Electronic Supplementary Material (ESI) for Faraday Discussions.

Electronic Supplementary Information

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Part 1: Auger transition

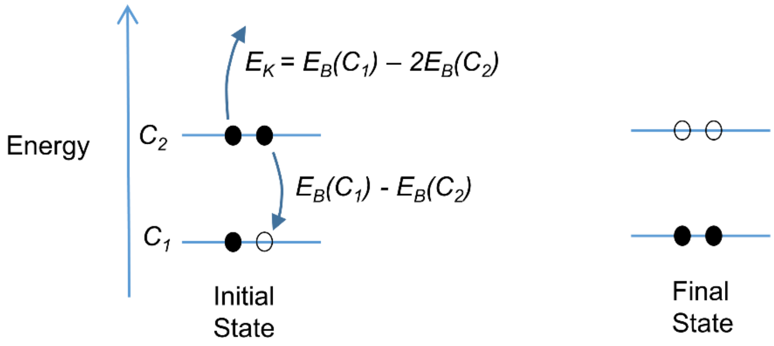


Figure S1: Schematic of the Auger process. E_K refers to kinetic energy of the emitted Auger electron.

Part 2: XP Spectra Used to Obtain S $2p_{3/2}$ values

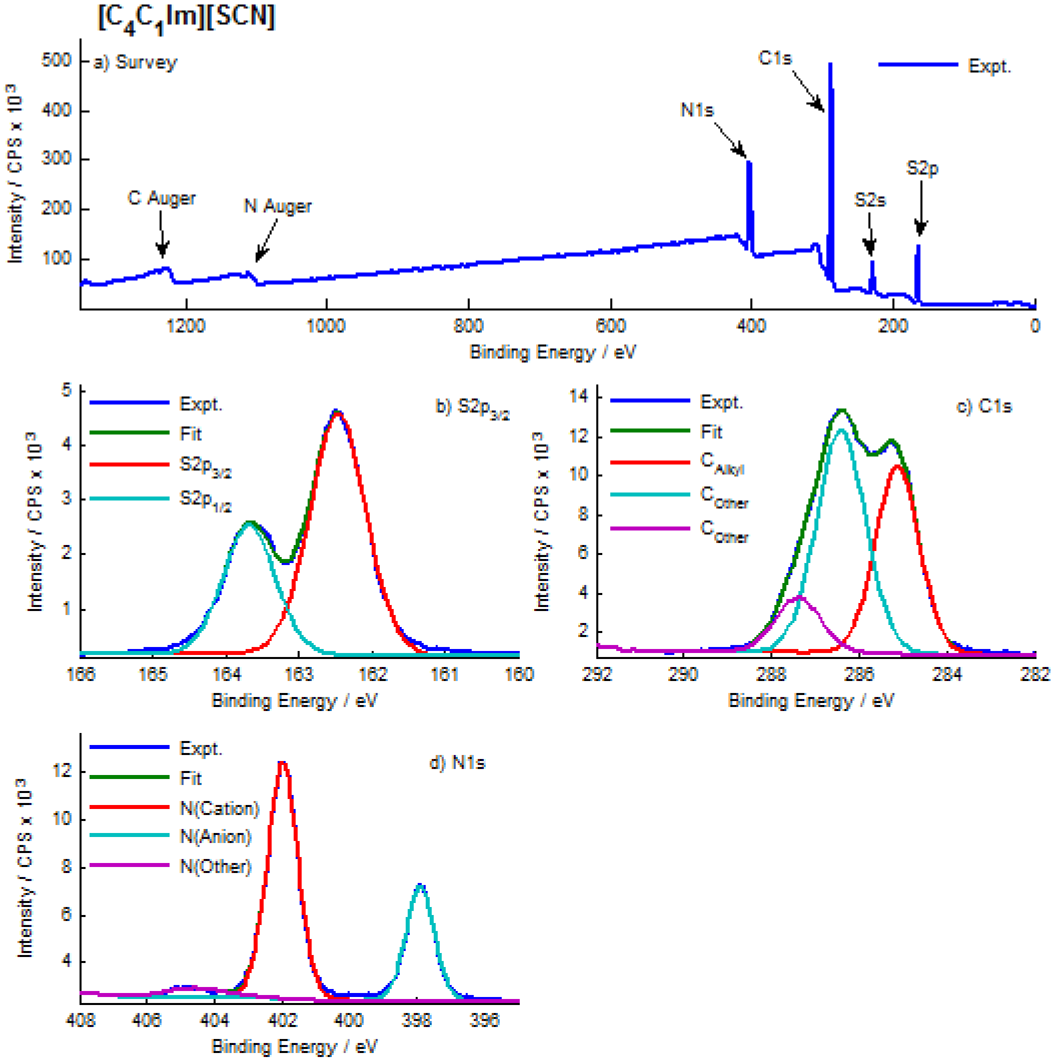


Figure S2: a) Survey and b-d) core level XP spectra for $[C_4C_1Im][SCN]$. All spectra are charge referenced to N_{cation} 1s = 401.9 eV. The N(Other) feature is assigned as a shake-up satellite.

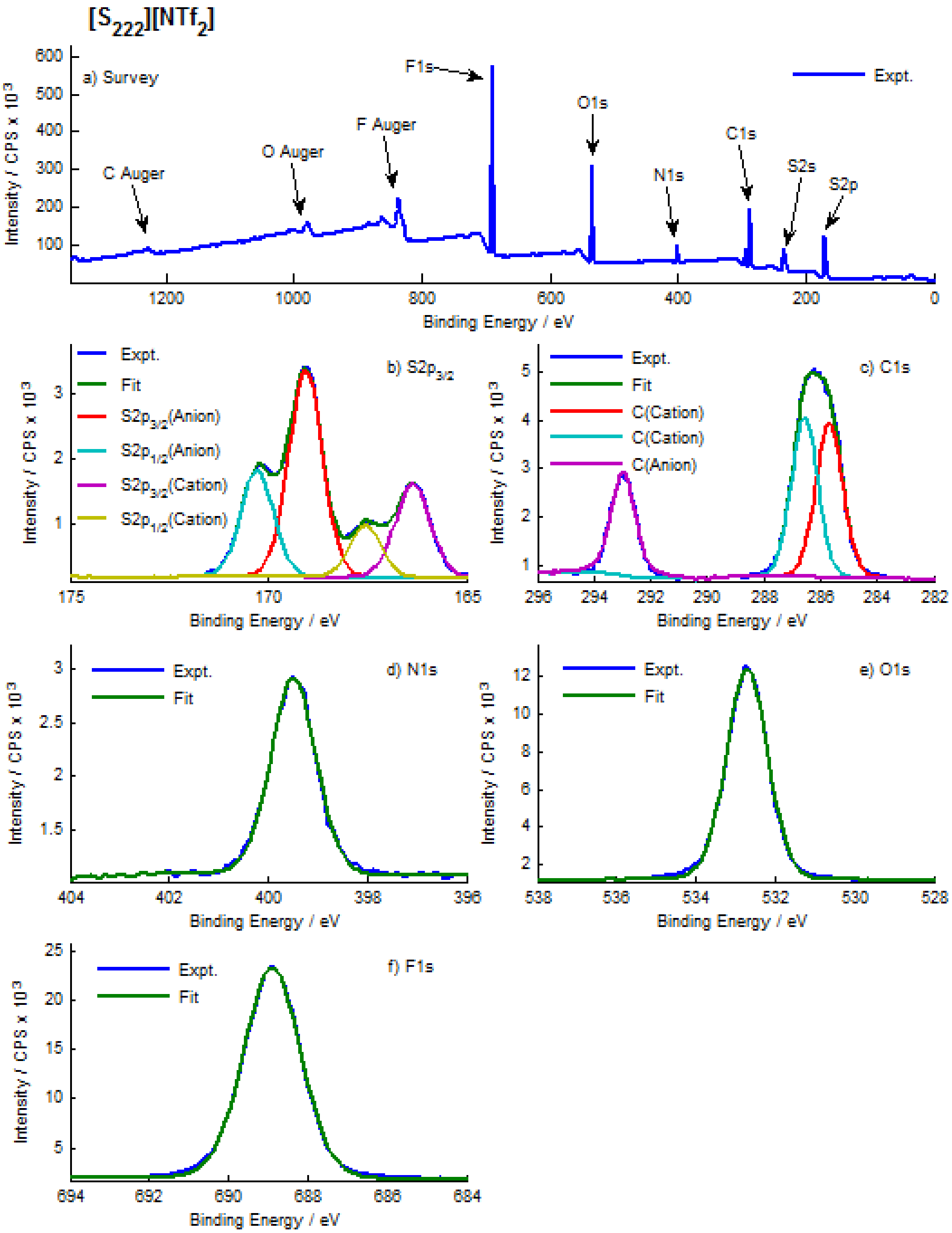


Figure S3: a) Survey and b-f) core level XP spectra for $[S_{2,2,2}][NTf_2]$. All spectra are charge referenced to CF_3 C 1s = 293.0 eV.

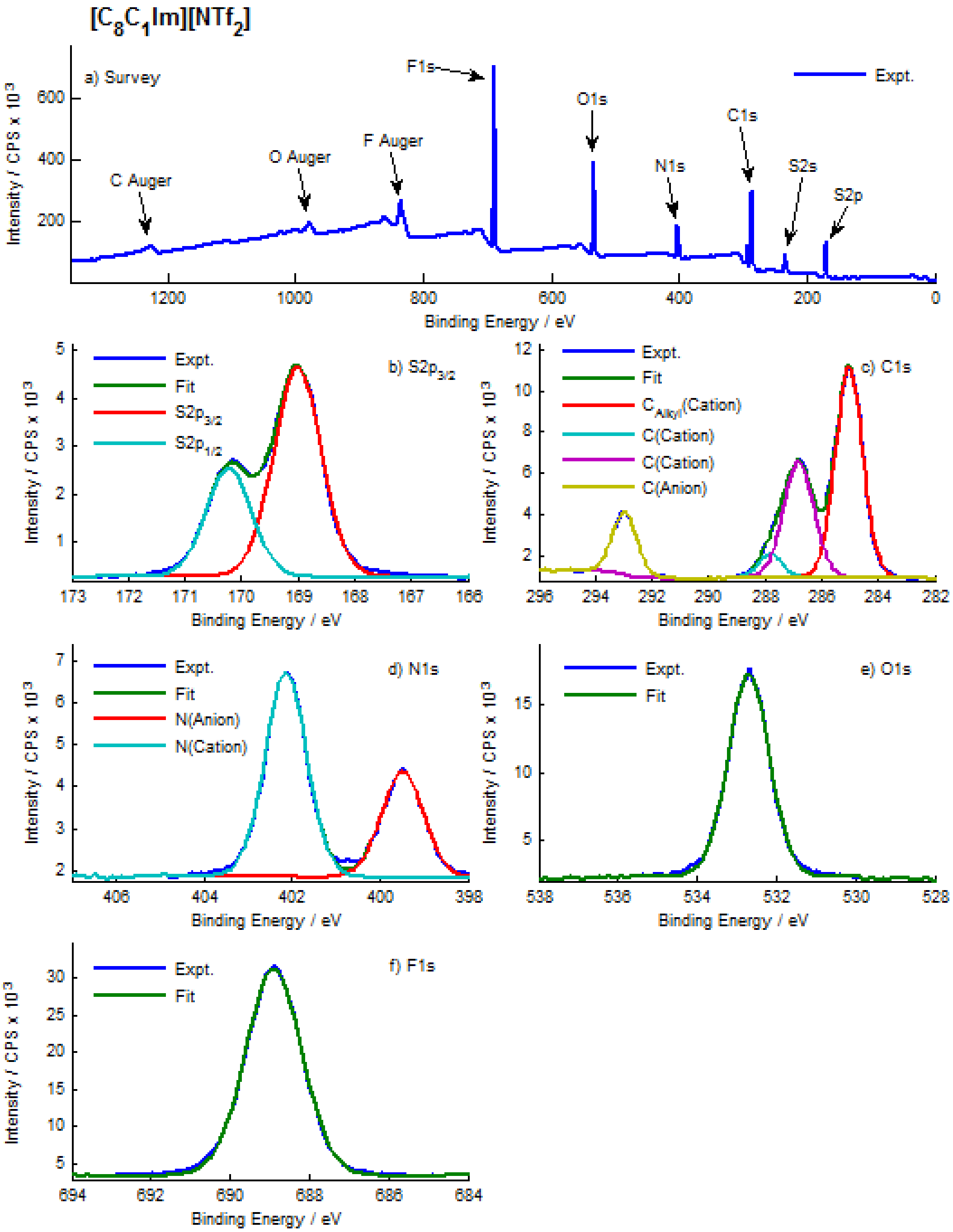


Figure S4: a) Survey and b-f) core level XP spectra for $[C_8C_1Im][NTf_2]$. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV.

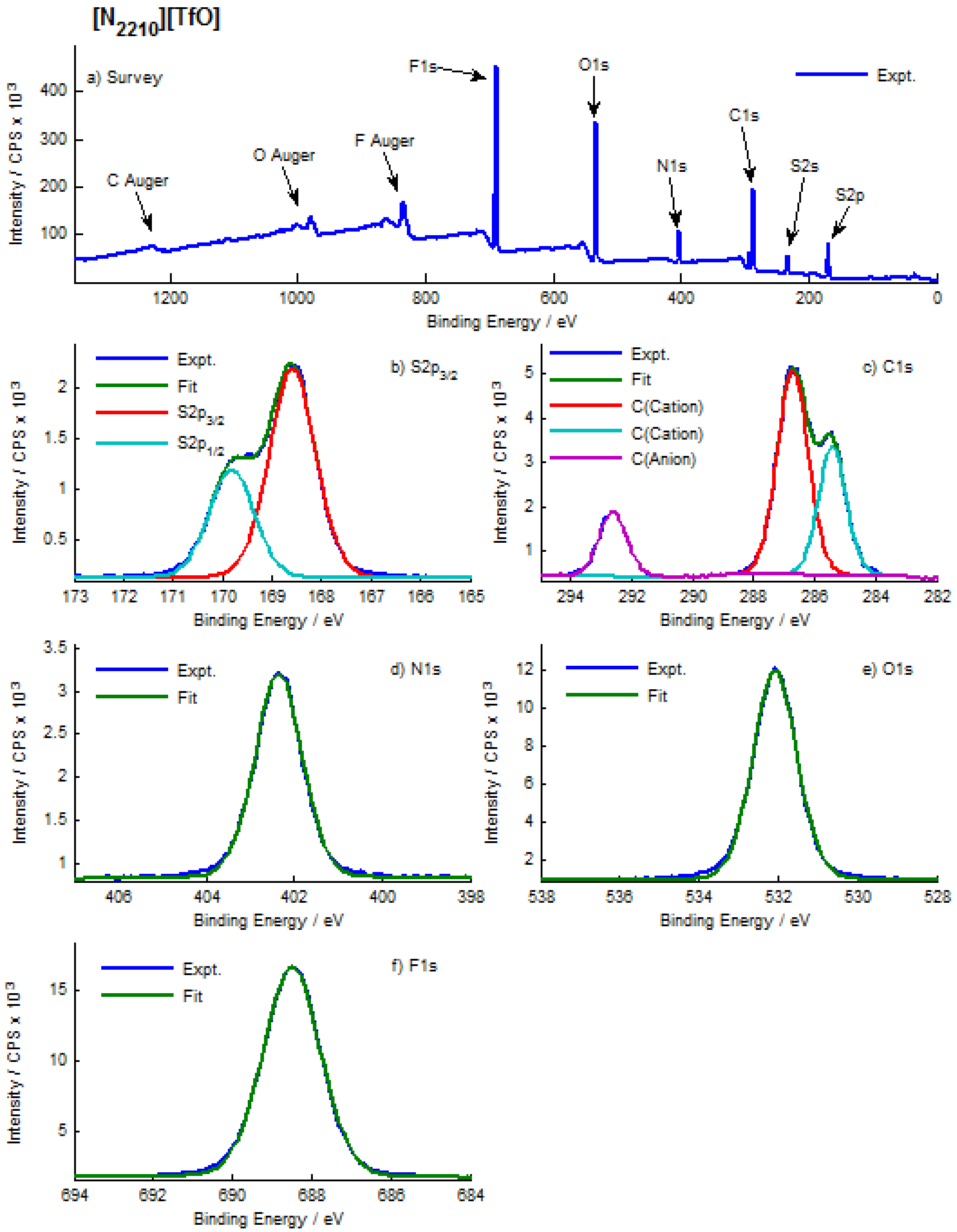


Figure S5 a) Survey and b-f) core level XP spectra for [N$_{2,2,1,0}$][TfO]. All spectra are charge referenced to F$_{anion}$ 1s = 688.5 eV.

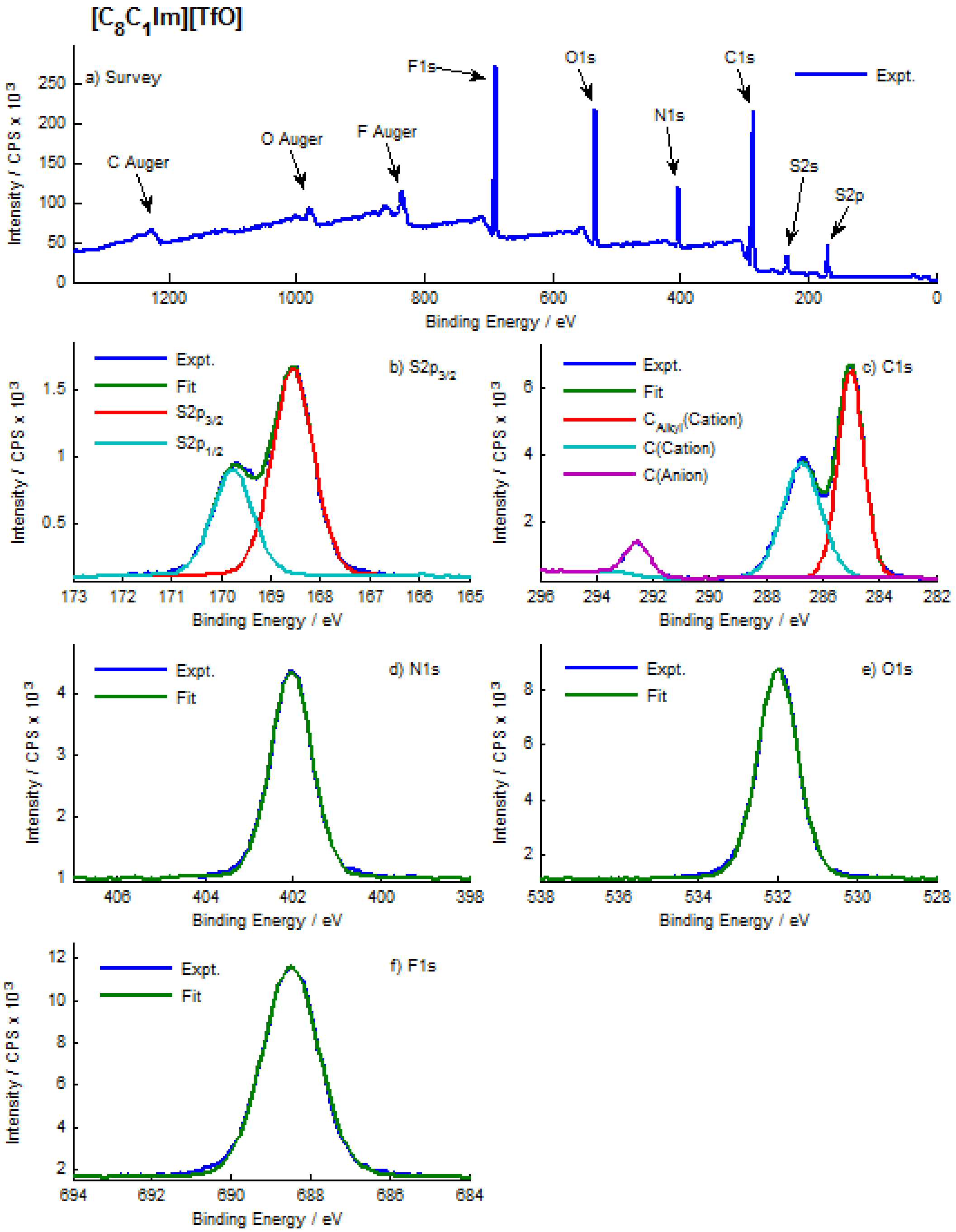


Figure S6: a) Survey and b-f) core level XP spectra for [C_8C_1Im][TfO]. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV.

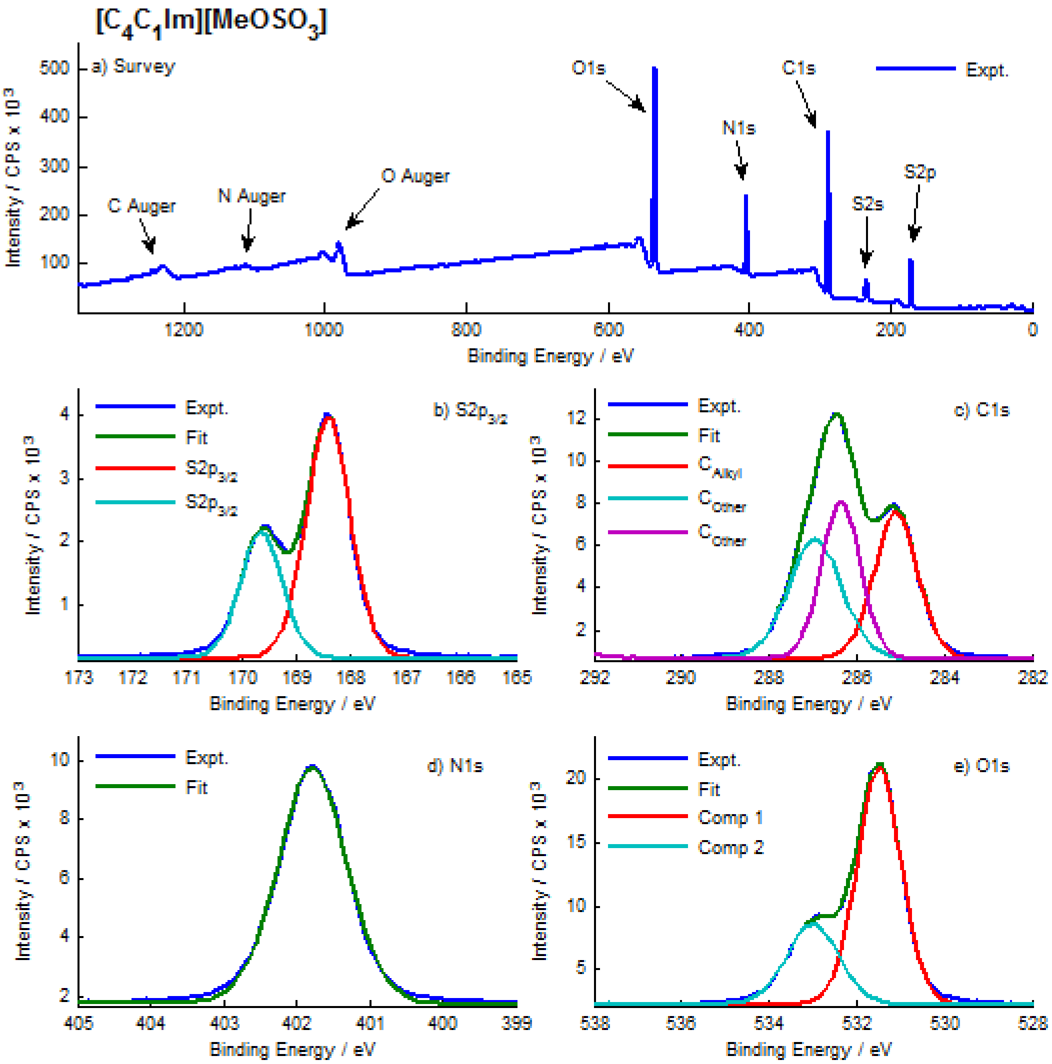


Figure S7: a) Survey and b-e) core level XP spectra for [C_4C_1Im][$MeOSO_3$]. All spectra are charge referenced to N_{cation} 1s = 401.8 eV.

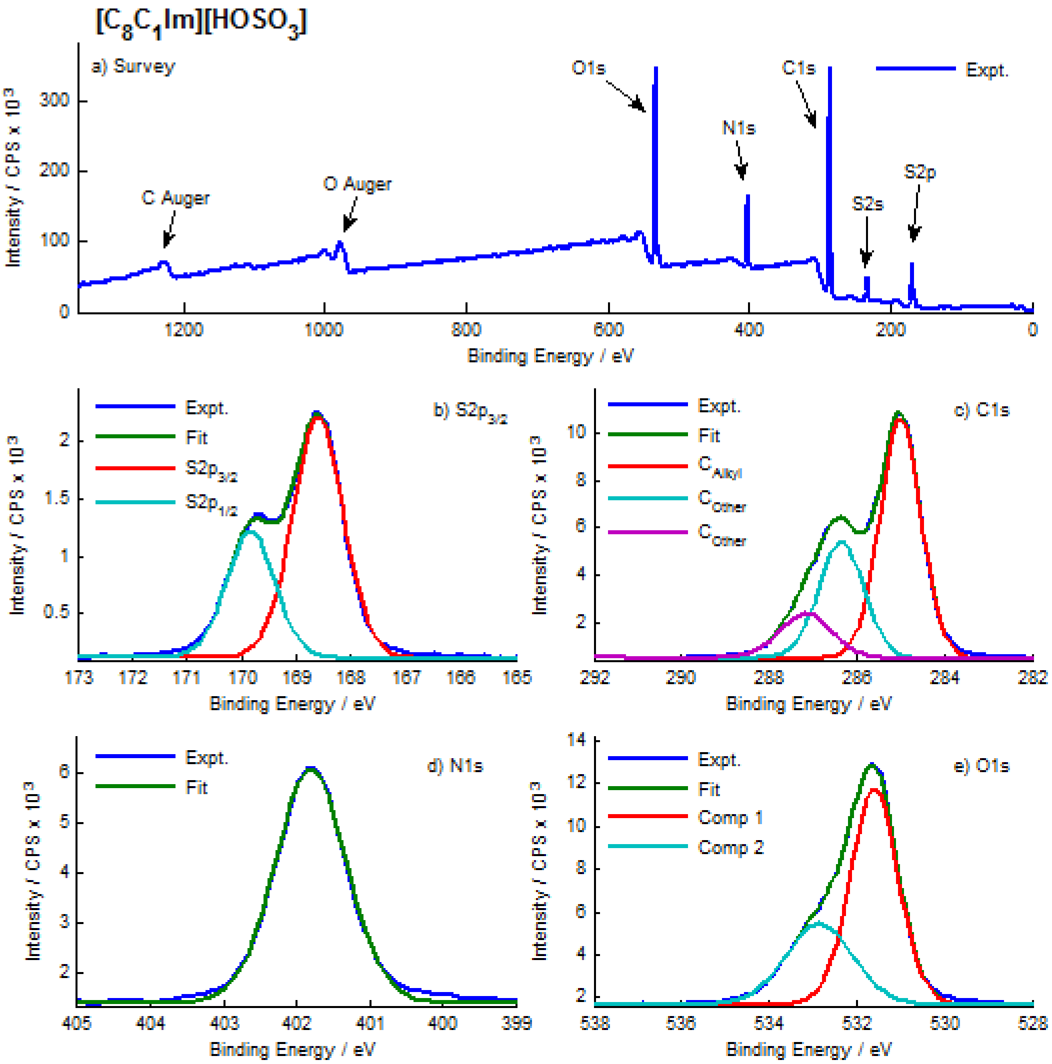


Figure S8: a) Survey and b-e) core level XP spectra for $[C_8C_1Im][HOSO_3]$. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV.

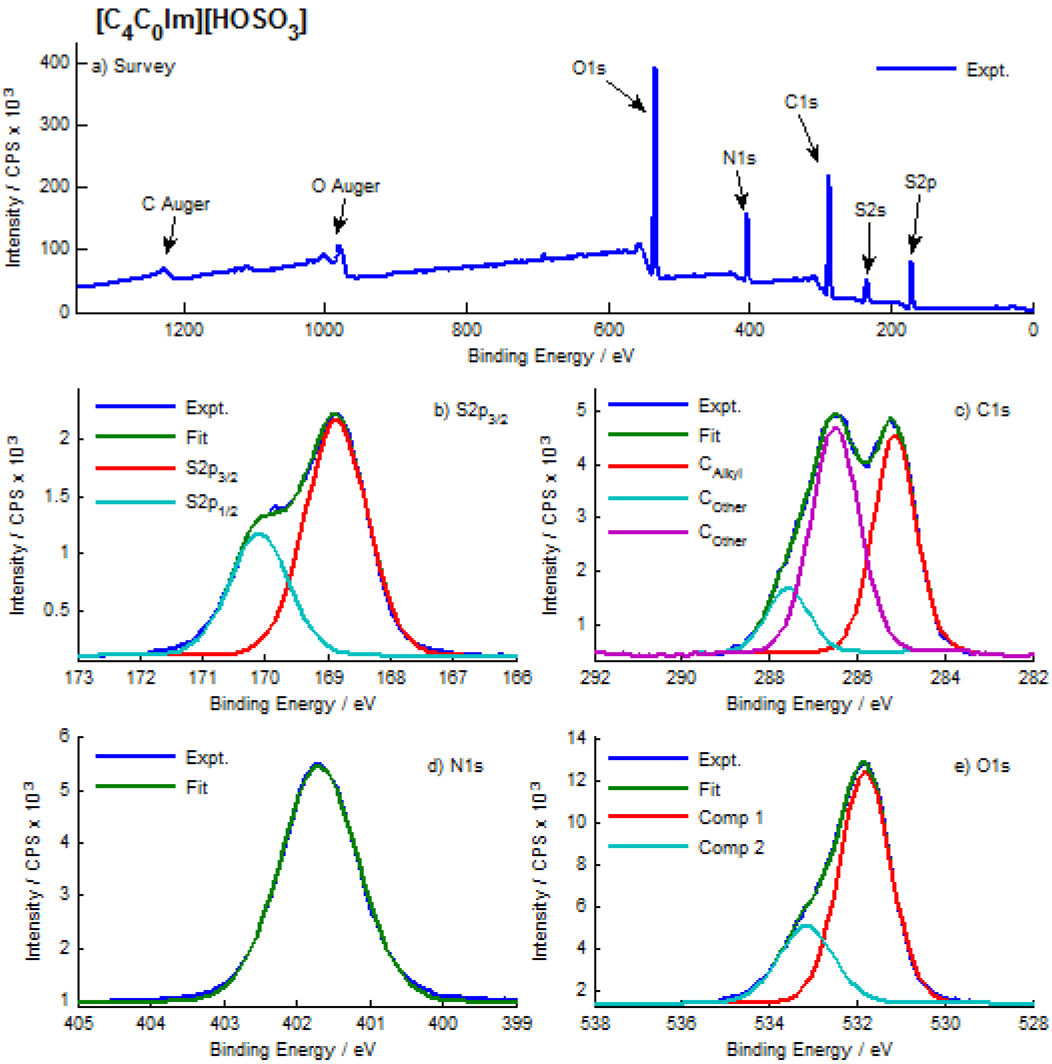


Figure S9: a) Survey and b-e) core level XP spectra for [C_4C_0Im][$HOSO_3$]. All spectra are charge referenced to C_{alkyl} 1s = 285.2 eV.

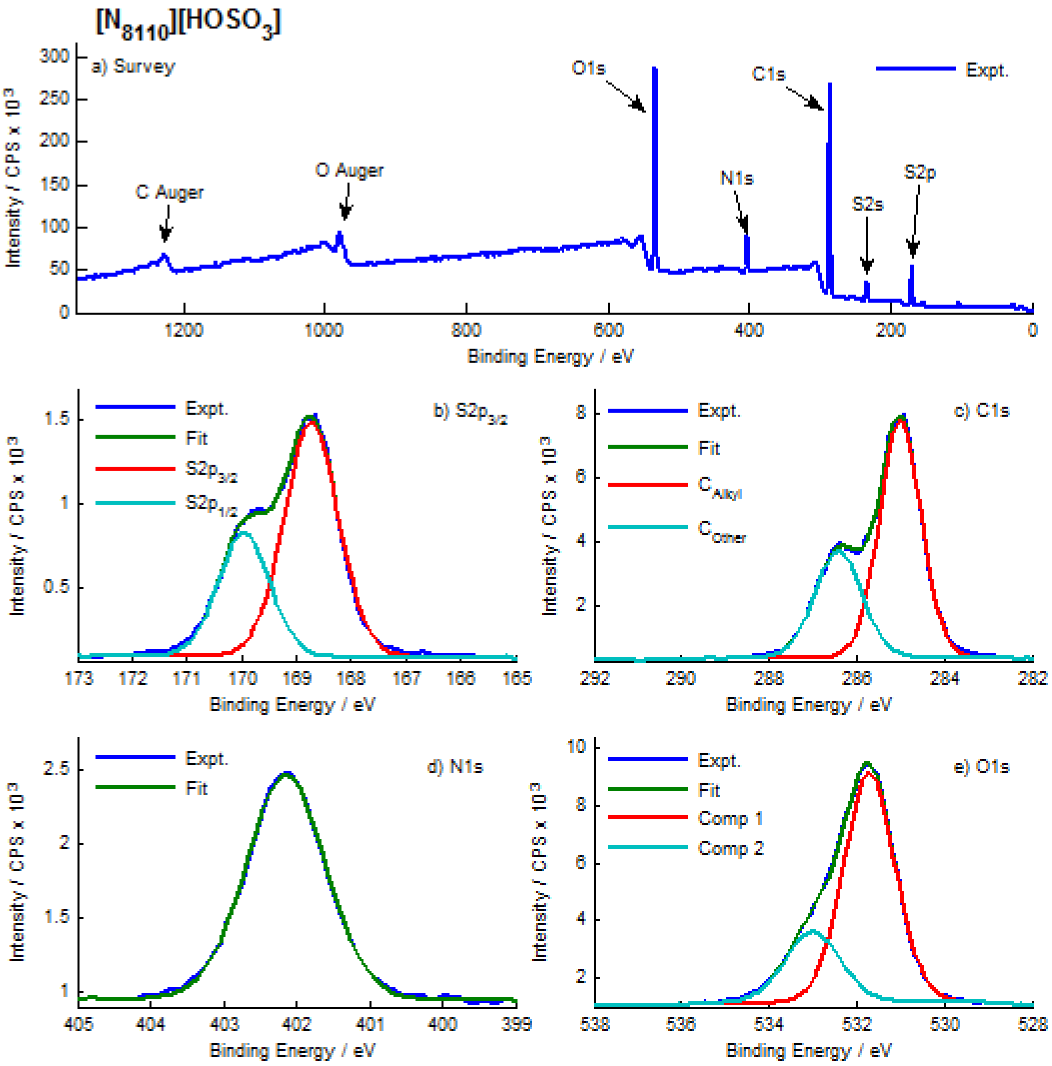


Figure S10: a) Survey and b-e) core level XP spectra for $[N_{8,1,1,0}][HSO_4]$. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV.

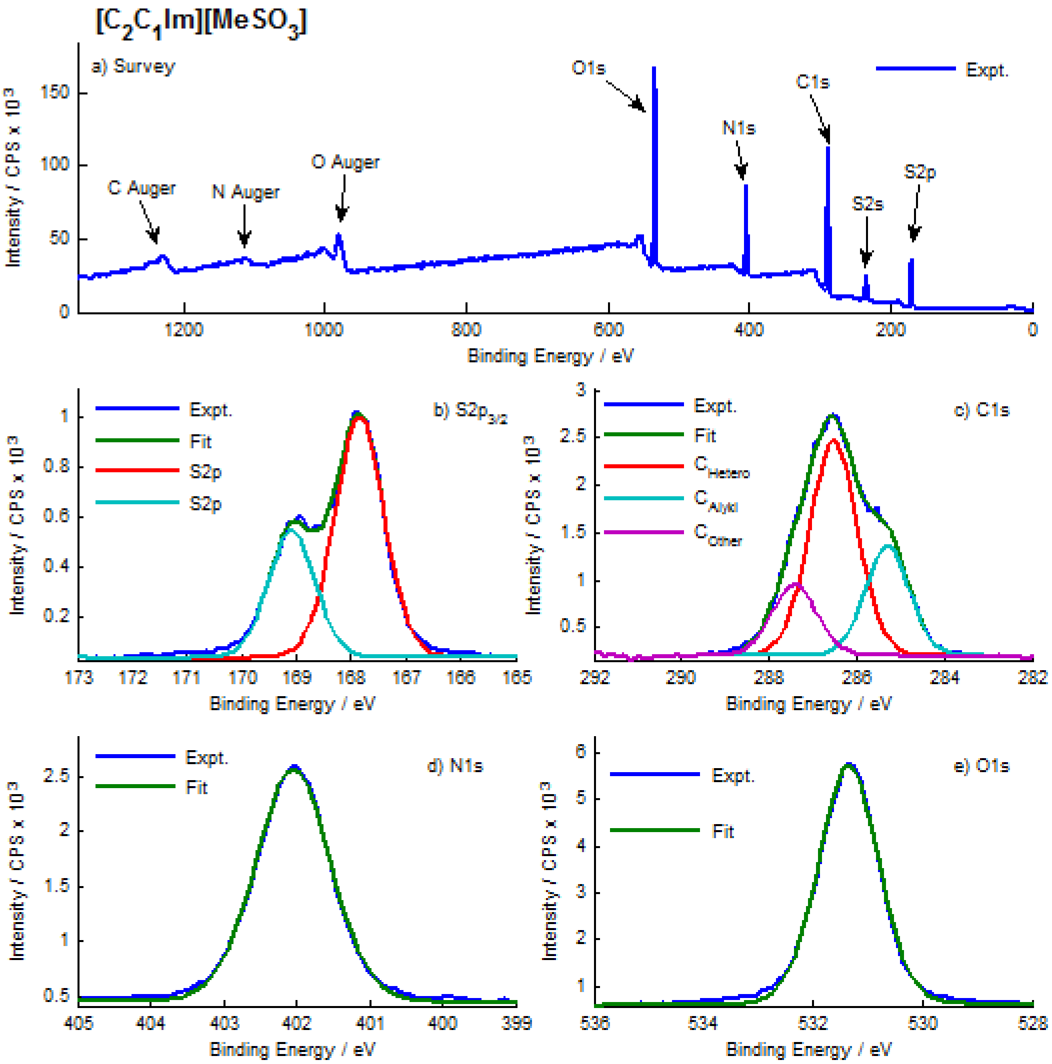


Figure S11: a) Survey and b-e) core level XP spectra for [C_2C_1Im][$MeSO_3$]. All spectra are charge referenced to C_{alkyl} 1s = 285.3 eV.

Part 3: XP Spectra Used to Obtain *β* values

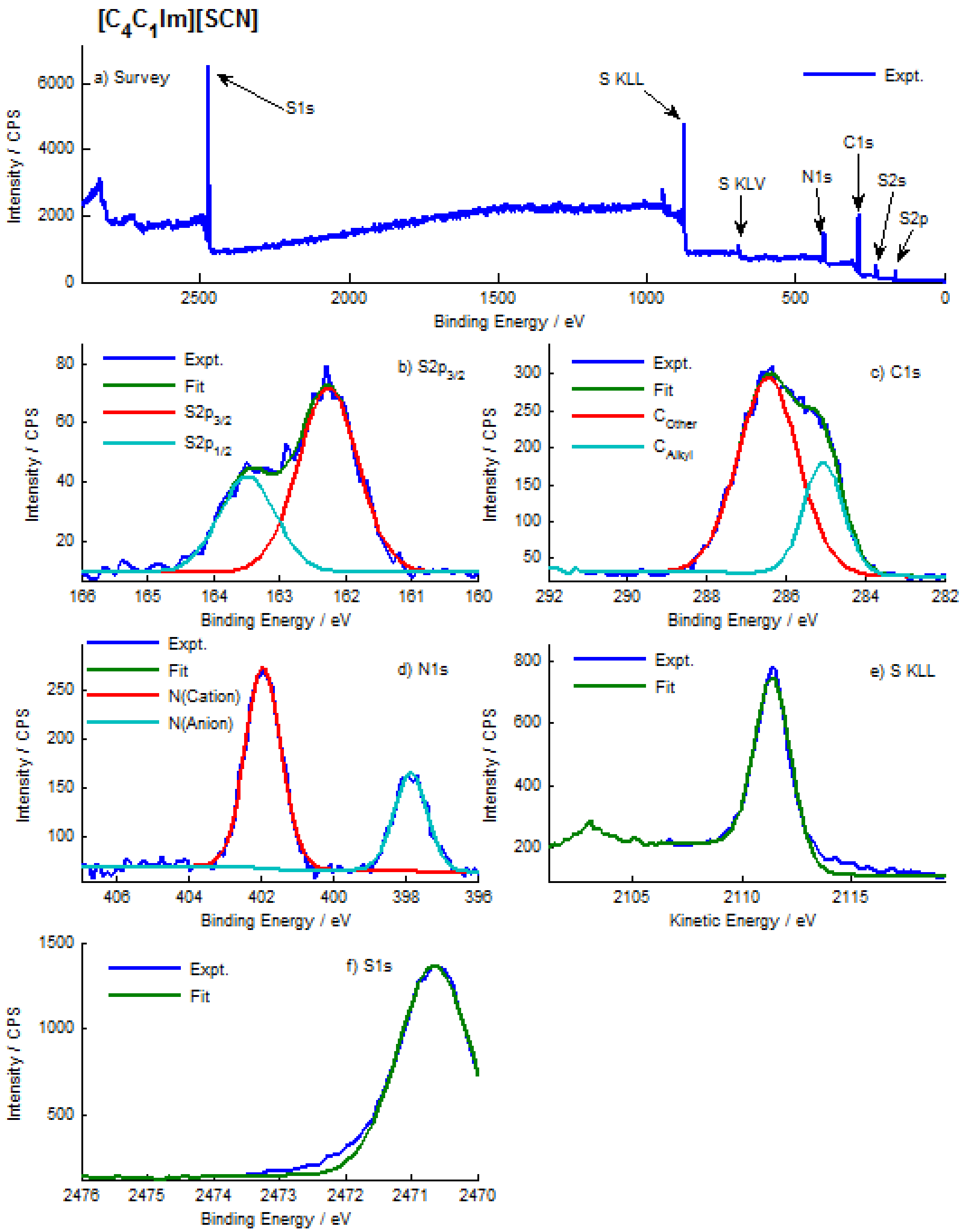


Figure S12: a) Survey and b-f) core level XP spectra for [C_4C_1Im][SCN]. All spectra are charge referenced to N_{cation} 1s = 401.9 eV. Note panel e) shows S $KL_{2,3}L_{2,3}$ Auger data.

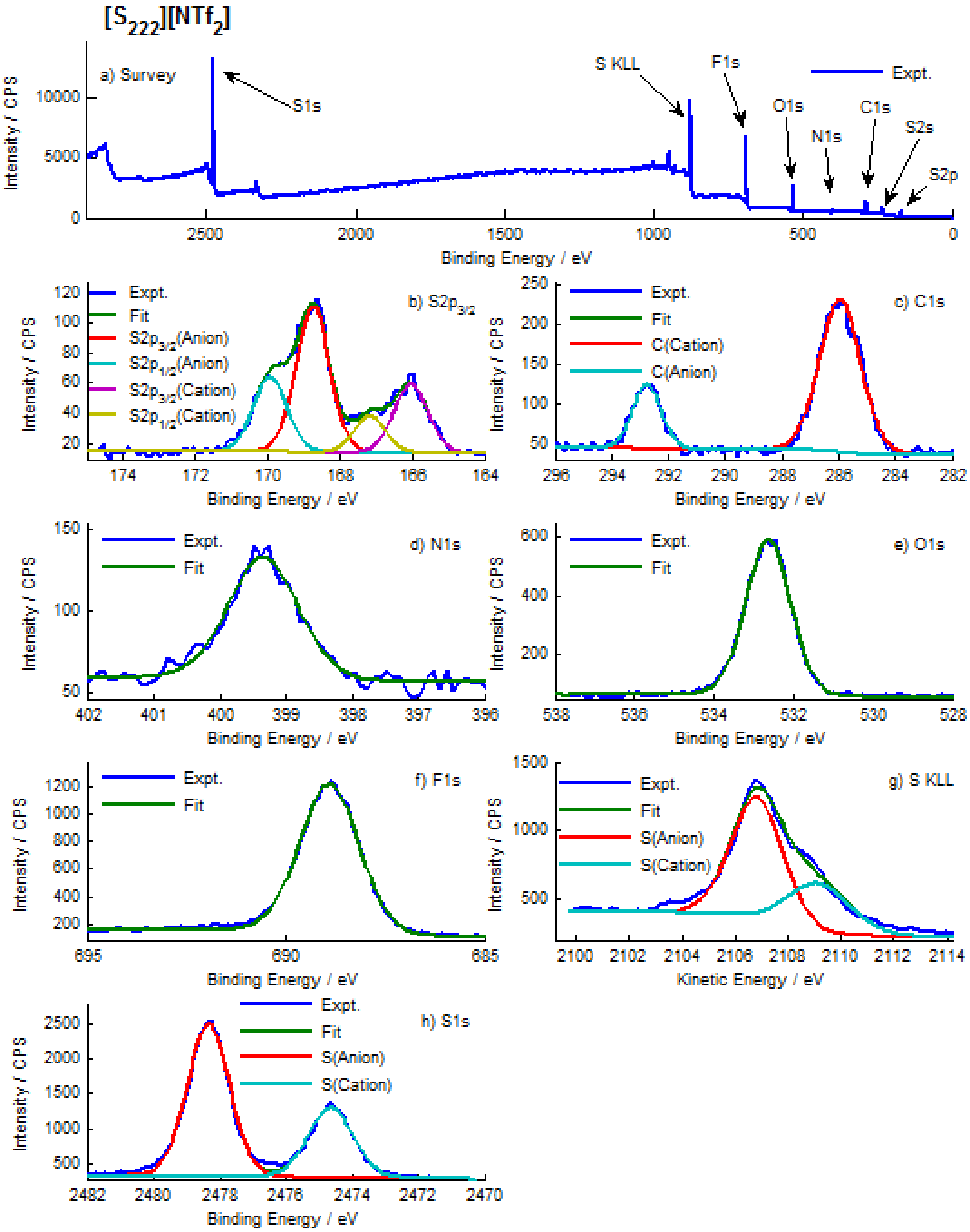


Figure S13: a) Survey and b-h) core level XP spectra for $[S_{2,2,2}][NTf_2]$. All spectra are charge referenced to CF_3 C 1s = 293.0eV. Note panel g) shows S $KL_{2,3}L_{2,3}$ Auger data.

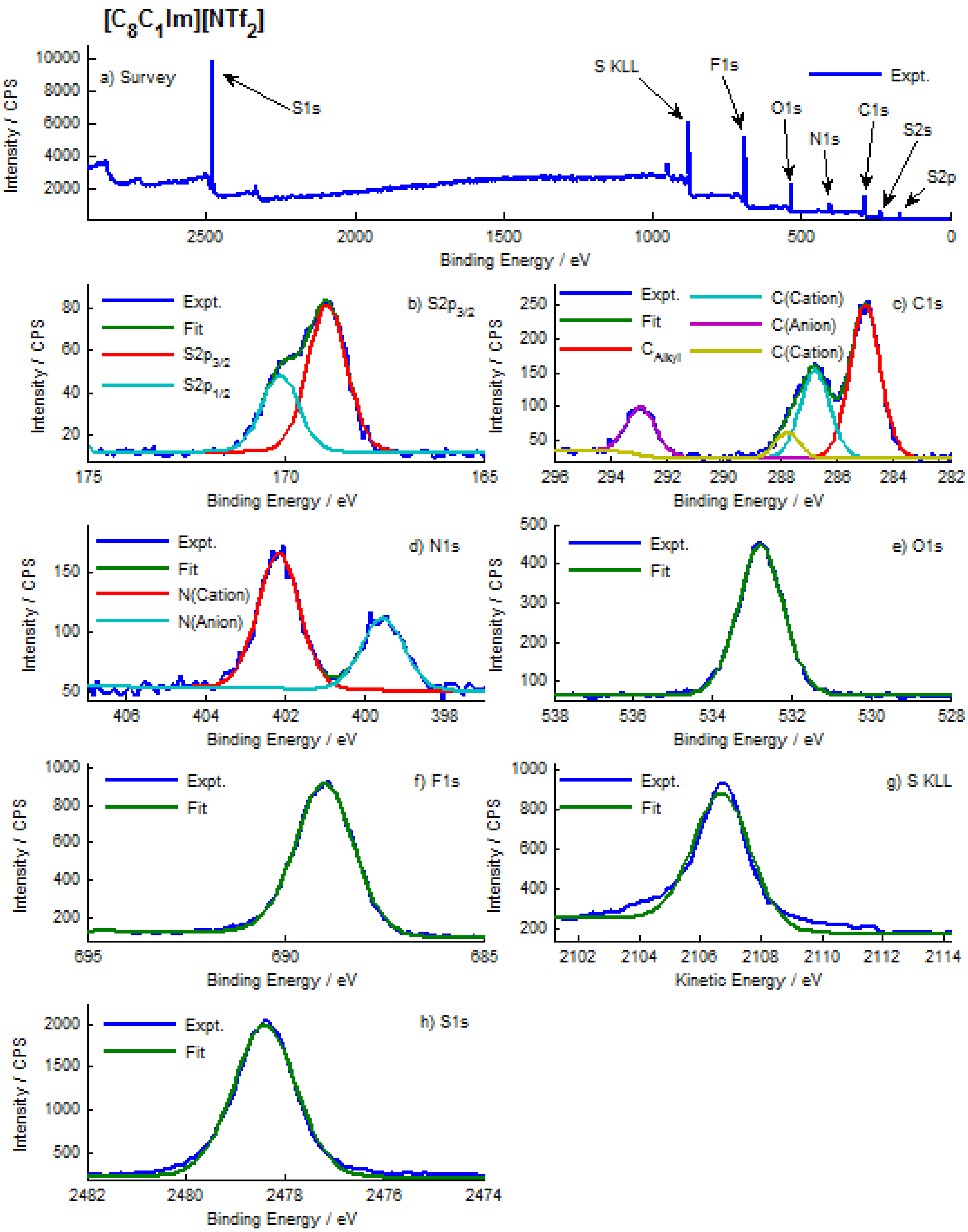


Figure S14: a) Survey and b-h) core level XP spectra for [C_8C_1Im][NTf_2]. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV. Note panel g) shows S $KL_{2,3}L_{2,3}$ Auger data.

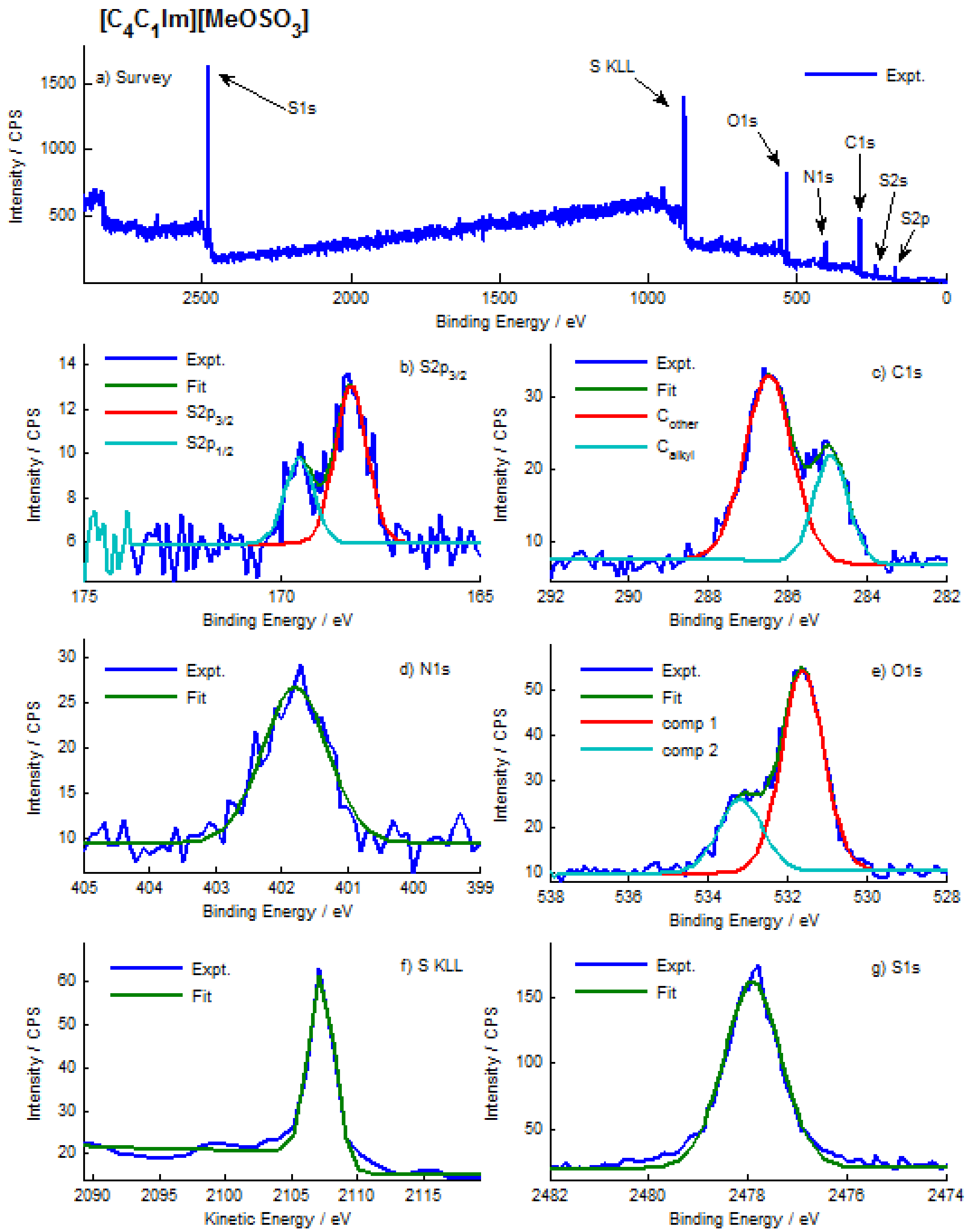


Figure S15: a) Survey and b-g) core level XP spectra for [C_4C_1Im][$MeSO_4$]. All spectra are charge referenced to N_{cation} 1s = 401.8 eV. Note panel f) shows S $KL_{2,3}L_{2,3}$ Auger data.

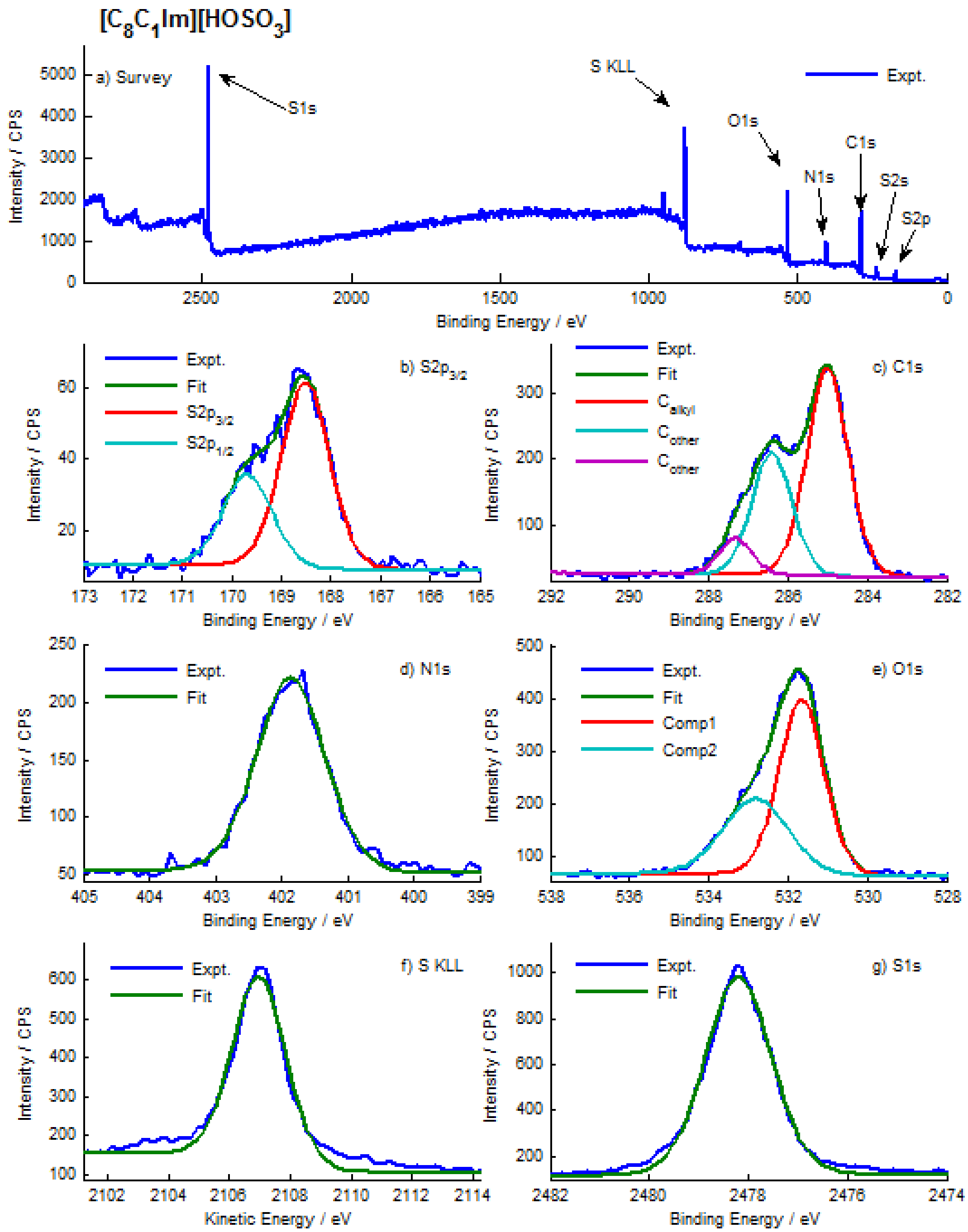


Figure S16: a) Survey and b-g) core level XP spectra for [C_8C_1Im][HSO_4]. All spectra are charge referenced to C_{alkyl} 1s = 285.0 eV. Note panel f) shows S $KL_{2,3}L_{2,3}$ Auger data.

Part 4: Charge Referencing

Ionic Liquid	Core orbital used for charge referencing	Core orbital E_B used for charge referencing / eV
$[C_8C_1Im][NTf_2]$	C_{alkyl} 1s	285.0
$[C_8C_1Im][HSO_4]$	C_{alkyl} 1s	285.0
$[C_8C_1Im][TfO]$	C_{alkyl} 1s	285.0
$[N_{8,1,1,0}][HSO_4]$	C_{alkyl} 1s	285.0
$[C_4C_1Im][SCN]$	N_{cation} 1s	401.9
$[C_4C_1Im][MeSO_4]$	N_{cation} 1s	401.8
$[S_{2,2,2}][NTf_2]$	C_{CF3} 1s	293.0
$[N_{2,2,1,0}][TfO]$	F_{anion} 1s	688.5
$[C_2C_1Im][MeSO_3]$	C_{alkyl} 1s	285.3
$[C_4C_0Im][HSO_4]$	C_{alkyl} 1s	285.2

Table S1: Description of how all ILs were charge referenced.

A major advantage of XPS over NEXAFS spectroscopy is that all E_B values can potentially be matched to the same reference level; usually the Fermi level, E_F, is used for condensed-phase measurements.[1] Careful charge referencing of XPS data is required to obtain E_B values that can be compared between different ILs.[2] The most common charge referencing method for ILs is to use a well-characterised internal reference E_B, allowing all E_B values for different ILs to be referenced to the same E_F. The most commonly used internal standard for XPS is such that all E_B values are referenced to C_{alkyl} 1s peak E_B = 285.0 eV relative to E_F.[3] Internal referencing of C_{alkyl} 1s peak E_B = 285.0 eV has previously been successfully employed for a wide range of $[C_nC_1Im][A]$ ILs[2, 4, 5] and other ILs[6-11].

XP spectra for the three $[C_8C_1Im][A]$ ILs studied here were charge referenced by shifting all core orbitals so that C_{alkyl} 1s peak = 285.0 eV. XP spectra for $[N_{8,1,1,0}][HSO_4]$ were also referenced to C_{alkyl} 1s peak E_B = 285.0 eV. The other six ILs studied here did not contain sufficient amounts of alkyl carbon for this value to be obtained directly from C 1s spectrum. Therefore, we use indirect methods to match E_B to C_{alkyl} 1s peak E_B = 285.0 eV.

We measured XPS of $[C_8C_1Im][SCN]$ and set C_{alkyl} 1s peak E_B = 285.0 eV; this gave N_{cation} 1s peak E_B = 401.9 eV. Consequently, for $[C_4C_1Im][SCN]$ N_{cation} 1s peak E_B = 401.9 eV was used for charge referencing. The assumption that the N_{cation} 1s peak has constant E_B for the same anion and different n has been demonstrated to hold for a wide range of $[C_nC_1Im][A]$ ILs.[2] A similar procedure was used to charge reference $[C_4C_1Im][MeSO_4]$. We measured XPS of $[C_4C_1Im][OcSO_4]$ and set C_{alkyl} 1s peak E_B = 285.0 eV; this gave N_{cation} 1s peak E_B = 401.8 eV. Consequently, for $[C_4C_1Im][MeSO_4]$ N_{cation} 1s peak E_B = 401.8 eV was used for charge referencing.

For $[S_{2,2,2}][NTf_2]$, there is insufficient alkyl carbon to use the C_{alkyl} 1s peak E_B = 285.0 eV as a reference. Therefore, we used C_{CF3} 1s peak E_B = 293.0 eV as the charge reference (obtained from XPS of $[C_8C_1Im][NTf_2]$), as the anion peaks are not expected to be significantly affected by the identity of the aprotic cation, as can be demonstrated by comparing anionic E_B for

$[C_8C_1Im][NTf_2]$, $[C_8C_1Pyrr][NTf_2]$ and $[C_8C_1Py][NTf_2]$ ILs.[2, 5-7] For $[N_{2,2,1,0}][TfO]$, we used F_{anion} 1s peak E_B = 688.5 eV as the charge reference (obtained from XPS of $[C_8C_1Im][TfO]$). For $[S_{2,2,2}][NTf_2]$, we did not use the F_{anion} 1s peak for charge referencing as this led to problems when using the monochromated Ag Lα' source ($h\nu$ =2984.6 eV); an S $KL_{2,3}V$ Auger peak occurs at E_K ~2295 eV (*i.e*. apparent E_B ~689 eV). Therefore, the more intense F_{anion} 1s peak at E_B ~688.8 eV could not be used due to overlap with this small Auger peak.

For $[C_2C_1Im][MeSO_3]$ and $[C_4C_0Im][HSO_4]$ no reliable anionic peak E_B references are readily available. For $[C_2C_1Im][MeSO_3]$, we estimated C_{alkyl} 1s peak E_B = 285.3 eV, based upon XPS for a wide range of $[C_2C_1Im][A]$ ILs, for which C_{alkyl} 1s peak E_B = 285.3 eV was the average value.[2] For $[C_4C_0Im][HSO_4]$, we potentially could have used an anionic $[HSO_4]^-$ peak obtained for $[C_8C_1Im][HSO_4]$ as a charge reference. However, as $[C_4C_0Im][HSO_4]$ is a protic IL, we were unsure whether the cation might affect E_B values for the $[HSO_4]^-$ anion. Therefore, we estimated C_{alkyl} 1s peak E_B = 285.2 eV, based upon XPS for a wide range of $[C_4C_1Im][A]$ ILs, for which C_{alkyl} 1s peak E_B = 285.2 eV was the average value.[2]

Part 5: Other Information

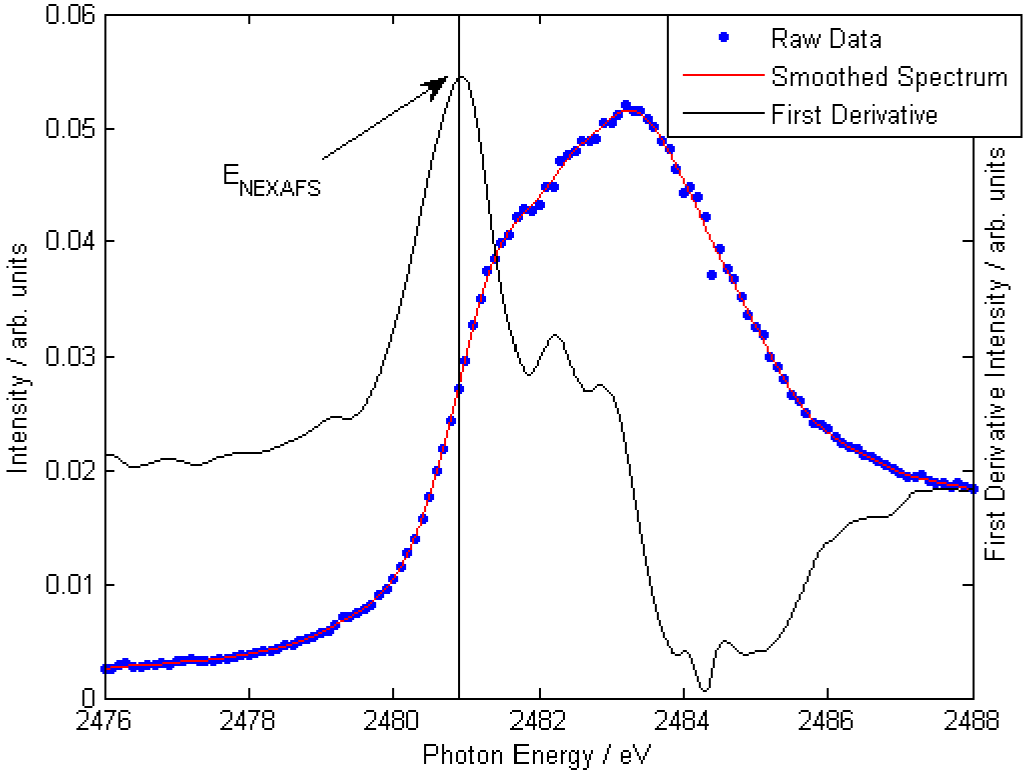


Figure S17: Raw experimental and smoothed NEXAFS spectrum for the S 1s edge of $[C_8C_1Im][HSO_4]$.

Ionic Liquid	Number of Conformers for GP	Number of Conformers for IL(SMD)
$[C_4C_1Im][NTf_2]$	7	6
$[C_4C_1Im][TfO]$	7	7
$[C_4C_1Im][HSO_4]$	6	5
$[C_4C_1Im][MeSO_4]$	5	5
$[C_4C_1Im][SCN]$	10	10
$[C_2C_1Im][MeSO_3]$	5	5
$[C_4C_0Im][HSO_4]$	6	4
$[N_{2,2,1,0}][TfO]$	4	4
$[N_{4,1,1,0}][HSO_4]$	8	4
$[S_{2,2,2}][NTf_2]$	23	21

Table S2: Number of conformers used to find atomic charges for all ILs studied.

Ionic Liquid	E_{NEXAFS} / eV
$[C_2C_1Im][NTf_2]$	2479.7
$[C_4C_1Im][NTf_2]$	2479.6
$[C_8C_1Im][NTf_2]$	2479.7
$[C_{12}C_1Im][NTf_2]$	2479.7

Table S3: Measured E_{NEXAFS} values for $[C_nC_1Im][NTf_2]$ of varying alkyl chain lengths.

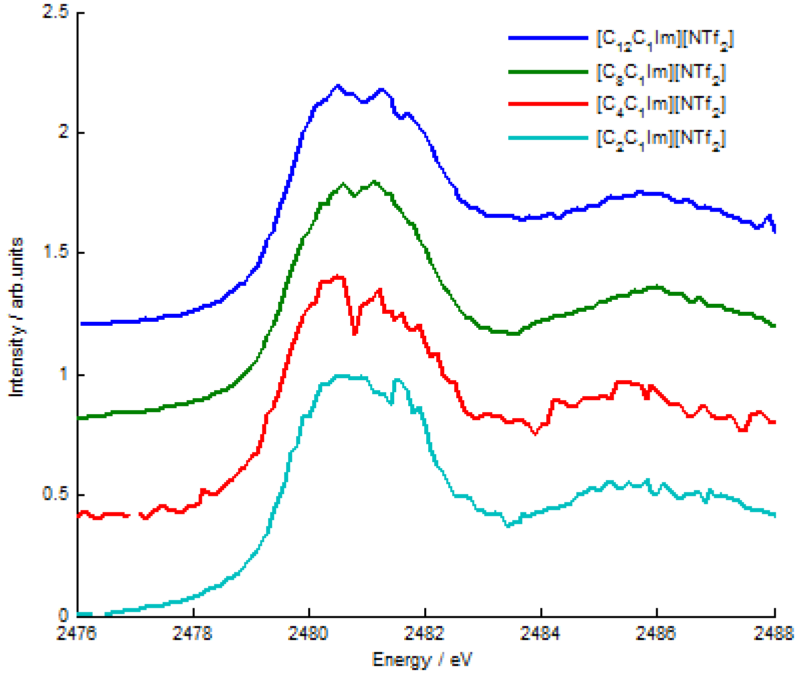


Figure S18: S 1s edge NEXAFS spectra for $[C_nC_1Im][NTf_2]$ based ILs with varying chain lengths.

System	E_B S $2p_{3/2}$ (±0.2 eV) / eV	E_B S1s (±0.2 eV) / eV	E_K S KLL (±0.2 eV) / eV	β (±0.6 eV) / eV	$\frac{\Delta\beta}{2}$ (±0.3 eV) / eV
$[C_4C_1Im][SCN]$	162.4	2470.6	2111.5	-34.3	0.0
$[S_{2,2,2}][Tf_2N]$(Cation)	166.3	2474.8	2108.9	-33.3	0.5
$[S_{2,2,2}][Tf_2N]$(Anion)	169.0	2478.6	2106.6	-34.0	0.1
$[C_8C_1Im][Tf_2N]$	169.0	2478.4	2106.7	-33.7	0.3
$[C_4C_1Im][C_1OSO_3]$	168.4	2477.9	2107.3	-33.8	0.3
$[C_8C_1Im][C_0OSO_3]$	168.6	2478.2	2107	-34.0	0.1
$[C_2C_1Im][MeSO_3]$	167.8	2477.3	2107.6	-33.8	0.3
$[C_8C_1Im][TfO]$	168.6	2478.2	2106.7	-34.3	0.0

Table S4: Electron binding energies (E_B) and Auger kinetic energies (E_K) used to calculate β values. All values are charge referenced, see Table S1 for core orbitals used for referencing.

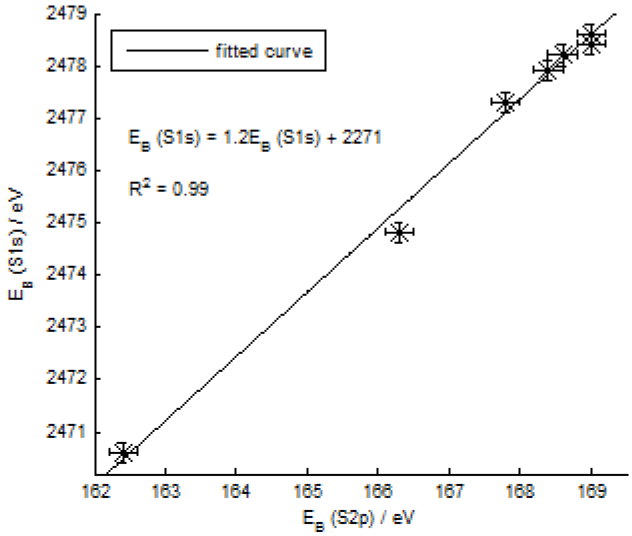


Figure S19: Correlation between measured electron binding energies (E_B) for the S 1s and the S $2p_{3/2}$ core orbitals for a range of ionic liquids.

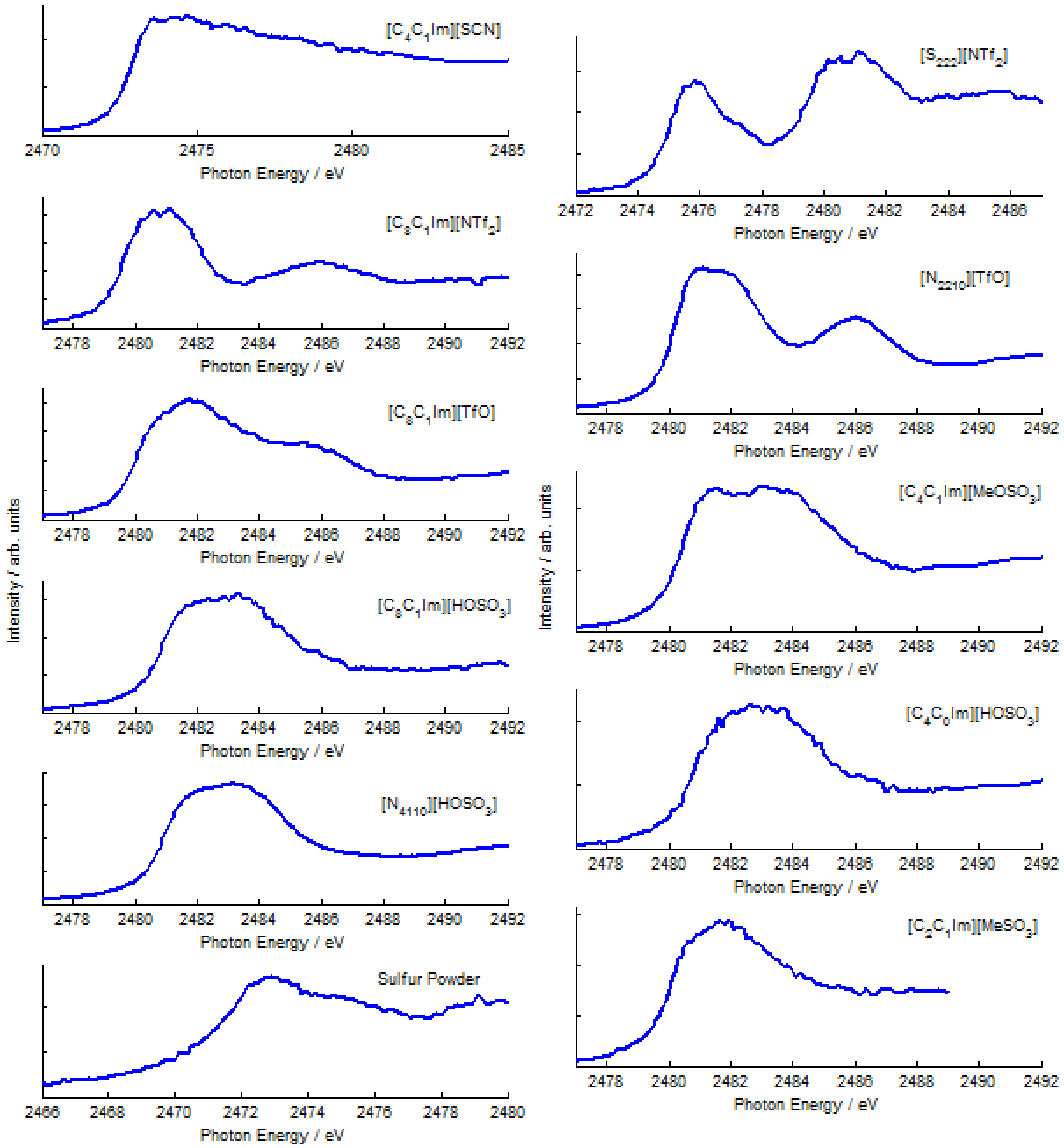


Figure S20: NEXAFS S 1s edge spectra for all ILs studied.

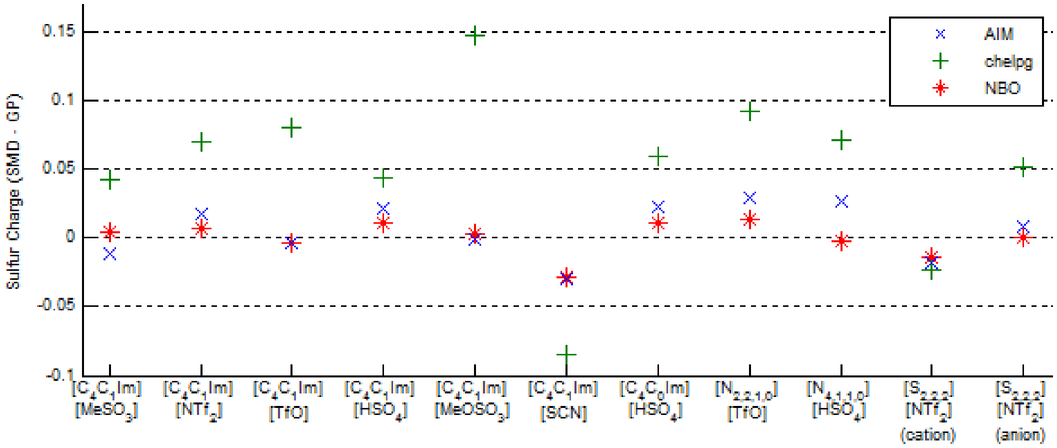


Figure S21: Difference between average sulfur charges, *q*(S), calculated for ion pair conformers in a solvent continuum model and in the gas phase. *q*(S) are from an unweighted average of all identified conformers.

	Calculated Sulfur Charge, *q*(S), for IL(SMD)		
Ionic Liquid	AIM	ChelpG	NBO
$[C_4C_1Im][SCN]$	-0.1	-0.6	-0.4
$[S_{2,2,2}][NTf_2]$ (cation)	0.3	0.0	0.8
$[S_{2,2,2}][NTf_2]$ (anion)	3.0	1.0	2.1
$[C_4C_1Im][NTf_2]$	3.0	1.1	2.1
$[C_4C_1Im][MeSO_3]$	3.0	1.0	2.1
$[N_{2,2,1,0}][TfO]$	3.2	1.1	2.2
$[C_4C_1Im][TfO]$	3.2	1.2	2.2
$[C_4C_1Im][MeOSO_3]$	3.5	1.5	2.5
$[C_4C_1Im][HOSO_3]$	3.5	1.5	2.5
$[C_4C_0Im][HOSO_3]$	3.5	1.5	2.5
$[N_{4,1,1,0}][HOSO_3]$	3.5	1.5	2.5

Table S5: Calculated sulfur atomic charge, *q*(S), for a range of ion pair structures and methods. All calculations were carried out using a solvent continuum (SMD) model parameterised for $[C_4C_1Im][PF_6]$. Charges reported are from an unweighted average of all conformers.

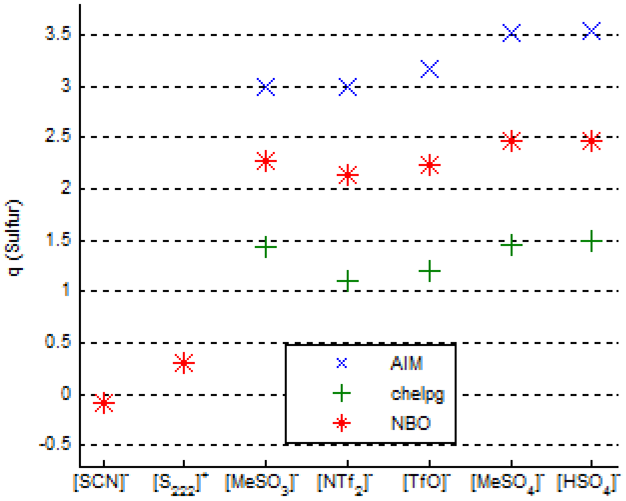


Figure S22: Calculated sulfur atomic charge, *q*(S), for different ions with varying methods. $[C_4C_1Im][Anion]$ charges were used in cases where charges were calculated for multiple cations and a single anion. All calculations were carried out using the SMD solvent continuum model.

	AIM		ChelpG		NBO	
Ionic Liquid	*q*(S) range (GP) / *e*	*q*(S) range (SMD) / *e*	*q*(S) range (GP) / *e*	*q*(S) range (SMD) / *e*	*q*(S) range (GP) / *e*	*q*(S) range (SMD) / *e*
$[C_4C_1Im][MeSO_3]$	0.01	0.00	0.14	0.11	0.01	0.00
$[C_4C_1Im][NTf_2]$	0.02	0.01	0.16	0.08	0.02	0.01
$[C_4C_1Im][TfO]$	0.05	0.01	0.29	0.20	0.03	0.01
$[C_4C_1Im][HSO_4]$	0.05	0.00	0.19	0.14	0.01	0.00
$[C_4C_1Im][MeSO_4]$	0.00	0.01	0.08	0.09	0.00	0.00
$[C_4C_1Im][SCN]$	0.06	0.03	0.05	0.04	0.04	0.02
$[C_4C_0Im][HSO_4]$	0.08	0.04	0.05	0.08	0.04	0.02
$[N_{2,2,1,0}][TfO]$	0.01	0.01	0.27	0.30	0.02	0.01
$[N_{4,1,1,0}][HSO_4]$	0.06	0.02	0.06	0.05	0.01	0.01
$[S_{2,2,2}][NTf_2]$ (cation)	0.14	0.06	0.51	0.40	0.11	0.04
$[S_{2,2,2}][NTf_2]$ (anion)	0.05	0.02	0.19	0.23	0.02	0.01

Table S6: Range of charges calculated for different conformers for calculations carried out in the gas phase, and calculations carried out using the SMD solvent continuum model parameterised for $[C_4C_1Im][PF_6]$.

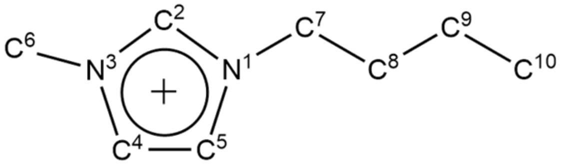


Figure S23: Atomic labelling scheme used for the imidazolium cation.

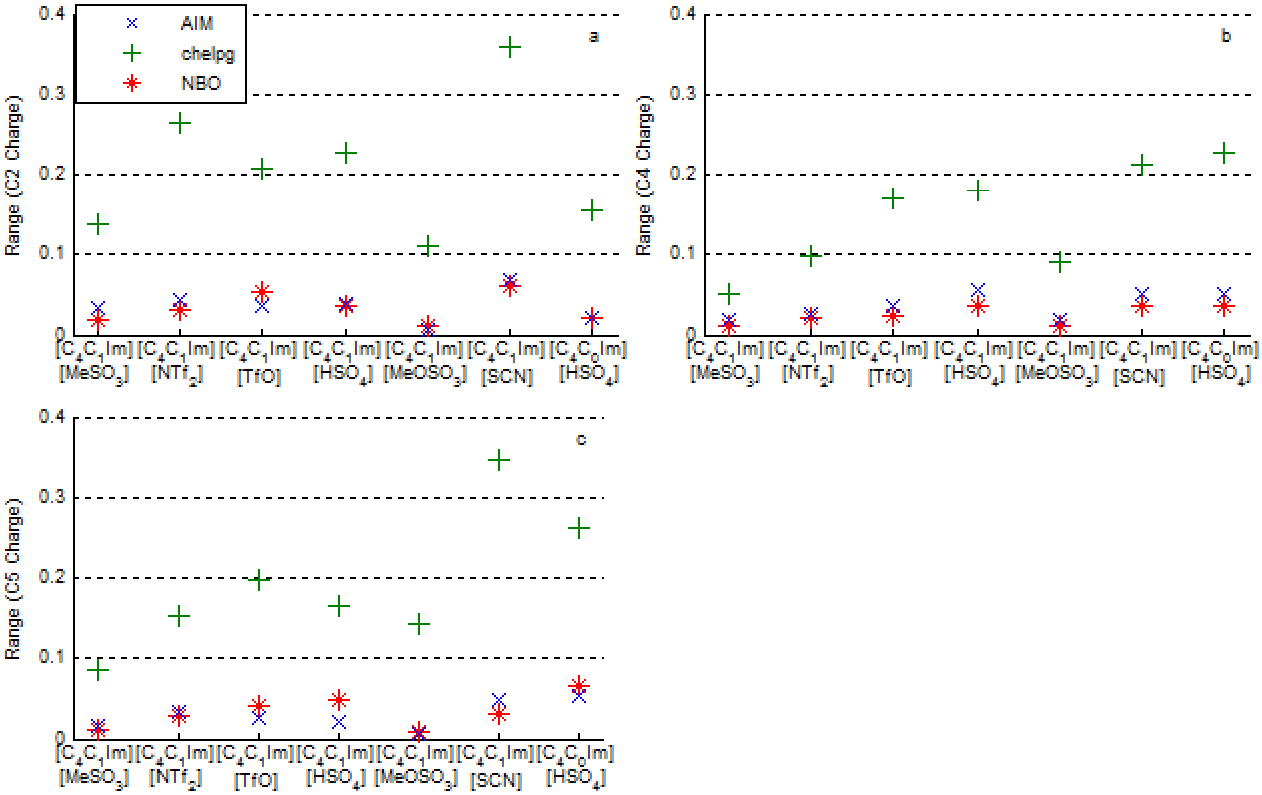


Figure S24: Range of calculated *q*(A) using three different computational methods for gas phase calculations for a) the C^2 carbon, b) the C^4 carbon and c) the C^5 carbon. See Figure S23 for definitions of the atom labels.

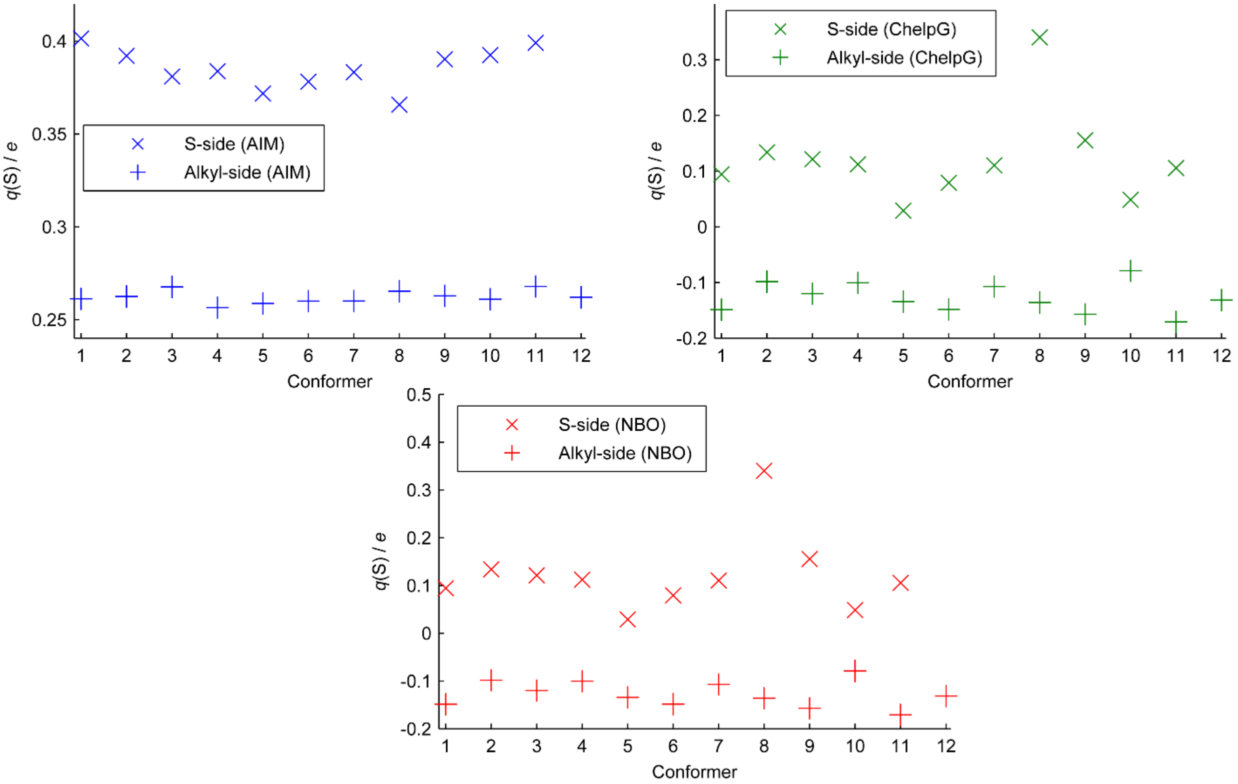


Figure S25: Conformational dependence of cationic *q*(S) for [$S_{2,2,2}$][NTf_2] using AIM (top left), ChelpG (top right) and NBO (bottom left) charge schemes. S-side and alkyl-side refer to the two types of conformer of [$S_{2,2,2}$][NTf_2] and are defined in the main text, *q*(S) are from gas phase calculations.

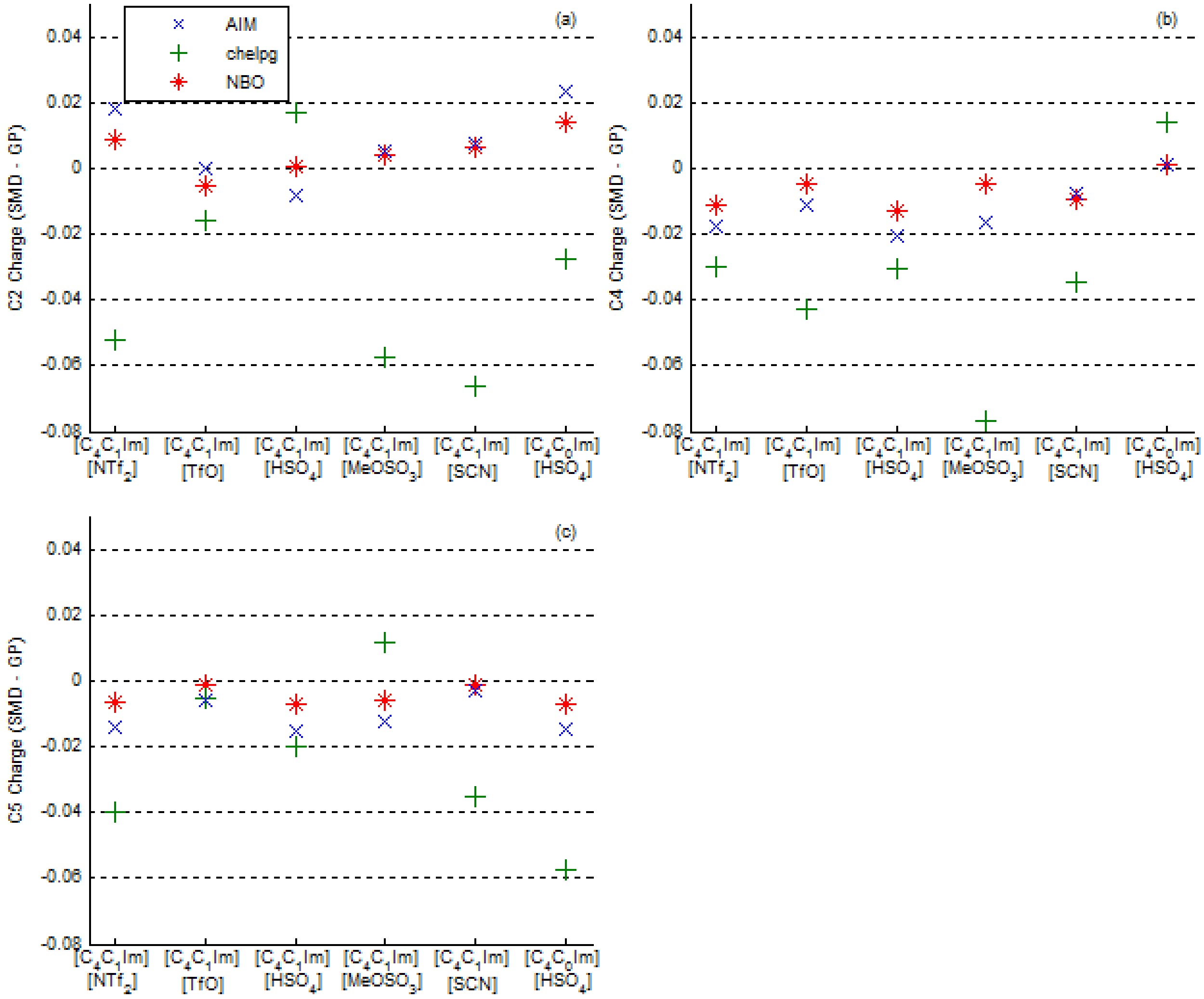


Figure S26: Difference between the calculated *q*(A) for ion pair conformers in a solvent continuum (SMD) and gas phase for the (a) C2 atom (b) C4 atom and (c) C5 atom. Values are from an unweighted average of all ion pair conformers.

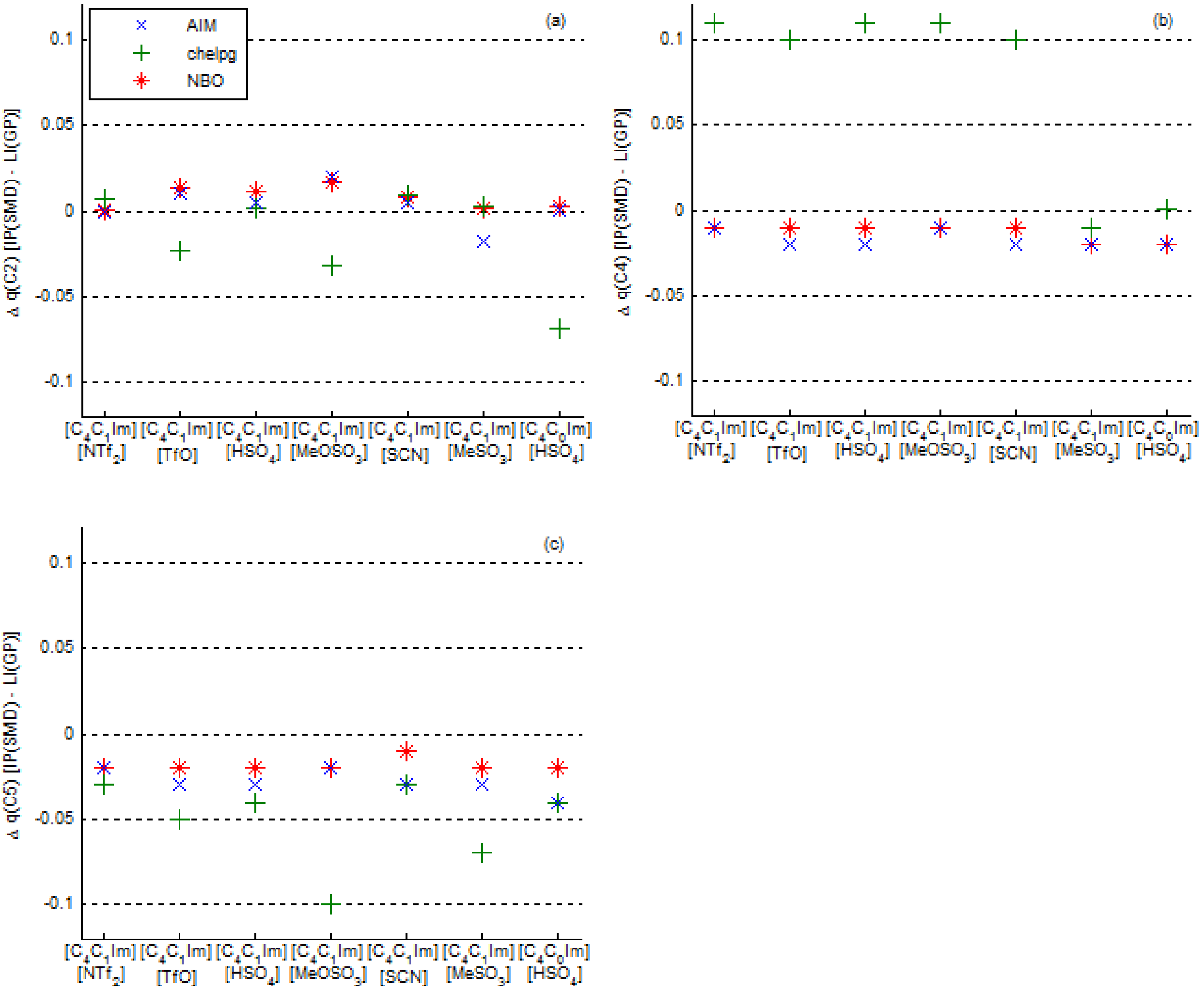


Figure S27: Difference between the calculated *q*(A) for ion pair conformers in a solvent continuum (SMD) and lone ions in the gas phase for the (a) C^2 atom (b) C^4 atom and (c) C^5 atom. Values are from an unweighted average of all ion pair conformers.

	Δ*q*(N-H Nitrogen, IP(SMD) – LI(GP))			Δ*q*(N-H Hydrogen, IP(SMD) – LI(GP))		
Ionic Liquid	AIM	ChelpG	NBO	AIM	ChelpG	NBO
$[N_{4,1,1,0}][HSO_4]$	-0.05	0.28	-0.04	0.08	-0.01	0.05
$[N_{2,2,1,0}][TfO]$	-0.05	0.18	-0.04	0.07	0.02	0.05

Table S7: Difference between *q*(S) in ion pair (SMD) and lone ions (GP) systems for the N-H group nitrogen and hydrogen atoms. Charges are from an unweighted average of conformers, but for the ion pairs only conformers with the anion directly interacting with the N-H hydrogen were considered.

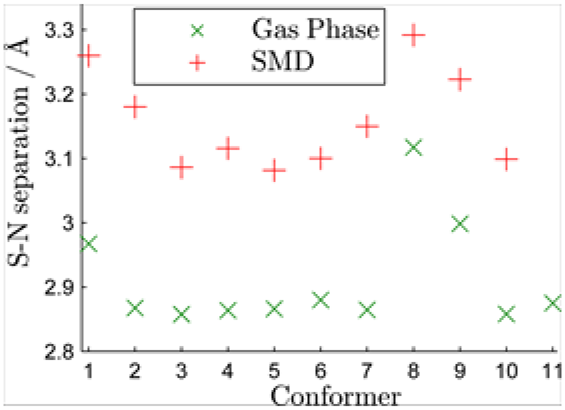


Figure S28: Distance between cationic sulfur and anionic nitrogen in the S-side conformers of $[S_{2,2,2}][NTf_2]$ for calculations in the GP and IL(SMD).

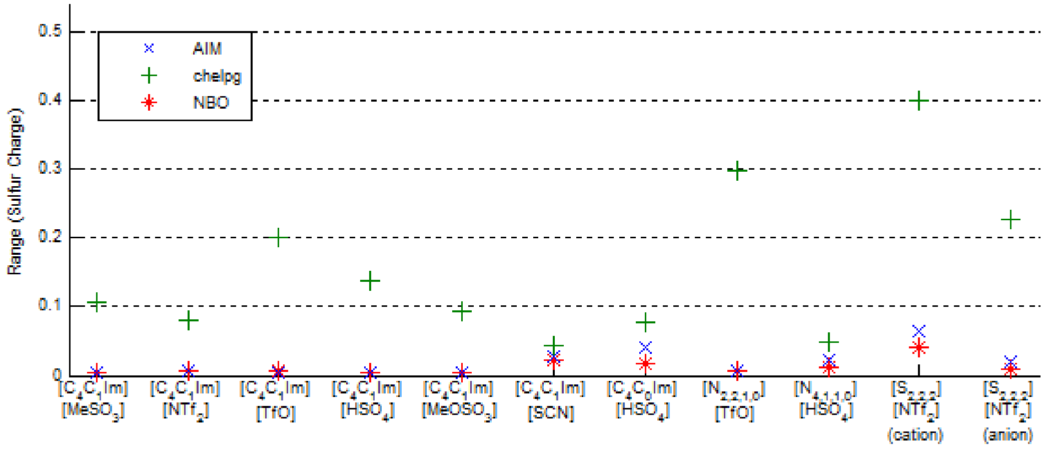


Figure S29: Conformational dependence of *q*(S) for calculations using a solvent continuum model parameterised for [C_4C_1Im][PF_6].

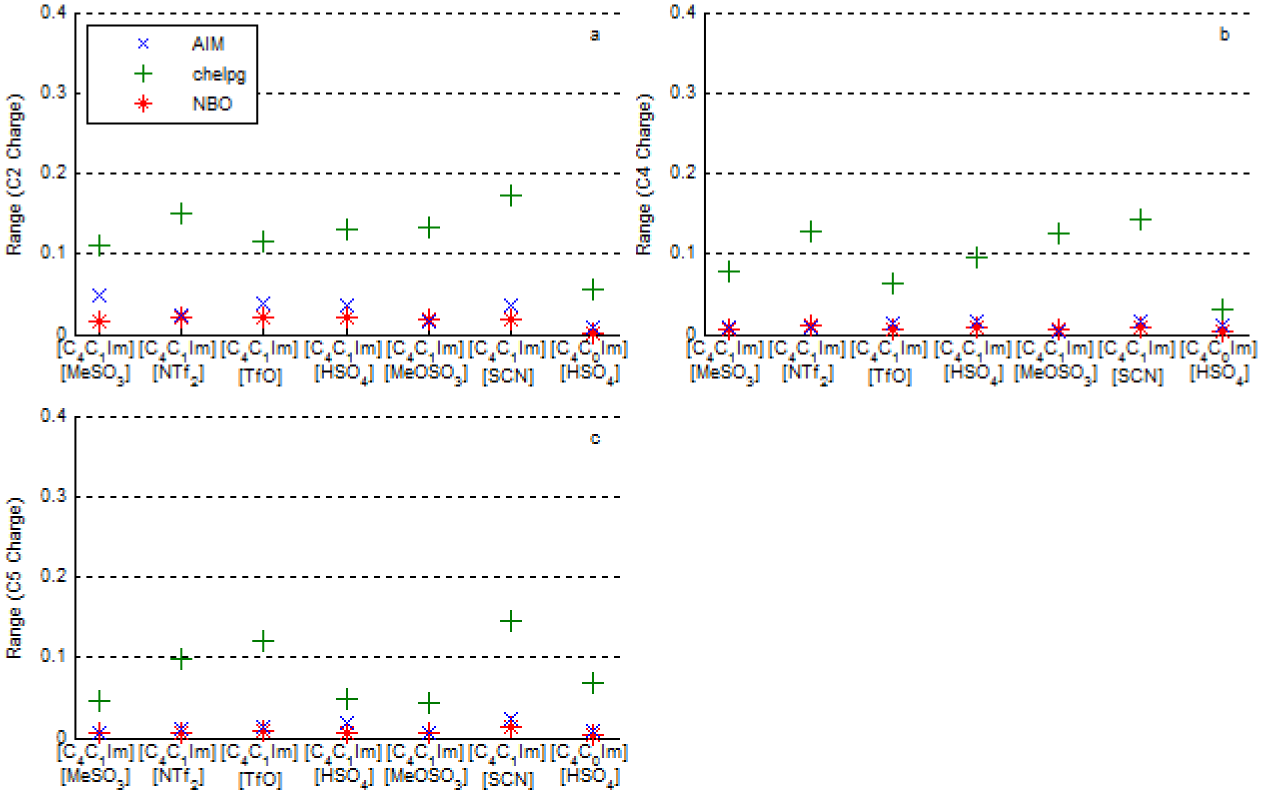


Figure S30: Range of calculated *q*(A) using three different computational methods for IL(SMD) calculations for a) the C^2 carbon, b) the C^4 carbon and c) the C^5 carbon. See Figure S23 for definitions of the atom labels.

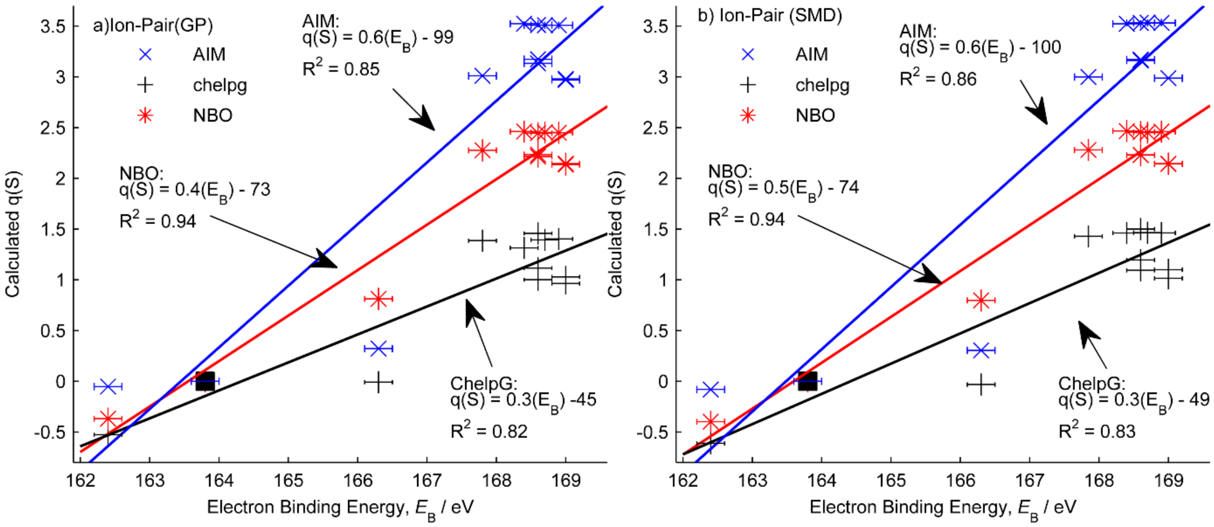


Figure S31: Comparison of S 2p E_B with calculated *q*(S) derived from a) ion-pair (GP) calculations and b) ion pair IL(SMD) calculations. Charges are from an unweighted average of all conformers. A black square represents the data point for S_8.

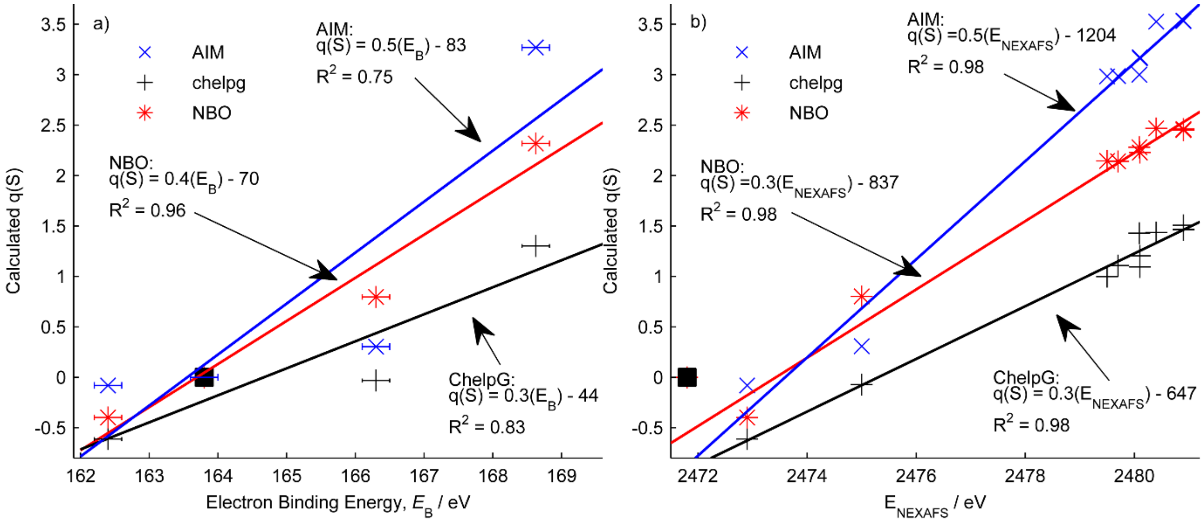


Figure S32: Comparison of calculated *q*(S) with a) S $2p_{3/2}$ electron binding energies (E_B) and b) S 1s NEXAFS edge energies (E_{NEXAFS}). For a) all $[YSO_x]^-$ data points were averaged so they did not overly affect the linear regression analysis. All charges were derived from ion pair IL(SMD) calculations (an unweighted average of all conformers was used). A black square represents the data point for S_8

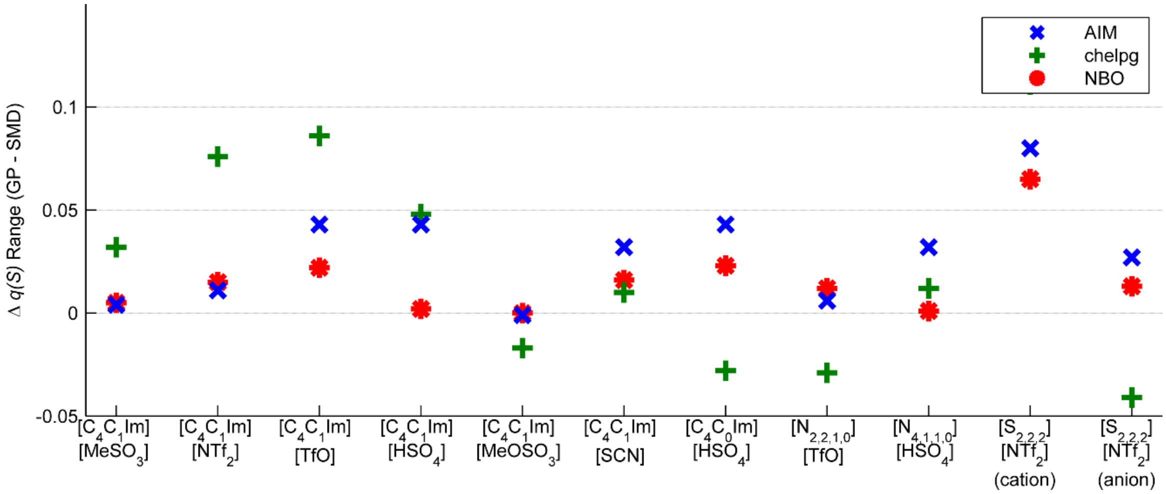


Figure S33**.** The difference in the range of sulfur atomic charges, *q*(S), calculated for ion pair (GP) and ion pair IL(SMD). In each case the range is difference in the maximum and minimum *q*(S) calculated for a conformer (larger range means greater conformational dependence). Positive values on the graph y-axis indicate a greater conformational dependence in GP calculations; negative values indicate a greater conformational dependence for IL(SMD) calculations.

Ionic Liquid	Calculated $q(SO_x)$		
	AIM	ChelpG	NBO
$[C_4C_1Im][NTf_2]$	0.44	-0.07	0.29
$[C_4C_1Im][TfO]$	-0.71	-0.74	-0.70
$[C_4C_1Im][HSO_4]$	-0.43	-0.62	-0.53
$[C_4C_1Im][MeSO_4]$	-0.43	-0.62	-0.53
$[C_4C_0Im][HSO_4]$	-0.39	-0.58	-0.47
$[N_{2,2,1,0}][TfO]$	-0.74	-0.86	-0.71
$[N_{4,1,1,0}][HSO_4]$	-0.39	-0.60	-0.47
$[S_{2,2,2}][NTf_2]$	0.47	-0.09	0.32
$[C_4C_1Im][MeSO_3]$	-0.96	-0.81	-0.80

Table S8: Calculated charge for the SO_x groups from ion pair (GP) calculations.

Data used to obtain S_8 average electron binding energy, E_B

Note that for the literature data for which an S 2p peak is reported, we subtracted 0.3 eV from the S 2p E_B to obtain an S $2p_{3/2}$ E_B value (this 0.3 eV value was obtained by fitting S 2p spectra with one peak and two peaks and taking the E_B difference in the maximum peak intensity E_B). S_8 average electron binding energy, E_B = 163.8 eV.

- E_B(S $2p_{3/2}$) = 164.45 eV.[12]
- E_B(S $2p_{3/2}$) = 163.3 eV.[13]
- E_B(S 2p) = 163.9 eV.[14]
  - E_B(S $2p_{3/2}$) = 163.6 eV.
- E_B(S 2p) = 165.0 eV.[15]
  - E_B(S $2p_{3/2}$) = 164.7 eV.

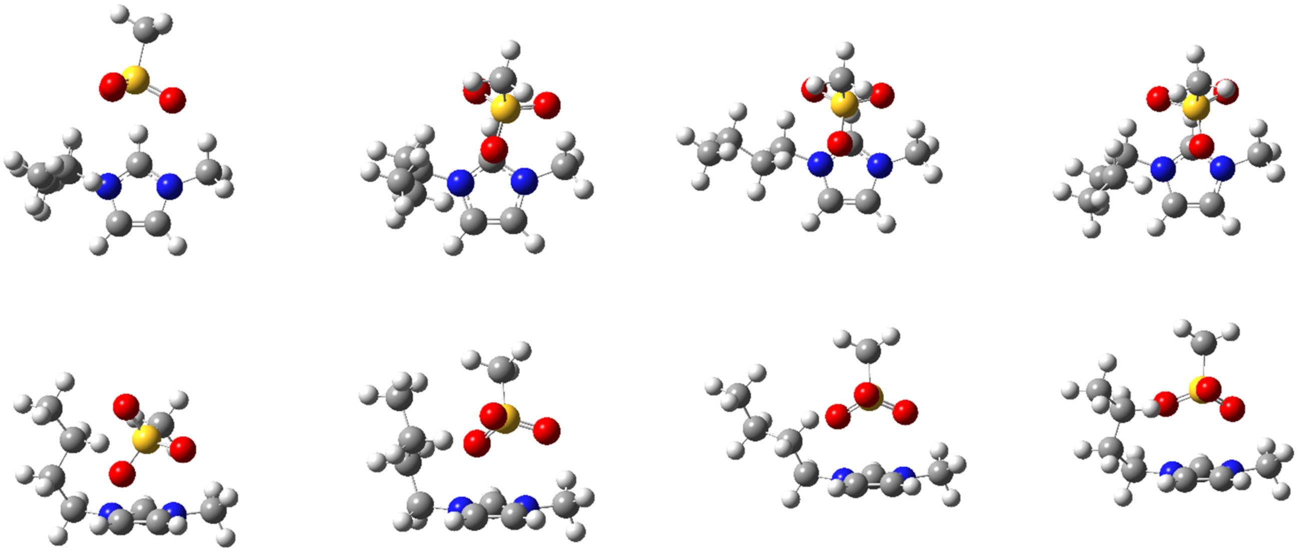
- E_B(S 2p) = 163.1 eV.[16]
    - E_B(S $2p_{3/2}$) = 162.8 eV.
- E_B(S $2p_{3/2}$) = 164.35 eV.[17]
- E_B(S $2p_{3/2}$) = 164.6 eV.[18]
- E_B(S 2p) = 164.2 eV.[19]
    - E_B(S $2p_{3/2}$) = 163.9 eV.
- E_B(S 2p) = 164.3 eV.[20]
    - E_B(S $2p_{3/2}$) = 164.0 eV.
- E_B(S $2p_{3/2}$) = 164.4 eV.[21]
- E_B(S 2p) = 163.8 eV.[22]
    - E_B(S $2p_{3/2}$) = 163.5 eV.
- E_B(2p) = 162.2 eV.[23]
    - E_B(S $2p_{3/2}$) = 161.9 eV.

References

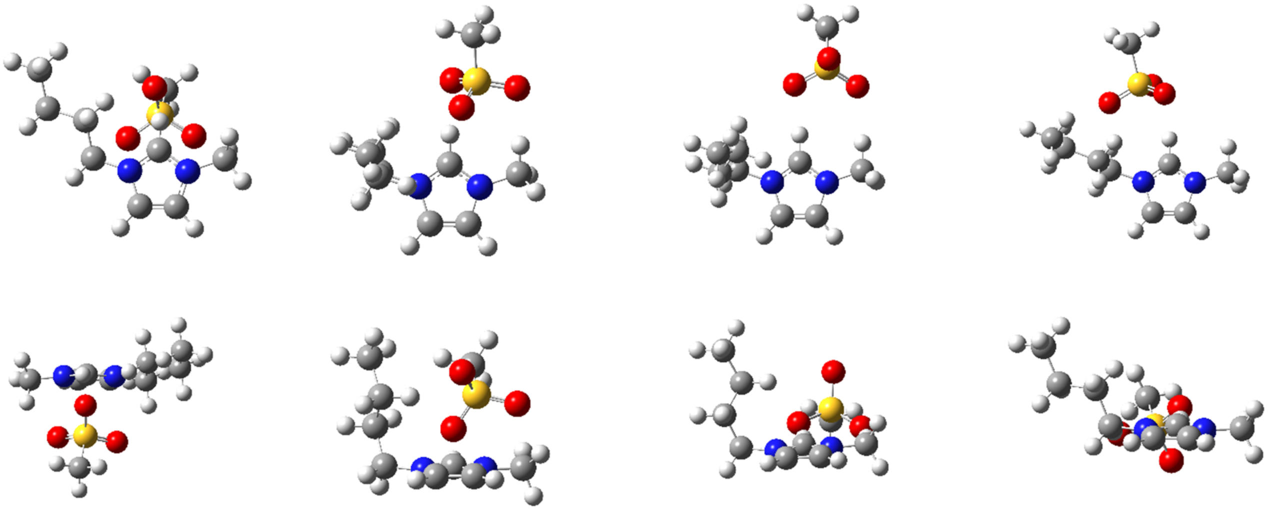
1. A. Cros, *J. Electron Spectrosc. Relat. Phenom.*, 1992, **59**, 1-14.
2. I. J. Villar-Garcia, E. F. Smith, A. W. Taylor, F. L. Qiu, K. R. J. Lovelock, R. G. Jones and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2797-2808.
3. D. Briggs and G. Beamson, eds., *The XPS of Polymers Database*, SurfaceSpectra, Manchester, 2000.
4. T. Cremer, C. Kolbeck, K. R. J. Lovelock, N. Paape, R. Wölfel, P. S. Schulz, P. Wasserscheid, H. Weber, J. Thar, B. Kirchner, F. Maier and H. P. Steinrück, *Chem.-Eur. J.*, 2010, **16**, 9018-9033.
5. I. J. Villar-Garcia, K. R. J. Lovelock, S. Men and P. Licence, *Chemical Science*, 2014, **5**, 2573-2579.
6. S. Men, K. R. J. Lovelock and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15244-15255.
7. S. Men, D. S. Mitchell, K. R. J. Lovelock and P. Licence, *ChemPhysChem*, 2015, **16**, 2211-2218.
8. R. K. Blundell and P. Licence, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15278-15288.
9. R. K. Blundell and P. Licence, *Chem. Commun.*, 2014, **50**, 12080-12083.
10. A. R. Santos, R. K. Blundell and P. Licence, *Phys. Chem. Chem. Phys.*, 2015, **17**, 11839-11847.
11. R. K. Blundell, A. E. Delorme, E. F. Smith and P. Licence, *Phys. Chem. Chem. Phys.*, 2016, **18**, 6122-6131.
12. J. Riga and J. J. Verbist, *J. Chem. Soc.-Perkin Trans. 2*, 1983, DOI: 10.1039/p29830001545, 1545-1551.
13. X. R. Yu, F. Liu, Z. Y. Wang and Y. Chen, *J. Electron Spectrosc. Relat. Phenom.*, 1990, **50**, 159-166.
14. S. R. Kelemen, G. N. George and M. L. Gorbaty, *Fuel*, 1990, **69**, 939-944.
15. J. M. Thomas, R. H. Williams, M. Barber and I. Adams, *Journal of the Chemical Society-Faraday Transactions Ii*, 1972, **68**, 755-764.
16. G. Hollinger, P. Kumurdjian, J. M. Mackowski, P. Pertosa, L. Porte and T. M. Duc, *J. Electron Spectrosc. Relat. Phenom.*, 1974, **5**, 237-245.
17. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder and G. E. Muilenberg, *Handbook of X-Ray Photoelectron Spectroscopy*, Perkin-Elmer Corporation, Physical Electronics Division, Eden Prairie, Minn., 1979.
18. A. S. Manocha and R. L. Park, *Applications of Surface Science*, 1977, **1**, 129-141.

19. B. J. Lindberg, K. Hamrin, G. Johansson, U. Gelius, A. Fahlman, C. Nordling and K. Siegbahn, *Phys. Scr.*, 1970, **1**, 286-298.
20. D. Brion, *Applications of Surface Science*, 1980, **5**, 133-152.
21. A. M. de Jong, H. J. Borg, L. J. van Ijzendoorn, V. G. F. M. Soudant, V. H. J. de Beer, J. A. R. van Veen and J. W. Niemantsverdriet, *J. Phys. Chem.*, 1993, **97**, 6477-6483.
22. H. Peisert, T. Chasse, P. Streubel, A. Meisel and R. Szargan, *J. Electron Spectrosc. Relat. Phenom.*, 1994, **68**, 321-328.
23. W. E. Swartz, K. J. Wynne and D. M. Hercules, *Anal. Chem.*, 1971, **43**, 1884-1887.

Part 6: Conformer Structures



Front 1 Front Top 1 Front Top 2 Front Top 3



Bottom Front 2(SMD) Front 3(SMD) Front 4(SMD)

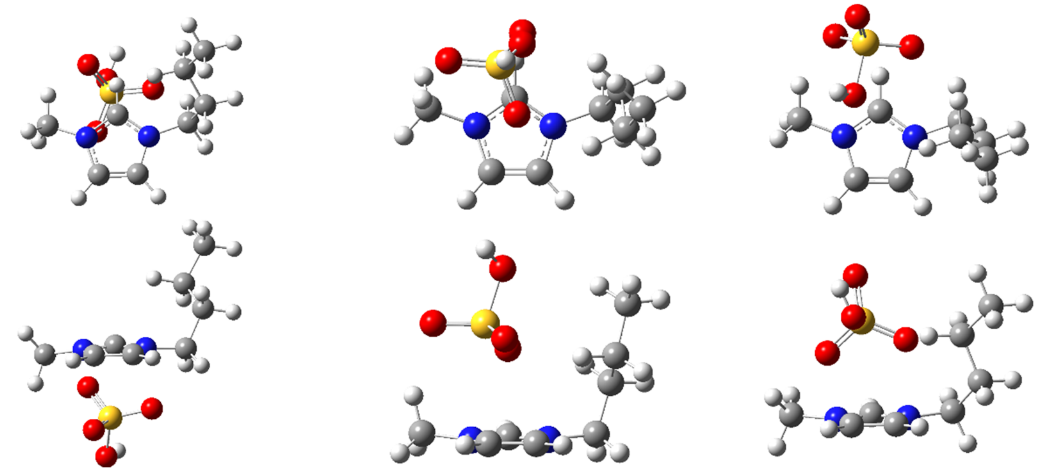
Figure S34: Optimised Ion Pair(GP) conformers for $[C_4C_1Im][MeSO_3]$. Conformers labelled (SMD) are structures which were found by re-optimising GP conformers in the SMD..

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Bottom	0.0	0.0	3.0	1.5	2.3	1.0	-0.1	0.3
Front Top 2	0.4	-2.6	3.0	1.4	2.3	1.0	-0.1	0.3
Front Top 1	0.7	-1.5	3.0	1.4	2.3	1.0	0.0	0.3
Front 1	3.4	2.6	3.0	1.4	2.3	1.0	0.0	0.3
Front Top 3	4.2	-1.2	3.0	1.3	2.3	1.0	-0.1	0.3

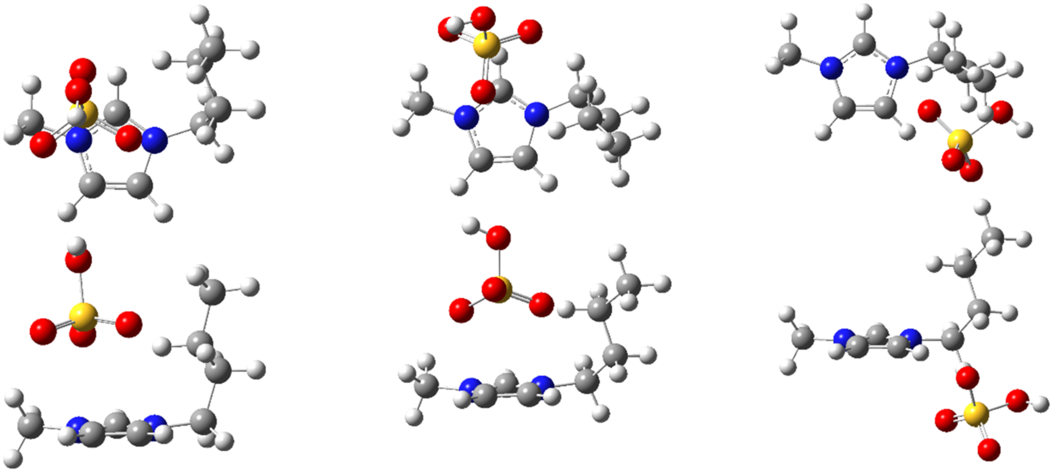
Table S9: Relative energies and calculated atomic charges for all $[C_4C_1Im][MeSO_3]$ conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front 4	0.0	0.0	3.0	1.4	2.3	1.0	-0.1	0.3
Front 1	0.3	-2.2	3.0	1.4	2.3	1.0	-0.1	0.3
Front 3	1.0	-1.6	3.0	1.4	2.3	1.0	-0.1	0.3
Front Top 2	3.0	2.6	3.0	1.5	2.3	1.0	-0.1	0.3
Front 2	4.2	-0.7	3.0	1.4	2.3	1.0	0.0	0.3

Table S10: Relative energies and calculated atomic charges for all $[C_4C_1Im][MeSO_3]$ conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.



Front Bot Top 1 Front Mid 2



Top 2 Front Mid 1 Back But

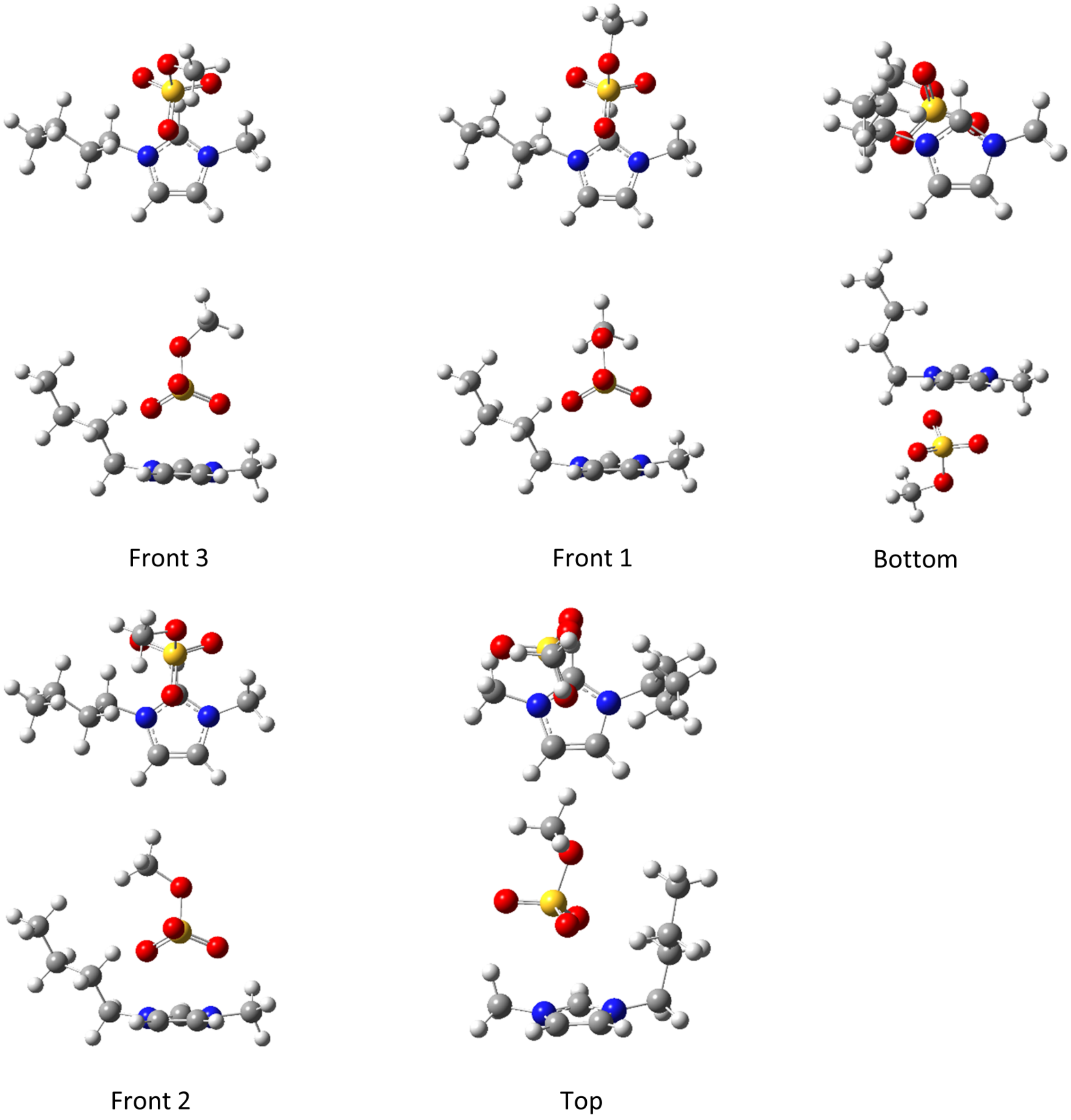
Figure S35: Optimised Ion Pair(GP) conformers for $[C_4C_1Im][HOSO_3]$.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front Bot	0.0	0.0	3.5	1.4	2.4	1.0	0.0	0.3
Top 1	0.8	-7.4	3.5	1.5	2.4	1.0	0.0	0.3
Front Mid 2	1.4	-3.8	3.5	1.5	2.4	1.0	-0.1	0.3
Top 2	2.4	-6.4	3.5	1.4	2.4	1.0	-0.1	0.3
Front Mid 1	3.8	-4.6	3.5	1.4	2.4	1.0	-0.1	0.3
Back But	32.6	30.3	3.5	1.4	2.4	1.0	-0.2	0.3

Table S11: Relative energies and calculated atomic charges for all $[C_4C_1Im][HOSO_3]$ conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front Mid 2	0.0	0.0	3.5	1.4	2.5	1.0	-0.1	0.3
Top 1	3.6	-0.8	3.5	1.5	2.5	1.0	0.0	0.3
Top 2	5.4	-0.6	3.5	1.6	2.5	1.0	-0.1	0.3
Back But	5.9	4.5	3.5	1.5	2.5	1.0	-0.1	0.3
Front Mid 1	6.1	0.3	3.5	1.5	2.5	1.0	0.0	0.3

Table S12: Relative energies and calculated atomic charges for all $[C_4C_1Im][HOSO_3]$ conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.


Front 3

Front 1

Bottom

Front 2

Top

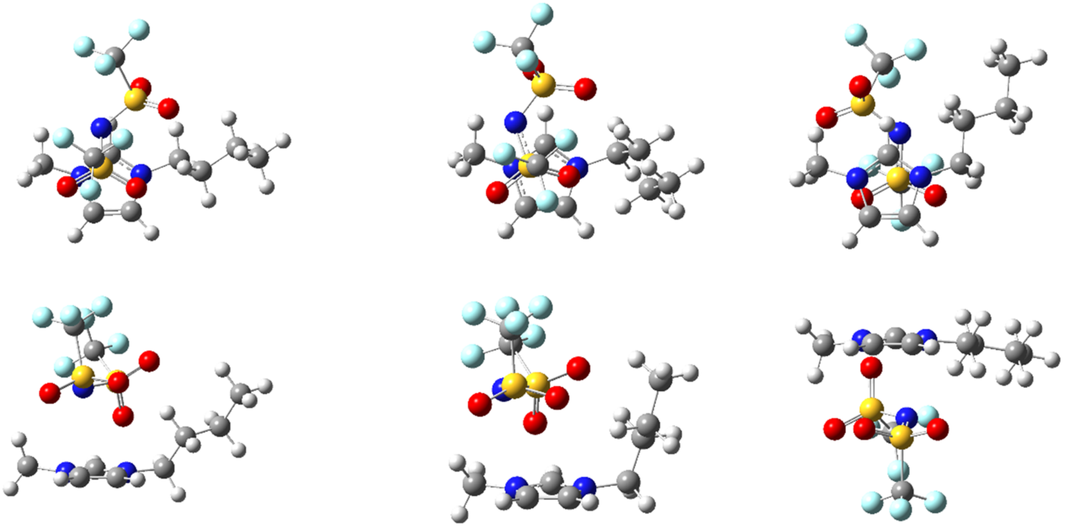
Figure S36: Optimised Ion Pair(GP) conformers for $[C_4C_1Im][MeOSO_3]$.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front 3	0.0	0.0	3.5	1.4	2.5	1.0	0.0	0.3
Front 1	0.2	-1.3	3.5	1.3	2.5	1.0	0.0	0.3
Bottom	0.9	5.8	3.5	1.3	2.5	1.0	-0.1	0.3
Front 2	1.3	0.2	3.5	1.3	2.5	1.0	-0.1	0.3
Top	1.9	-2.0	3.5	1.3	2.5	1.0	0.0	0.3

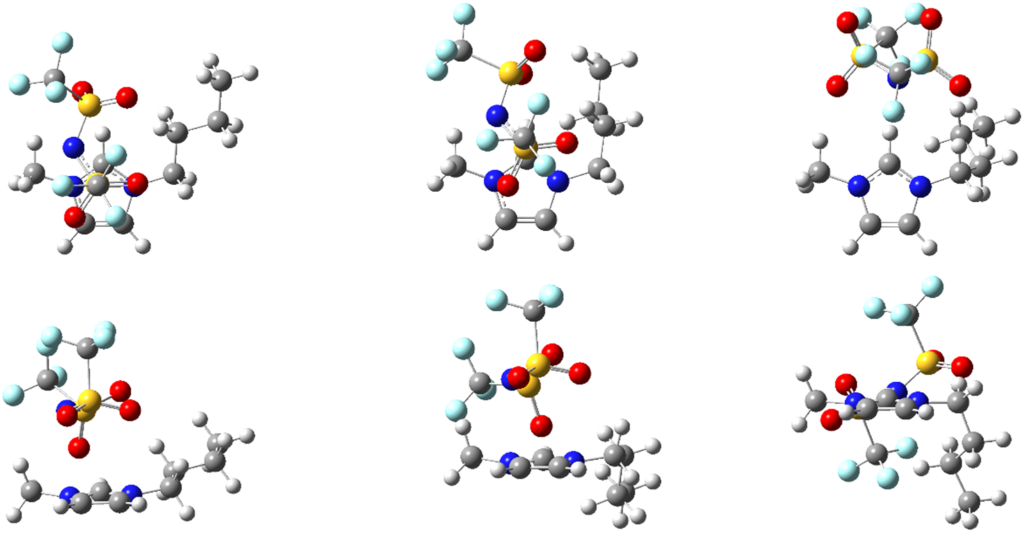
Table S13: Relative energies and calculated atomic charges for all [C_4C_1Im][MeOSO$_3$] conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Bottom	0.0	0.0	3.5	1.4	2.5	1.0	-0.2	0.3
Top	1.7	5.5	3.5	1.4	2.5	1.0	-0.1	0.3
Front 1	2.8	0.8	3.5	1.5	2.5	1.0	-0.1	0.3
Front 2	5.2	0.0	3.5	1.5	2.5	1.0	-0.1	0.3
Front 3	7.2	2.1	3.5	1.5	2.5	1.0	0.0	0.3

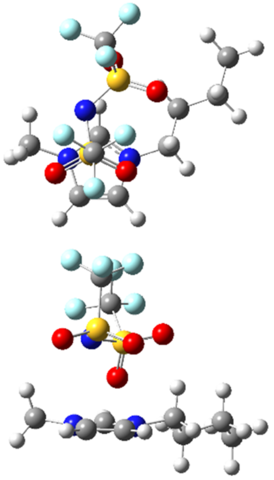
Table S14: Relative energies and calculated atomic charges for all [C_4C_1Im][MeOSO$_3$] conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.



Conf 6 Conf 5 Conf 1



Conf 3 Conf 2 Conf 4



Conf 7

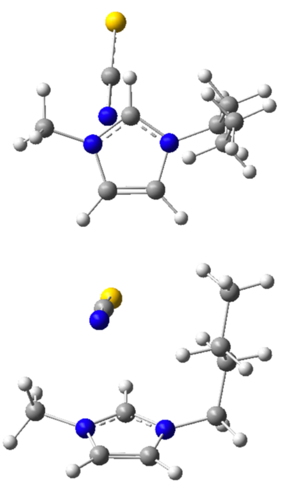
Figure S37: Optimised Ion Pair(GP) conformers for $[C_4C_1Im][NTf_2]$.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Conf 6	0.0	0.0	3.0	1.1	2.1	1.0	-0.1	0.3
Conf 5	0.2	0.2	3.0	1.0	2.1	1.0	0.0	0.3
Conf 1	1.4	1.2	3.0	1.0	2.1	1.0	-0.1	0.3
Conf 3	3.0	4.6	3.0	1.0	2.1	1.0	-0.1	0.3
Conf 2	4.8	5.3	3.0	1.0	2.1	1.0	0.0	0.3
Conf 4	5.0	10.5	3.0	1.0	2.2	1.0	0.2	0.3
Conf 7	5.2	3.4	3.0	1.1	2.1	1.0	-0.1	0.3

Table S15: Relative energies and calculated atomic charges for all [C_4C_1Im][NTf_2] conformers(GP). The value of q(S) is the average of the two anionic sulfur atoms.The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Conf 4	0.0	0.0	3.0	1.0	2.1	1.0	0.0	0.3
Conf 6	4.6	1.1	3.0	1.1	2.1	1.0	-0.1	0.3
Conf 3	6.7	3.4	3.0	1.1	2.1	1.0	0.0	0.3
Conf 1	7.0	4.0	3.0	1.1	2.1	1.0	-0.1	0.3
Conf 5	9.0	0.3	3.0	1.1	2.1	1.0	0.0	0.3
Conf 7	12.8	5.9	3.0	1.1	2.1	1.0	-0.1	0.3

Table S16: Relative energies and calculated atomic charges for all [C_4C_1Im][NTf_2] conformers(SMD). The value of q(S) is the average of the two anionic sulfur atoms.The value of q(C) is for the C2 carbon of the imidazolium ring.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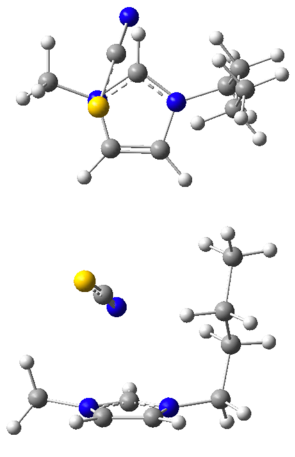
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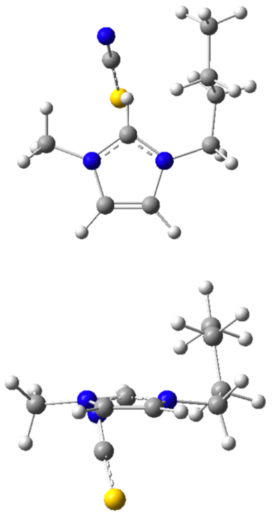
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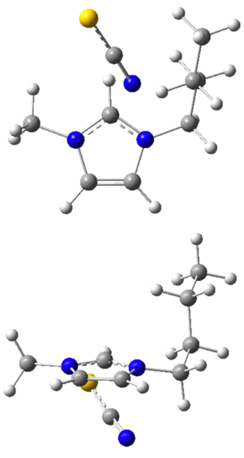
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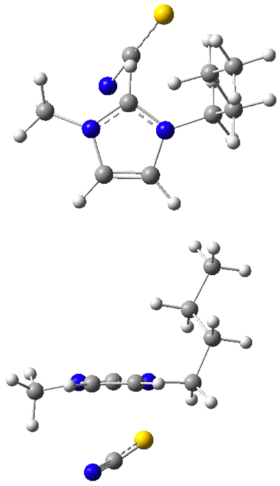
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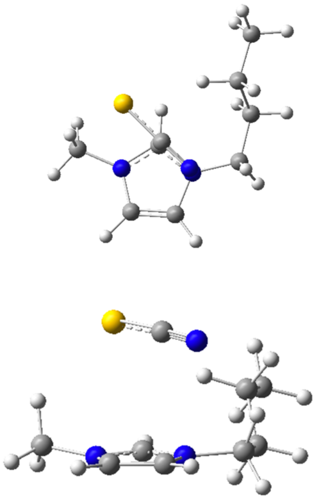
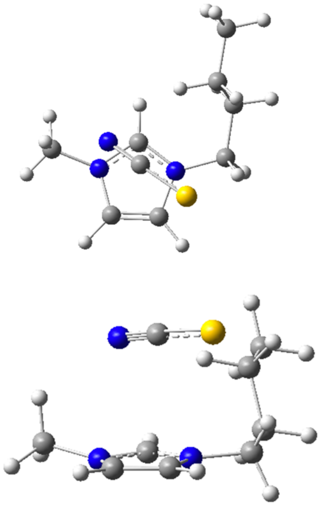
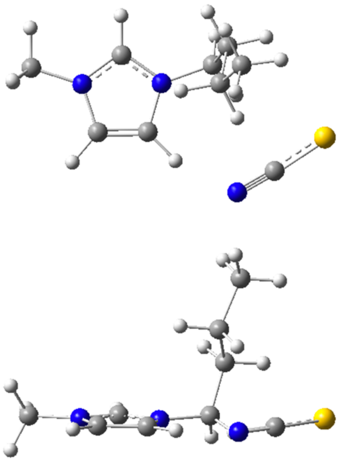
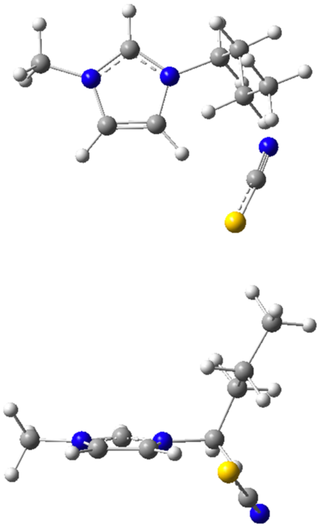

Tophoz1


Tophoz2


BBut1


BBut2

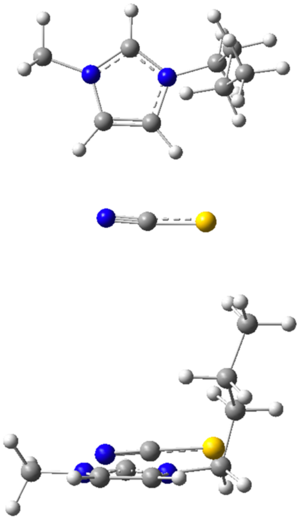

BMid2

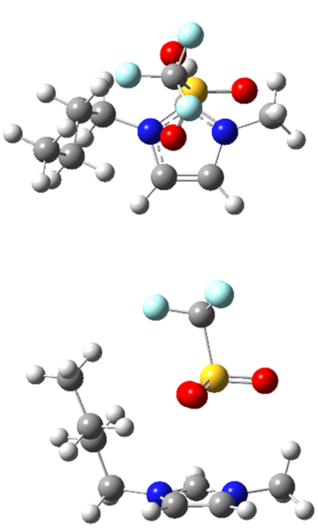
Figure S38: Optimised Ion Pair(GP) conformers for [C_4C_1Im][SCN].

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Sf2	0.0	0.0	-0.1	-0.5	-0.4	1.0	0.1	0.3
Nf2	3.5	1.4	0.0	-0.5	-0.4	1.0	0.0	0.3
CNbot2	4.8	9.2	0.0	-0.5	-0.3	1.0	0.1	0.3
CNbot1	7.9	8.5	-0.1	-0.5	-0.4	1.0	0.2	0.3
CNbot3	13.8	10.3	-0.1	-0.5	-0.4	1.0	0.1	0.3
TopHoz1	17.1	13.6	-0.1	-0.6	-0.4	1.0	0.0	0.3
Tophoz2	20.3	13.8	0.0	-0.5	-0.4	1.0	-0.1	0.3
BBut1	38.5	41.7	0.0	-0.5	-0.3	1.0	-0.1	0.3
BBut2	40.1	43.5	-0.1	-0.5	-0.4	1.0	-0.1	0.3
BMid2	45.5	51.4	-0.1	-0.6	-0.4	1.0	-0.1	0.3

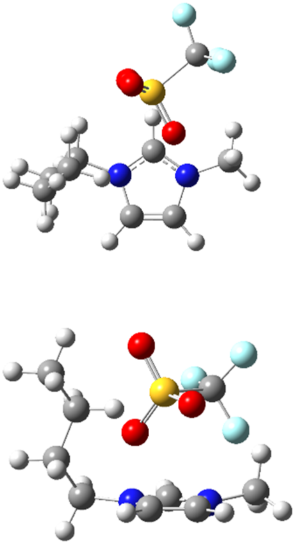
Table S17: Relative energies and calculated atomic charges for all [C_4C_1Im][SCN] conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
CNbot2	0.0	0.0	-0.1	-0.6	-0.4	1.0	-0.1	0.3
Sf2	4.4	-2.6	-0.1	-0.6	-0.4	1.0	0.0	0.3
CNbot3	5.7	2.7	-0.1	-0.6	-0.4	1.0	0.0	0.3
CNbot1	5.7	1.8	-0.1	-0.6	-0.4	1.0	0.0	0.3
Nf2	7.3	-2.4	-0.1	-0.6	-0.4	1.0	0.0	0.3
BMid2	8.2	8.3	-0.1	-0.6	-0.4	1.0	0.0	0.3
BBut1	8.8	4.2	-0.1	-0.6	-0.4	1.0	-0.1	0.3
BBut2	8.9	5.7	-0.1	-0.6	-0.4	1.0	-0.1	0.3
Tophoz2	13.1	7.0	-0.1	-0.6	-0.4	1.0	-0.2	0.3
TopHoz1	14.5	6.4	-0.1	-0.6	-0.4	1.0	-0.2	0.3

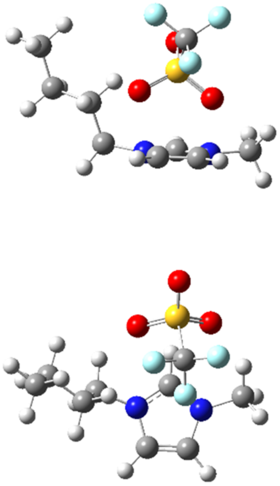
Table S18: Relative energies and calculated atomic charges for all [C_4C_1Im][SCN] conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.



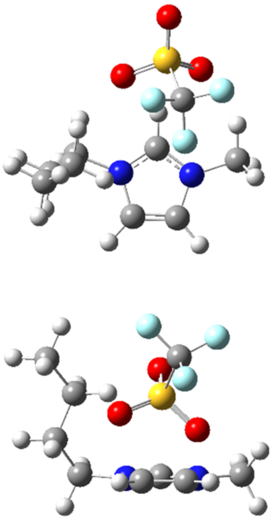
top 1



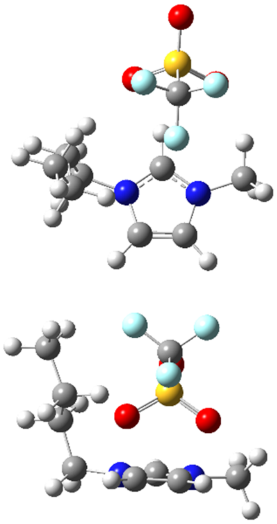
top 2



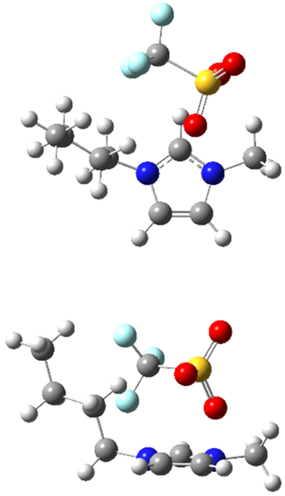
front 4



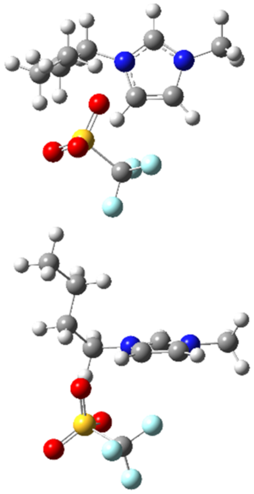
front 3



front 1



front 2



but side 1

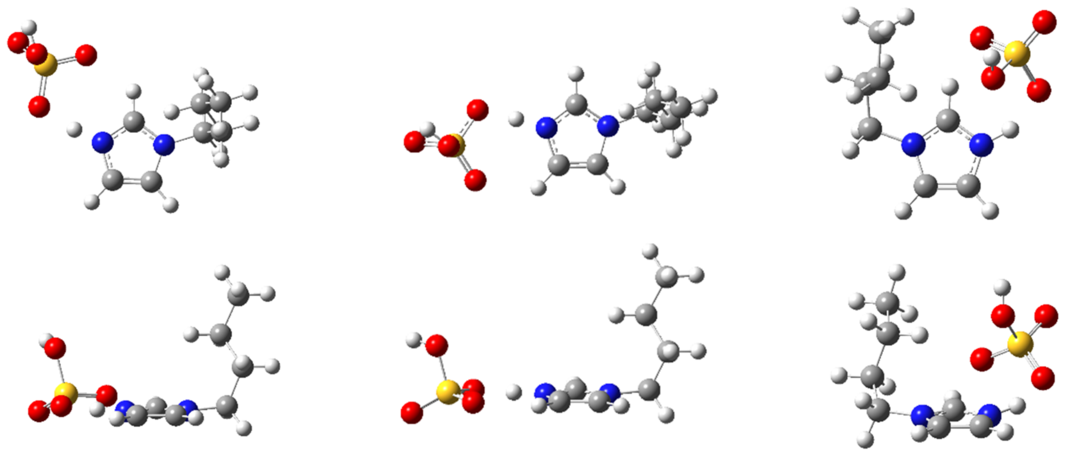
Figure S39: Optimised Ion Pair(GP) conformers for [C_4C_1Im][TfO].

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
top 1	0.0	0.0	3.1	1.1	2.2	1.0	-0.1	0.3
top 2	1.1	2.6	3.2	0.9	2.2	1.0	-0.1	0.3
front 4	2.3	2.9	3.2	1.1	2.2	1.0	-0.1	0.3
front 3	3.4	1.0	3.2	1.2	2.2	1.0	-0.1	0.3
front 1	3.5	3.7	3.2	1.2	2.2	1.0	0.0	0.3
front 2	7.4	4.9	3.2	1.1	2.2	1.0	0.0	0.3
but side 1	30.5	37.2	3.2	1.2	2.2	1.0	-0.2	0.3

Table S19: Relative energies and calculated atomic charges for all [C_4C_1Im][TfO] conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
top 1	0.0	0.0	3.2	1.2	2.2	1.0	0.0	0.3
front 3	4.4	-2.3	3.2	1.2	2.2	1.0	-0.1	0.3
top 2	5.6	-1.0	3.2	1.1	2.2	1.0	-0.1	0.3
front 4	6.3	0.0	3.2	1.2	2.2	1.0	-0.1	0.3
front 2	6.4	1.5	3.2	1.2	2.2	1.0	-0.1	0.3
front 1	8.3	-0.7	3.2	1.2	2.2	1.0	-0.1	0.3
but side 1	11.5	6.2	3.2	1.3	2.2	1.0	-0.1	0.3

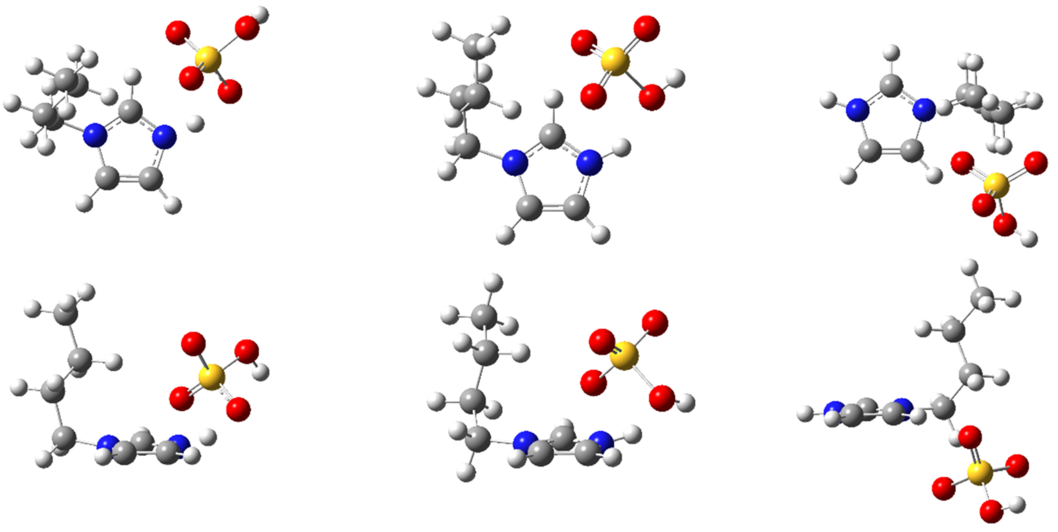
Table S20: Relative energies and calculated atomic charges for all [C_4C_1Im][TfO] conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.



Front NH

Back Hy

Front NH 3



Top

Front NH 2

Back But

Figure S40: Optimised Ion Pair(GP) conformers for [C_4C_0Im][HSO_4].

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front NH	0.0	0.0	3.5	1.4	2.5	1.0	-0.1	0.3
Back Hy	10.7	-0.1	3.5	1.4	2.5	1.0	0.0	0.3
Front NH 3	12.3	-6.5	3.5	1.4	2.5	1.0	0.1	0.3
Top	13.2	-6.1	3.5	1.4	2.5	1.0	0.0	0.3
Front NH 2	22.4	0.3	3.5	1.4	2.4	1.0	0.0	0.3
Back But	67.7	49.1	3.5	1.4	2.4	1.0	-0.1	0.3

Table S21: Relative energies and calculated atomic charges for all [C_4C_0Im][HSO_4] conformers(GP). The value of q(C) is for the C2 carbon of the imidazolium ring.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)	q(C) (AIM)	q(C) (ChelpG)	q(C) (NBO)
Front NH	0.0	0.0	3.5	1.4	2.5	1.0	-0.1	0.3
Back Hy	1.8	2.0	3.5	1.4	2.5	1.0	0.0	0.3
Front NH 2	9.1	8.1	3.5	1.4	2.5	1.0	-0.1	0.3
Back But	17.9	20.3	3.5	1.5	2.5	1.0	0.0	0.3

Table S22: Relative energies and calculated atomic charges for all [C_4C_0Im][HSO_4] conformers(SMD). The value of q(C) is for the C2 carbon of the imidazolium ring.

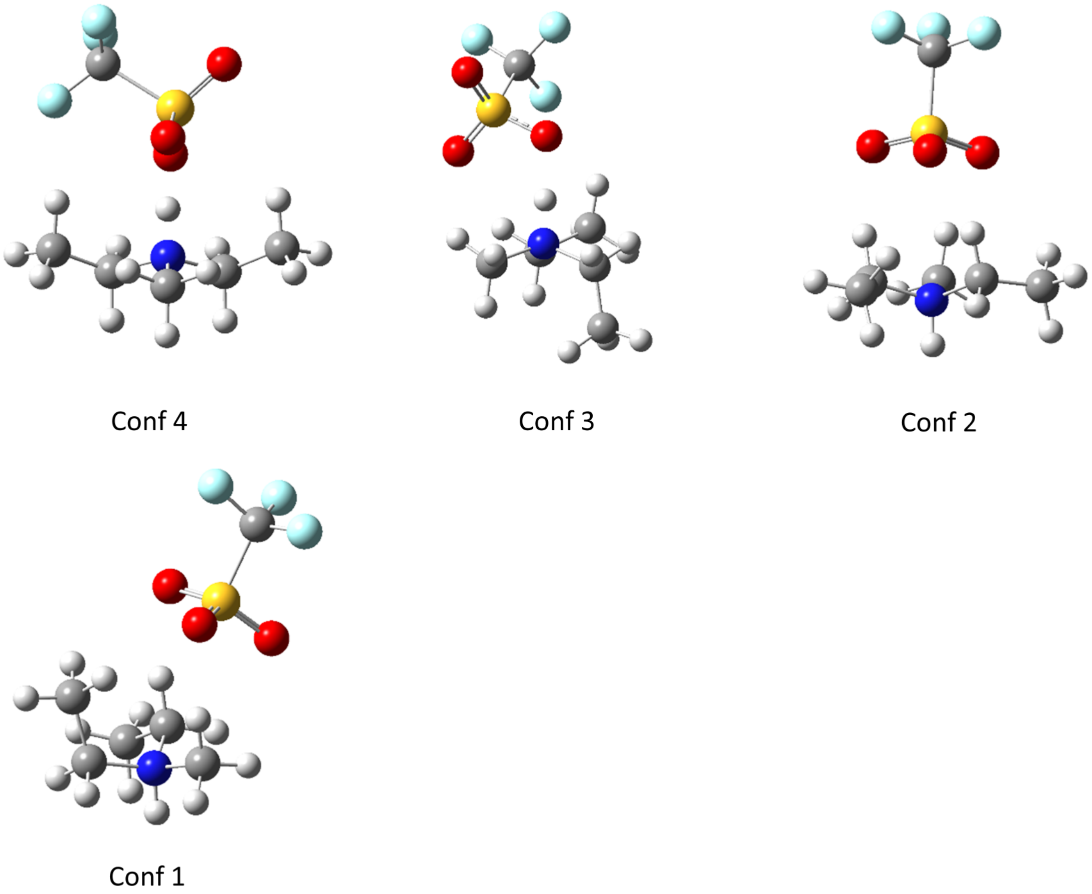


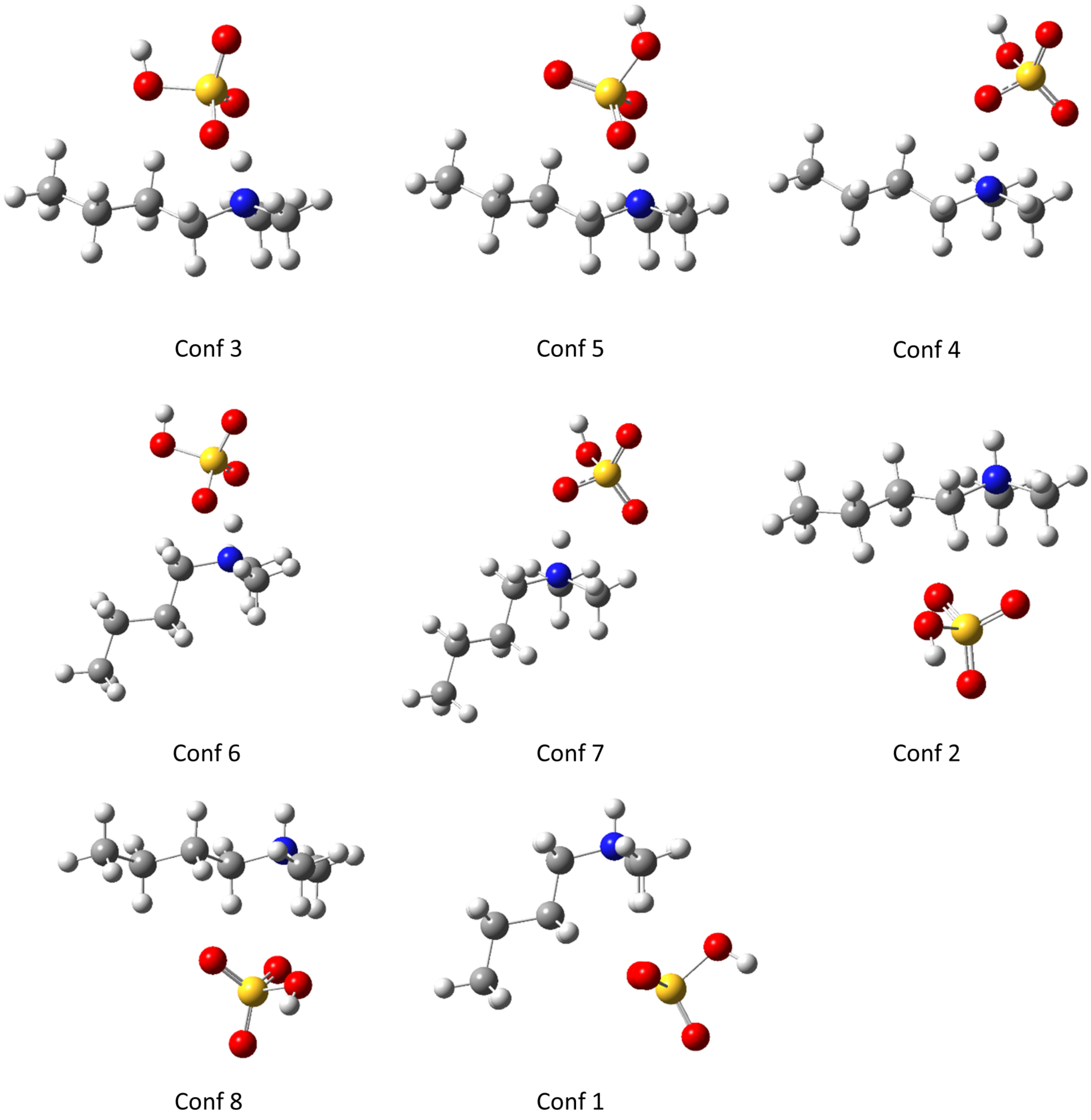
Figure S41: Optimised Ion Pair(GP) conformers for [N_{2210}][TfO].

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Conf 4	0.0	0.0	3.1	1.1	2.2
Conf 3	4.7	4.2	3.1	1.1	2.2
Conf 2	61.4	61.9	3.1	0.9	2.2
Conf 1	71.6	71.2	3.1	0.9	2.2

Table S23: Relative energies and calculated atomic charges for all [N_{2210}][TfO] conformers(GP).

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Conf 4	0.0	0.0	3.2	1.2	2.2
Conf 3	2.6	1.2	3.2	1.2	2.2
Conf 2	25.5	26.8	3.2	1.0	2.2
Conf 1	26.3	27.8	3.2	0.9	2.2

Table S24: Relative energies and calculated atomic charges for all [N_{2210}][TfO] conformers(SMD).


Conf 3

Conf 5

Conf 4

Conf 6

Conf 7

Conf 2

Conf 8

Conf 1

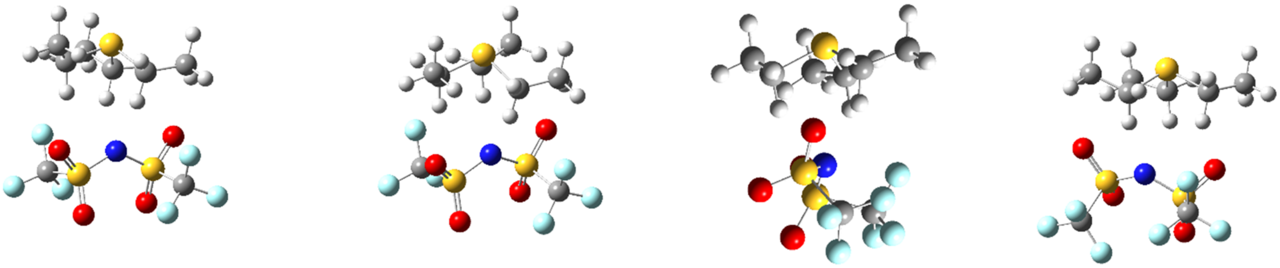
Figure S42: Optimised Ion Pair(GP) conformers for [N_{4110}][HSO_4].

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Conf 3	0.0	0.0	3.5	1.4	2.5
Conf 5	0.0	1.8	3.5	1.4	2.5
Conf 4	1.9	5.8	3.5	1.4	2.5
Conf 6	6.0	10.4	3.5	1.4	2.5
Conf 7	6.5	10.9	3.5	1.4	2.5
Conf 2	65.0	62.3	3.5	1.4	2.4
Conf 8	66.3	64.4	3.5	1.4	2.4
Conf 1	77.0	77.6	3.5	1.4	2.4

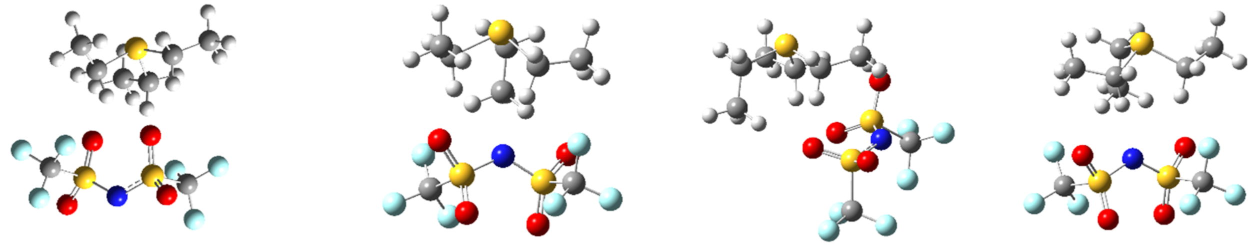
Table S25: Relative energies and calculated atomic charges for all [N_{4110}][HSO_4] conformers(GP).

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Conf 3	0.0	0.0	3.5	1.4	2.5
Conf 5	0.5	0.7	3.5	1.5	2.5
Conf 2	23.5	26.7	3.5	1.5	2.4
Conf 1	25.5	31.1	3.5	1.5	2.4

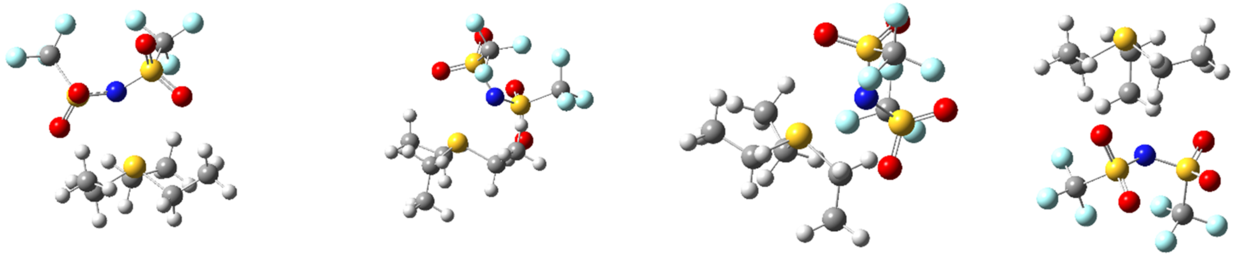
Table S26: Relative energies and calculated atomic charges for all [N_{4110}][HSO_4] conformers(SMD).



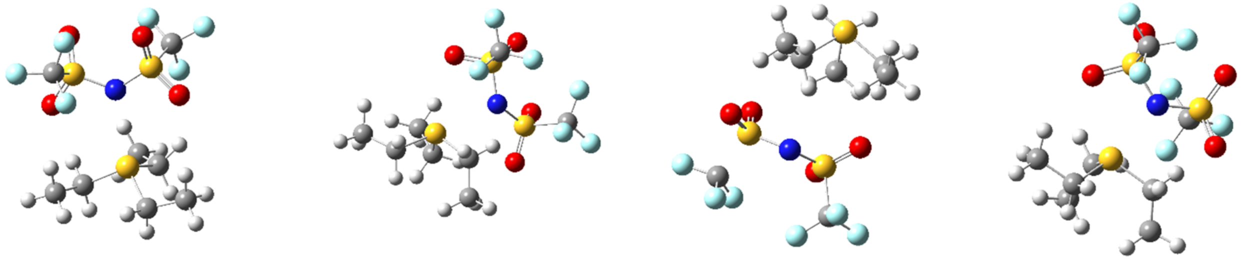
Bot-prop-flat-Trans-2 Bot-aprop-flat-Trans Bot-prop-flat-Cis Bot-aprop-flat-Cis



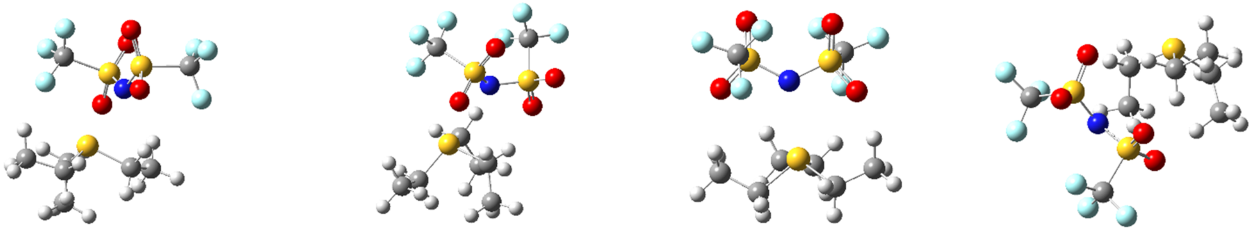
Bot-prop-flat-Trans Bot-prop-1down-Trans Bot-prop-1down-Cis-2 Bot-spread-1down-Trans



Top-aprop-flat-Cis Top-spread-1down-Cis Top-aprop-1down-Trans Bot-prop-1down-Cis



Top-prop-flat-Trans Top-aprop-1down-Cis Bot-aprop-1down-Cis Top-2down-Trans



Top-spread-1down-Trans Top-2down-Cis Top-aprop-flat-Trans Bot-2down-Cis

Top-prop-aflat-Cis Bot-2down-Trans Top-3down-Cis

Figure S43: Optimised Ion Pair(GP) conformers for $[S_{222}][NTf_2]$.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Bot-prop-flat-Trans-2	0.0	0.0	0.3/3.0	-0.2/0.9	0.8/2.1
Bot-aprop-flat-Trans	2.0	2.4	0.3/3.0	-0.1/0.9	0.8/2.1
Bot-prop-flat-Cis	2.8	4.1	0.3/3.0	-0.1/1.0	0.8/2.1
Bot-aprop-flat-Cis	5.0	5.7	0.3/3.0	-0.1/1.0	0.8/2.1
Bot-prop-flat-Trans	6.4	6.6	0.3/3.0	-0.1/1.1	0.8/2.2
Bot-prop-1down-Trans	11.1	12.3	0.3/3.0	-0.1/1.0	0.8/2.1
Bot-prop-1down-Cis-2	11.5	14.2	0.3/3.0	-0.1/0.9	0.8/2.1
Bot-spread-1down-Trans	12.2	11.4	0.3/3.0	-0.2/0.9	0.8/2.1
Top-aprop-flat-Cis	12.3	12.4	0.4/3.0	0.3/0.9	0.8/2.1
Top-spread-1down-Cis	14.1	11.9	0.4/3.0	0.0/1.0	0.9/2.1
Top-aprop-1down-Trans	15.6	12.3	0.4/3.0	0.1/1.0	0.9/2.1
Bot-prop-1down-Cis	16.4	16.3	0.3/3.0	-0.1/1.0	0.8/2.1
Top-prop-flat-Trans	16.8	18.2	0.4/3.0	0.1/0.9	0.9/2.1
Top-aprop-1down-Cis	17.8	14.6	0.4/3.0	0.1/1.0	0.9/2.1
Bot-aprop-1down-Cis	20.8	19.8	0.3/3.0	-0.1/0.9	0.8/2.1
Top-2down-Trans	21.9	19.4	0.4/3.0	0.1/1.0	0.9/2.1
Top-spread-1down-Trans	22.1	20.3	0.4/3.0	0.1/0.9	0.9/2.1
Top-2down-Cis	22.6	21.3	0.4/3.0	0.1/1.0	0.9/2.1
Top-aprop-flat-Trans	25.6	24.4	0.4/3.0	0.2/1.0	0.9/2.1
Bot-2down-Cis	26.0	23.1	0.3/3.0	-0.1/0.9	0.8/2.1
Top-prop-aflat-Cis	30.1	27.5	0.4/3.0	0.1/1.1	0.9/2.2
Bot-2down-Trans	34.1	30.5	0.3/3.0	-0.1/1.0	0.8/2.1
Top-3down-Cis	39.3	34.8	0.4/3.0	0.0/1.0	0.9/2.1

Table S27: Relative energies and calculated atomic charges for all $[S_{222}][NTf_2]$ conformers(GP). The Cationic q(S) value is on the left of the ”/”. The value of anionic q(S) is the average of the two anionic sulfur atoms.

Conformer	ΔG / $kJ\ mol^{-1}$	ΔE / $kJ\ mol^{-1}$	q(S) (AIM)	q(S) (ChelpG)	q(S) (NBO)
Bot-spread-1down-Trans	0.0	0.0	0.3/3.0	-0.1/1.0	0.8/2.1
Top-spread-1down-Cis	2.6	0.9	0.3/3.0	0.0/1.1	0.8/2.1
Top-aprop-1down-Trans	2.7	-0.4	0.3/3.0	0.0/1.0	0.8/2.1
Bot-prop-flat-Trans	3.6	3.4	0.3/3.0	-0.1/1.1	0.8/2.1
Bot-prop-flat-Trans-2	3.8	-3.2	0.3/3.0	-0.1/0.9	0.8/2.1
Bot-aprop-flat-Trans	4.8	0.0	0.3/3.0	-0.1/0.9	0.8/2.1
Bot-prop-flat-Cis	5.3	2.5	0.3/3.0	-0.1/1.0	0.8/2.1
Bot-prop-1down-Cis	5.4	4.8	0.3/3.0	-0.1/1.1	0.8/2.1
Top-aprop-1down-Cis	5.8	4.0	0.3/3.0	0.0/1.0	0.8/2.1
Bot-aprop-flat-Cis	6.2	5.4	0.3/3.0	-0.1/1.0	0.8/2.1
Top-aprop-flat-Cis	6.2	7.2	0.3/3.0	0.3/1.0	0.8/2.1
Top-prop-flat-Trans	6.3	0.4	0.3/3.0	0.2/1.0	0.8/2.1
Bot-prop-1down-Cis-2	6.5	7.2	0.3/3.0	0.0/0.9	0.8/2.1
Bot-prop-1down-Trans	7.3	0.6	0.3/3.0	-0.1/1.0	0.8/2.1
Top-aprop-flat-Trans	7.8	7.3	0.3/3.0	0.1/1.0	0.8/2.1
Top-prop-aflat-Cis	9.3	6.7	0.3/3.0	0.0/1.1	0.8/2.1
Top-2down-Trans	10.0	7.5	0.3/3.0	0.0/1.0	0.8/2.1
Top-2down-Cis	14.4	10.5	0.3/3.0	0.0/1.1	0.8/2.1
Bot-2down-Trans	15.8	10.1	0.3/3.0	-0.1/1.0	0.8/2.1
Bot-2down-Cis	17.4	14.9	0.3/3.0	-0.1/1.0	0.8/2.1
Top-3down-Cis	26.3	21.5	0.3/3.0	-0.1/1.0	0.8/2.1

Table S28: Relative energies and calculated atomic charges for all $[S_{222}][NTf_2]$ conformers(SMD). The Cationic q(S) value is on the left of the ”/”. The value of anionic q(S) is the average of the two anionic sulfur atoms.