[1] Nicholas A. Besley,[8] Kevin R. J. Lovelock.*[9]

[1] Department of Chemistry, Imperial College London, UK
[2] Department of Chemical Engineering, Imperial College London, UK
[3] Department of Chemistry, University College London, UK
[4] School of Chemical and Process Engineering, University of Leeds, UK
[5] Institute of Process Research and Development, School of Chemistry, University of Leeds, UK
[6] Department of Chemistry, KU Leuven, Belgium
[7] XMaS, UK CRG, ESRF, France, and Department of Physics, University of Liverpool, UK
[8] School of Chemistry, University of Nottingham, UK
[9] Department of Chemistry, University of Reading, UK
Contact E–mail: k.r.j.lovelock@reading.ac.uk; nick.besley@nottingham.ac.uk

Information relevant to Section 2 of the Main Article

Information relevant to Section 3.1 of the Main Article

Information relevant to Section 3.2 of the Main Article

Information relevant to Section 3.3 of the Main Article

Information relevant to Section 2 of the Main Article

Beamline Set–up: I09

S 1s NEXAFS experiments using partial electron yield (PEY) detection were performed at the Beamline I09 at Diamond Light Source, UK. The pressure during experiments was ~5×10^{-10} mbar. The end–chamber contains a VG Scienta EW4000 HAXPES hemispherical electron analyser. Note that no data from I09 was presented in the main paper, it is used solely in the ESI to demonstrate the similarities between spectra shapes for PEY and fluorescence yield (FY). Furthermore, we make no comments on the absolute energies measured for this data; hence, energy calibration is irrelevant for this data.

Energy Scale Calibration

Comparing our S 1s FY results to literature values shows that our measured white line energies (E_{WL}) and edge energies (E_{NEXAFS}) are calibrated to the same level as found in the literature.

The S 1s FY NEXAFS spectrum for solid elemental sulfur was very similar to a literature spectrum, in both peak $h\nu$ and spectrum shape.[1] Clearly, self–absorption occurred for this solid, highly concentrated sample, as was the case for the literature spectrum. For the ILs studied, excellent matches were observed between our FY data (for neat ILs) and literature data (for relatively dilute samples dissolved in water) (where self–absorption was not expected to occur), *e.g.* $[MeSO_4]^-$,[2] $[HSO_4]^-$,[1] and $[MeSO_3]^-$.[1] Therefore, self–absorption for our IL experiments using FY detection does not appear to occur.

For the S 1s edge, our experimental white line energies, E_{WL}(exp), are very similar to those reported in the literature (see Table S1). These similarities between our results and the literature show that the S 1s energy calibration for the results recorded at BM28 is valid.

Our measured cationic nitrogen N 1s E_{WL}(exp) ~401.8 eV for all four $[C_nC_1Im][A]$ ILs is in excellent agreement with the literature value of ~401.9 eV,[3-8] demonstrating that our energy calibration for the N 1s NEXAFS results does not need shifting.

Edge	IL	E_{WL} (ILs in this work) / eV	Literature compound	Literature E_{WL} / eV	Ref.
S 1s	$[S_{2,2,2}][NTf_2]$ (sulfonium)	2475.8	Aqueous $[S_{1,1,1}]^+$ $[S_{1,1,\mathrm{propionate}}]^+$	2475.5 2476.2	9 10
S 1s	$[C_2C_1Im][MeSO_3]$ (alkylsulfonate)	2481.6	Various $[RSO_3]^-$ compounds	2481.7	10
S 1s	$[C_4C_1Im][RSO_4]$ (alkylsulfate)	2482.8	Various $[RSO_4]^-$ compounds	2483.2	10
S 1s	S_8 (solid)	2472.9	S_8 (solid) S_8 (solid)	2473.1 2472.9	1 11
N 1s	$[C_nC_1Im][A]$	Three ILs gave 401.8 eV and one IL gave 401.7 eV	$[C_nC_1Im][NTf_2]$ (n = 1, 2, 4) $[C_4C_1Im][BF_4]$ $[C_4C_1Im][PF_6]$ $[C_4C_1Im]Cl$ $[C_nC_1Im]Br$ (n = 2, 4) $[C_4C_1Im]I$	401.9, 402.0 401.9 401.9 401.9 401.9 401.9	5-7 3, 8 3, 5 3, 5 3, 5, 6 7

Table S1. Comparison of ionic liquid E_{WL} values (measured in this work) with literature E_{WL} values for related compounds. R = alkyl chain, C_nH_{2n+1}.

Energy Scale Stability Over Time

Figure S1a shows two S 1s NEXAFS spectra for [C_4C_1Im][SCN] taken six months apart using the same methodology (including beamline). These spectra show identical shapes and differences between the spectra for both E_{NEXAFS} and E_{WL} are within experimental error; E_{WL}= 2474.4 eV for the January spectrum and 2474.3 eV for the June spectrum, E_{NEXAFS} = 2473.0 eV for the January spectrum and 2472.9 eV for the June spectrum. These results demonstrate that the beamline energy calibration is not changing over time. All S 1s spectra in the Main Article were recorded during a single beamtime (*i.e.* over the course of a few days); therefore, if the beamline calibration does not change over 6 months it will not change over this far shorter period.

For the N 1s NEXAFS data we have an internal standard for the [C_nC_1Im][A] ILs, namely the cationic nitrogen. The cationic N 1s E_{WL} was ~401.8 eV for all four [C_nC_1Im][A] ILs, which demonstrates that our energy calibration is stable over time. Furthermore, Figure S1b shows two N 1s spectra for [$N_{4,1,1,0}$][HSO_4] taken 12 hours apart. These spectra appear identical to the eye. This observation is strongly supported by E_{WL} and E_{NEXAFS} being the same (within experimental error) for these two spectra; for the spectra in Figure S1b E_{WL} = 405.6 eV (t = 0 h) and 405.7 eV (t = 12 h) and E_{NEXAFS} = 405.0 eV (for both t = 0 h and t = 12 h). All N 1s spectra were taken in a single beamtime (over six days), so instability in energy scale calibration over this timescale would be highly unlikely regardless.

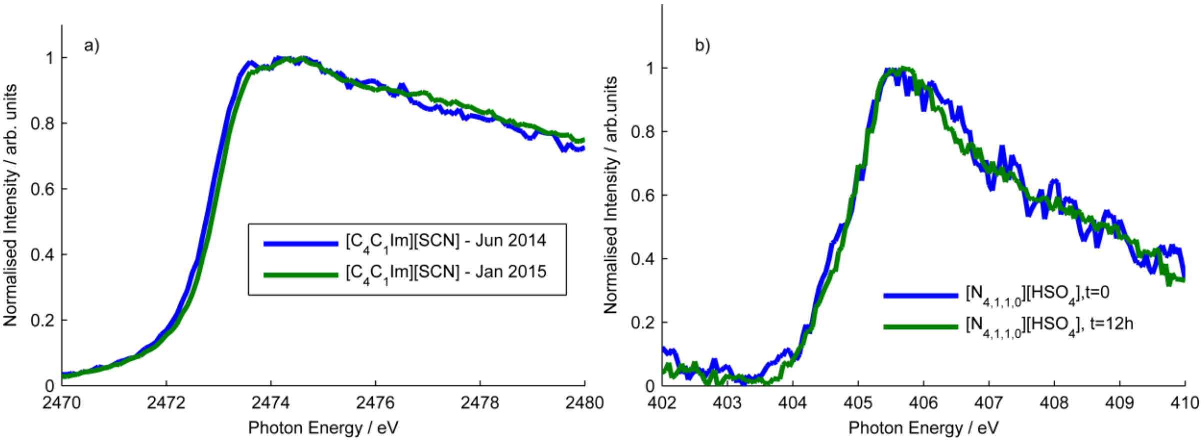


Figure S1. (a) Two experimental S 1s edge NEXAFS spectra for [C_4C_1Im][SCN] taken 6 months apart under the same conditions. Note the both E_{NEXAFS} and E_{WL} are the same within experimental error for both spectra (see the text). Spectra were taken at the ESRF using FY detection. (b) Two experimental N 1s edge NEXAFS spectra for [$N_{4,1,1,0}$][HSO_4] taken 12 hours apart under the same conditions. Note the both E_{NEXAFS} and E_{WL} are the same within experimental error for both spectra (see the text).

Information relevant to Section 3.1 of the Main Article

Counterion Dependence

There is no significant counterion dependence observed for any of the S 1s data recorded here. S 1s NEXAFS spectra for all four $[C_nC_1Im][NTf_2]$ ILs were similar in terms of both the relative peak areas and energies (Figure S2).

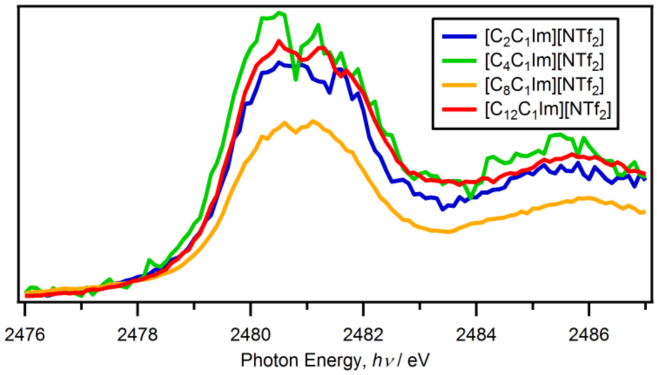


Figure S2. Experimental S 1s edge NEXAFS spectra for four $[C_nC1Im][NTf_2]$ ILs (n = 2, 4, 8, 12) using fluorescence yield (FY) detection.

Fluorescence Yield versus Partial Electron Yield

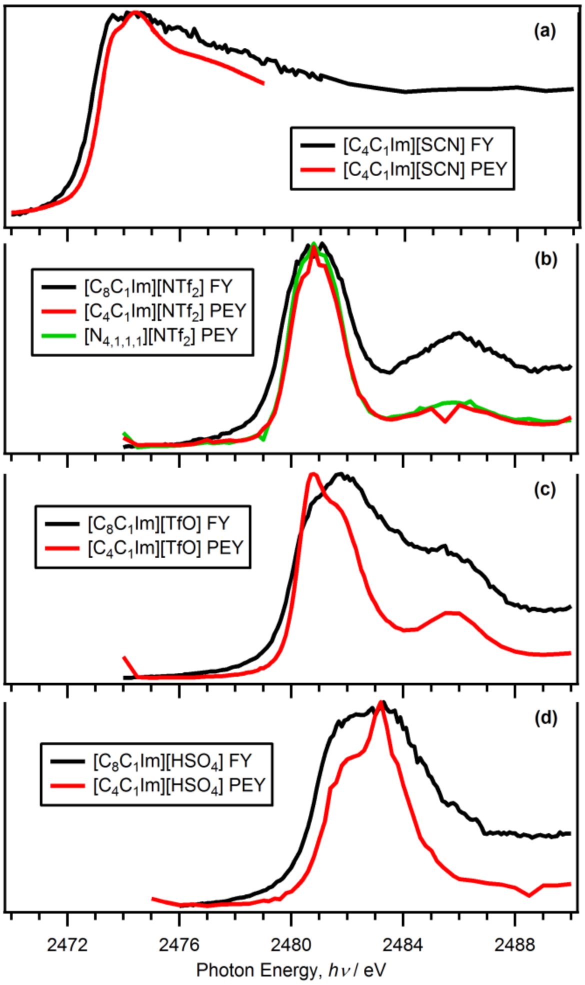


Figure S3. Experimental S 1s edge NEXAFS spectra using fluorescence yield (FY) and partial electron yield (PEY) detection. (a) $[C_4C_1Im][SCN]$, (b) $[cation][NTf_2]$, (c) $[C_nC_1Im][TfO]$ and (d) $[C_nC_1Im][HSO_4]$.

Once a single linear energy shift was applied to account for different beamline $h\nu$ calibrations, the visual match between FY (recorded on BM28 at the ESRF) and PEY (recorded on I09 at Diamond Light Source) detection was good overall for the four ILs studied. Subtle differences in relative peak intensities between FY and PEY detection were observed for $[C_nC_1Im][HSO_4]$ and $[C_nC_1Im][TfO]$ (Figure S3), which have two possible origins. Firstly, different processes were monitored, *i.e.* FY and PEY, although broadly both monitor the absorption probability (FY and PEY can provide subtly different measures of absorption, as the physical processes following core–hole filling are different[12, 13]). Secondly, the resolution of the two experiments may have been slightly different; it would appear that the resolution for PEY detection was slightly better than for FY detection. These results demonstrate that our calculations are valid whether either FY or PEY detection methods are used.

Experimental S 1s and N 1s energies

System	Experimental S 1s E_{NEXAFS}(exp) ±0.1 / eV	Experimental S 1s E_{WL}(exp) ±0.2 / eV
Solid S_8	2471.8	2472.9
$[C_4C_1Im][SCN]$	2472.9	2474.3
$[S_{2,2,2}][NTf_2]$	2475.0/2479.5 (cation/anion)	2475.8/2480.8 (cation/anion)
$[C_8C_1Im][NTf_2]$	2479.7	2481.1
$[C_8C_1Im][TfO]$	2480.1	2481.9
$[C_2C_1Im][MeSO_3]$	2480.1	2481.6
$[C_4C_1Im][MeSO_4]$	2480.4	2482.8
$[C_8C_1Im][HSO_4]$	2480.9	2483.3

Table S2. Experimental S 1s E_{NEXAFS}(exp) values and E_{WL}(exp) values for all systems studied. For systems with a sulfur atom on both cation and anion, the cationic value is to the left of the "/", the anionic value to the right. E_{NEXAFS}(exp) and E_{WL}(exp) were determined from fluorescence yield (FY) data.

System	Experimental N 1s E_{NEXAFS}(exp) ±0.1 / eV	Experimental N 1s E_{WL}(exp) ±0.2 / eV
$[C_8C_1Im][C(CN)_3]$	401.4/398.8 (cation/anion)	401.7/399.0 (cation/anion)
$[C_8C_1Im]Cl$	401.5	401.8
$[C_4C_1Im][SCN]$	401.5/399.3 (cation/anion)	401.8/399.5 (cation/anion)
$[C_8C_1Im][NTf_2]$	401.5/X (cation/anion)	401.8
$[P_{6,6,6,14}][NO_3]$	404.8	405.1
$[N_{2,2,1,0}][TfO]$	404.8	406.0
$[N_{4,1,1,0}][HSO_4]$	404.9	405.7

Table S3. Experimental N 1s E_{NEXAFS}(exp) values for all systems studied. For systems with a nitrogen atom on both cation and anion, the cationic value is to the left of the "/", the anionic value to the right. Edge energies were determined using partial electron yield (PEY) data. The X for $[C_8C_1Im][NTf_2]$ demonstrates that no well–resolved peak was observed for the $[NTf_2]^-$ anion.

Information relevant to Section 3.2 of the Main Article

More Experimental *vs*. Calculations Comparisons for the S 1s Edge

The calculated S 1s spectra for [C_4C_1Im][$MeSO_3$] vary significantly between lone ions and ion pairs (Figure S3h). For [C_4C_1Im][$MeSO_3$] the spectrum calculated with lone ions contains two peaks (~2477.7 eV and ~2480.6 eV) compared to a single peak for the ion pair (~2480.6 eV). For [C_4C_1Im][$MeSO_3$] the lone ions system was also found to be too small for calculating S 1s NEXAFS spectra, predicting a peak at ~2477 eV which is absent in experimental and ion pair calculated spectra (Figure S3h).

For the S 1s edge, the only IL to show noteworthy ion pair conformational dependence is the [$S_{2,2,2}$]$^+$ cation for [$S_{2,2,2}$][NTf_2] (Figure S3a); the [NTf_2]$^-$ anion shows no conformational dependence for [$S_{2,2,2}$][NTf_2] (Figure S3e). Both conformers for [$S_{2,2,2}$][NTf_2] give a peak at 2474.9 eV. A relatively subtle but noticeable difference occurs at larger $h\nu$. This dependence arises due to two very different conformers, either with the anion closest to the cationic sulfur atom or with the anion closest to the cationic alkyl chains. Such a conformer dependence is also observed for cationic sulfur atomic charges for [$S_{2,2,2}$][NTf_2].[14]

The shape matches between S 1s experimental spectra and calculated spectra (for both lone ions and ion pairs) for [$S_{2,2,2}$][NTf_2], [C_4C_1Im][NTf_2] and [C_4C_1Im][TfO] are excellent (Figure S6). For both [C_4C_1Im][NTf_2] and [$S_{2,2,2}$][NTf_2], lone ions and ion pairs are very similar in terms of both peak shape and peak $h\nu$ (Figure S3). Effects of using ion pair calculations (rather than lone ions) on calculated S 1s spectra were similar for three ILs, ([C_4C_1Im][$MeSO_4$], [C_4C_1Im][TfO] and [C_4C_1Im][HSO_4]) (Figure S3). For example, for both lone [$MeSO_4$]$^-$ ions and [C_4C_1Im][$MeSO_4$] ion pairs two peaks are observed, but small differences are observed in the peak $h\nu$ separations (Figure S3). The two peaks are separated by ~3.4 eV for lone [$MeSO_4$]$^-$ ions and by ~2.0 eV for both [C_4C_1Im][$MeSO_4$] ion pairs.

Comparing Calculations to Each Other and to Experimental Data

Ionic liquid	Lone ion calculations *vs*. ion pair calculations	Significant ion pair conformational dependence?	Shift for ion pair calculations to match experimental spectra / eV
$[C_4C_1Im][SCN]$	Different. Very large peak in lone ion calculations not present in ion pair calculations.	No	0.0
$[C_nC_1Im][NTf_2]$	Very similar	No	+1.0
$[C_nC_1Im][TfO]$	Very small differences	No	+1.3
$[C_nC_1Im][MeSO_3]$	Different. Peak in lone ion calculations not present in ion pair calculations.	No	+1.1
$[C_4C_1Im][MeSO_4]$	Very small differences	No	+1.2
$[C_nC_1Im][HSO_4]$	Very small differences	No	+1.3
$[S_{2,2,2}][NTf_2]$	Almost identical	Very subtle at larger $h\nu$.	+1.0

Table S4. S 1s NEXAFS results: comparing calculations to each other and to experimental data.

Ionic liquid	Lone ion calculations *vs*. ion pair calculations	Significant ion pair conformational dependence?	Shift for ion pair calculations to match experimental spectra / eV
$[P_{6,6,6,14}][NO_3]$	Very similar	No	+0.8
$[C_nC_1Im]Cl$	Very similar	Yes. Back butyl conformer gives two peaks. Other two conformers give one peak.	–0.9
$[C_nC_1Im][NTf_2]$	Very similar	No	–0.8
$[C_nC_1Im][C(CN)_3]$	Very similar	No	–0.8
$[C_4C_1Im][SCN]$	Very similar	Yes. Sf conformer gives two peaks. CNbot gives one peak.	–0.9
$[N_{4,1,1,0}][HSO_4]$	Yes. NH–O ion pair conformers give one peak. Lone ions give two peaks.	Yes. NH–O conformers give one peak. Alkyl–O conformers give two peaks.	–0.4
$[N_{2,2,1,0}][TfO]$	Yes. NH–O ion pair conformers give one peak. Lone ions give two peaks.	Yes. NH–O conformers give one peak. Alkyl–O conformers give two peaks.	–0.4

Table S5. N 1s NEXAFS results: comparing calculations to each other and to experimental data.

Nomenclature used for labelling ion pair and ion pair dimer calculations

The three [C_4C_1Im]Cl ion pair structures are labelled Front, Top and Back–Butyl respectively. The name refers to the position of the anion relative to the imidazolium ring. “Front” refers to Cl^- sitting in the plane of the imidazolium ring near the C^2–H group (Figure S4 for atomic numbering). “Top” refers to the Cl^- sitting above the imidazolium ring plane; “above” is determined by the position of the alkyl group, the alkyl group and Cl^- both being on the same side of the imidazolium plane makes this a “top” conformer. The “Back–Butyl” name indicates that Cl^- is in the imidazolium ring plane, but on the opposite side to the C^2–H group (hence, “back” rather than “front”). The “butyl” part of “Back–Butyl” refers to the Cl^- being closer to the imidazolium alkyl chain than the methyl group. This nomenclature has been used in previous works, hence these names were chosen for consistency as well as clarity.[15-17]

The three [C_4C_1Im][SCN] structures are labelled Sf, Nf and CNbot. These names refer to the position of the anion, relative to the cation. “Sf” is short for “Sulfur front”, indicating that the sulfur group of $[SCN]^-$ interacts with the C^2–H (“front”) group of the imidazolium cation. Similarly Nf is short for “Nitrogen front”, indicating that the nitrogen group of [SCN] interactions with the C^2–H (“front”) group of the imidazolium cation. “CNbot” means that the anion sits “below” the imidazolium ring plane; it is “below” (rather than above) as the butyl group is on the opposite side of imidazolium plane. This nomenclature has previously been employed in another publication, hence is continued here for reasons of consistency.[14]

The [$N_{4,1,1,0}$][HSO_4] conformers are divided into two groups; NH–O and Alkyl–O. The NH–O conformers involve an interaction between the ammonium N–H group and an oxygen group on the anion. The Alkyl–O conformers do not possess this NH–O interaction, but instead possess only C–H–O intermolecular interactions (hence the name Alkyl–O).

The [C_2C_1Im]Cl dimer conformers are named in a consistent manner based on previous work (see reference [18] for a more thorough explanation of the naming scheme).[18] An example name is “D_BtF_FBt_A”. The first letter denotes the general structural motif, in the current work this is either “diagonal”(D) or “Middle”(M). A diagonal motif is one where the ion positions essentially form a rectangle, with an ion in each corner. The middle motif involves one cation ring sitting above the other, and the anions being in between the two ring planes. The “BtF” part of the name refers to the positions of both anions to one of the cations, the same names are used here as in the case of [C_4C_1Im]Cl ion pairs; Bt means “Bottom”, T means “Top”, F means “Front” and B means “Back” (and represents a similar position to back–butyl). Therefore the “BtF” means anion 1 is Bottom with respect to cation 1, and anion 2 is “Front” with respect to cation 1. Similarly, the “FBt” part of the name means anion 1 is “Front” with respect to cation 2 and “Bottom” with respect to cation 2. Note the assignment of one ion to “cation 1” or “cation 2” is arbitrary (for example, this conformer could also have been named D_FBt_BtF_A). The final letter in a dimer name corresponds to the relative positions of the cations. “A” means antiparallel (ring planes are parallel but the two C^2–H groups face opposite directions), “P” means parallel (ring planes are parallel but the two C^2–H groups face the same direction), “R” means rotated (ring planes are parallel but the direction of one C^2–H group is ~90^o to the other), “T” stands for T–shaped (the imidazolium ring planes are ~90^o to each other).

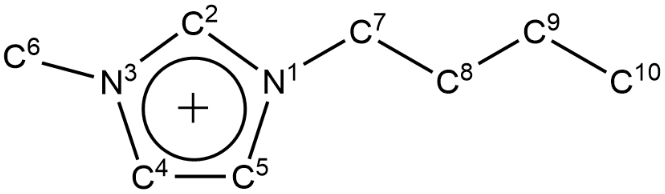


Figure S4: Numbering used for the $[C_4C_1Im]^+$ cation (we employ the same ring atom numbering for the $[C_2C_1Im]^+$ cation used in $[C_2C_1Im]Cl$ dimers.

Calculated *vs*. FY Experimental NEXAFS Spectra

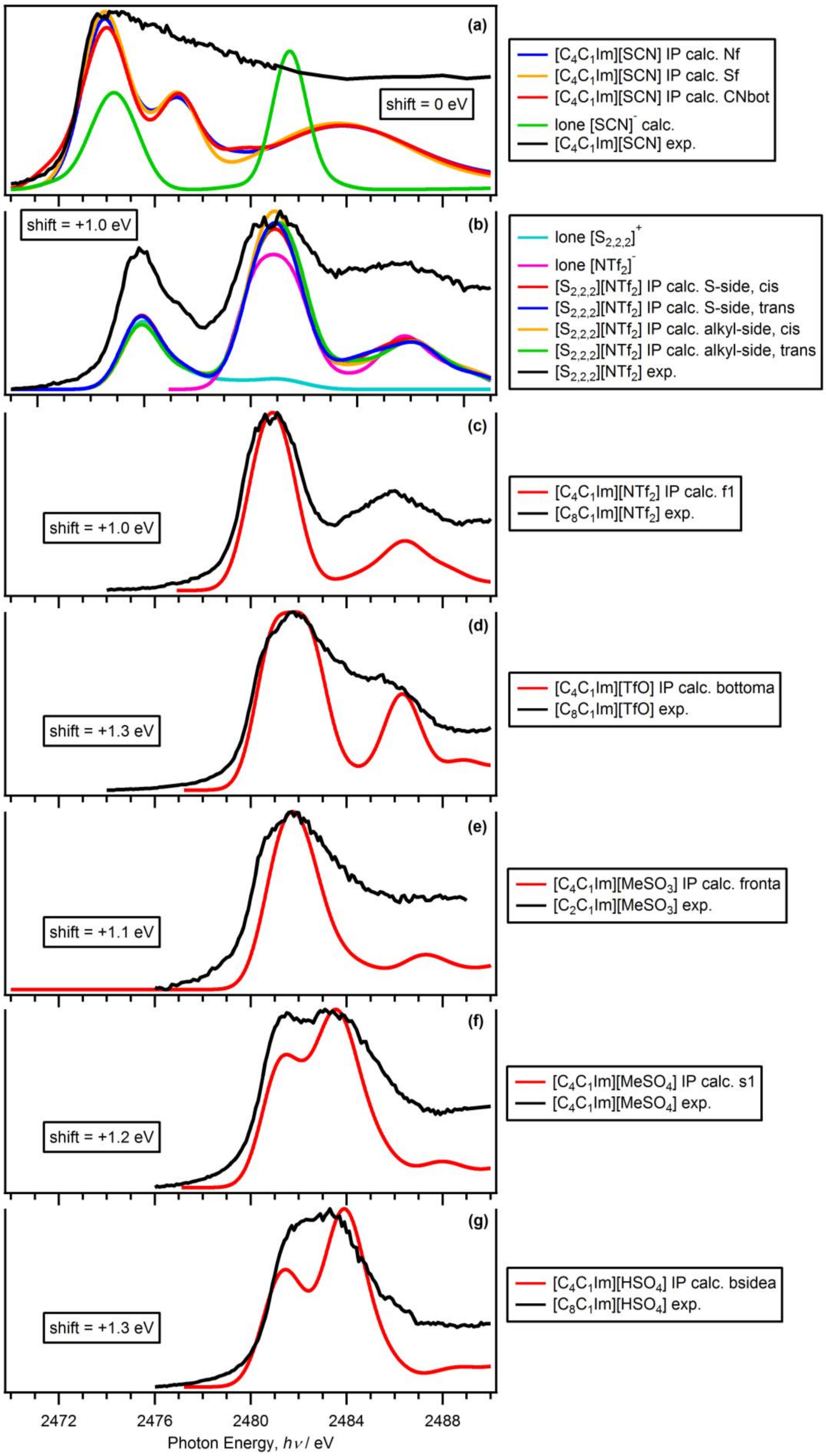


Figure S5. S 1s calculated *vs*. FY experimental NEXAFS spectra. Shifts for the calculated spectra are given in each graph. (a) $[C_4C_1Im][SCN]$, (b) $[S_{2,2,2}][NTf_2]$ (For S–side conformers, $[NTf_2]^-$ interacts directly with the sulfur centre in the cation. For alkyl–side conformers, $[NTf_2]^-$ sits further from the sulfur centre in the cation and interacts only with the alkyl chains.[14]), (c) $[C_4C_1Im][NTf_2]$, (d) $[C_4C_1Im][TfO]$, (e) $[C_4C_1Im][MeSO_3]$, (f) $[C_4C_1Im][MeSO_4]$, (g) $[C_4C_1Im][HSO_4]$.

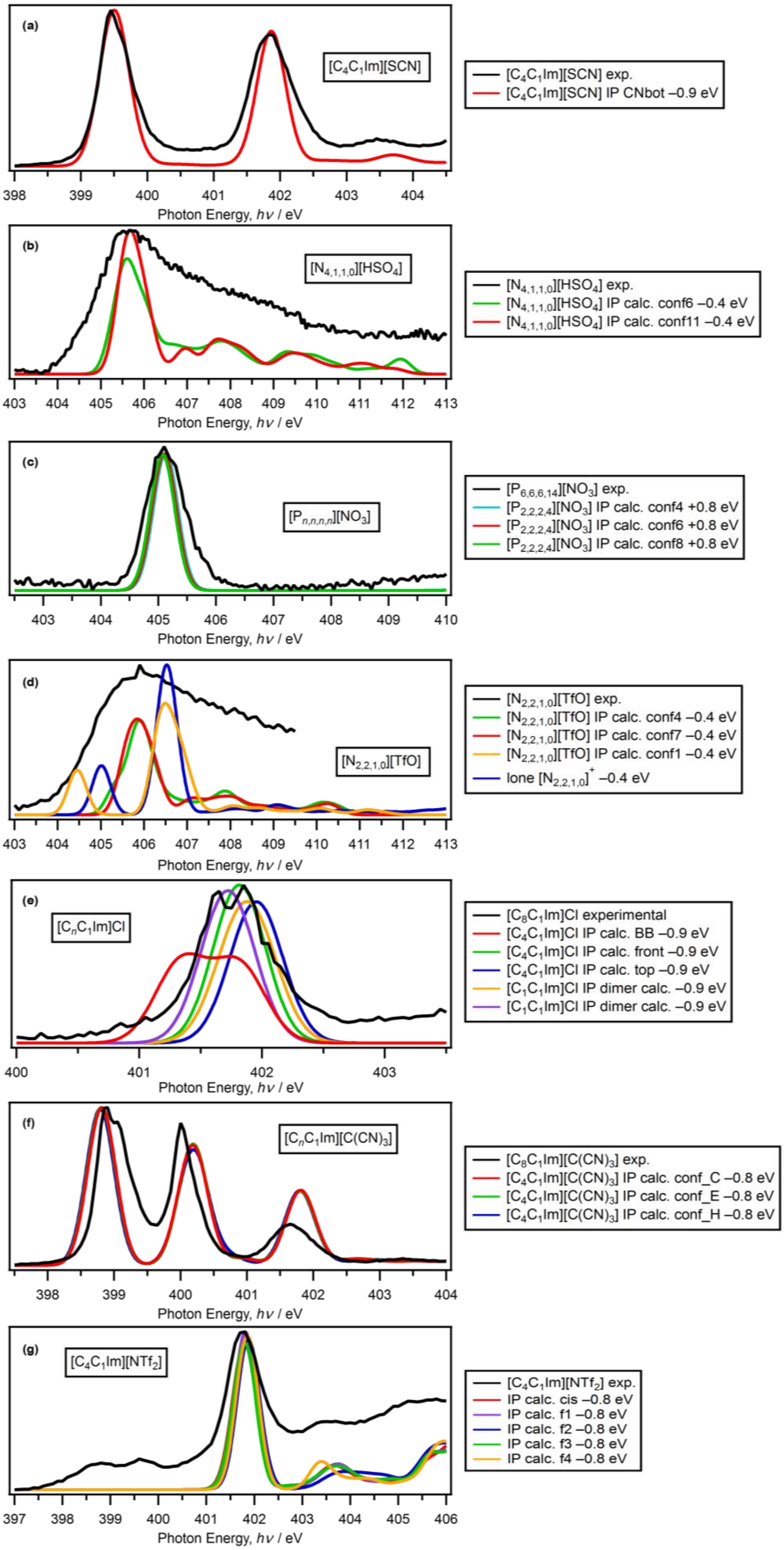

(a)
[C4C1Im][SCN]
[C4C1Im][SCN] exp.
[C4C1Im][SCN] IP CNbot –0.9 eV
398 399 400 401 402 403 404
Photon Energy, hν / eV
(b)
[N4,1,1,0][HSO4]
[N4,1,1,0][HSO4] exp.
[N4,1,1,0][HSO4] IP calc. conf6 –0.4 eV
[N4,1,1,0][HSO4] IP calc. conf11 –0.4 eV
403 404 405 406 407 408 409 410 411 412 413
Photon Energy, hν / eV
(c)
[Pn,n,n,n][NO3]
[P6,6,6,14][NO3] exp.
[P2,2,2,4][NO3] IP calc. conf4 +0.8 eV
[P2,2,2,4][NO3] IP calc. conf6 +0.8 eV
[P2,2,2,4][NO3] IP calc. conf8 +0.8 eV
403 404 405 406 407 408 409 410
Photon Energy, hν / eV
(d)
[N2,2,1,0][TfO]
[N2,2,1,0][TfO] exp.
[N2,2,1,0][TfO] IP calc. conf4 –0.4 eV
[N2,2,1,0][TfO] IP calc. conf7 –0.4 eV
[N2,2,1,0][TfO] IP calc. conf1 –0.4 eV
lone [N2,2,1,0]+ –0.4 eV
403 404 405 406 407 408 409 410 411 412 413
Photon Energy, hν / eV
(e)
[CnC1Im]Cl
[C8C1Im]Cl experimental
[C4C1Im]Cl IP calc. BB –0.9 eV
[C4C1Im]Cl IP calc. front –0.9 eV
[C4C1Im]Cl IP calc. top –0.9 eV
[C1C1Im]Cl IP dimer calc. –0.9 eV
[C1C1Im]Cl IP dimer calc. –0.9 eV
400 401 402 403
Photon Energy, hν / eV
(f)
[CnC1Im][C(CN)3]
[C8C1Im][C(CN)3] exp.
[C4C1Im][C(CN)3] IP calc. conf_C –0.8 eV
[C4C1Im][C(CN)3] IP calc. conf_E –0.8 eV
[C4C1Im][C(CN)3] IP calc. conf_H –0.8 eV
398 399 400 401 402 403 404
Photon Energy, hν / eV
(g)
[C4C1Im][NTf2]
[C4C1Im][NTf2] exp.
IP calc. cis –0.8 eV
IP calc. f1 –0.8 eV
IP calc. f2 –0.8 eV
IP calc. f3 –0.8 eV
IP calc. f4 –0.8 eV
397 398 399 400 401 402 403 404 405 406
Photon Energy, hν / eV

Figure S6. N 1s calculated *vs*. PEY experimental NEXAFS spectra. Shifts for the calculated spectra are given in each graph. (a) [C_4C_1Im][SCN], (b) [$N_{4,1,1,0}$][HSO_4], (c) [$P_{2,2,2,4}$][NO_3] ion pair calculations *vs*. [$P_{6,6,6,14}$][NO_3] experimental, (d) [$N_{2,2,1,0}$][TfO], (e) [C_4C_1Im]Cl, (f) [C_4C_1Im][$C(CN)_3$], (g) [C_4C_1Im][NTf_2].

Information relevant to Section 3.3 of the Main Article

Calculated NEXAFS Spectra: Ion Pairs *vs*. Lone Ions

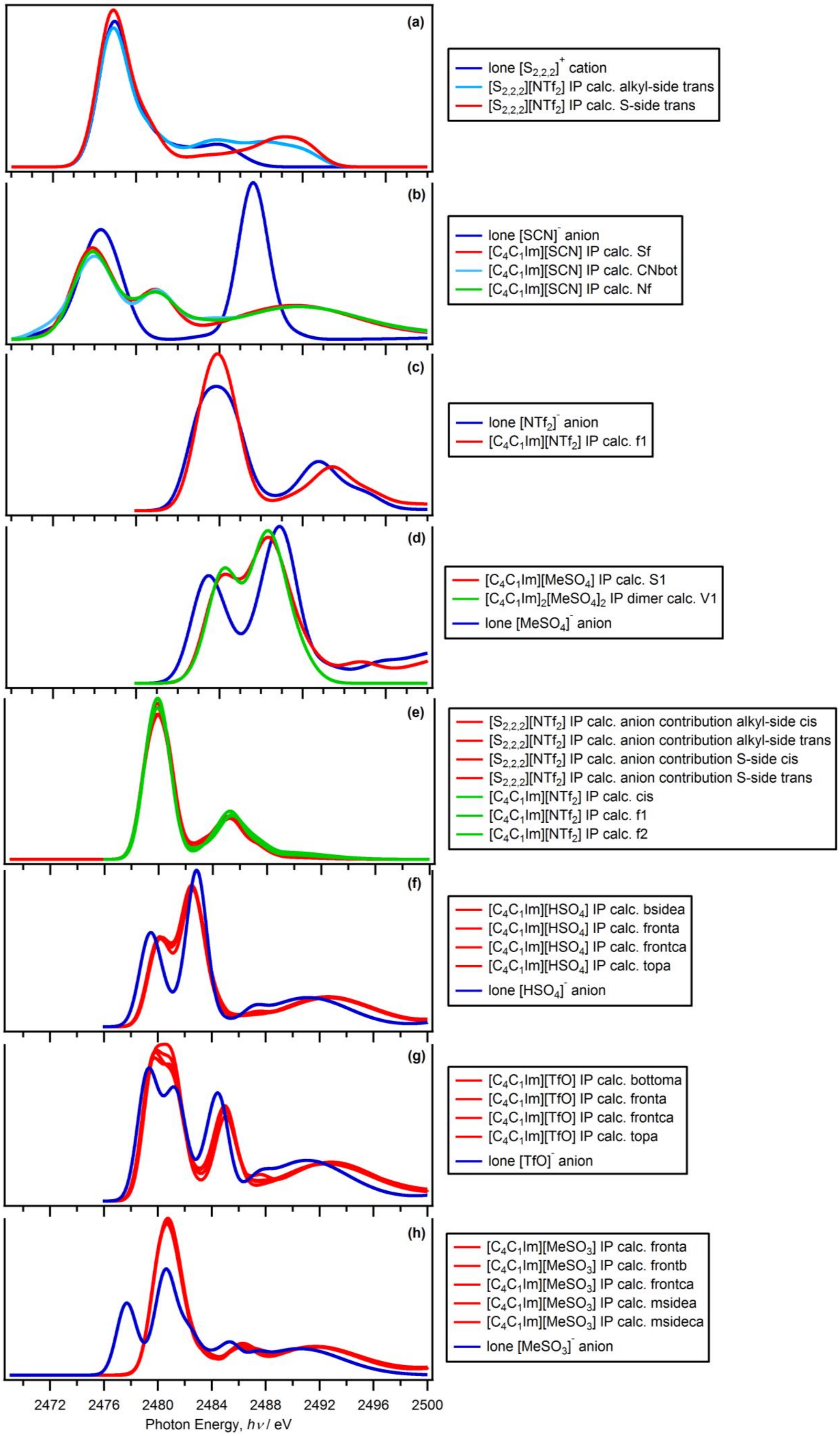

(a)
lone $[S_{2,2,2}]^+$ cation
$[S_{2,2,2}][NTf_2]$ IP calc. alkyl-side trans
$[S_{2,2,2}][NTf_2]$ IP calc. S-side trans
(b)
lone $[SCN]^-$ anion
$[C_4C_1Im][SCN]$ IP calc. Sf
$[C_4C_1Im][SCN]$ IP calc. CNbot
$[C_4C_1Im][SCN]$ IP calc. Nf
(c)
lone $[NTf_2]^-$ anion
$[C_4C_1Im][NTf_2]$ IP calc. f1
(d)
$[C_4C_1Im][MeSO_4]$ IP calc. S1
$[C_4C_1Im]_2[MeSO_4]_2$ IP dimer calc. V1
lone $[MeSO_4]^-$ anion
(e)
$[S_{2,2,2}][NTf_2]$ IP calc. anion contribution alkyl-side cis
$[S_{2,2,2}][NTf_2]$ IP calc. anion contribution alkyl-side trans
$[S_{2,2,2}][NTf_2]$ IP calc. anion contribution S-side cis
$[S_{2,2,2}][NTf_2]$ IP calc. anion contribution S-side trans
$[C_4C_1Im][NTf_2]$ IP calc. cis
$[C_4C_1Im][NTf_2]$ IP calc. f1
$[C_4C_1Im][NTf_2]$ IP calc. f2
(f)
$[C_4C_1Im][HSO_4]$ IP calc. bsidea
$[C_4C_1Im][HSO_4]$ IP calc. fronta
$[C_4C_1Im][HSO_4]$ IP calc. frontca
$[C_4C_1Im][HSO_4]$ IP calc. topa
lone $[HSO_4]^-$ anion
(g)
$[C_4C_1Im][TfO]$ IP calc. bottoma
$[C_4C_1Im][TfO]$ IP calc. fronta
$[C_4C_1Im][TfO]$ IP calc. frontca
$[C_4C_1Im][TfO]$ IP calc. topa
lone $[TfO]^-$ anion
(h)
$[C_4C_1Im][MeSO_3]$ IP calc. fronta
$[C_4C_1Im][MeSO_3]$ IP calc. frontb
$[C_4C_1Im][MeSO_3]$ IP calc. frontca
$[C_4C_1Im][MeSO_3]$ IP calc. msidea
$[C_4C_1Im][MeSO_3]$ IP calc. msideca
lone $[MeSO_3]^-$ anion
2472
2476
2480
2484
2488
2492
2496
2500
Photon Energy, $h\nu$ / eV

Figure S7. S 1s calculated NEXAFS spectra: ion pairs *vs*. lone ions. (a) $[S_{2,2,2}][NTf_2]$ ion pairs *vs*. lone $[S_{2,2,2}]^+$, (b) $[C_4C_1Im][SCN]$ *vs*. lone $[SCN]^-$, (c) $[C_4C_1Im][NTf_2]$ *vs*. lone $[NTf_2]^-$, (d) $[C_4C_1Im][MeSO_4]$ ion pairs *vs*. $[C_4C_1Im][MeSO_4]$ ion pair dimers *vs*. lone $[MeSO_4]^-$, (e) $[S_{2,2,2}][NTf_2]$ anion contribution *vs*. $[C_4C_1Im][NTf_2]$ anion contribution, (f) $[C_4C_1Im][HSO_4]$ *vs*. lone $[HSO_4]^-$, (g) $[C_4C_1Im][TfO]$ *vs*. lone $[TfO]^-$, (h) $[C_4C_1Im][MeSO_3]$ *vs*. lone $[MeSO_3]^-$.

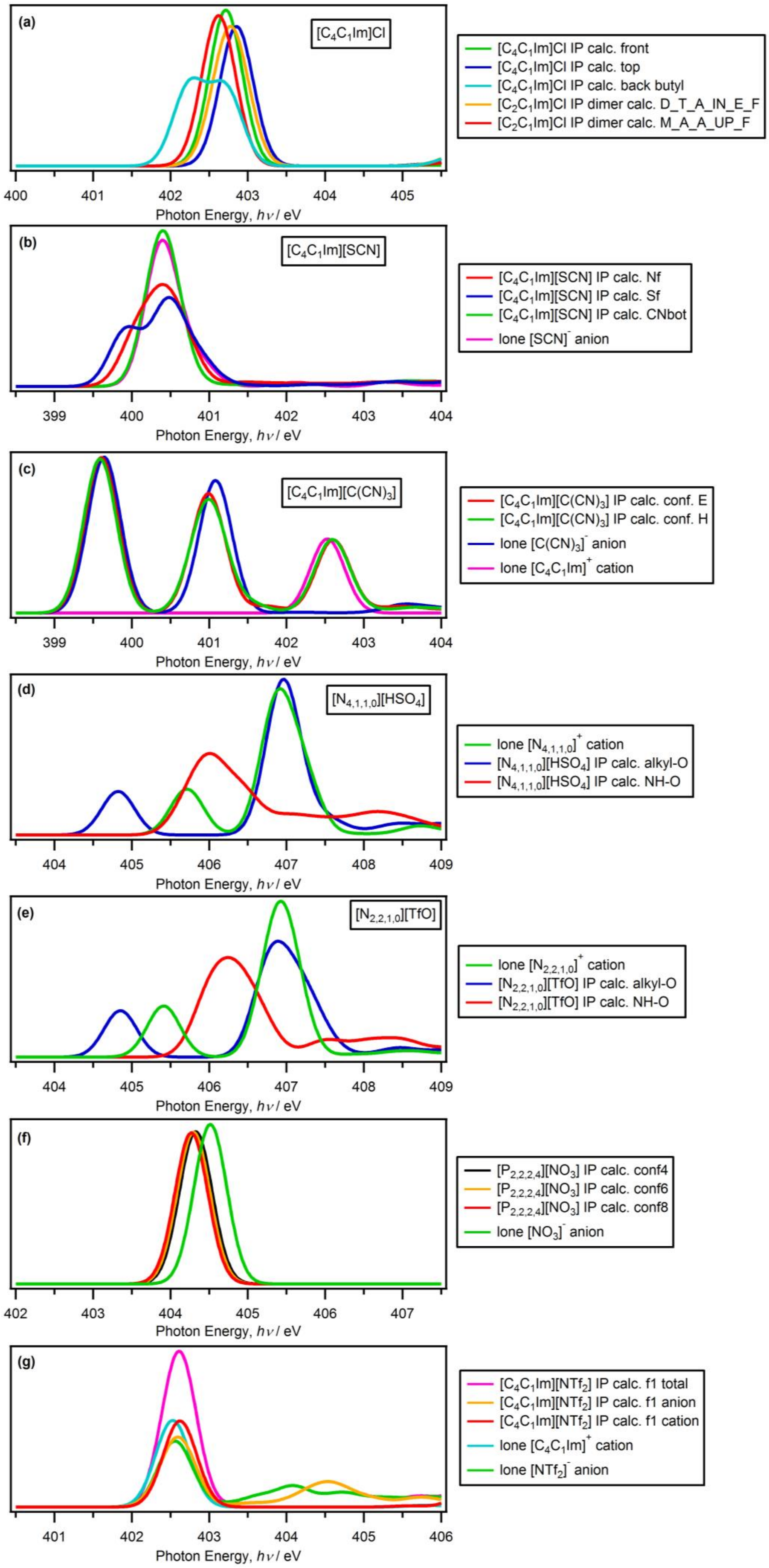

(a)
$[C_4C_1Im]Cl$
$[C_4C_1Im]Cl$ IP calc. front
$[C_4C_1Im]Cl$ IP calc. top
$[C_4C_1Im]Cl$ IP calc. back butyl
$[C_2C_1Im]Cl$ IP dimer calc. D_T_A_IN_E_F
$[C_2C_1Im]Cl$ IP dimer calc. M_A_A_UP_F
400
401
402
403
404
405
Photon Energy, $h\nu$ / eV
(b)
$[C_4C_1Im][SCN]$
$[C_4C_1Im][SCN]$ IP calc. Nf
$[C_4C_1Im][SCN]$ IP calc. Sf
$[C_4C_1Im][SCN]$ IP calc. CNbot
lone $[SCN]^-$ anion
399
400
401
402
403
404
Photon Energy, $h\nu$ / eV
(c)
$[C_4C_1Im][C(CN)_3]$
$[C_4C_1Im][C(CN)_3]$ IP calc. conf. E
$[C_4C_1Im][C(CN)_3]$ IP calc. conf. H
lone $[C(CN)_3]^-$ anion
lone $[C_4C_1Im]^+$ cation
399
400
401
402
403
404
Photon Energy, $h\nu$ / eV
(d)
$[N_{4,1,1,0}][HSO_4]$
lone $[N_{4,1,1,0}]^+$ cation
$[N_{4,1,1,0}][HSO_4]$ IP calc. alkyl-O
$[N_{4,1,1,0}][HSO_4]$ IP calc. NH-O
404
405
406
407
408
409
Photon Energy, $h\nu$ / eV
(e)
$[N_{2,2,1,0}][TfO]$
lone $[N_{2,2,1,0}]^+$ cation
$[N_{2,2,1,0}][TfO]$ IP calc. alkyl-O
$[N_{2,2,1,0}][TfO]$ IP calc. NH-O
404
405
406
407
408
409
Photon Energy, $h\nu$ / eV
(f)
$[P_{2,2,2,4}][NO_3]$ IP calc. conf4
$[P_{2,2,2,4}][NO_3]$ IP calc. conf6
$[P_{2,2,2,4}][NO_3]$ IP calc. conf8
lone $[NO_3]^-$ anion
402
403
404
405
406
407
Photon Energy, $h\nu$ / eV
(g)
$[C_4C_1Im][NTf_2]$ IP calc. f1 total
$[C_4C_1Im][NTf_2]$ IP calc. f1 anion
$[C_4C_1Im][NTf_2]$ IP calc. f1 cation
lone $[C_4C_1Im]^+$ cation
lone $[NTf_2]^-$ anion
401
402
403
404
405
406
Photon Energy, $h\nu$ / eV

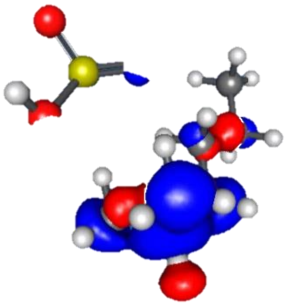
Figure S8. N 1s calculated NEXAFS spectra: ion pairs *vs*. lone ions. (a) $[C_4C_1Im]Cl$ ion pairs *vs*. $[C_2C_1Im]Cl$ ion pair dimers *vs*. lone $[C_4C_1Im]^+$, (b) $[C_4C_1Im][SCN]$ *vs*. lone $[C_4C_1Im]^+$, (c) $[C_4C_1Im][C(CN)_3]$ *vs*. lone $[C_4C_1Im]^+$, (d) $[N_{4,1,1,0}][HSO_4]$ ion pairs *vs*. lone $[N_{4,1,1,0}]^+$, (e) $[N_{2,2,1,0}][TfO]$ ion pairs *vs*. lone $[N_{2,2,1,0}]^+$, (f) $[P_{2,2,2,4}][NO_3]$ *vs*. lone $[NO_3]^-$, (g) $[C_4C_1Im][NTf_2]$ ion pair total *vs*. $[C_4C_1Im][NTf_2]$ ion pair anion contribution *vs*. $[C_4C_1Im][NTf_2]$ ion pair cation contribution *vs*. lone $[NTf_2]^-$ *vs*. lone $[C_4C_1Im]^+$.

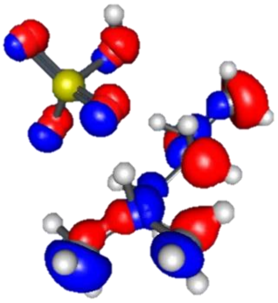
UMOs for Two Different $[N_{4,1,1,0}][HSO_4]$ Conformers

'Alkyl–O, Conf 1':

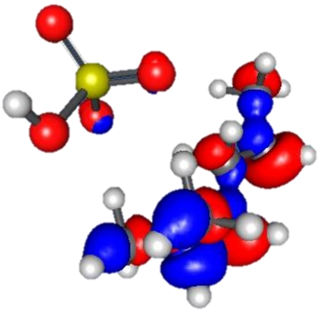
'NH–O, Conf 6':

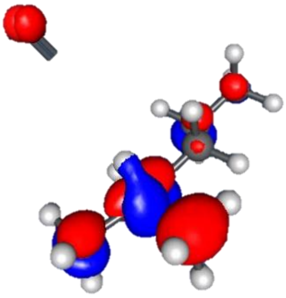
LUMO



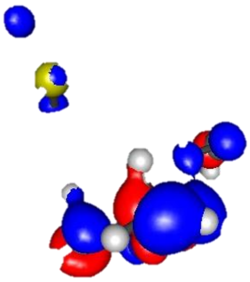


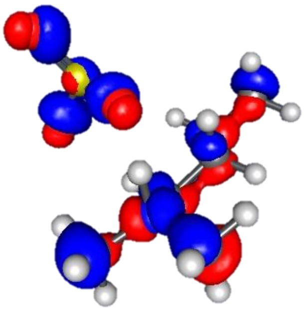
LUMO+1





LUMO+2





LUMO+4

Figure S9. Selected UMOs for $[N_{4,1,1,0}][HSO_4]$: images of the four lowest energy UMOs for the two conformers.

Figure S9 shows that the orbitals for the conf6 configuration are more delocalised across both the anion and the cation compared with conf1. For the conf6 configuration there is good evidence for a strong hydrogen bond between anion and cation. This observation rationalises why the conf6 spectra is very different from the lone cation spectrum.

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Conformer Structures

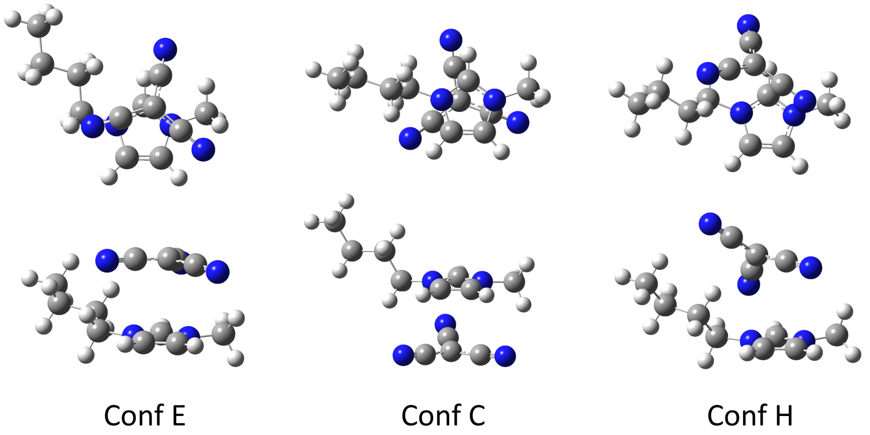


Figure S10:Optimised Ion Pair conformers for $[C_4C_1Im][C(CN)_3]$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
Conf E	0.0	0.0	0.0
Conf C	2.1	2.8	-2.6
Conf H	6.8	6.9	3.0

Table S6:Relative energies for $[C_4C_1Im][C(CN)_3]$ Ion Pair conformers.

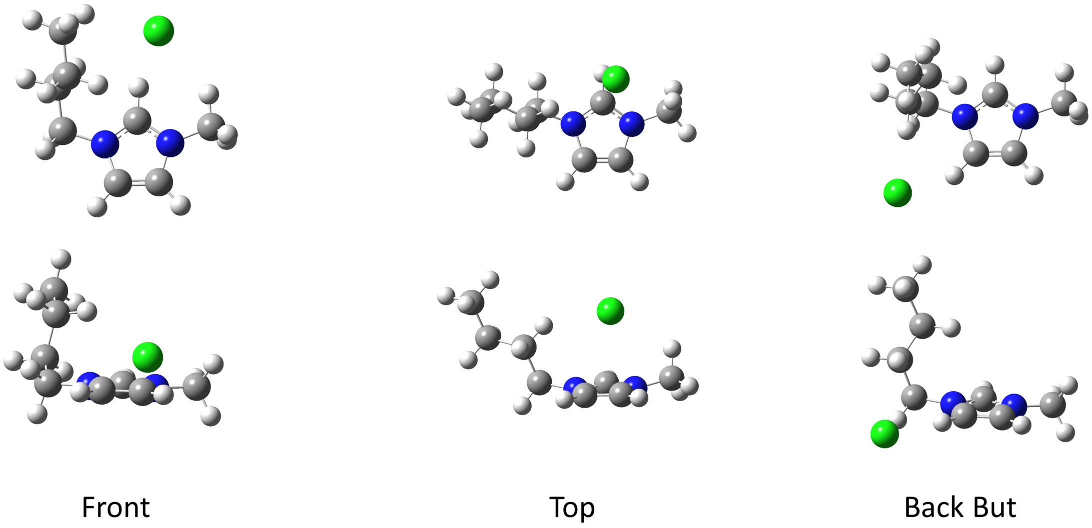
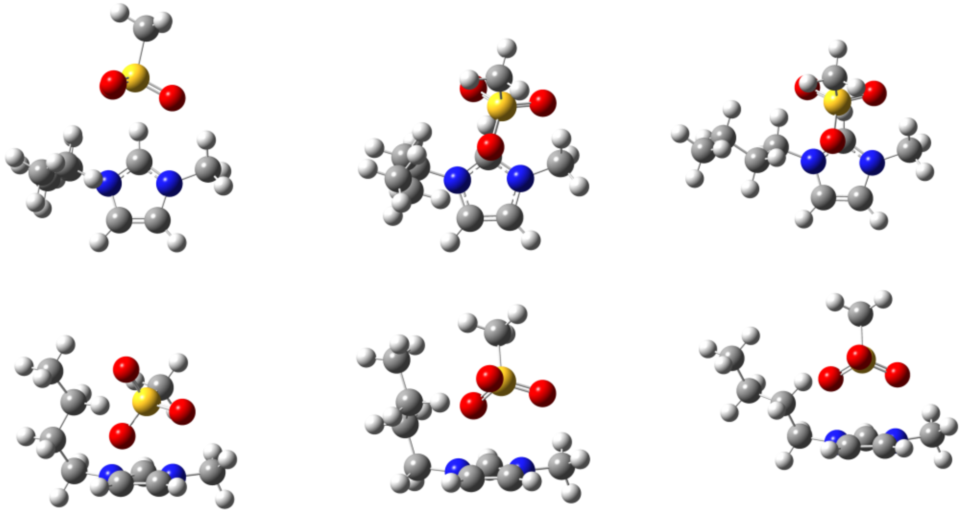


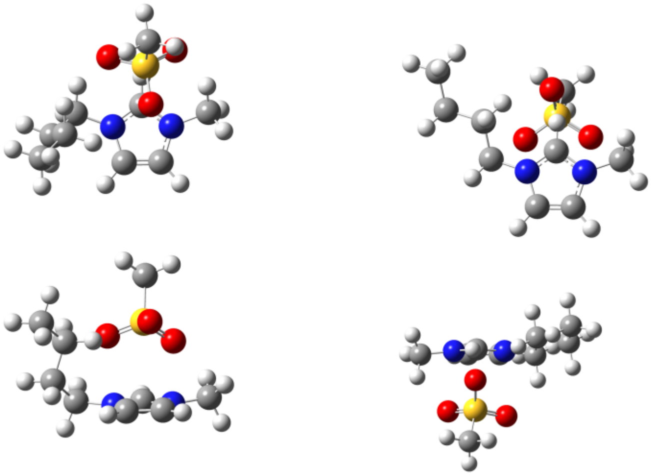
Figure S11:Optimised Ion Pair conformers for $[C_4C_1Im]\,Cl$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
Front	0.0	0.0	0.0
Top	4.6	3.4	4.8
Back Butyl	37.6	38.1	35.3

Table S7:Relative energies for $[C_4C_1Im]\,Cl$ Ion Pair conformers.



fronta frontb frontca

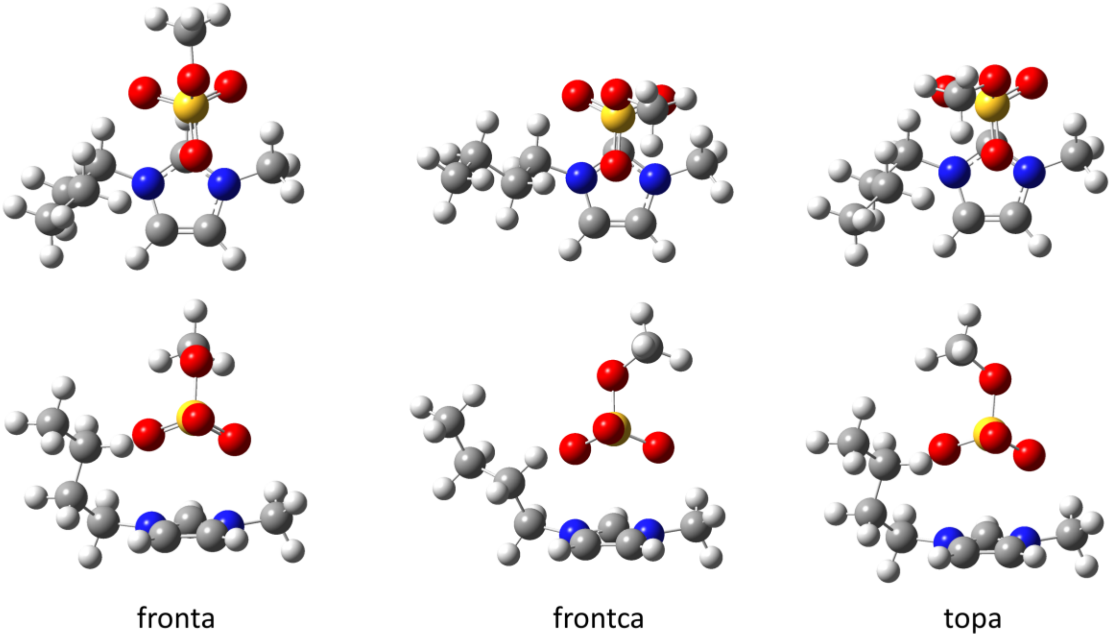


msidea msideca

Figure S12:Optimised Ion Pair conformers for [C_4C_1Im][$MeOSO_3$].

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
frontca	0.0	0.0	0.0
frontb	1.0	1.1	0.3
msidea	1.7	1.4	3.8
msideca	2.3	2.6	-0.4
fronta	4.8	5.2	3.0

Table S8:Relative energies for [C_4C_1Im][$MeOSO_3$] Ion Pair conformers.

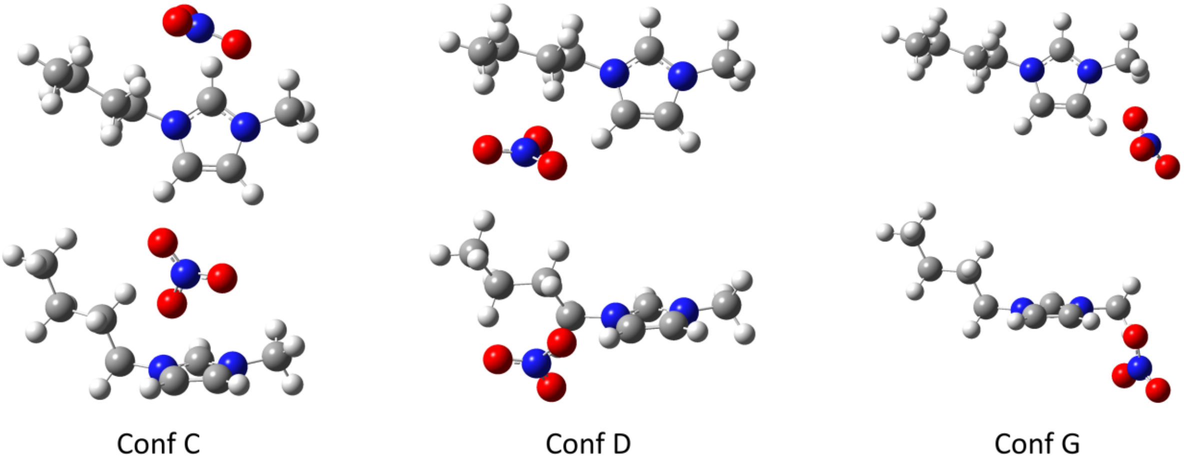


fronta frontca topa

Figure S13:Optimised Ion Pair conformers for [C_4C_1Im][$MeSO_4$].

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
fronta	0.0	0.0	0.0
topa	1.5	1.7	0.6
frontca	35.5	34.3	34.3

Table S9:Relative energies for [C_4C_1Im][$MeSO_4$] Ion Pair conformers.

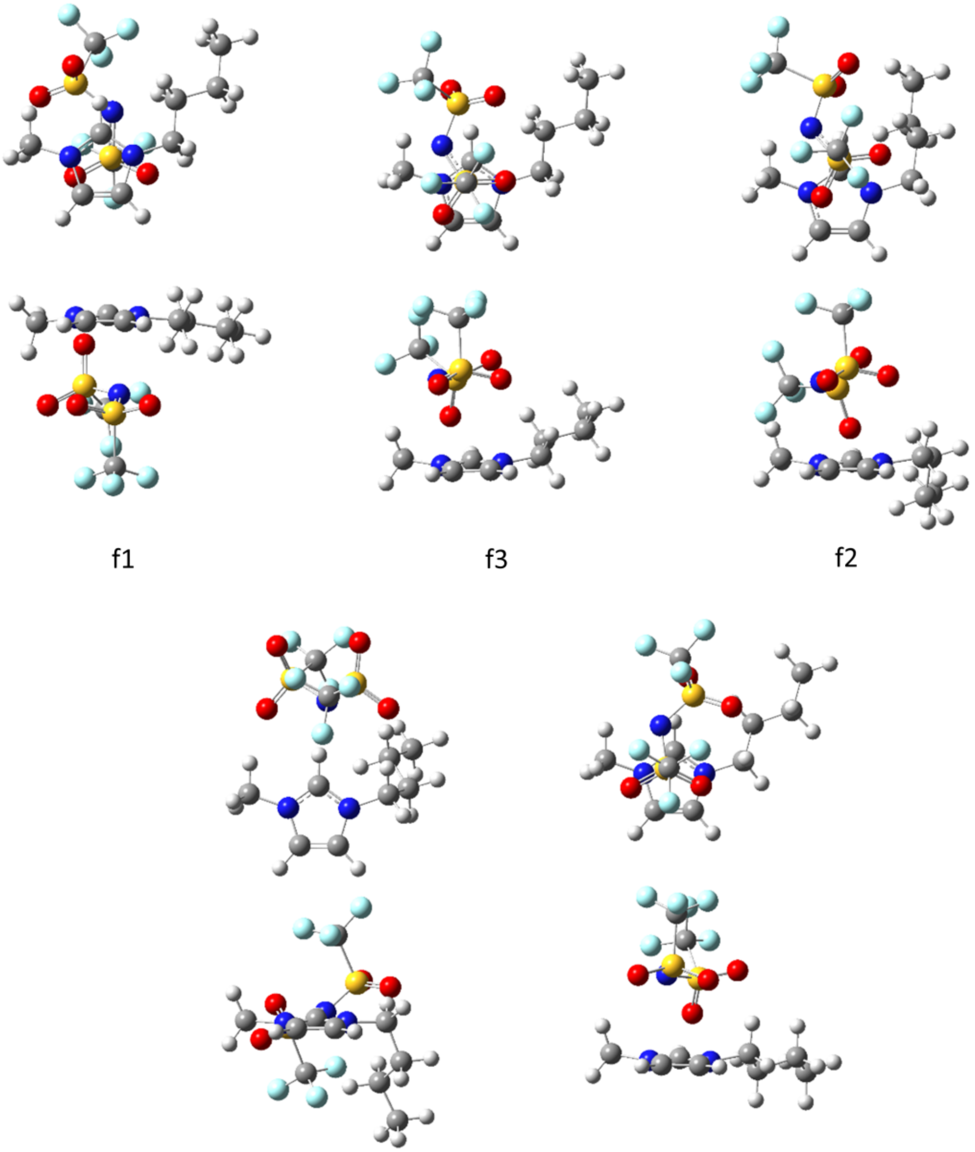


Conf C Conf D Conf G

Figure S14:Optimised Ion Pair conformers for [C_4C_1Im][NO_3].

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
Conf C	0.0	0.0	0.0
Conf D	32.4	32.9	32.4
Conf G	40.1	41.4	35.2

Table S10:Relative energies for [C_4C_1Im][NO_3] Ion Pair conformers.



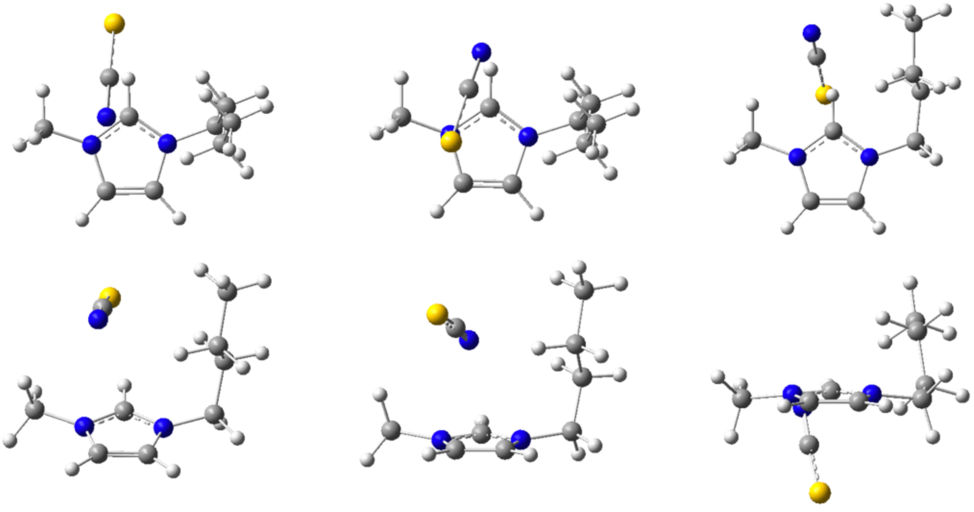
f1 f3 f2

f4 cis

Figure S15:Optimised Ion Pair conformers for [C_4C_1Im][NTf_2].

Conformer	$\Delta E(ZPE)\ /\ kJ\ mol^{-1}$	$\Delta E\ /\ kJ\ mol^{-1}$	$\Delta G\ /\ kJ\ mol^{-1}$
f1	0.0	0.0	0.0
cis	2.2	2.2	3.8
f3	2.9	3.3	1.7
f2	4.0	4.1	3.4
f4	8.3	9.3	3.7

Table S11:Relative energies for $[C_4C_1Im][NTf_2]$ Ion Pair conformers.

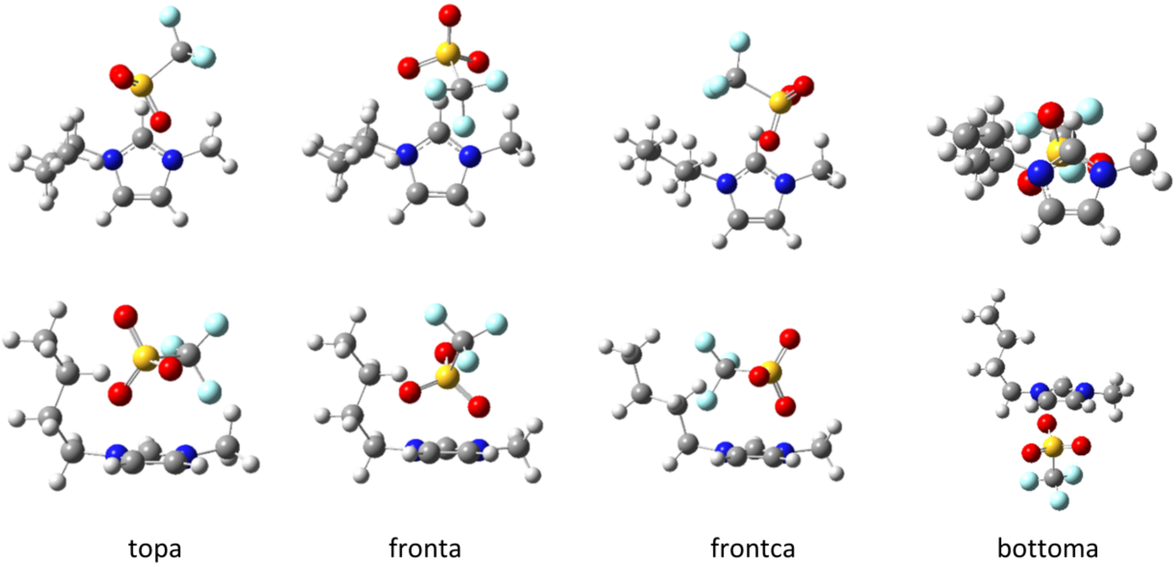


Sf **Nf** **CNbot**

Figure S16:Optimised Ion Pair conformers for $[C_4C_1Im][SCN]$.

Conformer	$\Delta E(ZPE)\ /\ kJ\ mol^{-1}$	$\Delta E\ /\ kJ\ mol^{-1}$	$\Delta G\ /\ kJ\ mol^{-1}$
Sf	0.0	0.0	0.0
Nf	1.7	1.4	3.5
CNbot	9.6	9.2	4.8

Table S12:Relative energies for $[C_4C_1Im][SCN]$ Ion Pair conformers.

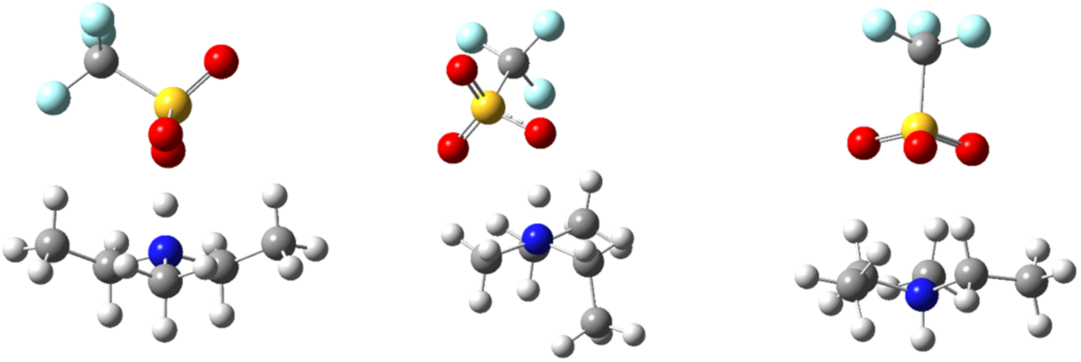


topa fronta frontca bottoma

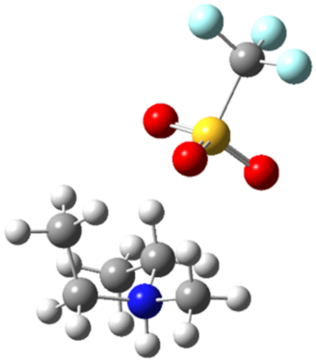
Figure S17:Optimised Ion Pair conformers for $[C_4C_1Im][TfO]$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
fronta	0.0	0.0	0.0
topa	1.3	1.6	-2.2
bottoma	4.5	5.8	4.3
frontca	4.6	3.8	4.0

Table S13:Relative energies for $[C_4C_1Im][TfO]$ Ion Pair conformers. Note the bottoma conformer has a small negative frequency ($\approx$ -4cm^{-1}).



NH-O, Conf 4   NH-O,Conf 3   Alkyl-O,Conf 2



Alkyl-O,Conf 1

Figure S18:Optimised Ion Pair conformers for [N$_{2,2,1,0}$][TfO].

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
NH-O,Conf 4	0.0	0.0	0.0
NH-O,Conf 3	4.5	4.2	4.7
Alkyl-O,Conf 2	64.2	61.9	61.4
Alkyl-O,Conf 1	72.9	71.2	71.6

Table S14:Relative energies for [N$_{2,2,1,0}$][TfO] Ion Pair conformers.

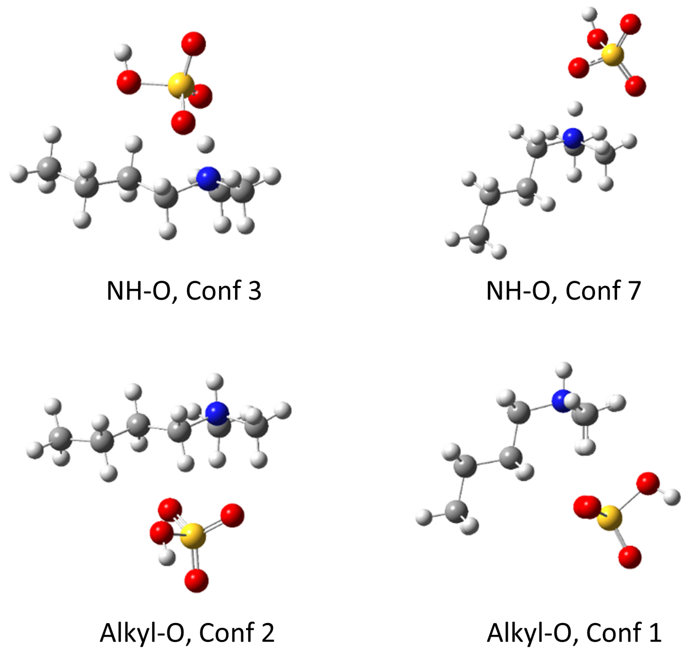


Figure S19:Optimised Ion Pair conformers for $[\mathrm{N}_{4,1,1,0}][\mathrm{HSO}_4]$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
NH-O,Conf 3	0.0	0.0	0.0
NH-O,Conf 7	10.1	10.9	6.5
Alkyl-O,Conf 2	65.5	62.3	65.0
Alkyl-O,Conf 1	79.6	77.6	77.0

Table S15:Relative energies for $[\mathrm{N}_{4,1,1,0}][\mathrm{HSO}_4]$ Ion Pair conformers.

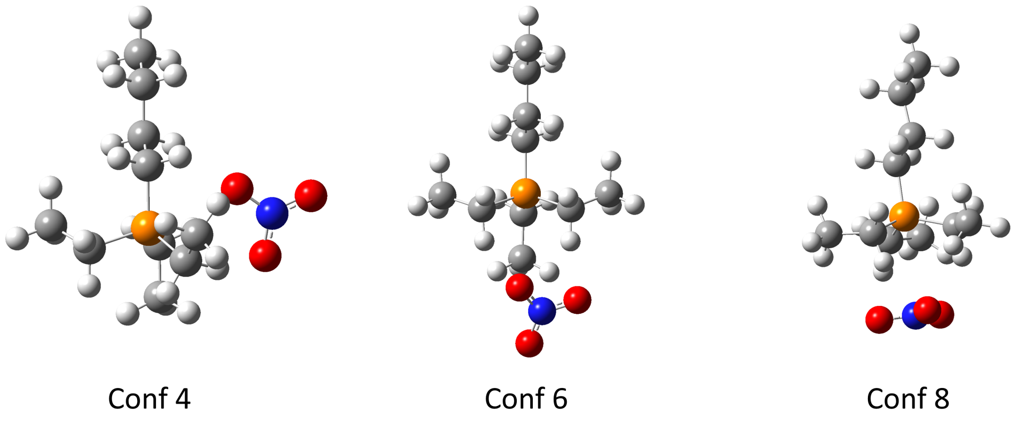
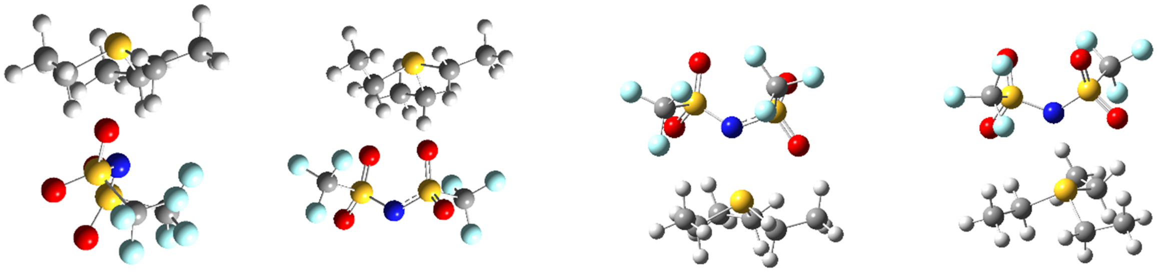


Figure S20:Optimised Ion Pair conformers for $[\mathrm{P}_{2,2,2,4}][\mathrm{NO}_3]$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
Conf 8	0.0	0.0	0.0
Conf 4	1.2	0.4	-0.7
Conf 6	13.5	15.3	7.2

Table S16:Relative energies for $[\mathrm{P}_{2,2,2,4}][\mathrm{NO}_3]$ Ion Pair conformers.

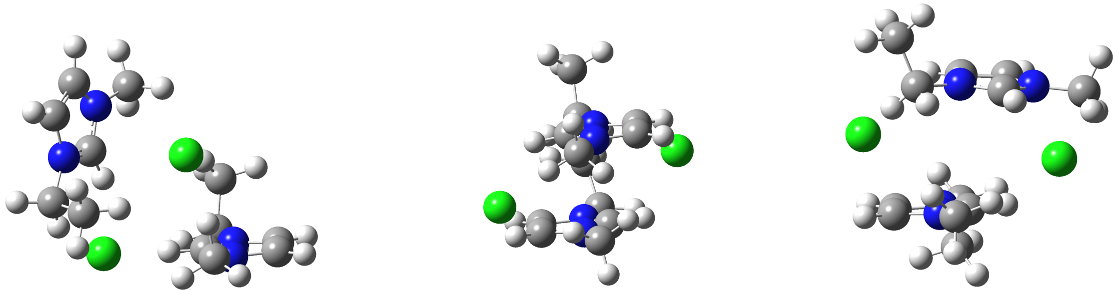


Alkyl-side, Cis　Alykl-side, Trans　S-side, Cis　S-side, Trans

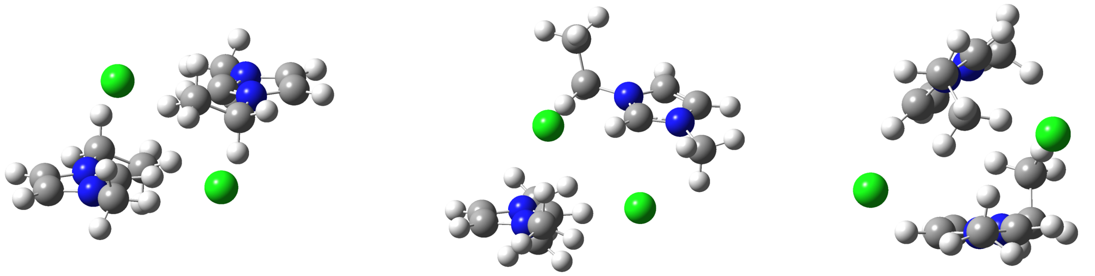
Figure S21:Optimised Ion Pair conformers for $[S_{2,2,2}][NTf_2]$.

Conformer	$\Delta E(ZPE)$ / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	ΔG / $kJ\ mol^{-1}$
Alkyl-side, Cis	0.0	0.0	0.0
Alkyl-side, Trans	2.4	2.5	3.6
S-side, Trans	14.5	14.2	14.0
S-side, Cis	23.4	23.4	27.3

Table S17:Relative energies for $[S_{2,2,2}][NTf_2]$ Ion Pair conformers.



D_FF_TT_T　M_BF_FB_A　M_FF_BB_R



D_BtF_FBt_A　D_BtF_FBt_R　M_BB_TT_P

Figure S22:Optimised Dimer conformers for $[C_2C_1Im]Cl$.

Conformer	$\Delta E(ZPE)\ /\ kJ\ mol^{-1}$	$\Delta E\ /\ kJ\ mol^{-1}$	$\Delta G\ /\ kJ\ mol^{-1}$
D_FF_TT_T	0.0	0.0	0.0
M_BF_FB_A	0.2	0.5	0.8
M_FF_BB_R	1.4	2.4	0.1
D_BtF_FBt_A	3.8	3.9	5.6
D_BtF_FBt_R	5.3	6.8	-6.2
M_BB_TT_P	32.2	33.1	36.6

Table S18:Relative energies for [C_2C_1Im]Cl Dimer conformers.

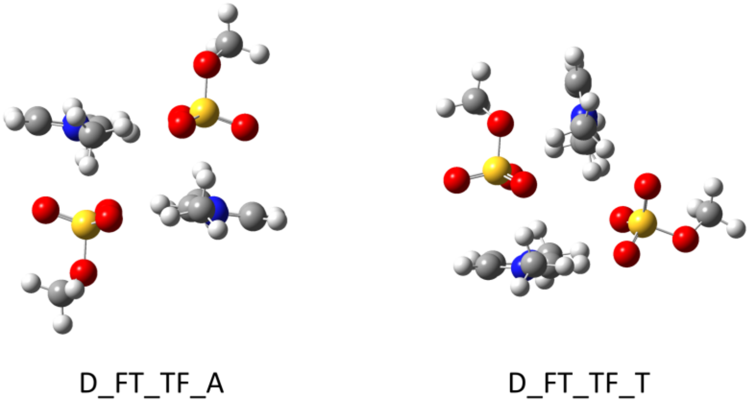


Figure S23:Optimised Dimer conformers for [C_1C_1Im][$MeSO_4$].

Conformer	$\Delta E(ZPE)\ /\ kJ\ mol^{-1}$	$\Delta E\ /\ kJ\ mol^{-1}$	$\Delta G\ /\ kJ\ mol^{-1}$
D_FT_TF_A	0.0	0.0	0.0
D_FT_TF_T	3.4	2.8	7.3

Table S19:Relative energies for [C_1C_1Im][$MeSO_4$] Dimer conformers.