Electronic Supplementary Material (ESI) for ChemComm.

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

Supplementary Information

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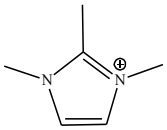
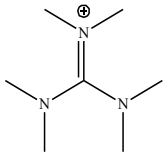
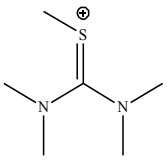
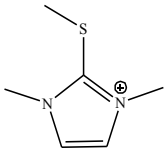
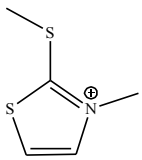
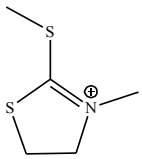
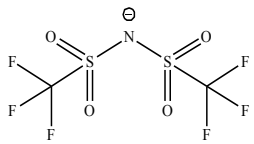
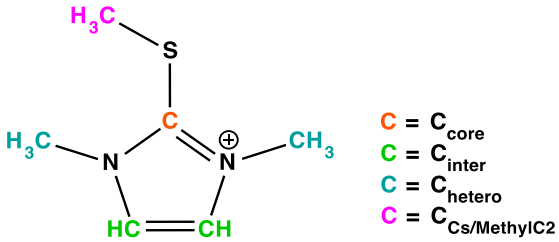
Supplementary Information

Ionic liquids

Table 1. Structures and abbreviations of cations and anion investigated in this study.

Structure	Name	Abbreviation
	1-Methyl-3-methylimidazolium	$[C_1C_1Im]^+$
	1,2,3-Trimethylimidazolium	$[C_1C_1C_1Im]^+$
	Hexamethylguanidinium	$[(C_1C_1)_2dmg]^+$
	Pentamethylthiuronium	$[(C_1)_5TU]^+$
	1-Methyl-3-alkyl-2-methylthioimidazolium	$[C1(C_1)_2ThioIm]^+$
	3-Methyl-2-(methylthio)thiazolium	$[(C_1)_2Thio]^+$
	3-Methyl-2-methylsulfanyl-4,5-dihydro-1,3-thiazolium	$[(C_1)_2Thiz]^+$
	Bis(trifluoromethanesulfonyl)imide	$[NTf_2]^-$

Model proposed for nitrogen-based ionic liquids[1] and corresponding nomenclature regarding this work:



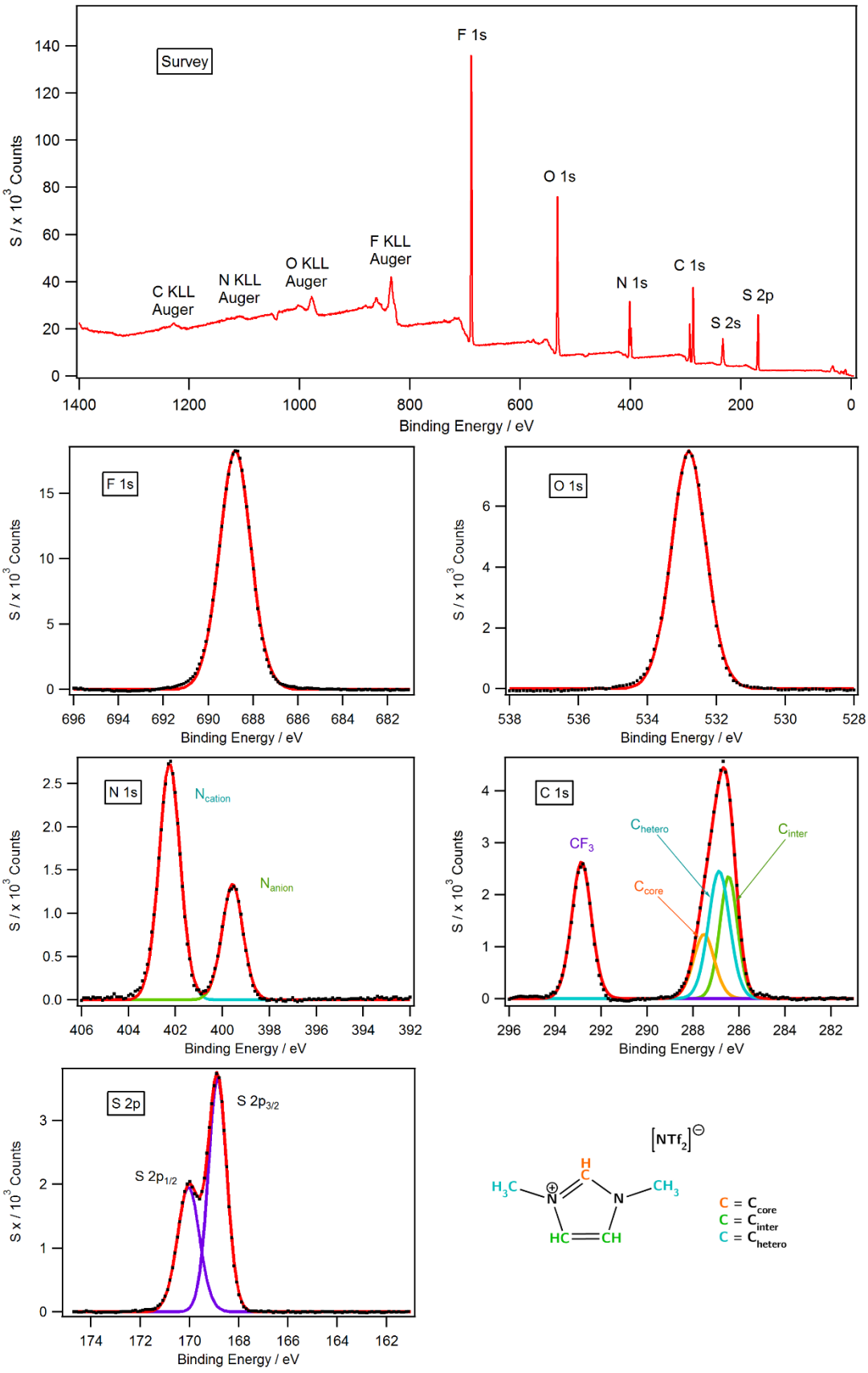
XP spectra of Ionic Liquids

All experiments were carried out on a Kratos Axis Ultra Spectrometer. Survey and fitted high resolution spectra for all ionic liquids studied are presented. Spectra are charge corrected by indirect charge referencing as all the ionic liquids have short alkyl chains ($n < 8$). This was achieved by setting the F 1s component to 688.8 eV as all ionic liquids studied share the $[NTf_2]^-$ anion. This agrees with the F 1s literature binding energy attributed to the $[NTf_2]^-$ anion for various ionic liquid families.[1-3]

C 1s high-resolution spectra were fitted according to the models described.[1, 4] S 2p high-resolution spectra was fitted taking into account spin-orbit coupling, whereby the area ratio of $2p_{1/2}$: $2p_{3/2}$ components is set to 1 : 2. The O 1s and S 2p high-resolution spectra for ionic liquids containing the $[NTf_2]^-$ anion are affected by shake up/off phenomena and a 4% intensity loss (per oxygen/sulfur atom involved in double bonding) was taken into account when calculating atomic percentages for these elements. This was also applied to the sulfur in the cation when involved in double bonding. Likewise, the C_{core} 1s and N_{cation} 1s high-resolution spectra of all cations are affected by shake up/off phenomena and a 20% and 12%, respectively, intensity loss (per carbon/nitrogen atom involved in double bonding) was taken into account when calculating atomic percentages for these elements.[5]

Binding energies, full width at half maximum and composition tables for all guanidinium-, imidazolium- and sulfur-based ionic liquids investigated can be found on this ESI.

IL 1 [C_1C_1Im][NTf_2] survey and high-resolution scans



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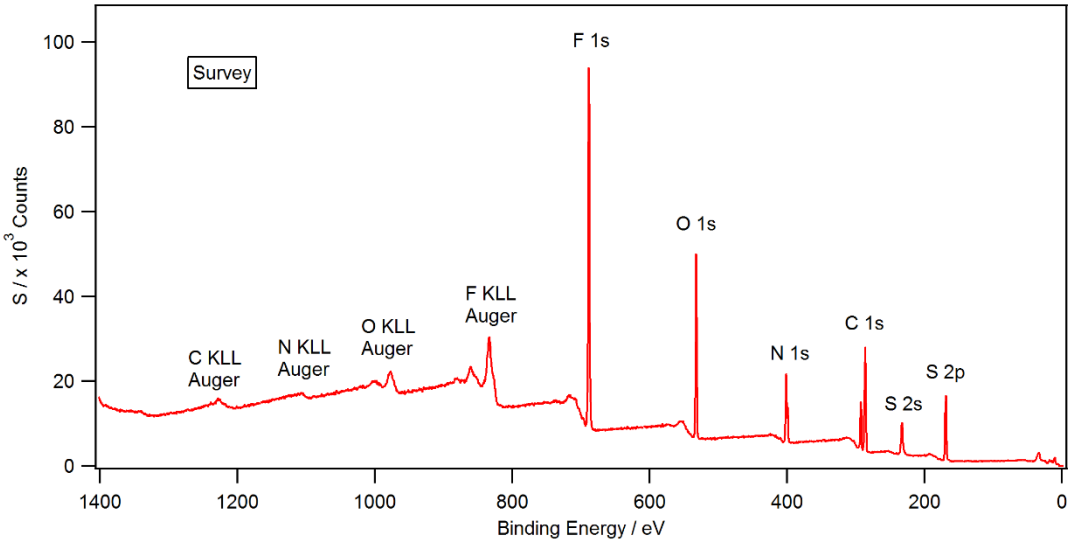

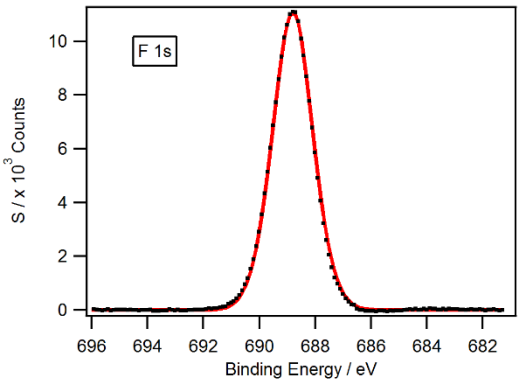

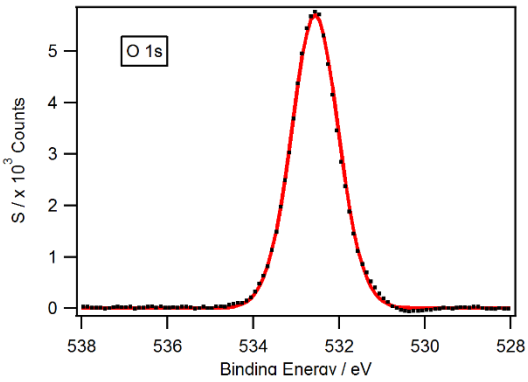

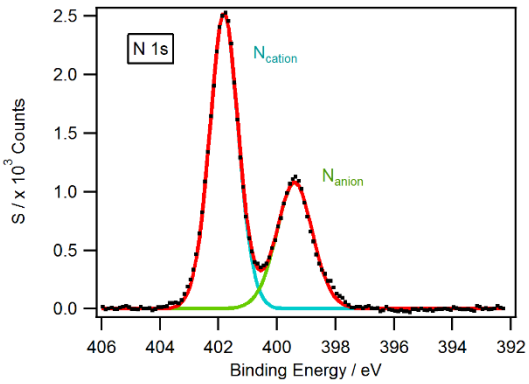

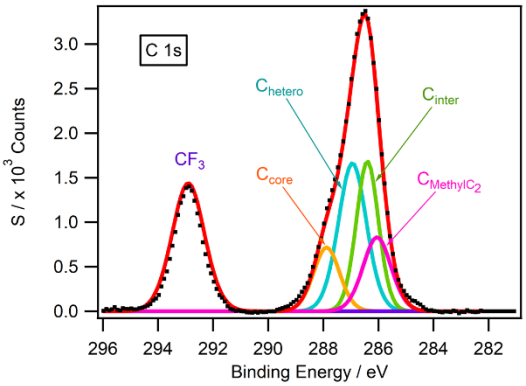

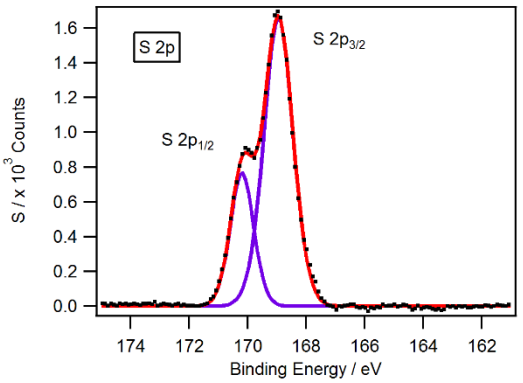

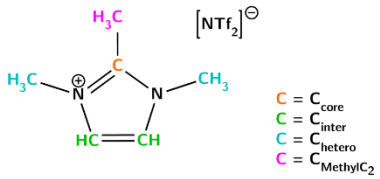

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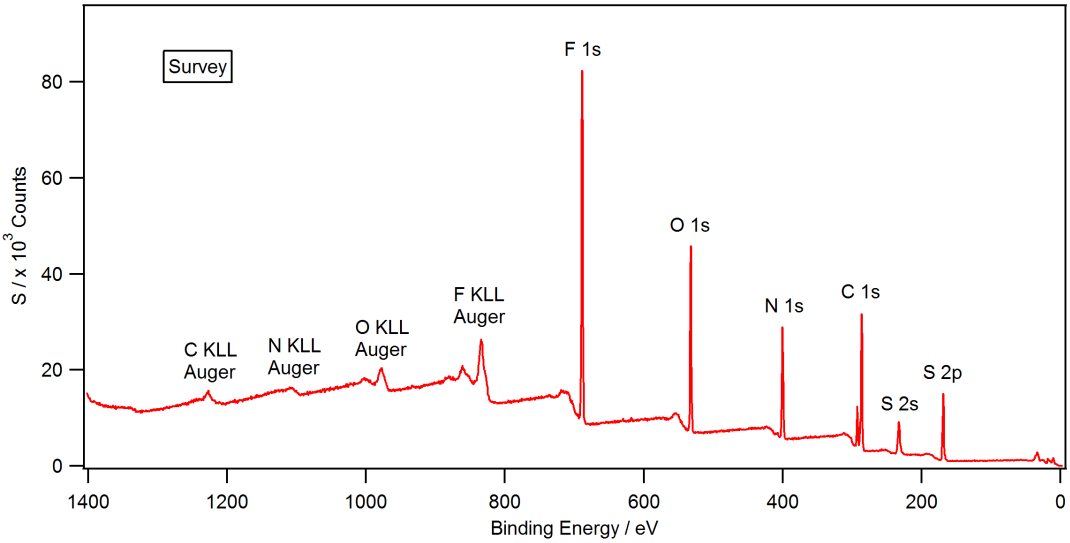
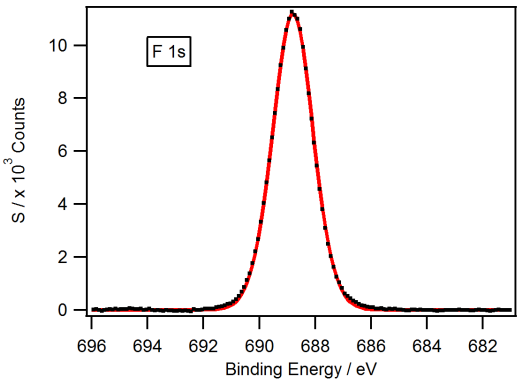
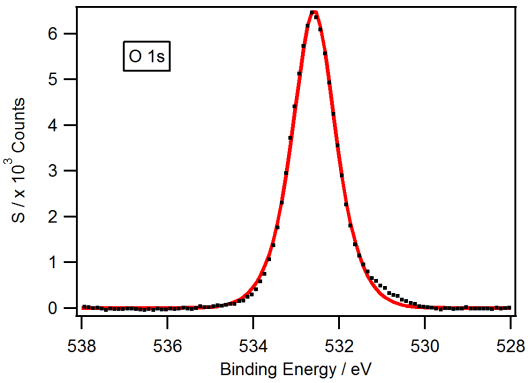
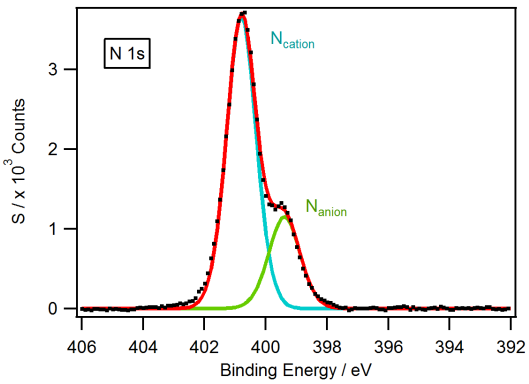
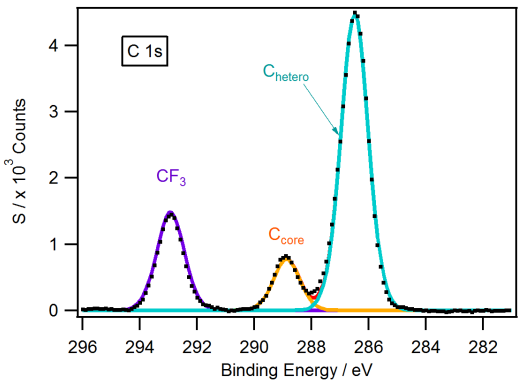
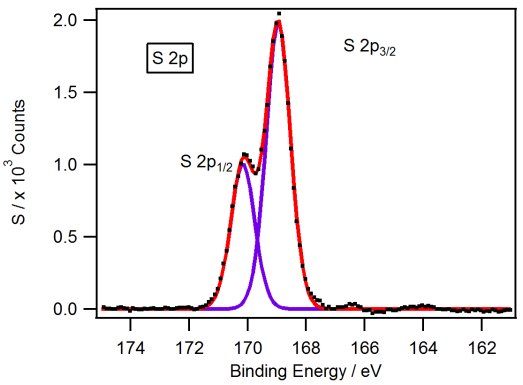


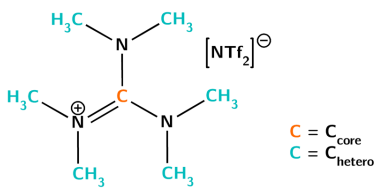




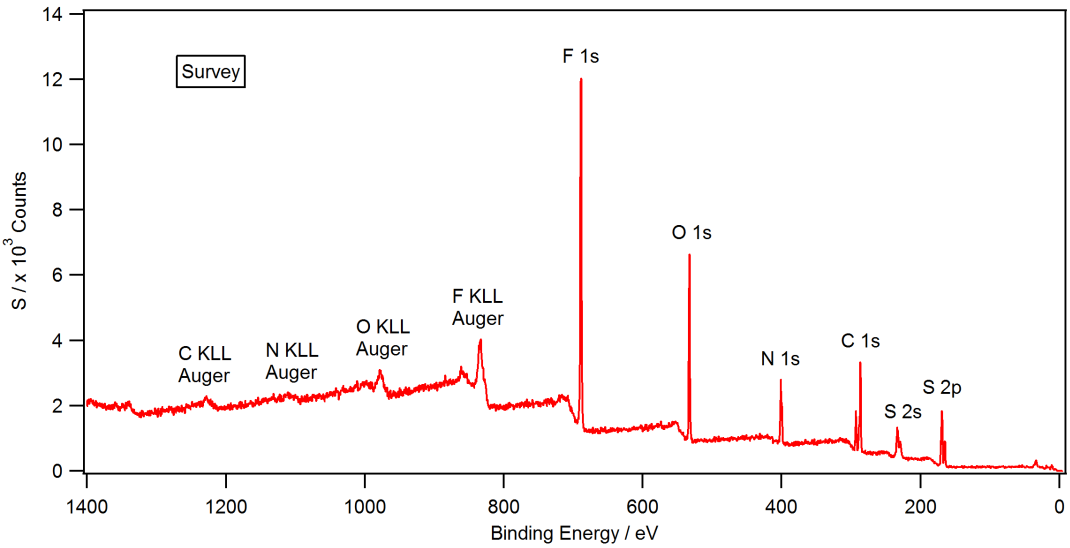


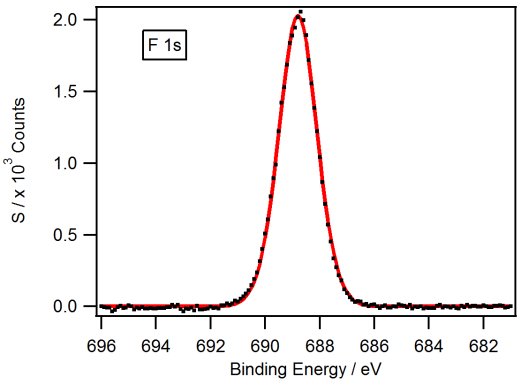


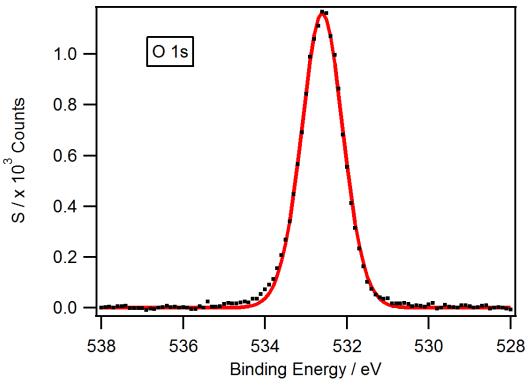


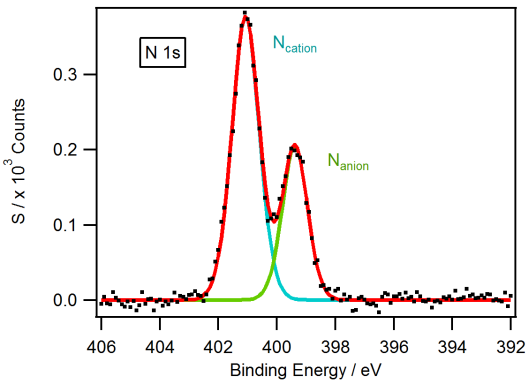


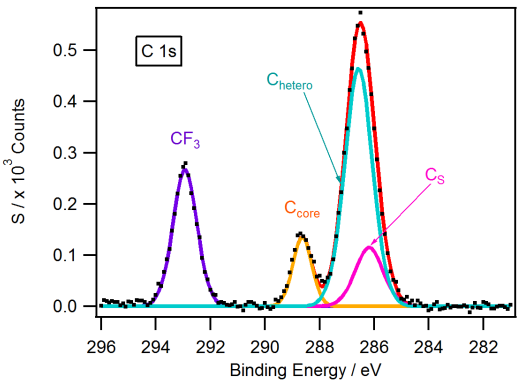
IL 4 $[(C_1)_5TU][NTf_2]$ survey and high-resolution scans

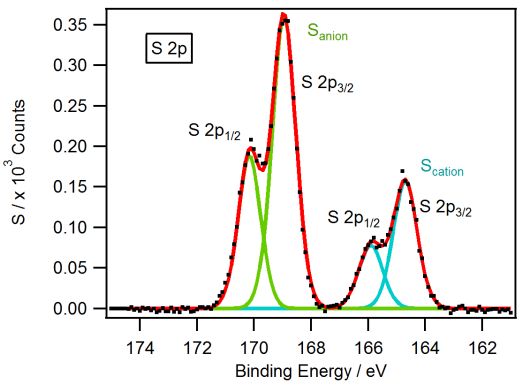


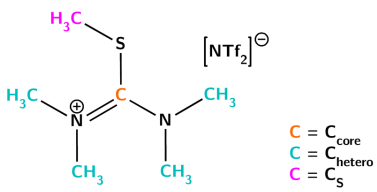




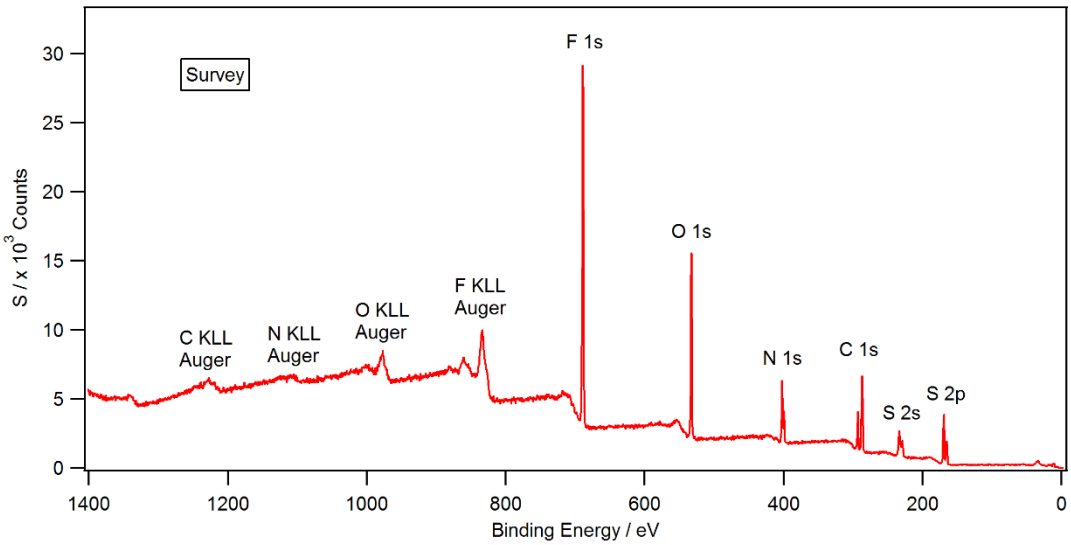


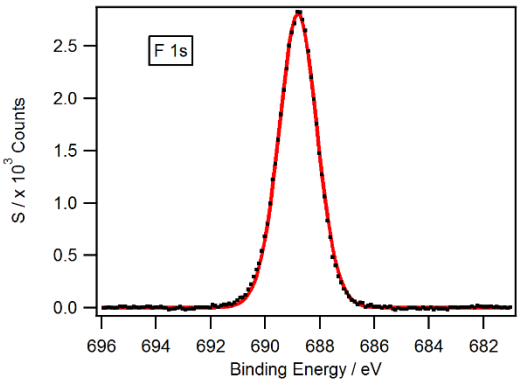


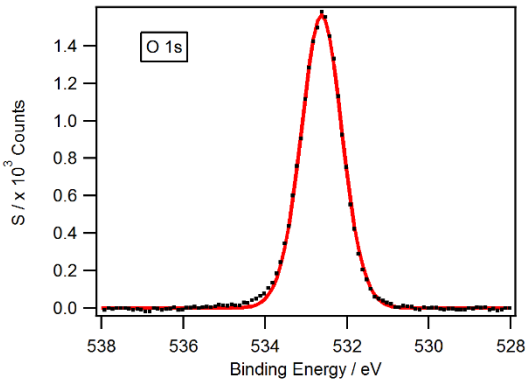


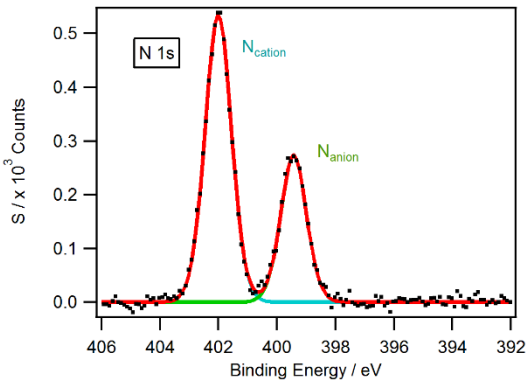


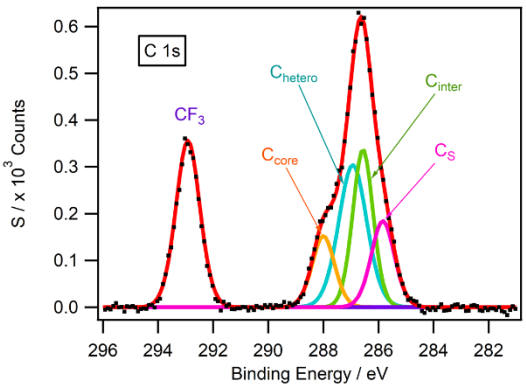
IL 5 [$C_1(C_1)_2$ThioIm][NTf_2] survey and high-resolution scans

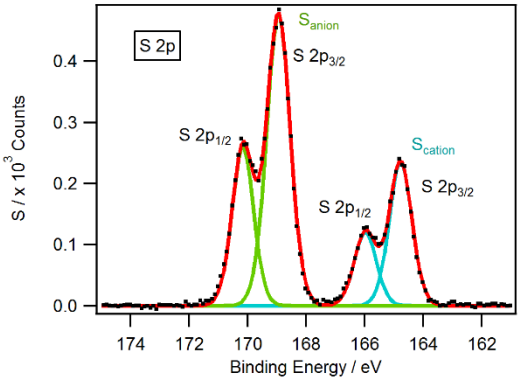


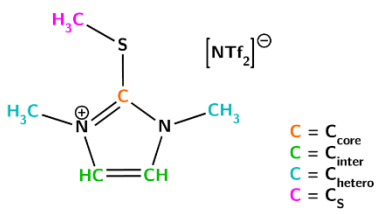




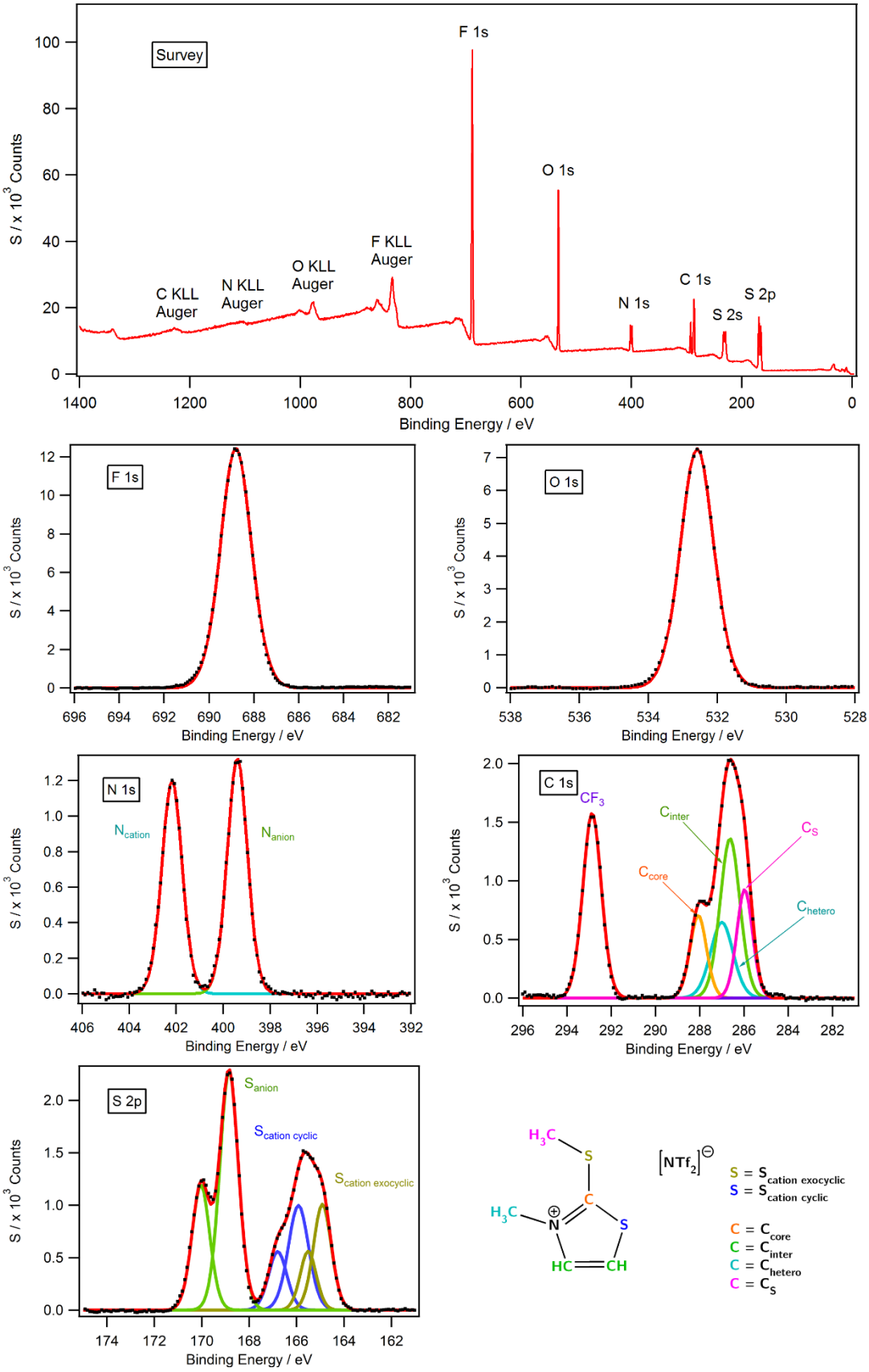








IL 6 [$(C_1)_2$Thio][NTf_2] survey and high-resolution scans



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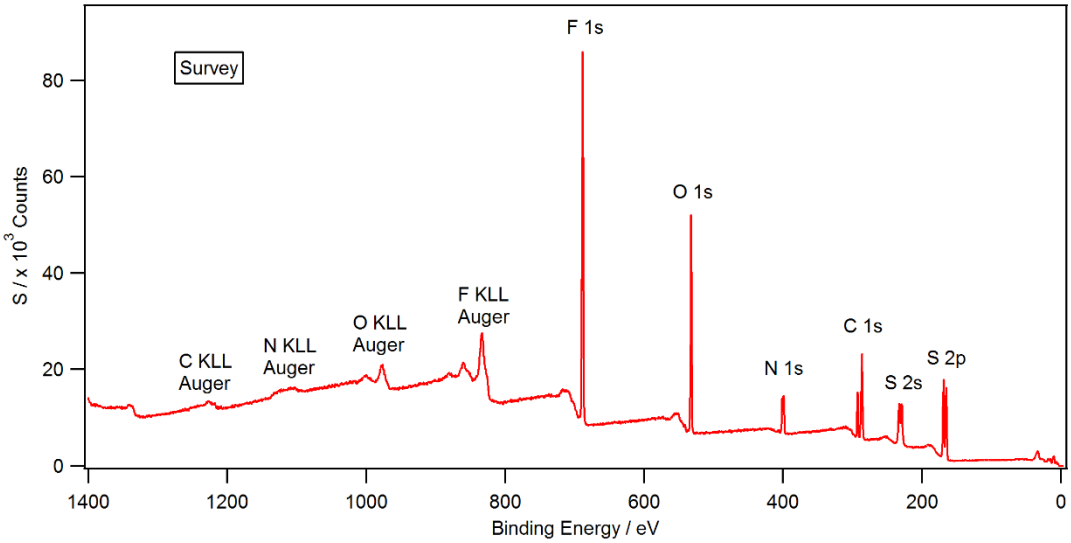
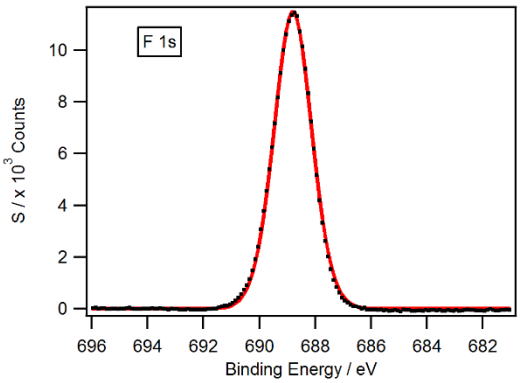
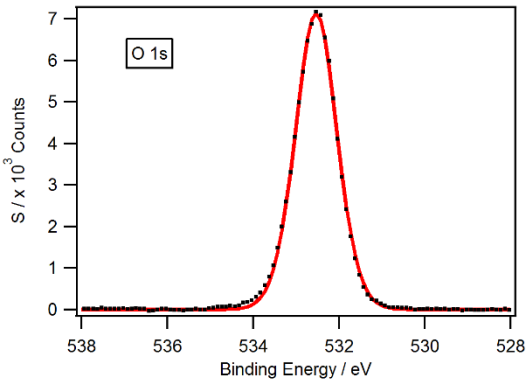
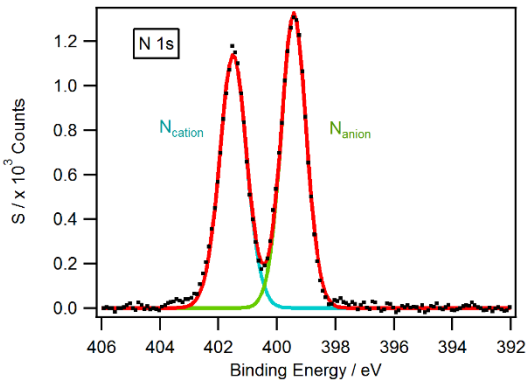
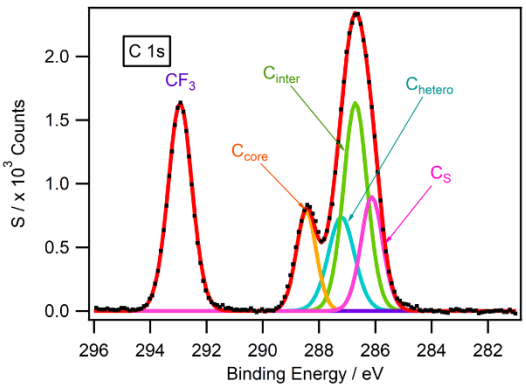
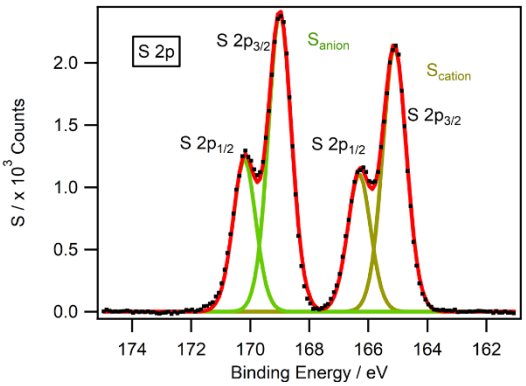


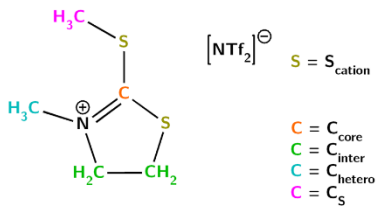












Valence Band scans for IL 3, IL 4 and IL 5

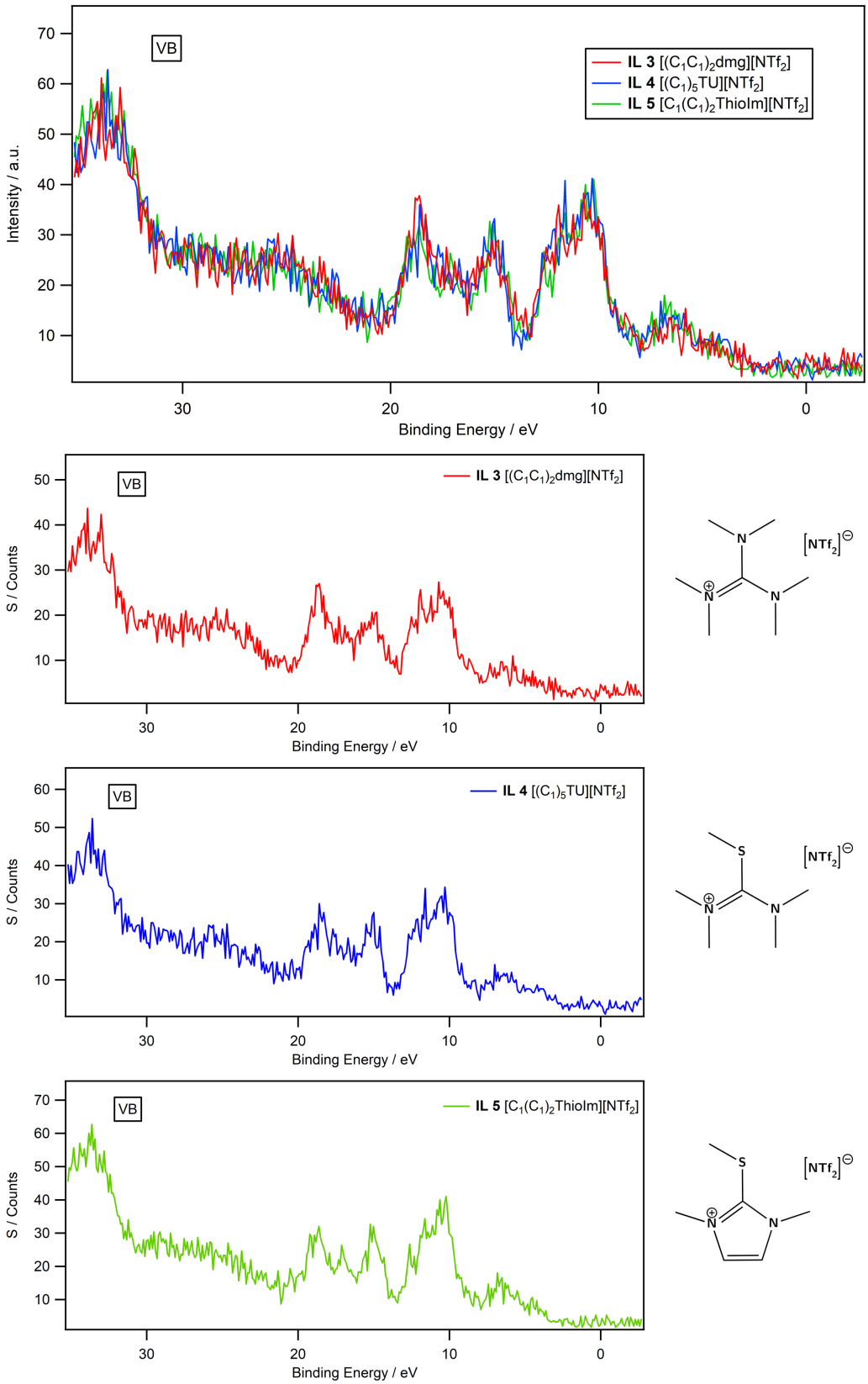
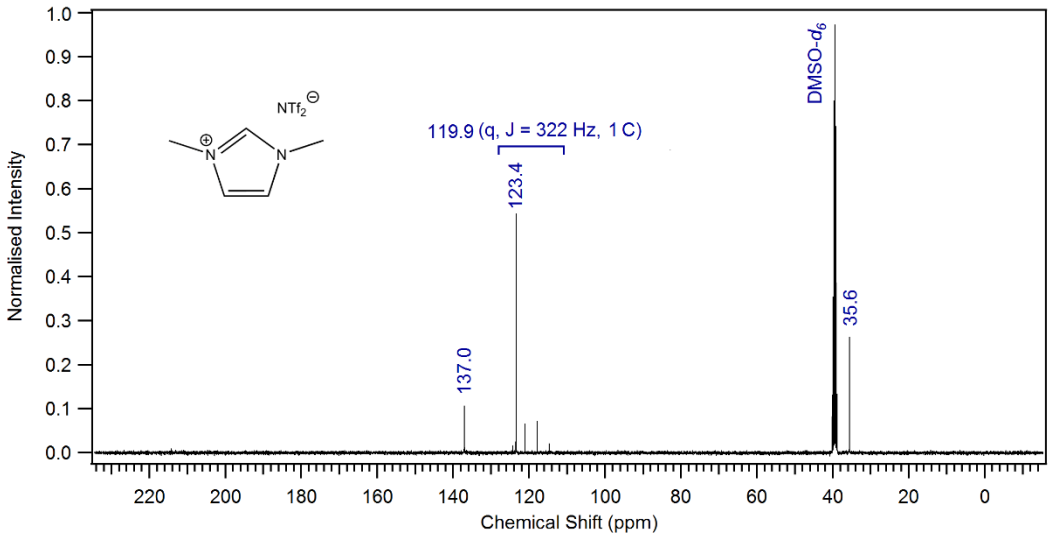


Figure 1 Individual VB spectrum for **IL 3** (red), **IL 4** (blue) and **IL 5** (green) (bottom), and normalised VB spectra of all 3 overlapped, showing minimal impact of cationic structure upon the VB region (top).

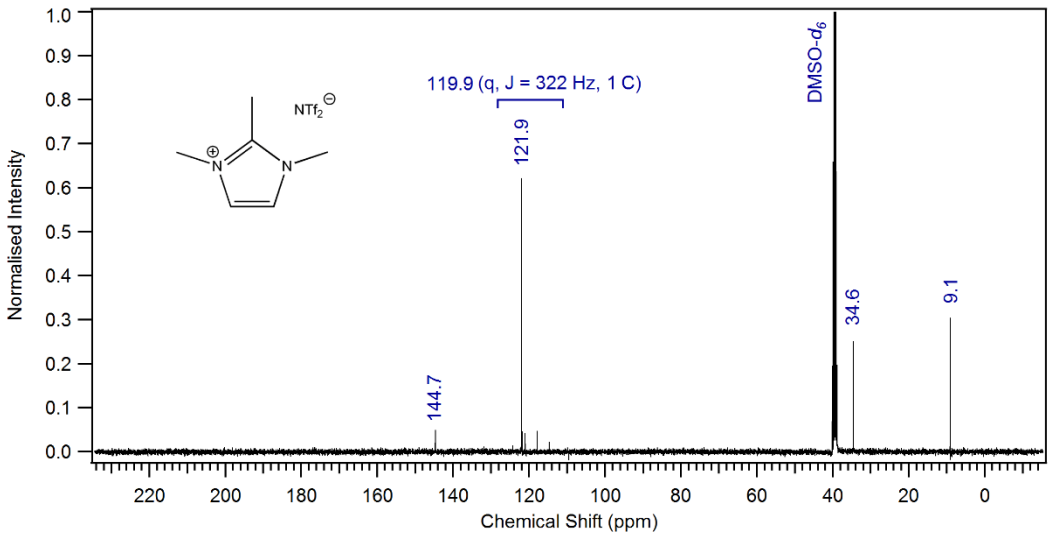
^{13}C NMR of Ionic Liquids

All compounds were dried *in vacuo* ($p \leq 10^{-3}$ mbar) at 50 °C and stored under argon before being characterised by ^{1}H, ^{13}C, and ^{19}F-{^{1}H} recorded at room temperature on a Bruker AV3400HD spectrometer; Chemical shifts (δ) are reported in parts per million (ppm) with reference to residual traces of protonated solvents in commercial NMR solvent, protonated dimethyl sulfoxide (δ_H 2.50) and DMSO-d_6 (δ_C 39.5); Coupling constants (J) are given in Hz.

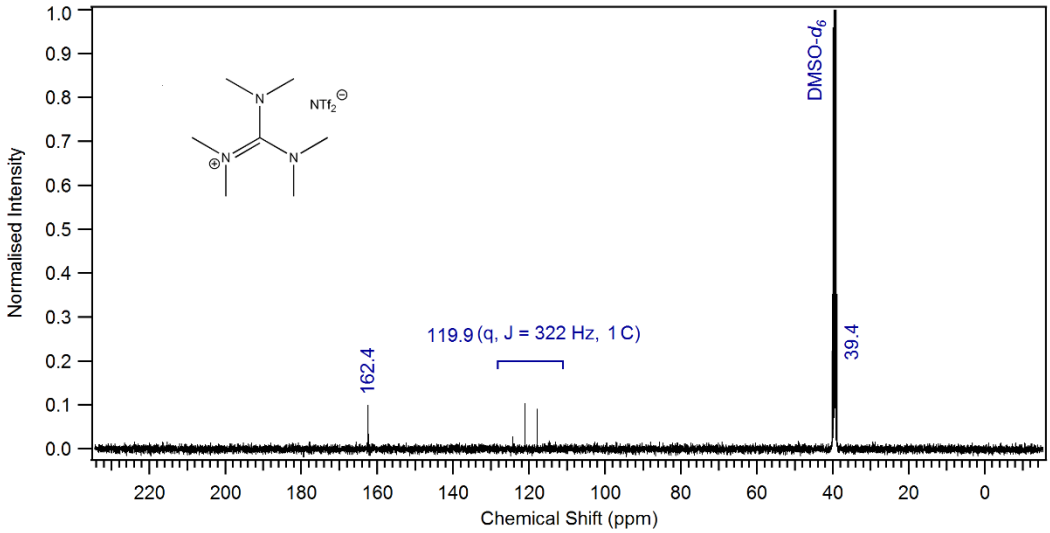
IL 1 [C_1C_1Im][NTf_2] ^{13}C NMR spectrum



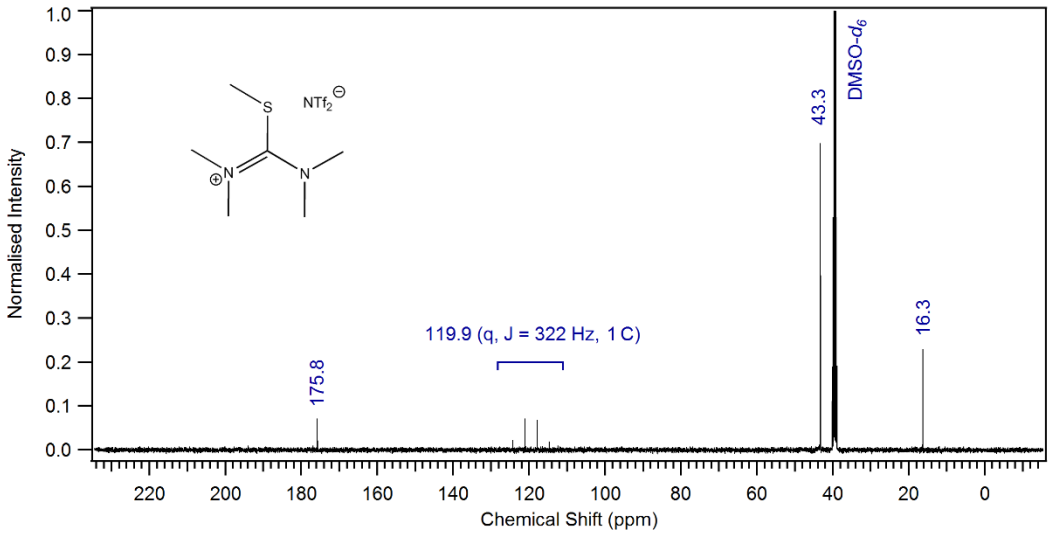
IL 2 [$C_1C_1C_1$Im][NTf_2] ^{13}C NMR spectrum



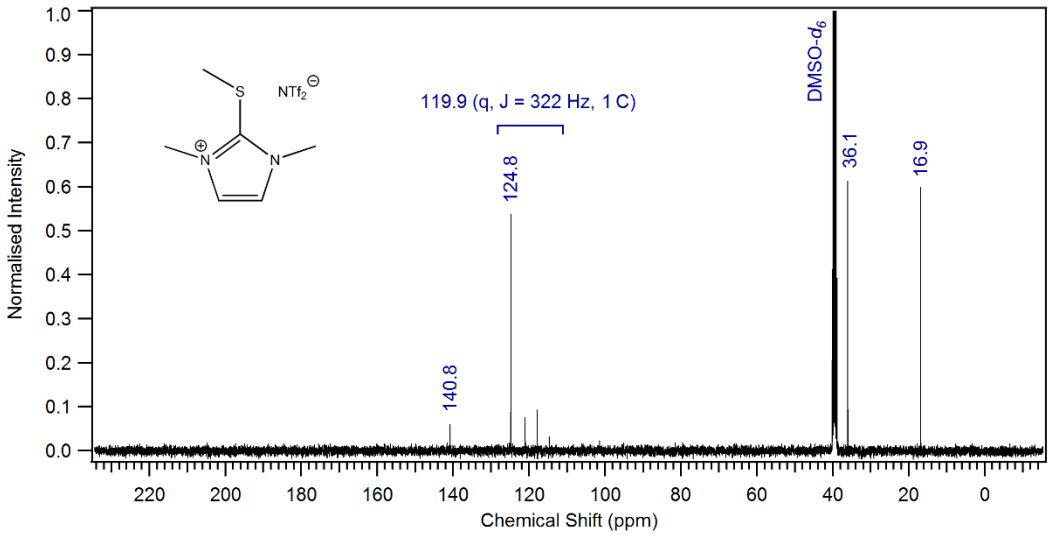
IL 3 [$(C_1C_1)_2$dmg][NTf_2] ^{13}C NMR spectrum



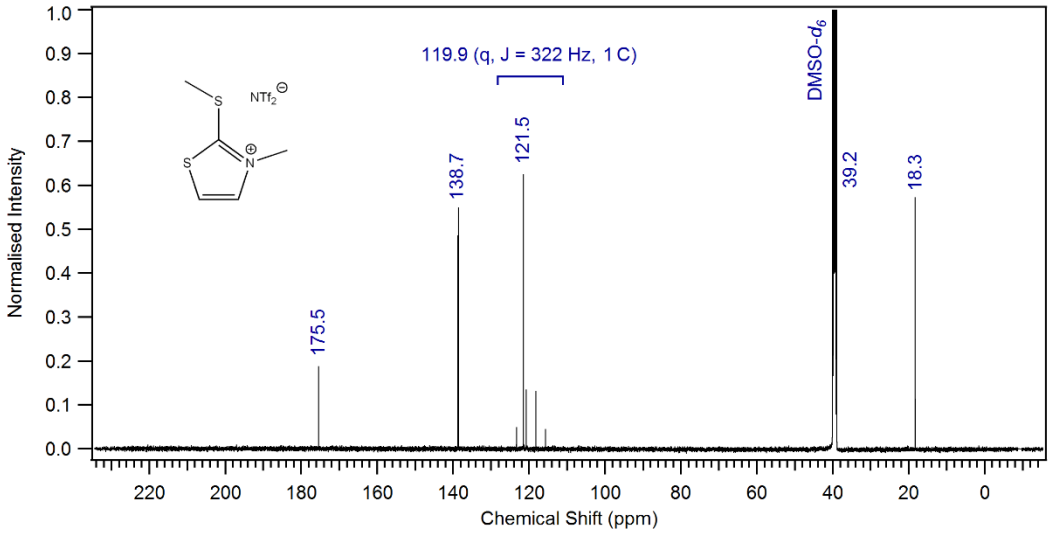
IL 4 [$(C_1)_5$TU][NTf_2] ^{13}C NMR spectrum



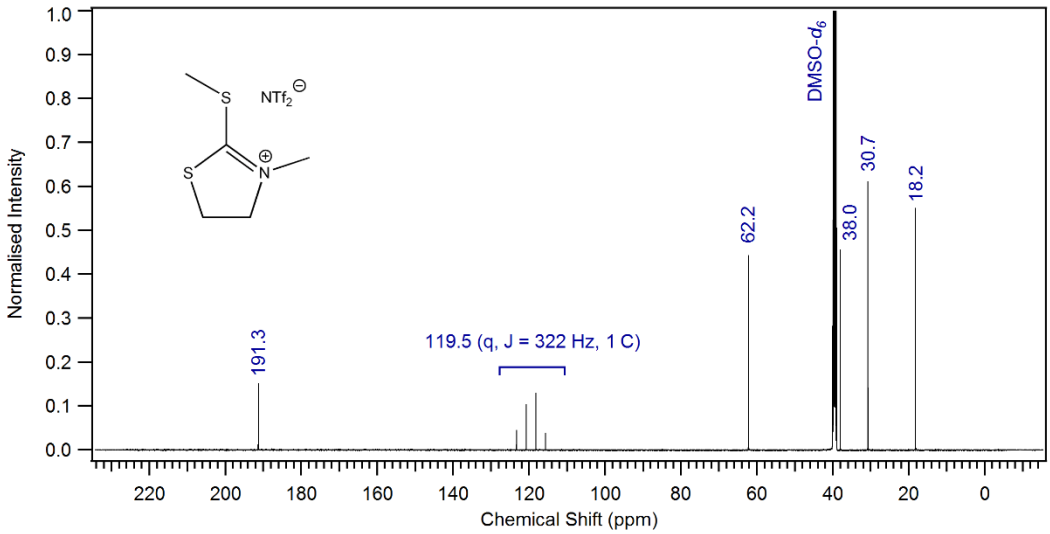
IL 5 [$C_1(C_1)_2$ThioIm][NTf_2] ^{13}C NMR spectrum



IL 6 [$(C_1)_2$Thio][NTf_2] ^{13}C NMR spectrum



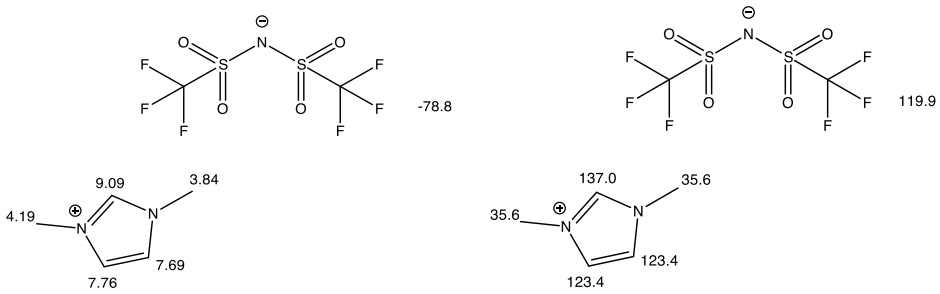
IL 7 [$(C_1)_2$Thiz][NTf_2] ^{13}C NMR spectrum



Synthesis of Ionic Liquids

^{1}H NMR and ^{19}F NMR chemical shifts are represented together in the compound structure on the left. ^{13}C NMR chemical shifts are represented separately on the right. ESI-MS measured on a Brücker MicroTOF 62 spectrometer.

IL 1: 1,3-Dimethylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_1C_1Im][NTf_2]$[6]



1,3-Dimethylimidazolium methyl sulphate (1.10 g, 5.30 mmol) was transferred to a round bottom flask followed by the addition of water (10 mL). $LiNTf_2$ (1.83 g, 6.36 mmol) in water (10 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (20 mL) was added to recover the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and dried *in vacuo* overnight at 50 °C. The salt (1.98 g, 99.1%) was obtained as colourless liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 9.09 (br. s, 1 H), 7.76 (t, J = 1.8 Hz, 1 H), 7.69 (t, J = 1.8 Hz, 1 H), 4.19 (s, 3 H), 3.84 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 137.0, 123.4, 119.9 (q, $^{1}J_{C\text{-}F}$ = 322 Hz, 1 C), 35.6;

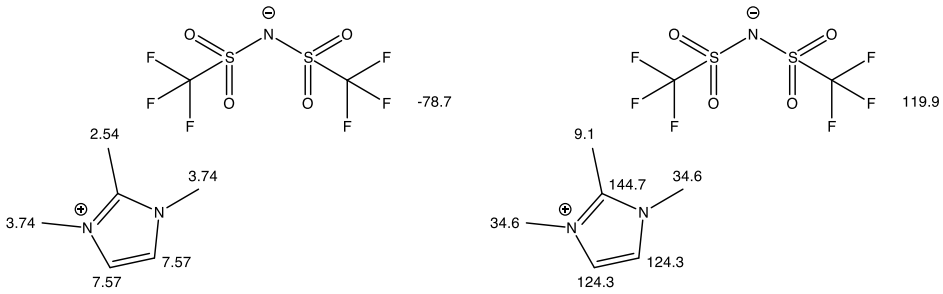
^{19}F NMR (376 MHz, DMSO-d_6): δ -78.8 (s, 6 F).

ESI-MS (+ve) $[C_5H_9N_2]^+$: calcd 97.0760, found 97.0777.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9185.

Data in agreement with literature values.[6]

IL 2: 1,2,3-Trimethylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_1C_1C_1Im][NTf_2]$



1,2,3-Trimethylimidazolium iodide (0.610 g, 2.56 mmol) was transferred to a round bottom flask followed by the addition of water (5 mL). $LiNTf_2$ (0.880 g, 3.07 mmol) in water (5 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (10 mL) was added to recover the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and dried *in vacuo* overnight at 50 °C. The salt (0.990 g, 98.7%) was obtained as white powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.57 (s, 2 H), 3.74 (s, 6 H), 2.54 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 144.7, 121.9, 119.9 (q, $^1J_{C\text{-}F}$ = 322 Hz, 1 C), 34.6, 9.1;

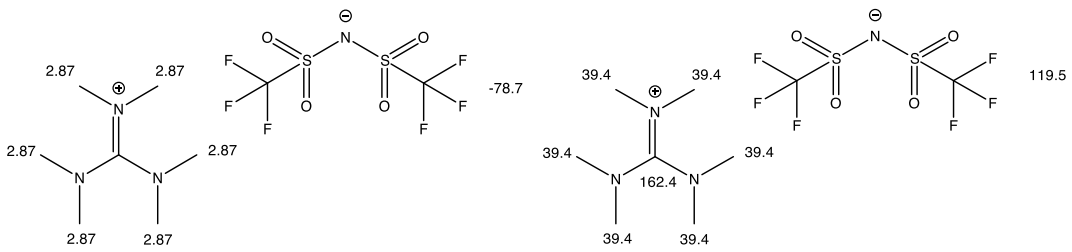
^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

ESI-MS (+ve) $[C_6H_{11}N_2]^+$: calcd 111.0917, found 111.0929.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9181.

CHN Analysis: Calc. for $[C_1C_1C_1Im][NTf_2]$, ($C_8H_{11}F_6N_3O_4S_2$): N 10.74, C 24.56, H 2.83. Found: N 10.51, C 24.78, H 2.64.

IL 3: Hexamethylguanidinium bis(trifluoromethanesulfonyl)imide, $[(C_1C_1)_2dmg][NTf_2]$



Hexamethylguanidinium chloride (0.50 g, 2.78 mmol) was transferred to a round bottom flask followed by the addition of water (5 mL). Lithium bis(trifluoromethanesulfonyl)imide (0.960 g, 3.34 mmol) in water (5 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (10 mL) was added to extract the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 °C. The salt $[(C_1C_1)_2dmg][NTf_2]$ (1.11 g, 94.0%) was obtained as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 2.87 (s, 18 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 162.4, 119.9 (q, $^1J_{C\text{-}F}$ = 322 Hz, 1 C), 39.4;

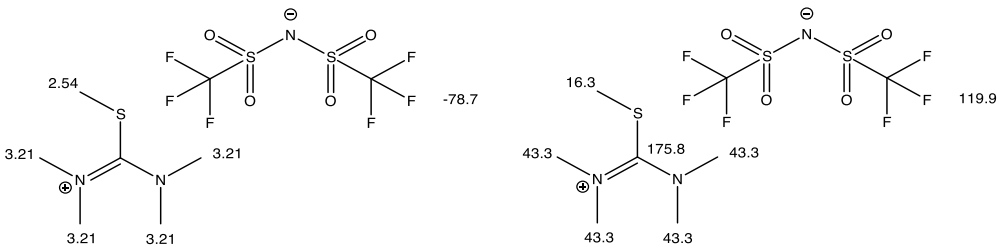
^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

ESI-MS (+ve) $[C_7H_{18}N_3]^+$: calcd 144.1495, found 144.1484.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9178, found 279.9175.

CHN Analysis: Calc. for $[(C_1C_1)_2dmg][NTf_2]$, ($C_9H_{18}F_6N_4O_4S_2$): N 13.20, C 25.47, H 4.28. Found: N 13.00, C 25.51, H 4.07.

IL 4: Pentamethylthiouronium bis(trifluoromethanesulfonyl)imide, $[(C_1)_5TU][NTf_2]$



Pentamethylthiouronium iodide (1.92 g, 7.02 mmol) was transferred to a round bottom flask followed by the addition of water (15 mL). Lithium bis(trifluoromethanesulfonyl)imide (2.42 g, 8.42 mmol) in water (15 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (20 mL) was added to recover the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 °C. The salt (2.81 g, 93.6%) was obtained as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 3.21 (s, 12 H), 2.54 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.8, 119.9 (q, $^{1}J_{C\text{-}F}$ = 322 Hz, 1 C), 43.3, 16.3;

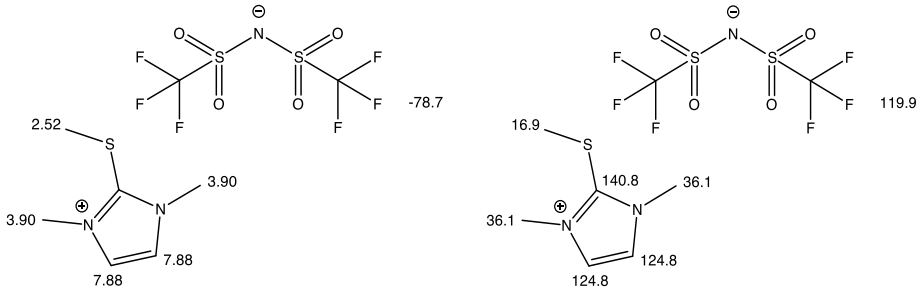
^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

ESI-MS (+ve) $[C_6H_{15}N_2S]^+$: calcd 147.0950, found 147.0941.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9193.

CHN Analysis: Calc. for $[(C_1)_5TU][NTf_2]$, ($C_8H_{15}F_6N_3O_4S_3$): N 9.83, C 22.48, H 3.54. Found: N 9.43, C 22.43, H 3.25.

IL 5: 1,3-Dimethyl-2-methylthioimidazolium bis(trifluoromethanesulfonyl)imide, $[C_1(C_1)_2ThioIm][NTf_2]$[7]



1,3-Dimethyl-2-methylthioimidazolium iodide (0.770 g, 2.83 mmol) was transferred to a round bottom flask followed by the addition of water (5 mL). Lithium bis(trifluoromethanesulfonyl)imide (0.980 g, 3.40 mmol) in water (5 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (10 mL) was added to recover the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and stirred *in vacuo* overnight at 50 °C. The salt (1.19 g, 99.6%) was obtained as a colourless viscous liquid.

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.88 (br.s, 2 H), 3.90 (s, 6 H), 2.52 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 140.8, 124.8, 119.9 (q, $^1J_{C\text{-}F}$ = 322 Hz, 1 C), 36.1, 16.9;

^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

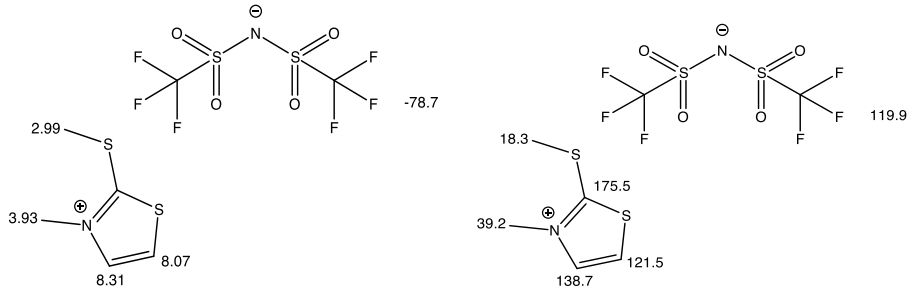
ESI-MS (+ve) $[C_6H_{11}N_2S]^+$: calcd 143.0637, found 143.0890.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9171.

CHN Analysis: Calc. for $[C_1(C_1)_2ThioIm][NTf_2]$, ($C_8H_{11}F_6N_3O_4S_3$): N 9.93, C 22.70, H 2.62. Found: N 9.84, C 22.72, H 2.34.

Data in agreement with literature values.[7]

IL 6: 3-Methyl-2-(methylthio)thiazolium bis(trifluoromethylsulfonyl)imide, $[(C_1)_2Thio][NTf_2]$



3-Methyl-2-(methylthio)thiazolium iodide (1.28 g, 4.69 mmol) was transferred to a round bottom flask followed by the addition of water (10 mL). $LiNTf_2$ (1.62 g, 5.63 mmol) in water (10 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (20 mL) was added to recover the ionic liquid and washed with cold water (5 x 5 mL). The organic layer was collected, the solvent removed and dried *in vacuo* overnight at 50 °C. The salt (1.90 g, 95.2%) was obtained as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.31 (d, J = 4.1 Hz, 1 H), 8.07 (d, J = 4.1 Hz, 1 H), 3.93 (s, 3 H), 2.99 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 175.5, 138.7, 121.5, 119.9 (q, $^1J_{C\text{-}F}$ = 322 Hz, 1 C), 39.2, 18.3;

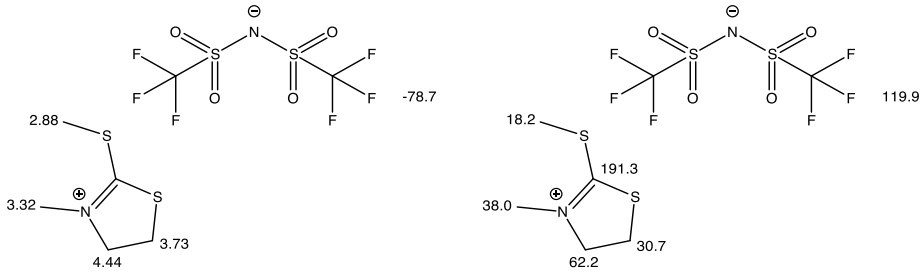
^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

ESI-MS (+ve) $[C_5H_8NS_2]^+$: calcd 146.0093, found 146.0090.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9196.

CHN Analysis: Calc. for $[(C_1)_2Thio][NTf_2]$, ($C_7H_8F_6N_2O_4S_3$): N 6.57, C 19.72, H 1.89. Found: N 6.77, C 19.83, H 1.90.

IL 7: 3-Methyl-2-methylsulfanyl-4,5-dihydro-1,3-thiazolium bis(trifluoromethylsulfonyl)imide, $[(C_1)_2Thiz][NTf_2]$



3-Methyl-2-methylsulfanyl-4,5-dihydro-1,3-thiazolium iodide (1.28 g, 4.67 mmol) was transferred to a round bottom flask followed by the addition of water (10 mL). $LiNTf_2$ (1.61 g, 5.60 mmol) in water (10 mL) was added and the mixture stirred at 0 °C and gradually allowed to warm up to room temperature for 24 h. Dichloromethane (20 mL) was added to recover the ionic liquid and washed with cold water (5 x 10 mL). The organic layer was collected, the solvent removed and dried *in vacuo* overnight at 50 °C. The salt (1.86 g, 93.1%) was obtained as a white powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ 4.44 (t, J = 8.8 Hz, 2 H), 3.73 (t, J = 8.8 Hz, 2 H), 3.32 (s, 3 H), 2.88 (s, 3 H);

^{13}C NMR (100 MHz, DMSO-d_6): δ 191.3, 119.9 (q, $^1J_{C\text{-}F}$ = 322 Hz, 1 C), 62.2, 38.0, 30.7, 18.2;

^{19}F NMR (376 MHz, DMSO-d_6): δ -78.7 (s, 6 F).

ESI-MS (+ve) $[C_5H_{10}NS_2]^+$: calcd 148.0249, found 148.0247.

ESI-MS (-ve) $[C_2F_6NO_4S_2]^-$: calcd 279.9173, found 279.9175.

CHN Analysis: Calc. for $[(C_1)_2Thiz][NTf_2]$, ($C_7H_{10}F_6N_2O_4S_3$): N 6.54, C 19.63, H 2.35. Found: N 6.62, C 19.78, H 2.52.

Table 2. XPS measured experimental and nominal (in brackets) stoichiometries for guanidinium, sulfur and imidazolium based ionic liquids studied in this work. Associated experimental error is ± 10 - 20%.

	Composition (%)				
Compound	C 1s	N 1s	O 1s	F 1s	S 2p
[a]RSF[5,8]	0.278	0.477	0.780	1.000	0.668
IL 1 $[C_1C_1Im][NTf_2]$	35.3 (31.8)	14.3 (13.6)	16.0 (18.2)	25.9 (27.3)	8.5 (9.1)
IL 2 $[C_1C_1C_1Im][NTf_2]$	38.2 (34.8)	14.6 (13.0)	15.8 (17.4)	23.4 (26.1)	8.1 (8.7)
IL 3 $[(C_1C_1)_2dmg][NTf_2]$	39.9 (36.0)	16.7 (16.0)	14.4 (16.0)	22.6 (24.0)	6.4 (8.0)
IL 4 $[(C_1)_5TU][NTf_2]$	37.8 (33.3)	11.5 (12.5)	14.2 (16.7)	23.3 (25.0)	13.3 (12.5)
IL 5 $[C_1(C_1)_2ThioIm][NTf_2]$	36.6 (33.3)	11.7 (12.5)	14.2 (16.7)	24.4 (25.0)	13.1 (12.5)
IL 6 $[(C_1)_2Thio][NTf_2]$	32.3 (30.4)	9.1 (8.7)	16.4 (17.4)	27.2 (26.1)	15.0 (17.4)
IL 7 $[(C_1)_2Thiz][NTf_2]$	33.8 (30.4)	9.1 (8.7)	16.2 (17.4)	25.0 (26.1)	15.8 (17.4)

[a] Relative sensitivity factors (RSF) taken from the Kratos Library. *N.B.* Hydrogen is undetectable by XPS due its low photoionisation cross-section; consequently, reported stoichiometries are determined without consideration of hydrogen content.[9]

Table 3. Experimental binding energies in eV for guanidinium, sulfur-based and imidazolium ionic liquids studied in this work. The associated experimental error is 0.1 eV. All compounds charge corrected by setting F 1s to 688.8 eV of the corresponding $[NTf_2]^-$ anion.

		Binding Energy / eV											
Compound		Cation							Anion				
Cation	Anion	C_{core} 1s	C_{hetero} 1s	C_{inter} 1s	$C_{Cs/MethylC2}$ 1s	N_{cation} 1s	$S_{exocyclic}$ $2p_{3/2}$	S_{cyclic} $2p_{3/2}$	C_{CF_3} 1s	N_{anion} 1s	O 1s	F 1s	S_{anion} $2p_{3/2}$
IL 1 $[C_1C_1Im]^+$	$[NTf_2]^-$	287.6	286.9	286.5	-	402.1	-	-	292.9	399.4	532.6	688.8	168.9
IL 2 $[C_1C_1C_1Im]^+$	$[NTf_2]^-$	287.9	286.9	286.4	286.1	401.8	-	-	292.9	399.4	532.6	688.8	168.9
IL 3 $[(C_1C_1)_2dmg]^+$	$[NTf_2]^-$	288.9	286.5	-	-	400.8	-	-	292.9	399.4	532.6	688.8	169.0
IL 4 $[(C_1)_5TU]^+$	$[NTf_2]^-$	288.6	286.6	-	286.2	401.1	164.7	-	292.9	399.4	532.6	688.8	169.0
IL 5 $[C_1(C_1)_2ThioIm]^+$	$[NTf_2]^-$	288.0	286.9	286.6	285.8	402.0	164.8	-	292.9	399.4	532.6	688.8	168.9
IL 6 $[(C_1)_2Thio]^+$	$[NTf_2]^-$	288.1	286.9	286.6	285.9	402.2	164.9	165.9	292.9	399.4	532.6	688.8	168.9
IL 7 $[(C_1)_2Thiz]^+$	$[NTf_2]^-$	288.4	286.9	286.7	286.1	401.5	165.1	-	292.9	399.4	532.6	688.8	169.0

Table 4. FWHM in eV for guanidinium, sulfur-based and imidazolium ionic liquids studied in this work.

		FWHM / eV											
Compound		Cation							Anion				
Cation	Anion	C_{core} 1s	C_{hetero} 1s	C_{inter} 1s	$C_{Cs/MethylC2}$ 1s	N_{cation} 1s	$S_{exocyclic}$ $2p_{3/2}$	S_{cyclic} $2p_{3/2}$	C_{CF_3} 1s	N_{anion} 1s	O 1s	F 1s	S_{anion} $2p_{3/2}$
IL 1 $[C_1C_1Im]^+$	$[NTf_2]^-$	1.0	1.1	0.9	-	1.0	-	-	1.0	1.0	1.2	1.6	0.9
IL 2 $[C_1C_1C_1Im]^+$	$[NTf_2]^-$	1.0	1.2	1.0	1.2	1.1	-	-	1.1	1.2	1.2	1.7	1.0
IL 3 $[(C_1C_1)_2dmg]^+$	$[NTf_2]^-$	1.0	1.1	-	-	1.1	-	-	1.1	1.2	1.2	1.7	1.0
IL 4 $[(C_1)_5TU]^+$	$[NTf_2]^-$	0.8	1.2	-	1.2	1.1	1.0	-	1.0	1.0	1.2	1.6	1.0
IL 5 $[C_1(C_1)_2ThioIm]^+$	$[NTf_2]^-$	0.9	1.2	0.9	1.0	1.0	0.9	-	1.0	1.0	1.2	1.6	0.9
IL 6 $[(C_1)_2Thio]^+$	$[NTf_2]^-$	0.8	1.2	0.9	0.9	1.0	1.1	1.0	0.9	1.0	1.1	1.6	0.9
IL 7 $[(C_1)_2Thiz]^+$	$[NTf_2]^-$	0.8	1.1	1.1	1.0	1.1	0.9	-	1.0	1.0	1.1	1.6	0.9

Computational Details

Density functional theory (DFT) calculations were performed using the Q-Chem software package.[10] The cation-anion complexes were optimized to minimum energy structures using the PBE0 functional and 6-31+G(d) basis set.[11] Core electron binding energies (CEBEs) and ^{13}C NMR chemical shifts were then calculated at the resulting geometries using the individual gauge for localized orbitals double-ζ basis set (IGLO-II) and a polarized continuum model (C-PCM) with a dielectric constant of 15.0 to represent the bulk effects of the ionic liquid. CEBEs have been computed from the difference between the energy of the ground state and the energy with a core electron removed with the maximum overlap method (MOM) used to prevent variational collapse during the SCF calculation of the core-ionized states,[12] and NMR chemical shifts have been calculated using the gauge invariant atomic orbital (GIAO) approach.

Table 5. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 1** $[(C_1C_1)Im]^+$.

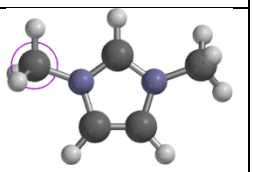
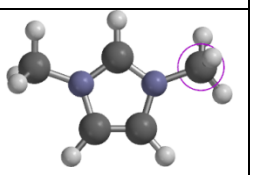
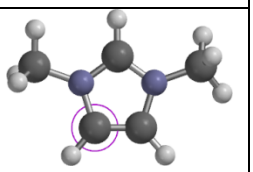
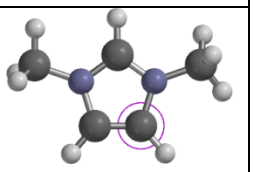
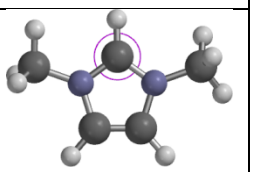
$[(C_1C_1)Im]^+$		
Shift	Assignment	
10.41	N-CH_3	
19.51	N-CH_3	
101.05	N-C=C	
105.82	N-C=C	
143.93	N-CH-N	

Table 6. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 2** $[(C_1C_1C_1)Im]^+$.

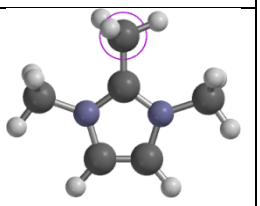
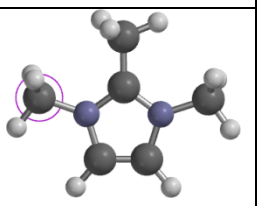
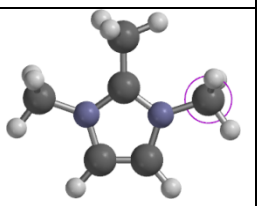
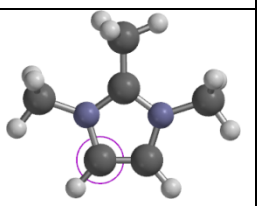
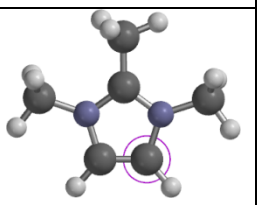
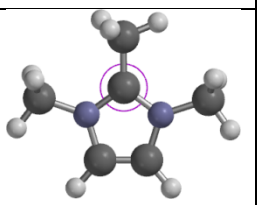
$[(C_1C_1C_1)Im]^+$		
Shift	Assignment	
-14.04	C-CH_3	
14.43	N-CH_3	
18.17	N-CH_3	
109.22	N-C=C	
113.00	N-C=C	
144.53	C-CH_3	

Table 7. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 3** $[(C_1C_1)_2dmg]^+$.

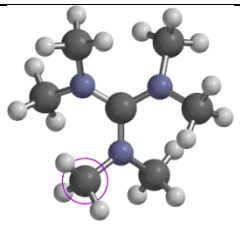
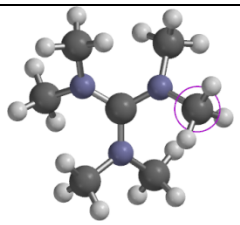
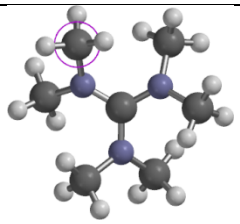
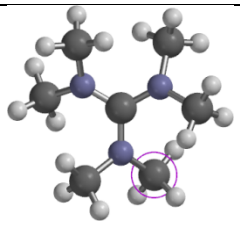
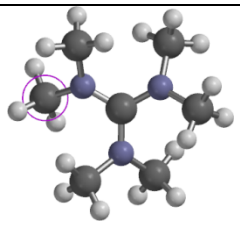
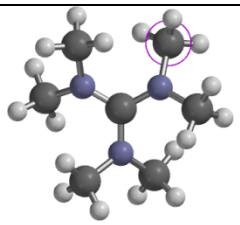
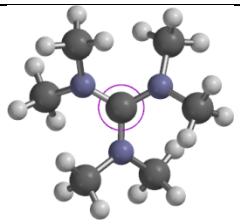
$[(C_1C_1)_2dmg]^+$		
Shift	Assignment	
16.99	N-CH_3	
17.34	N-CH_3	
25.40	N-CH_3	
26.97	N-CH_3	
34.52	N-CH_3	
34.59	N-CH_3	
169.83	CN_3	

Table 8. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 4** $[(C_1)_5TU]^+$.

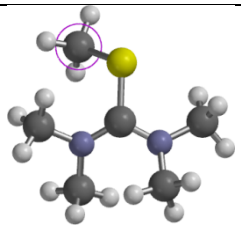
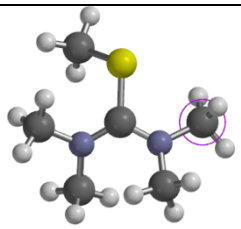
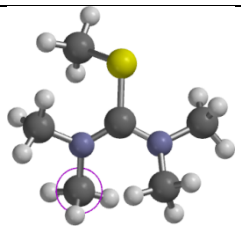
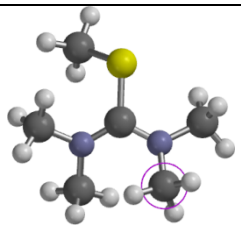
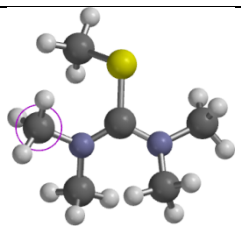
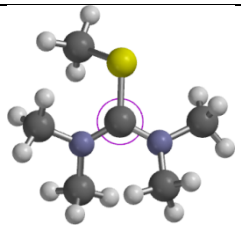
$[(C_1)_5TU]^+$		
Shift	Assignment	
0.51	S-CH_3	
21.51	N-CH_3	
28.45	N-CH_3	
37.44	N-CH_3	
39.01	N-CH_3	
181.11	SCN_2	

Table 9. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 5** $[C_1(C_1)_2ThioIm]^+$.

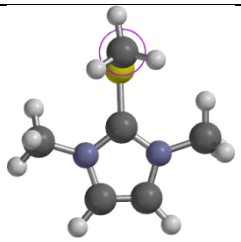
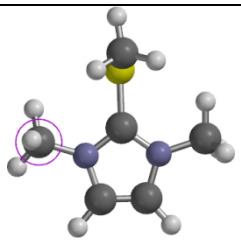
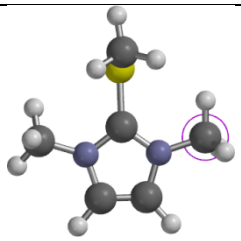
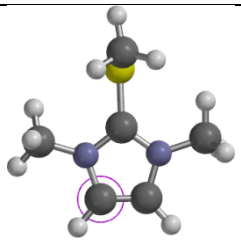
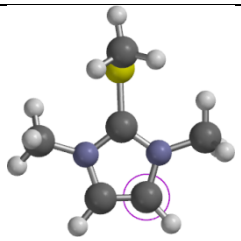
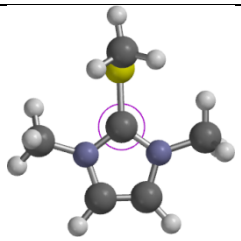
$[C_1(C_1)_2ThioIm]^+$		
Shift	Assignment	
12.82	S-CH_3	
18.14	N-CH_3	
19.01	N-CH_3	
115.77	N-C=C	
118.89	N-C=C	
138.59	SCN_2	

Table 10. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 6** $[(C_1)_2Thio]^+$.

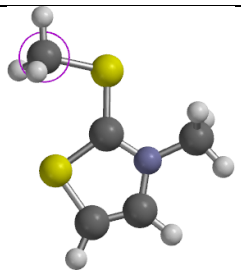
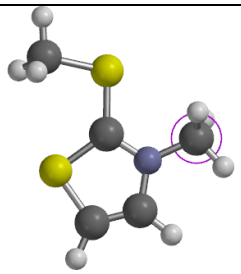
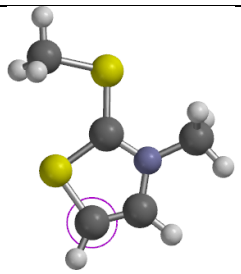
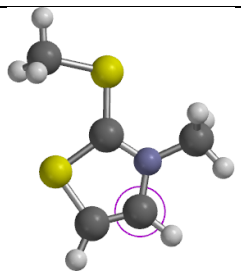
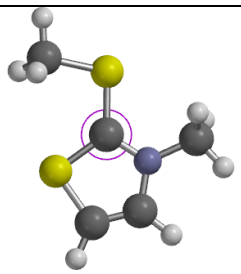
$[(C_1)_2Thio]^+$		
Shift	Assignment	
-0.05	S-CH_3	
24.15	N-CH_3	
105.57	S-C=C	
135.48	S-C=C	
176.24	S_2CN	

Table 11. Calculated NMR shifts in ppm and assignments for the ^{13}C NMR spectrum of **IL 7** $[(C_1)_2Thiz]^+$.

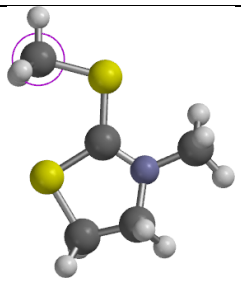
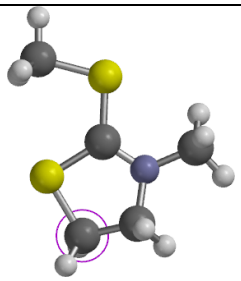
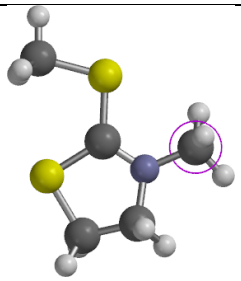
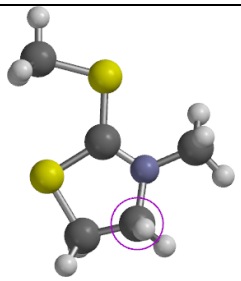
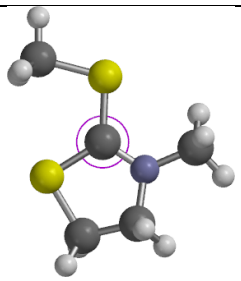
$[(C_1)_2Thiz]^+$		
Shift	Assignment	
4.71	S-CH_3	
5.89	S-C-C-N	
16.59	N-CH_3	
43.57	S-C-C-N	
204.79	S_2CN	

Table 12. Calculated CEBEs in eV and orbital assignments for **IL 1** $[(C_1C_1)Im]^+$.

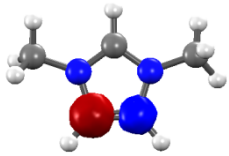
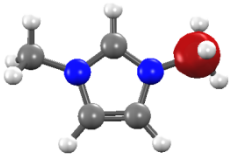
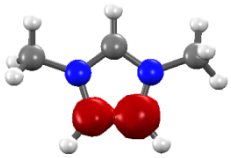
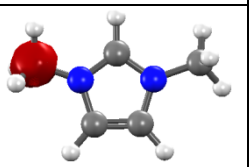
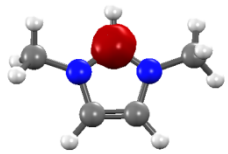
$[(C_1C_1)Im]^+$	
CEBE	Orbital
289.25	
289.25	
289.28	
289.33	
290.27	

Table 13. Calculated CEBEs in eV and orbital assignments for **IL 2** $[(C_1C_1C_1)Im]^+$.

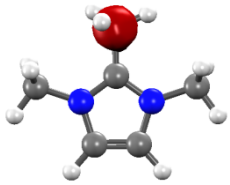
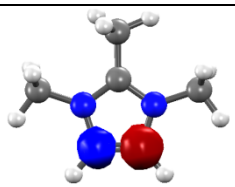
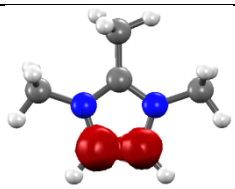
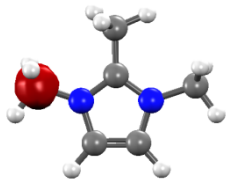
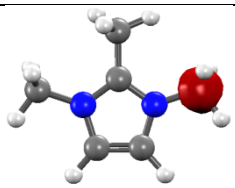
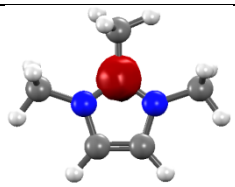
$[(C_1C_1C_1)Im]^+$	
CEBE	Orbital
288.46	
289.03	
289.04	
289.24	
289.24	
290.48	

Table 14. Calculated CEBEs in eV and orbital assignments for **IL 3** $[(C_1C_1)_2dmg]^+$.

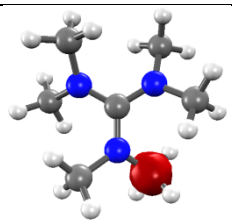
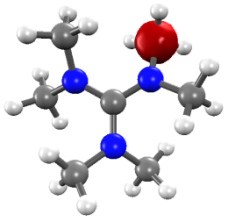
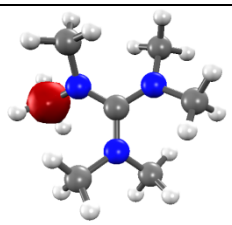
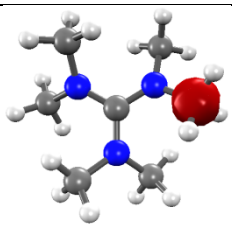
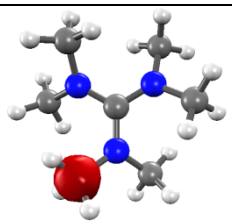
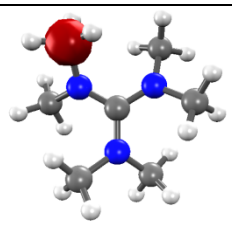
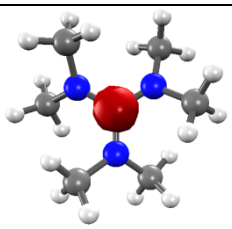
$[(C_1C_1)_2dmg]^+$	
CEBE	Orbital
288.66	
288.71	
288.75	
288.78	
288.81	
288.82	
291.52	

Table 15. Calculated CEBEs in eV and orbital assignments for **IL 4** $[(C_1)_5TU]^+$.

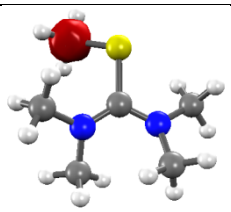
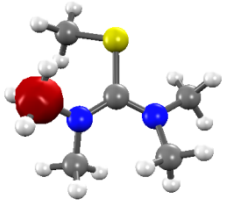
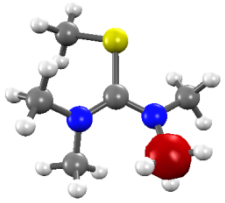
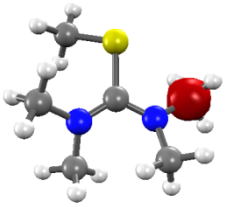
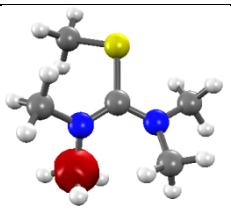
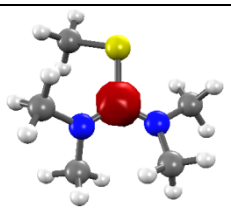
$[(C_1)_5TU]^+$	
CEBE	Orbital
288.59	
288.87	
288.90	
288.97	
288.97	
291.45	

Table 16. Calculated CEBEs in eV and orbital assignments for **IL 5** $[C_1(C_1)_2ThioIm]^+$.

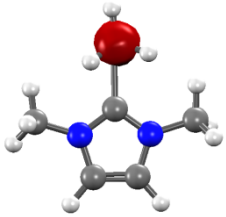
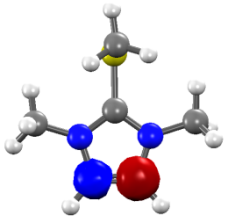
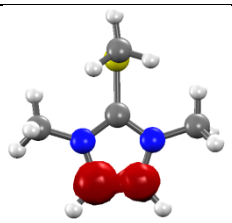
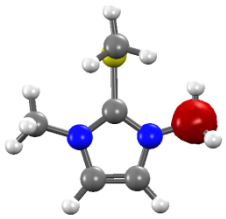
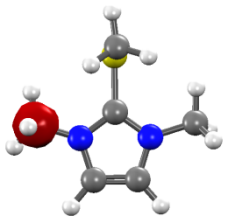
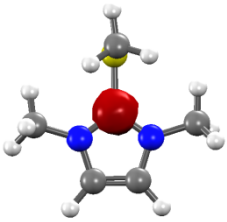
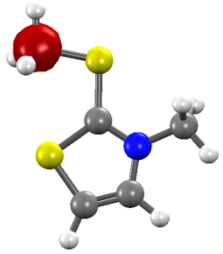
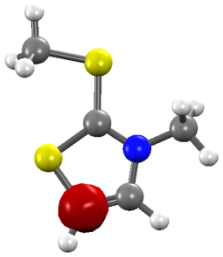
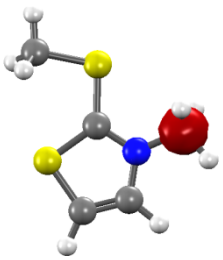
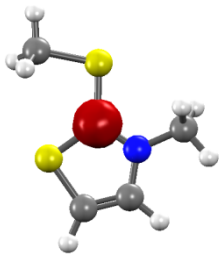
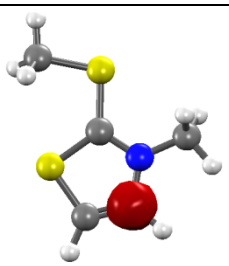
$[C_1(C_1)_2ThioIm]^+$	
CEBE	Orbital
288.29	
289.19	
289.20	
289.24	
289.25	
290.78	

Table 17. Calculated CEBEs in eV and orbital assignments for **IL 6** $[(C_1)_2Thio]^+$.

$[(C_1)_2Thio]^+$	
CEBE	Orbital
288.77	
288.92	
289.40	
290.97	
*289.53	

***When calculating the CEBE for orbital 20 of $[(C_1)_2Thio]^+$ (at 289.53 eV) it was necessary to use Hartree-Fock ground state orbitals as a starting guess in order to converge on the correct core-ionized state using the PBE0 functional.

Table 18. Calculated CEBEs in eV and orbital assignments for **IL 7** $[(C_1)_2Thiz]^+$.

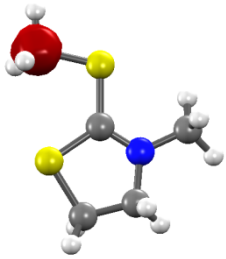
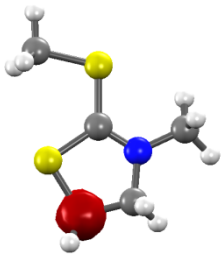
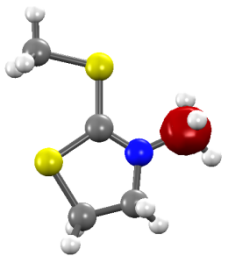
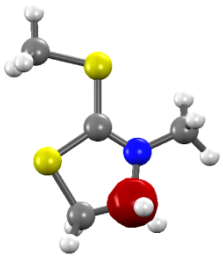
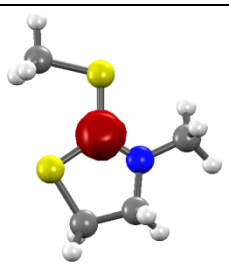
$[(C_1)_2Thiz]^+$	
CEBE	Orbital
288.74	
289.18	
289.22	
289.62	
291.33	

Table 19. XPS, ^{13}C-NMR and DFT calculations for the C_{core} for guanidinium, sulfur and imidazolium based ionic liquids 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 $[C_1C_1Im][NTf_2]$	287.6	290.27	137.0	143.93
IL 2 $[C_1C_1C_1Im][NTf_2]$	287.9	290.48	144.7	144.53
IL 3 $[(C_1C_1)_2dmg][NTf_2]$	288.9	291.52	162.4	169.83
IL 4 $[(C_1)_5TU][NTf_2]$	288.6	291.45	175.8	181.11
IL 5 $[C_1(C_1)_2ThioIm][NTf_2]$	288.0	290.78	140.8	138.59
IL 6 $[(C_1)_2Thio][NTf_2]$	288.1	290.97	175.5	176.24
IL 7 $[(C_1)_2Thiz][NTf_2]$	288.4	291.33	191.3	204.79

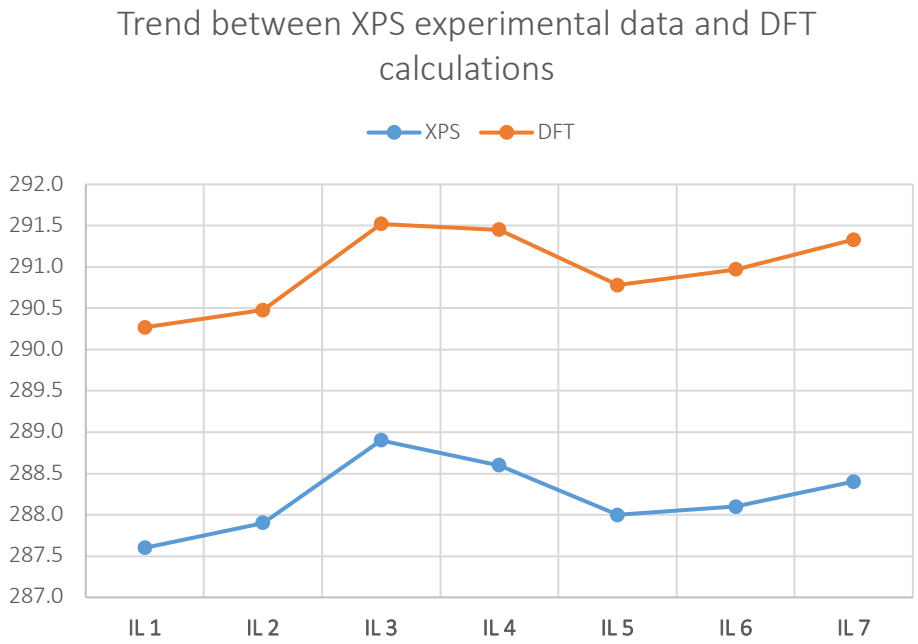


Figure 2 General trend between C_{core} 1s XPS experimental data (blue) and DFT calculations (orange).

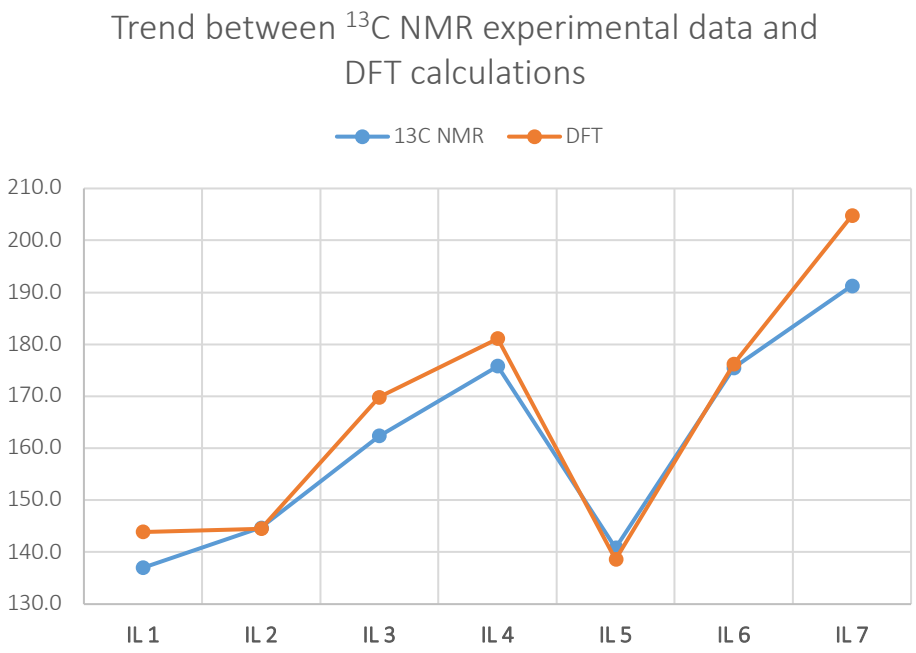


Figure 3 General trend between C_{core} ^{13}C NMR experimental data (blue) and DFT calculations (orange).

Table 20. Cartesian coordinates in Å for the DFT structure of **IL 1**

C	-1.7824349865	-1.8157964721	-0.5359162558
N	-3.0758190486	-1.5994738632	-0.2920366799
C	-3.4976368613	-2.4832881591	0.6738948625
C	-2.4205887476	-3.2454304952	1.0090281321
N	-1.3653775005	-2.8153734614	0.2395719349
H	-4.5142511649	-2.4947267566	1.0365266066
H	-2.3145264318	-4.0451690196	1.7261434984
C	-3.8908557059	-0.5840092307	-0.9472011202
H	-4.4246797411	-0.0115558890	-0.1862336575
H	-4.6020018148	-1.0635077072	-1.6245303551
H	-3.2268786873	0.0846325523	-1.4972223313
C	0.0115477755	-3.2938625706	0.3247810168
H	0.4575629852	-3.2758025164	-0.6702469198
H	-0.0040732496	-4.3200021598	0.6953948923
H	0.5911176507	-2.6451009133	0.9880382700
N	0.5393970817	0.1159233404	-0.1322761155
S	-0.0742721795	1.3862519380	-0.8995261453
S	1.9417896256	0.1240951243	0.6759219759

O	0.8470113436	2.3902580090	-1.3956483819
O	-1.1062998406	0.8420625666	-1.7974246402
O	2.4184791500	1.4196084333	1.1252999182
O	1.8939637035	-1.0055032645	1.6031219964
C	3.1555135042	-0.4349316946	-0.6268523928
C	-1.0915249689	2.2482422803	0.4083521269
F	4.3659414121	-0.5517265362	-0.0863361421
F	3.2089952810	0.4269293566	-1.6340219540
F	2.7903814348	-1.6321951868	-1.1100732159
F	-2.0234171453	1.4066963176	0.8915622924
F	-1.7191757965	3.2909623726	-0.1336968059
F	-0.3404435618	2.6652518757	1.4155957860
H	-1.1719871086	-1.2234820646	-1.2067744514

Table 21. Cartesian coordinates in Å for the DFT structure of **IL 2**

C	2.1328821393	-1.8064039700	0.5035516172
N	2.9566346157	-0.9091815889	-0.0551047137
C	2.8386195403	-0.9794706520	-1.4239173920
C	1.9319460463	-1.9523331915	-1.6946486336
N	1.5183476382	-2.4634231659	-0.4883016810
H	3.3848512577	-0.3181867916	-2.0781916096
H	1.5145686662	-2.2941876309	-2.6283914857
C	3.7982241201	0.0192288292	0.6843960986
H	4.3090955075	0.6607114658	-0.0334639737
H	4.5414926047	-0.5314747736	1.2678204074
H	3.1717723116	0.6336086829	1.3358079245
C	0.5309835952	-3.5180925324	-0.3195100980
H	-0.2643808036	-3.1781307955	0.3430165487
H	1.0082822288	-4.4193571783	0.0757752429
H	0.0886326262	-3.7266105996	-1.2922626498
N	-0.2504309517	0.0668045287	0.0895094916
S	-0.0436467873	1.4317862044	0.9162400712
S	-1.5357168452	-0.2394660803	-0.8403566284
O	-1.2431238624	2.1172653711	1.3641223594
O	1.0399855648	1.1669524417	1.8705890081

O	-2.1939175008	0.9118467457	-1.4332018004
O	-1.1721276380	-1.3860523206	-1.6738064763
C	-2.7945321616	-0.9636550798	0.3372428945
C	0.7571337725	2.6151398366	-0.2902477158
F	-3.8502211727	-1.3804362071	-0.3595908164
F	-3.1907517880	-0.0819851063	1.2419569897
F	-2.2738167017	-2.0248856770	0.9797680941
F	1.9192171214	2.1090254322	-0.7451245779
F	1.0267247334	3.7567207900	0.3404638344
F	-0.0214182874	2.8654381515	-1.3311116868
C	1.9311330262	-1.9908155983	1.9562430309
H	1.4381566151	-1.0983480519	2.3621579167
H	2.8875854883	-2.1262268061	2.4727877779
H	1.3057250472	-2.8625907177	2.1544787211

Table 22. Cartesian coordinates in Å for the DFT structure of **IL 3**

C	2.8496824422	0.7253720458	-0.1250802501
N	2.1873564999	1.8783531435	-0.2834552892
C	1.3683842553	2.4450592037	0.7790008547
H	1.8074374959	3.3748810004	1.1623901475
H	1.2489896299	1.7182182339	1.5811642346
H	0.3772314339	2.6505221402	0.3673817861
C	2.1043336184	2.5639357395	-1.5625219345
H	2.2760791601	3.6325419179	-1.3903170325
H	1.1150509916	2.4336052278	-2.0136384507
H	2.8752954634	2.1923439989	-2.2392792401
N	3.4112514651	0.4291936332	1.0664380796
N	3.0102432508	-0.1220352002	-1.1577073061
C	3.9293920080	1.4531755169	1.9521719617
H	4.0483803754	2.3931173211	1.4106210871
H	4.9117191844	1.1349830107	2.3207165755
H	3.2746450957	1.6172545274	2.8171467932
C	3.4035153754	-0.9241023857	1.5986356680
H	2.9664485945	-0.9054879821	2.6029756553
H	4.4194788514	-1.3346240481	1.6608759039

H	2.7711919708	-1.5610210139	0.9819150852
C	1.9636854138	-0.3544316369	-2.1440466141
H	2.2658780087	0.0141956270	-3.1319493977
H	1.0332087155	0.1189574205	-1.8299475409
H	1.7875324187	-1.4333542998	-2.2116126711
C	4.1981460088	-0.9424448805	-1.2970068936
H	4.9902871007	-0.5769555902	-0.6411907715
H	4.5456302124	-0.8824850525	-2.3348433956
H	3.9946516976	-1.9951924967	-1.0646805988
N	-2.1003419437	-0.5572366402	0.2526026535
S	-2.1171688040	0.5461993270	-0.9035655420
S	-0.8392875205	-1.1840029571	0.9849393744
O	-0.8175147332	1.1280840883	-1.2655447141
O	-3.0270311028	0.1658730024	-1.9699607927
O	0.4593425273	-0.5537584610	0.7097806577
O	-1.1630116097	-1.5102337303	2.3638553580
C	-0.6887918566	-2.8343951272	0.1350083693
C	-2.9788520942	1.9313329688	-0.0054251371
F	0.3859355504	-3.4799735841	0.6120919959
F	-0.5162675707	-2.6653587725	-1.1814818550
F	-1.7600120813	-3.5886596515	0.3331351524
F	-4.1893825683	1.5706825538	0.3973500975
F	-3.0904514091	2.9826655057	-0.8220479768
F	-2.2621298446	2.3060972763	1.0616997980

Table 23. Cartesian coordinates in Å for the DFT structure of **IL 4**

C	-2.6592743473	-0.7422043816	-0.2009988685
N	-2.7403536920	-0.3600173010	-1.4812188505
C	-1.6083797362	-0.4640301194	-2.4029694495
H	-1.8198419755	-1.1874755546	-3.1980908998
H	-0.6959971871	-0.7381176228	-1.8775348175
H	-1.4557984874	0.5214419679	-2.8541489897
C	-3.8596294250	0.4081185082	-2.0128363126
H	-4.7754263254	0.1987667794	-1.4605071163
H	-3.9963627855	0.1177020740	-3.0588006336

H	-3.6489371387	1.4832280424	-1.9725054031
N	-1.8951747831	-1.7623386146	0.1812984455
C	-1.2806161000	-1.8427006873	1.5035288332
H	-1.7834377325	-2.6008053684	2.1154580160
H	-1.2854173284	-0.8646258550	1.9861405928
H	-0.2356541935	-2.1261699651	1.3642941453
C	-1.5254667595	-2.8487876824	-0.7209352829
H	-2.2093654100	-2.8801249093	-1.5702216841
H	-1.6154390887	-3.7845237754	-0.1594477661
H	-0.4932039836	-2.7389963465	-1.0709608252
S	-3.6089947604	0.1762996405	0.9500190593
C	-4.1879315888	-1.0737520868	2.1296840795
H	-4.3307991898	-2.0375649506	1.6363821643
H	-5.1557640765	-0.7143655250	2.4890805651
H	-3.5074160751	-1.1760911851	2.9765611835
N	0.7919368234	0.0167921369	0.0367072831
S	0.8025825784	1.3620251758	0.9259710931
S	2.0395623962	-0.5275193875	-0.8243270775
O	-0.2788752520	1.2300279777	1.9016284550
O	2.1013177111	1.8631756622	1.3398591404
O	1.4780091292	-1.5033033633	-1.7641545118
O	3.0025267159	0.4540131947	-1.2910125728
C	2.9718078982	-1.6004679391	0.3858615292
C	0.1417707073	2.6465805544	-0.2574451364
F	3.9993722942	-2.1789419251	-0.2305240415
F	2.1663658890	-2.5668954357	0.8578703862
F	3.4223217696	-0.8932855814	1.4137842159
F	0.9314491815	2.7887703302	-1.3155904464
F	0.0321220702	3.8171481691	0.3650717842
F	-1.0822723017	2.2932663133	-0.6966551398

Table 24. Cartesian coordinates in Å for the DFT structure of **IL 5**

C	2.7955459861	-0.0463952727	-0.1004157254
N	2.6072682839	1.2427404617	-0.4435687990
C	2.1364342581	1.2991727658	-1.7266196256

C	2.0494450057	0.0198147075	-2.1823478363
N	2.4697674547	-0.7973092297	-1.1711596844
H	1.8704541378	2.2336511015	-2.1957562018
H	1.6760294406	-0.3751303439	-3.1140517331
C	2.7840586040	2.3948984811	0.4289954372
H	3.0905682143	3.2458399383	-0.1814487393
H	3.5606347954	2.1669482918	1.1600128378
H	1.8396906314	2.6034281729	0.9381082867
C	2.5152083321	-2.2484536580	-1.2599604328
H	1.5197230125	-2.6039335516	-1.5327175242
H	2.8104669996	-2.6481349279	-0.2900930529
H	3.2499183562	-2.5416276770	-2.0142398322
N	-0.5107228278	0.0118503482	-0.1203314545
S	-1.1593863910	1.1146429340	0.8578323351
S	-1.3788809116	-1.0714878843	-0.9428043608
O	-2.4244505940	0.7738684660	1.4843364686
O	-0.0599635815	1.6321816264	1.6805034889
O	-2.7518100621	-0.7118236738	-1.2502555195
O	-0.5071371440	-1.5873432420	-2.0013811883
C	-1.4991247932	-2.5242116869	0.2255012930
C	-1.5410756226	2.5652758063	-0.2569194777
F	-2.1174246517	-3.5310954303	-0.3865487563
F	-2.1578456164	-2.2163797353	1.3333946213
F	-0.2662562976	-2.9407425538	0.5706425197
F	-0.4090332856	3.0226897907	-0.8234698212
F	-2.0647532995	3.5499457002	0.4686804577
F	-2.3869742235	2.2375747012	-1.2224943037
S	3.4750276290	-0.6186451942	1.3978168482
C	1.9851858757	-0.8218191585	2.4359979613
H	1.3996318121	0.0991215784	2.4639761935
H	2.3693309199	-1.0576091203	3.4325554463
H	1.3739999129	-1.6476524497	2.0705372744

Table 25. Cartesian coordinates in Å for the DFT structure of **IL 6**

C	-2.6235112128	0.7116920347	0.4055724597
S	-2.8584537101	1.2534981032	-1.1982598423
C	-1.8666367817	2.6327616444	-0.9060924140
C	-1.3900318085	2.6238259846	0.3559960597
N	-1.8305739206	1.5418763695	1.0886717941
H	-1.6371547311	3.3328886912	-1.6968510433
H	-0.6817425551	3.3061683800	0.8043525886
C	-1.3874547874	1.2618896218	2.4506476266
H	-0.5862782454	1.9557203235	2.6988695703
H	-0.9857600613	0.2463543696	2.4835079346
H	-2.2260826340	1.3682691831	3.1453179756
S	-3.3208321097	-0.6856360296	1.1316148077
C	-3.9533769912	-1.5489334062	-0.3260578192
H	-4.7509339469	-0.9799843386	-0.8119323217
H	-4.3681632640	-2.4862912601	0.0528777986
H	-3.1230756582	-1.7656091710	-1.0039347056
N	0.5115223121	0.1030487950	-0.0721569769
S	1.8527840520	0.9089384048	0.3130827849
S	0.4822272177	-1.3474216747	-0.7755670338
O	1.4348703523	1.9662689325	1.2395879055
O	3.0274375734	0.1087301736	0.6138321437
O	-0.9006057354	-1.5515347198	-1.2168033659
O	1.5786915282	-1.6620001896	-1.6750134921
C	0.6469696853	-2.5620203628	0.6373097035
C	2.3004425934	1.8656952230	-1.2289048964
F	0.3605955461	-3.7851591276	0.1904994163
F	-0.2227881382	-2.2609335480	1.6149748833
F	1.8690758440	-2.5611115305	1.1462136050
F	2.5375867120	1.0614002407	-2.2550844262
F	3.3871115124	2.5951115219	-0.9842009500
F	1.3038527033	2.7004240202	-1.5659399698

Table 26. Cartesian coordinates in Å for the DFT structure of **IL 7**

C	-2.4957053741	-0.9770994774	0.0285494963

S	-2.6530953382	-0.2777766883	-1.5404820187
C	-3.6077527516	1.1182338566	-0.8442605432
C	-3.2367846427	1.1604535493	0.6312037898
N	-2.9313029540	-0.2196594185	1.0174626219
C	-2.7133861572	-0.5397590432	2.4193461198
H	-3.3796792273	0.0789291945	3.0229873748
H	-1.6701950045	-0.3316684455	2.6828268566
H	-2.9503557205	-1.5915184576	2.6013549954
S	-1.8380096235	-2.5304893162	0.3285895957
C	-1.5019580880	-3.1445742855	-1.3392823726
H	-2.4166962508	-3.1901571512	-1.9349565813
H	-1.1150136280	-4.1562286912	-1.1919951930
H	-0.7279840088	-2.5268812375	-1.8021905419
H	-4.6729471247	0.9278312477	-1.0033487060
H	-4.0636635437	1.5302648223	1.2442560691
H	-2.3387454645	1.7608462264	0.8143403416
H	-3.3167189274	2.0338033649	-1.3626215821
N	2.1423213392	0.7518565197	0.0888980586
S	1.0108460643	1.5209971803	0.9044266006
S	1.9197895921	-0.5442538965	-0.8245587162
O	-0.2623646736	0.8084339102	1.0938957738
O	1.5977636032	2.1932328458	2.0500691110
O	0.5388140011	-0.8056265421	-1.2441183610
O	2.9783866222	-0.6204278105	-1.8144757963
C	2.2939786775	-1.9333163830	0.3649129821
C	0.5421162954	2.9079343684	-0.2512316024
F	2.0132808180	-3.1046089548	-0.2257477827
F	1.5396084602	-1.8348200304	1.4638480061
F	3.5707567107	-1.9336915492	0.7230134411
F	1.5621413905	3.7211669094	-0.4809807878
F	-0.4563391756	3.6180287811	0.3030711489
F	0.0982298177	2.4290345109	-1.4183038540

References

1. I. J. Villar-Garcia, E. F. Smith, A. W. Taylor, F. Qiu, K. R. J. Lovelock, R. G. Jones and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2797-2808.
2. R. K. Blundell and P. Licence, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15278-15288.
3. S. Men, K. R. J. Lovelock and P. Licence, *Phys. Chem. Chem. Phys.*, 2011, **13**, 15244-15255.
4. A. R. Santos, R. K. Blundell and P. Licence, *Phy. Chem. Chem. Phys.*, 2015, **17**, 11839-11847.
5. E. F. Smith, F. J. M. Rutten, I. J. Villar-Garcia, D. Briggs and P. Licence, *Langmuir*, 2006, **22**, 9386-9392.
6. P. Bonhôte, A. P. Dias, M. Armand, N. Papageorgiou, K. Kalyanasundaram and M. Grätzel, *Inorg. Chem.*, 1996, **35**, 1168-1178.
7. R. Guterman, H. Miao and M. Antonietti, *J. Org. Chem.*, 2018, **83**, 684-689.
8. C. D. Wagner, L. E. Davis, M. V. Zeller, J. A. Taylor, R. H. Raymond and L. H. Gale, *Surf. Interface Anal.*, 1981, **3**, 211-225.
9. N. Stojilovic, *J. Chem. Educ.*, 2012, **89**, 1331-1332.
10. Y. H. Shao, Z. T. Gan, E. Epifanovsky, A. T. B. Gilbert, M. Wormit, J. Kussmann, A. W. Lange, A. Behn, J. Deng, X. T. Feng, D. Ghosh, M. Goldey, P. R. Horn, L. D. Jacobson, I. Kaliman, R. Z. Khaliullin, T. Kus, A. Landau, J. Liu, E. I. Proynov, Y. M. Rhee, R. M. Richard, M. A. Rohrdanz, R. P. Steele, E. J. Sundstrom, H. L. Woodcock, P. M. Zimmerman, D. Zuev, B. Albrecht, E. Alguire, B. Austin, G. J. O. Beran, Y. A. Bernard, E. Berquist, K. Brandhorst, K. B. Bravaya, S. T. Brown, D. Casanova, C. M. Chang, Y. Q. Chen, S. H. Chien, K. D. Closser, D. L. Crittenden, M. Diedenhofen, R. A. DiStasio, H. Do, A. D. Dutoi, R. G. Edgar, S. Fatehi, L. Fusti-Molnar, A. Ghysels, A. Golubeva-Zadorozhnaya, J. Gomes, M. W. D. Hanson-Heine, P. H. P. Harbach, A. W. Hauser, E. G. Hohenstein, Z. C. Holden, T. C. Jagau, H. J. Ji, B. Kaduk, K. Khistyaev, J. Kim, R. A. King, P. Klunzinger, D. Kosenkov, T. Kowalczyk, C. M. Krauter, K. U. Lao, A. D. Laurent, K. V. Lawler, S. V. Levchenko, C. Y. Lin, F. Liu, E. Livshits, R. C. Lochan, A. Luenser, P. Manohar, S. F. Manzer, S. P. Mao, N. Mardirossian, A. V. Marenich, S. A. Maurer, N. J. Mayhall, E. Neuscamman, C. M. Oana, R. Olivares-Amaya, D. P. O'Neill, J. A. Parkhill, T. M. Perrine, R. Peverati, A. Prociuk, D. R. Rehn, E. Rosta, N. J. Russ, S. M. Sharada, S. Sharma, D. W. Small, A. Sodt, T. Stein, D. Stuck, Y. C. Su, A. J. W. Thom, T. Tsuchimochi, V. Vanovschi, L. Vogt, O. Vydrov, T. Wang, M. A. Watson, J. Wenzel, A. White, C. F. Williams, J. Yang, S. Yeganeh, S. R. Yost, Z. Q. You, I. Y. Zhang, X. Zhang, Y. Zhao, B. R. Brooks, G. K. L. Chan, D. M. Chipman, C. J. Cramer, W. A. Goddard, M. S. Gordon, W. J. Hehre, A. Klamt, H. F. Schaefer, M. W. Schmidt, C. D. Sherrill, D. G. Truhlar, A. Warshel, X. Xu, A. Aspuru-Guzik, R. Baer, A. T. Bell, N. A. Besley, J. D. Chai, A. Dreuw, B. D. Dunietz, T. R. Furlani, S. R. Gwaltney, C. P. Hsu, Y. S. Jung, J. Kong, D. S. Lambrecht, W. Z. Liang, C. Ochsenfeld, V. A. Rassolov, L. V. Slipchenko, J. E. Subotnik, T. Van Voorhis, J. M. Herbert, A. I. Krylov, P. M. W. Gill and M. Head-Gordon, *Mol. Phys.*, 2015, **113**, 184-215.
11. C. Adamo and V. Barone, *J. Chem. Phys.*, 1999, **110**, 6158-6170.
12. A. T. B. Gilbert, N. A. Besley and P. M. W. Gill, *J. Phys. Chem. A*, 2008, **112**, 13164-13171.