Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Probing the Electronic Structure of Ether Functionalised Ionic Liquids Using X-ray Photoelectron Spectroscopy

Supporting Information

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XPS instrument calibration and data collection

XP spectra were recorded using a Kratos Axis Ultra spectrometer equipped with a focused, monochromated Al K_α source ($h\upsilon$ =1486.6 eV), hybrid (magnetic/electrostatic) optics, concentric hemispherical analyser, a multi-channel plate and delay line detector (DLD) with an X-ray incident angle of 30° and a collection angle of 0° (both relative to the surface normal). X-ray source was fixed at 10 mA emission current and 12 kV anode potential. All spectra were recorded using an entrance aperture of 300 x 700 μm with pass energy of 80 eV for survey scans and 20 eV for high resolution scans. The instrument sensitivity was 7.5 x 10^5 counts s^{-1} when measuring the Ag $3d_{5/2}$ photoemission peak for a clean Ag sample recorded at a pass energy of 20 eV and 450 W emission power. Ag $3d_{5/2}$ full width at half maximum (FWHM) was 0.55 eV for the same instrument settings. Charge neutralisation was used for solid samples only and was applied using a standard Kratos charge neutraliser consisting of a filament, coaxial with the electrostatic and magnetic transfer lenses, and a balance plate which creates a potential gradient between the neutraliser and sample. Charge neutralization was applied at 1.9 A filament current and 3.3 V balance plate voltage. Room temperature ionic liquid samples were prepared by placing a thin film (≈10 mg) of ionic liquid onto a 316 stainless steel multi-sample bar of area 8 cm x 1.5 cm, mounted 1 cm apart to minimize cross contamination.

XPS data analysis

Analysis of XPS data was carried out using CASAXPS (version 2.3.18 dev 1.1p) software, a full description of methods applied can be found elsewhere.[1, 2] Determination of elemental composition was achieved by taking relative sensitivity factors (RSFs) from the Kratos Library (RSF F 1s = 1.000).[3] Peak areas were measured after performing two-point linear or Shirley background subtractions, the estimated error in the relative atomic concentrations of each element is between 10 and 20%, depending on the experimental signal to noise ratio.[4] The photoelectron peaks from high resolution spectra were each fitted with components using GL(30) line shapes (70% Gaussian, 30% Lorentzian). The FWHM of the C 1s component was constrained to be between 0.8 ≤ FWHM ≤ 1.2 eV. Chemical state identification and fitting procedures for each photemission region were based upon the known stoichiometry of the sample.[4, 5] In the absence of long aliphatic side chain length, ($C_{aliphatic}$ $n \geq 8$), in PEG-functionalized systems measured, charge correction was achieved indirectly by setting the value of the F 1s = 688.8 eV, which is the value observed in a standard reference material, $[C_8C_1Im][Tf_2N]$.[4] This charge referencing method gave rise to consistent BEs as the error in

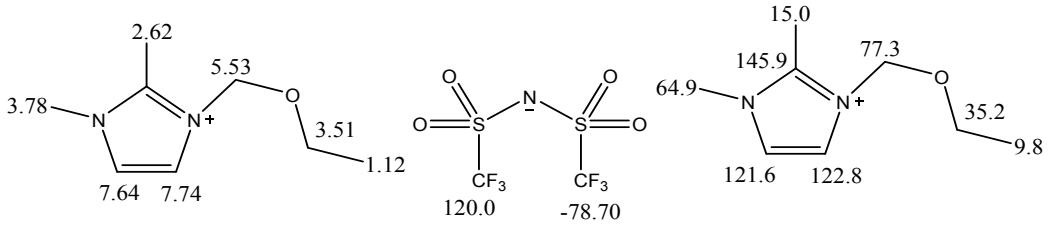
these binding energies has been shown by previous studies to vary by a maximum of ±0.01 eV across a range of different ionic liquid standards.[4, 6]

S 2p high-resolution spectra were 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 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] The BEs of the cationic and anionic O 1s for γ-IL is coincidental and hence fitted with one component, while that for the β-IL are different and as a result fitted with two components.

Ionic liquid synthesis

3-ethoxymethyl-1-methylimidazolium bis(trifluromethanesulfonyl)imide, $[(C_1OC_2)C_1Im][Tf_2N]$

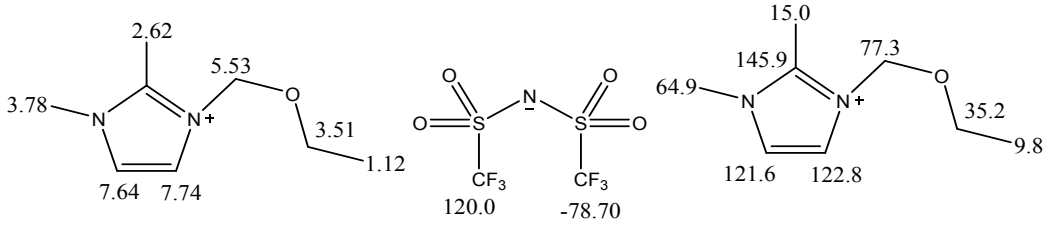
1 molar equivalent $[(C_1OC_2)C_1C_1Im]Cl$ (3.6 g, 26.2 mMol) was placed in a 100 ml single-neck round-bottomed flask and dissolved in ultra-pure water (10 ml). A corresponding 1.2 molar equivalent lithium bis(trifluoromethanesulfonyl)imide (6.9 g, 28.9 mMol) was added drop-wise at room temperature. The reaction vessel was sealed with parafilm and stirred for 18 h. Dichloromethane (10 ml) was added to the mixture to form a biphasic mixture. The organic phase was removed and washed with ultra-pure water (5 x 20 ml). Solvent was removed *in vacuo* (10^{-6} mbar) to yield a viscous orange-coloured liquid, (7.0 g, 16.1 mMol, 68.5 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, J = 2.1 Hz, 1H), 7.64 (d, J = 2.1 Hz, 1H), 5.53 (s, 2H), 3.78 (s, 3H), 3.51 (q, J = 7.0 Hz, 2H), 2.62 (s, 3H), 1.12 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 145.9, 122.8, 121.6, 120.0 (q, J_{CF} = 322.7 Hz, 2C, CF_3), 77.3, 64.9, 35.2, 15.0, 9.8. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.71 (s, 6 F, CF_3). **MS-ESI** for $C_8H_{15}N_2O$, M^+. Calcd 155.1179, found 155.1188.

3-ethoxymethyl-1,2-dimethylimidazolium bis(trifluromethanesulfonyl)imide, [$(C_1OC_2)C_1$ C_1Im][Tf_2N]

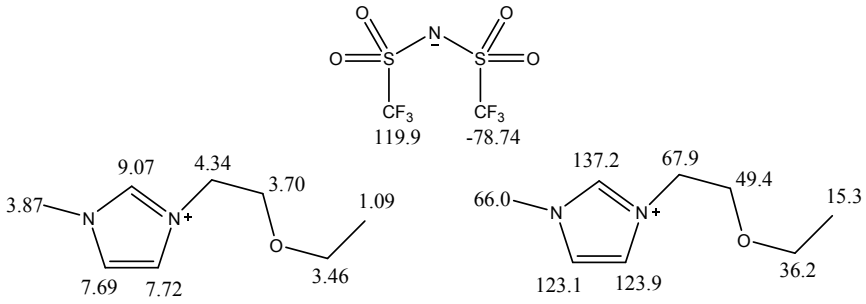
1 molar equivalent [$(C_1OC_2)C_1C_1$Im]Cl (3.6 g, 26.2 mMol) was placed in a 100 ml single-neck round-bottomed flask and dissolved in ultra-pure water (10 ml). A corresponding 1.2 molar equivalent lithium bis(trifluoromethanesulfonyl)imide (6.9 g, 28.9 mMol) was added drop-wise at room temperature. The solution was sealed with parafilm and stirred for 18 h. Dichloromethane (10 ml) was added to the solution to form a biphasic mixture. The organic phase was removed and washed with ultra-pure water (5 x 20 ml). Solvent was removed *in vacuo* (10^{-6} mbar) to yield a viscous orange-coloured liquid, (7.0 g, 16.1 mMol, 68.5 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.74 (d, J = 2.1 Hz, 1H), 7.64 (d, J = 2.1 Hz, 1H), 5.53 (s, 2H), 3.78 (s, 3H), 3.51 (q, J = 7.0 Hz, 2H), 2.62 (s, 3H), 1.12 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 145.9, 122.8, 121.6, 120.0 (q, J_{CF} = 322.7 Hz, 2C, CF_3), 77.3, 64.9, 35.2, 15.0, 9.8. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.71 (s, 6 F, CF_3). **MS-ESI** for $C_8H_{15}N_2O$, M^+. Calcd 155.1179, found 155.1188.

3-(2-ethoxyethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide, [$(C_2OC_2)C_1Im$][Tf_2N]

1.2 equivalent lithium bis(trifluoromethane sulfonyl)imide (3.9 g, 13.7 mMol) was placed in a single neck 100 mL round-bottomed flask and dissolved in ultra-pure water (ca. 10 mL). The solution was added drop-wise to a corresponding 1 molar equivalent [$(C_2OC_2)C_1Im$]Cl (2.17 g, 11.4 mMol), dissolved in ultra-pure (ca. 10 mL). The solution was stirred at room temperature for 18 h. Dichloromethane (10 ml) was added to the solution to form a biphasic mixture. The organic phase was removed and washed with ultra-pure water (5 x 20 ml). Solvent was removed *in vacuo* (10^{-6} mbar) to obtain a honey-coloured viscous liquid (6.2 g, 21.6 mMol, 79 %).

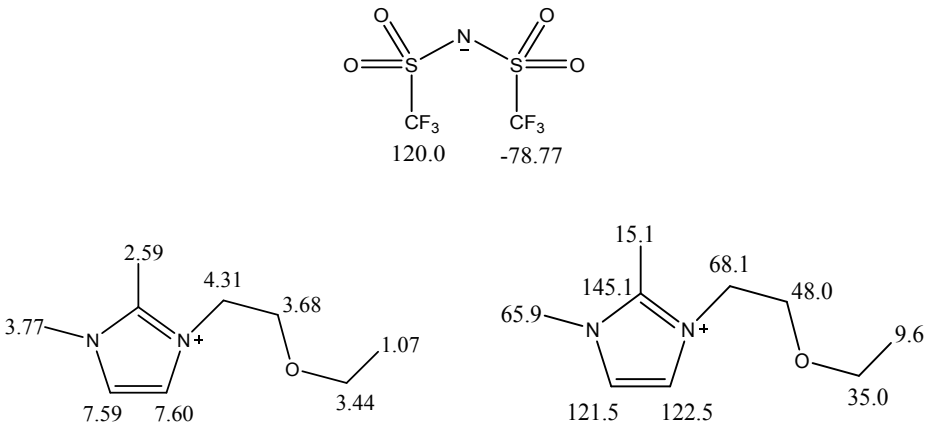


^{1}H NMR (400 MHz, DMSO-d_6) δ 9.07 (s, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.69 (d, J = 1.9 Hz, 1H), 4.34 (t, J = 5.2 Hz, 2H), 3.87 (s, 3H), 3.70 (t, J = 5.2 Hz 2H), 3.46 (q, J = 7.0 Hz, 2H), 1.09 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.2, 123.9, 123.1, 119.9 (q, J_{CF} = 318.7 Hz, 2C, CF_3), 67.9, 66.0, 49.4, 36.2, 15.3. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.74 (s, 6 F, CF_3). **MS-ESI** for $C_8H_{15}N_2O$, M^+: Calcd 155.1179, found 155.1174.

3-(2-ethoxyethyl)-1,2-dimethylimidazolium bis(trifluoromethanesulfonyl)imide,

$[(C_2OC_2)C_1C_1Im][Tf_2N]$

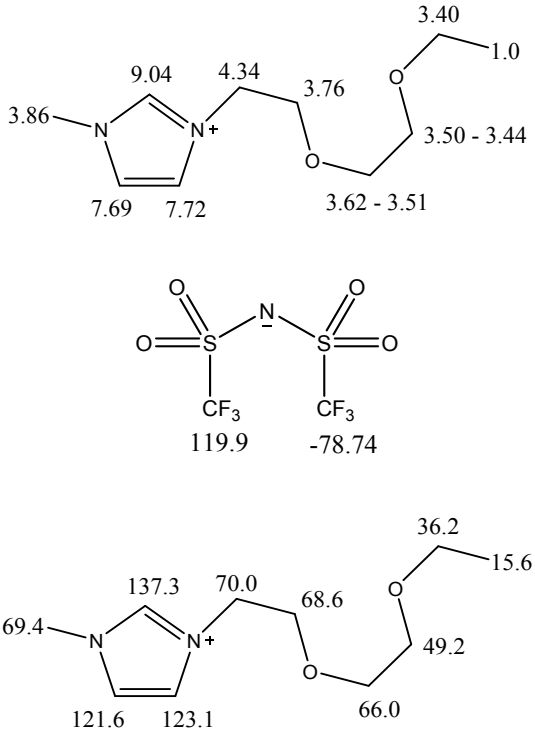
A similar procedure to that outlined for $[(C_2OC_2)C_1Im][Tf_2N]$ was used to obtain a honey-coloured viscous liquid (4.2 g, 9.3 mMol, 86 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 (d, J = 2.1 Hz, 1H), 7.59 (d, J = 2.1 Hz, 1H) 4.31 (t, J = 5.5 Hz, 2H), 3.77 (s, 3H), 3.68 (t, J = 5.5 Hz, 2H), 3.44 (q, J = 7.0 Hz, 2H), 2.59 (s, 3H), 1.07 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 145.1, 122.5, 121.5, 120.0 (q, J_{CF} = 320.0 Hz, 2C, CF_3), 68.1, 65.9, 48.0, 35.0, 15.1, 9.6 **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.77 (s, 6 F, CF_3). **MS-ESI** for $C_9H_{17}N_2O$, M^+: Calcd 169.1335, found 169.1339.

3-(2-(2-ethoxyethoxy)ethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide, [($C_2EG_1C_2$)C_1Im][Tf_2N]

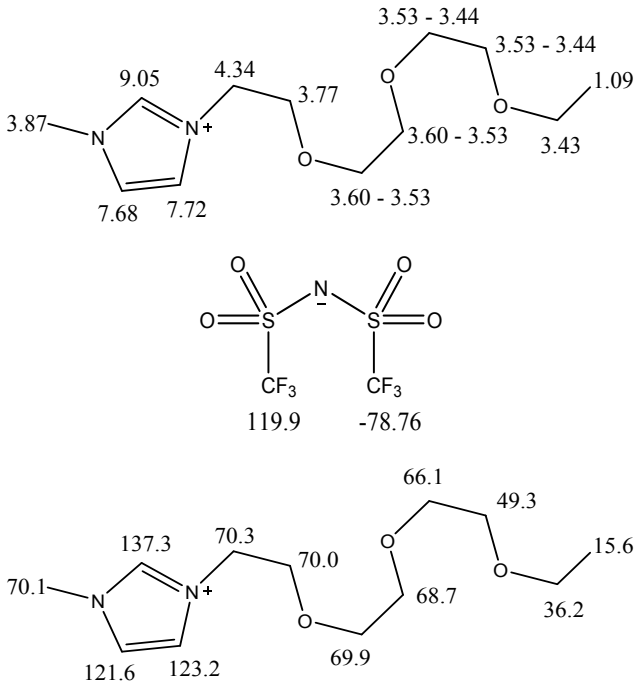
1 molar equivalent [($C_2EG_1C_2$)C_1Im]Cl (4.9 g, 8.6 mMol) was placed in a single neck 100 ml round-bottomed flask and dissolved in ultra-pure water (10 ml). A corresponding 1.2 molar equivalent bis(trifluoromethanesulfonyl)imide (9.8 g, 12.5 mMol) was dissolved in ultra-pure water and added dropwise into the stirring solution at room temperature. The resultant biphasic mixture was sealed with parafilm and allowed to stir for 18 h. The product was partitioned in dichloromethane (15 ml) and the organic phase washed with ultra-pure water (6 x 20 ml). Solvent was removed *in vacuo* (10^{-6} mbar) at 60 °C to obtain a viscous orange-coloured liquid. (3.8 g, 7.2 mMol, 86 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H), 7.72 (d, J = 1.9 Hz, 1H), 7.69 (d, J = 1.9 Hz, 1H), 4.34 (t, J = 5.6 Hz, 2H), 3.86 (s, 3H), 3.76 (t, J = 5.6 Hz, 2H), 3.62 – 3.51 (m, 2H), 3.50 – 3.44 (m, 2H), 3.40 (q, J = 7.0 Hz, 2H), 1.09 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.3, 123.1, 121.6, 119.9 (q, J_{CF} = 323.2 Hz, 2C, CF_3), 70.0, 69.4, 68.6, 66.0, 49.2, 36.2, 15.6. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.74 (s, 6 F, CF_3). **MS-ESI** for $C_8H_{15}N_2O$, M^+: Calcd 199.1441, found 199.1434.

3-(2-(2-2(-ethoxyethoxy)ethyl)-1-methylimidazolium bis(trifluoromethanesulfonyl)imide, $[(C_2EG_2C_2)C_1Im][Tf_2N]$

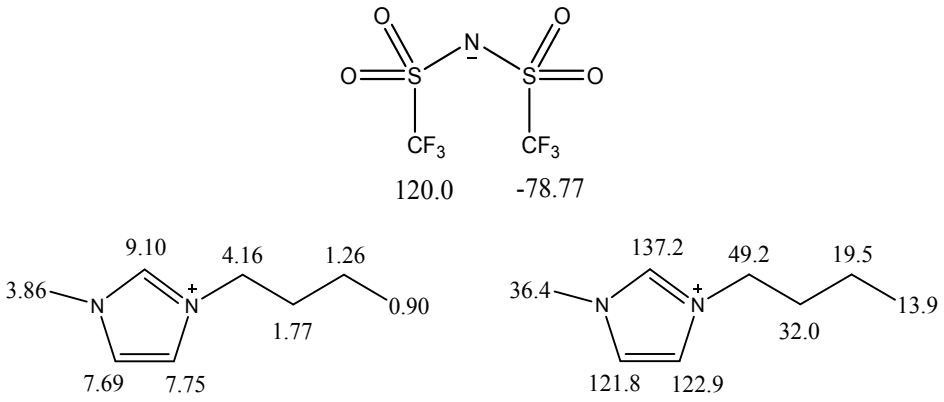
A similar procedure to that outlined for $[(C_2EG_1C_2)C_1Im][Tf_2N]$ was used to obtain a viscous colourless liquid (4.6 g, 8.8 mMol, 59 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.05 (s, 1H), 7.72 (d, J = 1.8 Hz, 1H), 7.68 (d, J = 1.8 Hz, 1H), 4.34 (t, J = 5.5 Hz, 2H), 3.87 (s, 3H), 3.77 (t, J = 5.8 2H), 3.60 – 3.53 (m, 4H), 3.53 – 3.44 (m, 4H), 3.43 (q, J = 7.0 Hz 2H), 1.09 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.3, 123.2, 121.6, 119.9 (q, J_{CF} = 323.2 Hz, 2C, CF_3), 70.3, 70.1, 70.0, 69.9, 68.7, 66.1, 49.3, 36.2, 15.6. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.76 (s, 6 F, CF_3). MS-ESI for $C_{12}H_{23}N_2O_3$, M^+: Calcd 242.1703, found 243.1704. **Elemental analysis (%):** Calcd for $[(C_2EG_2C_2)C_1Im][Tf_2N]$ ($C_{14}H_{23}F_6N_3O_6S_2$): C 32.12, H 4.43, N 8.03. Found: C 32.07, H 4.23, N 8.08.

3-butyl-1-methylimidazolium bis[(trifluoromethane sulfonyl)imide], [C_4C_1Im][Tf_2N]

A similar procedure to that outlined for [(C_2OC_2)C_1Im][Tf_2N] was used to obtain a honey-coloured viscous liquid (10.6 g, 25.3 mMol, 59 %).



^{1}H NMR (400 MHz, DMSO-d_6) δ 9.10 (s, 1H), 7.75 (d, J = 2.0 Hz, 1H), 7.69 (d, J = 2.0 Hz, 1H), 4.16 (t, J = 7.2, 1.9 Hz, 2H), 3.85 (s, 3H), 1.77 (m, 2H), 1.26 (m, 1.9 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, DMSO-d_6) δ 137.2, 122.9, 121.8, 120.0 (q, J_{CF} = 323.2 Hz, 2C, CF_3), 49.2, 36.4, 32.0, 19.5, 13.9. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -78.77 (s, 6 F, CF_3). MS-ESI for $C_8H_{15}N_2$, M^+: Calcd 139.1230, found 139.1230.

Ionic liquid XP spectra

SI 1 Fitting parameters for β-IL and γ-ILs

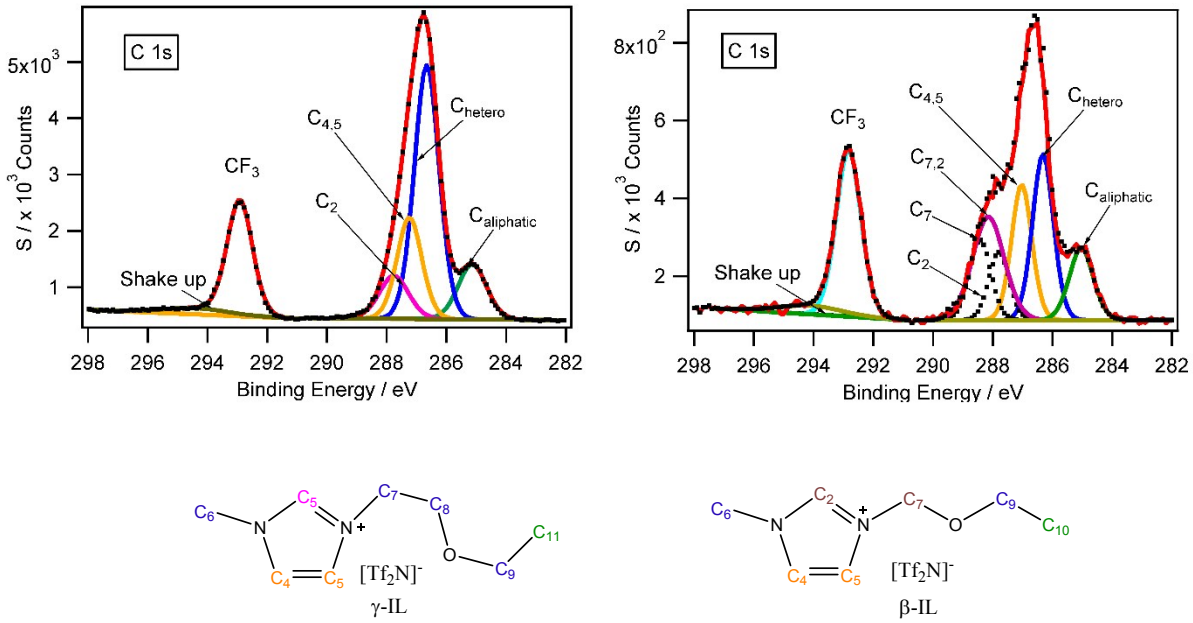
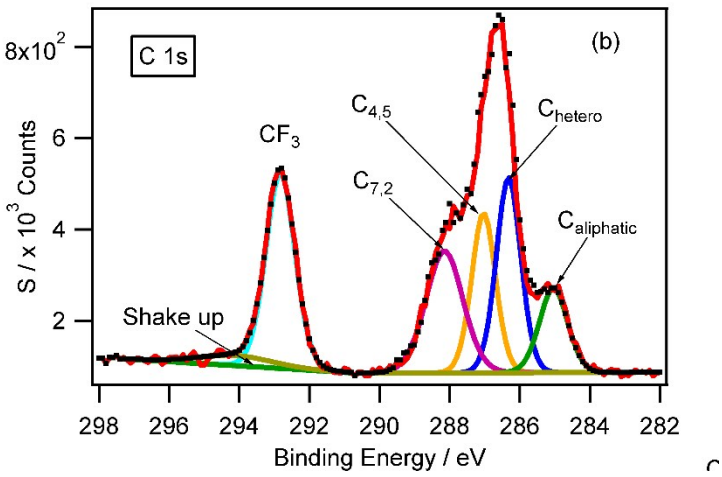


Table SI.1: Fitting parameters for the C 1s high resolution XP spectra for β and γ-ILs.

Ionic liquids	Component	BE / eV	FWHM	Relative area	Area constraint
γ-IL	C_2	287.7	1.02	220.2	0.8 x $C_{aliphatic}$
	$C_{4,5}$	287.1	0.94	440.4	1.6 x $C_{aliphatic}$
	C_{hetero}	286.5	0.93	825.7	4 x $C_{aliphatic}$
	$C_{aliphatic}$	285.1	1.12	275.2	-
	C_{CF_3}	292.9	1.03	441.6	2 x $C_{aliphatic}$
β-IL	C_7	288.3	1.12	250.5	1 x $C_{aliphatic}$
	C_2	287.7	1.03	200.4	0.8 x $C_{aliphatic}$
	$C_{4,5}$	287.0	0.94	400.8	1.6 x $C_{aliphatic}$
	C_{hetero}	286.5	1.03	501.0	4 x $C_{aliphatic}$
	$C_{aliphatic}$	285.1	1.12	250.5	-
	C_{CF_3}	292.8	1.02	442.5	2 x $C_{aliphatic}$



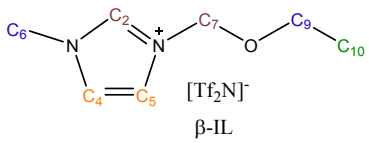
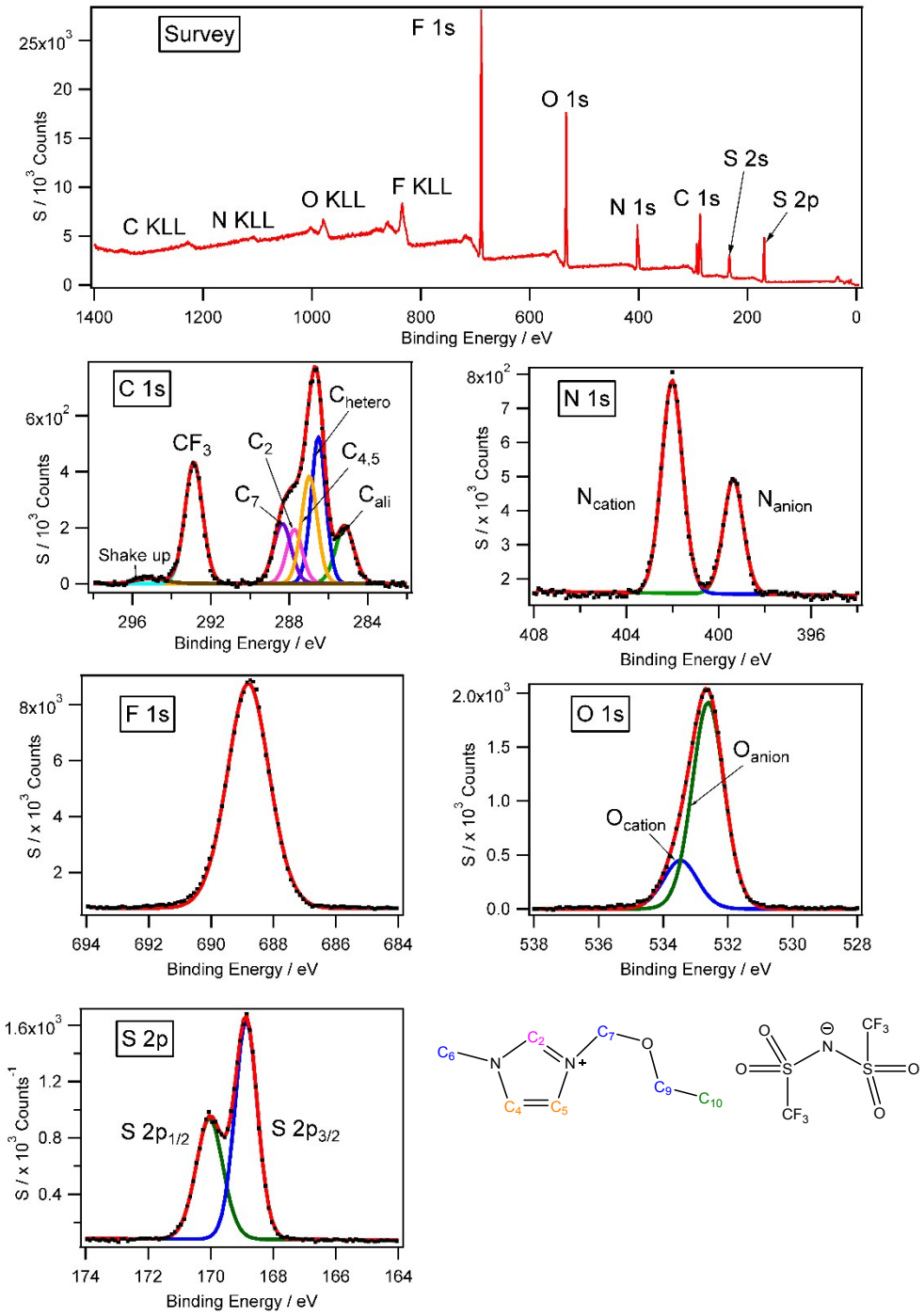


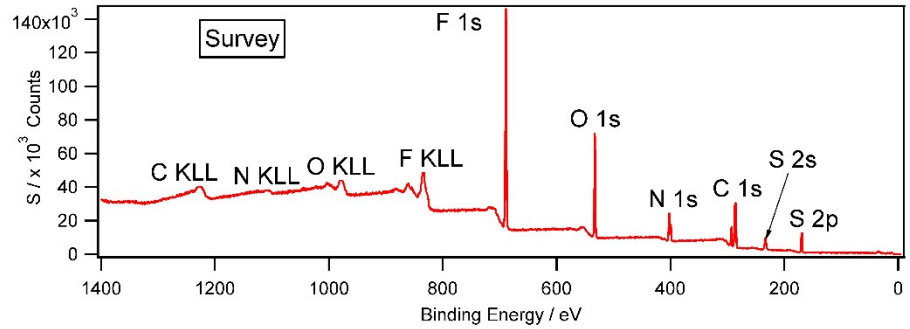
Table SI, 1 Continued

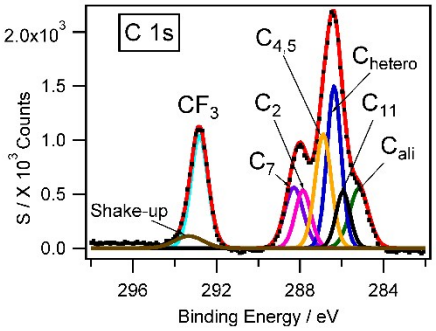
Ionic Liquids	Component	BE / eV	FWHM	Relative area	Area constraint
β-IL	$C_{7,2}$	288.1	1.18	360.1	1.8 x $C_{aliphatic}$
	$C_{4,5}$	287.0	0.91	303.2	1.6 x $C_{aliphatic}$
	C_{hetero}	286.4	0.91	379.0	2 x $C_{aliphatic}$
	$C_{aliphatic}$	285.0	1.01	225.9	-
	C_{CF_3}	292.8	1.03	452.6	2 x $C_{aliphatic}$

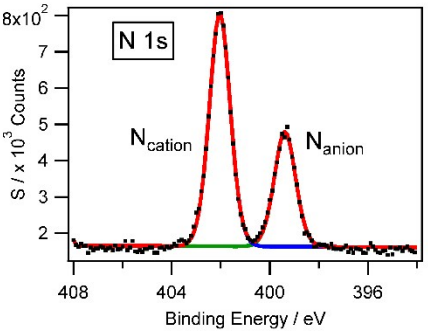
SI 2.1 Survey and high resolution scans of $[(C_1OC_2)C_1Im][Tf_2N]$

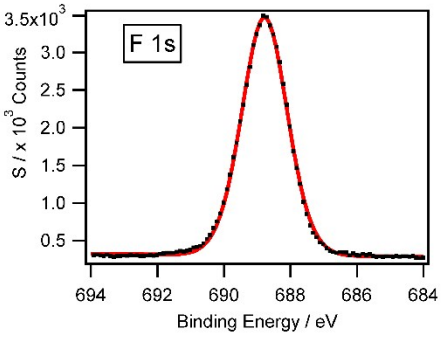


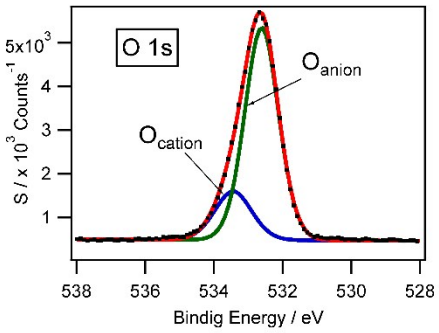
SI 2.2 Survey and high resolution scans of $[(C_1OC_2)C_1C_1Im][Tf_2N]$

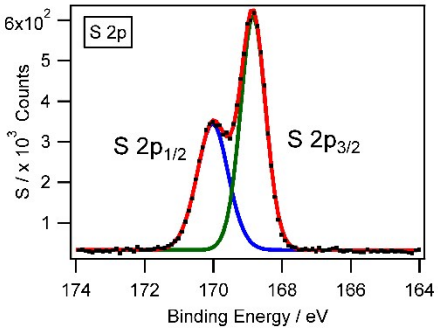


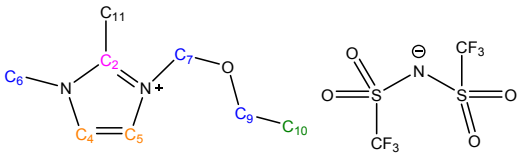




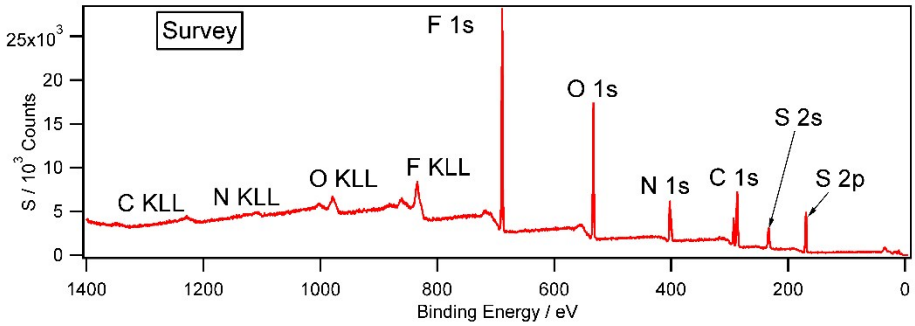


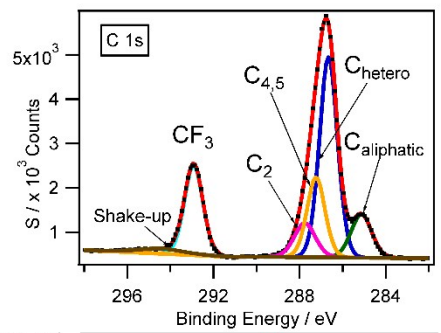


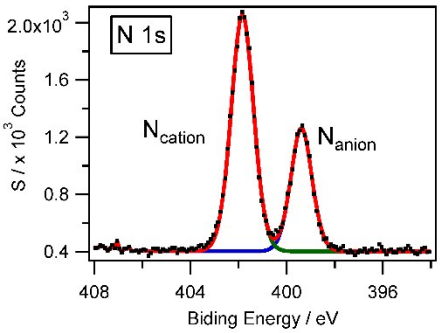


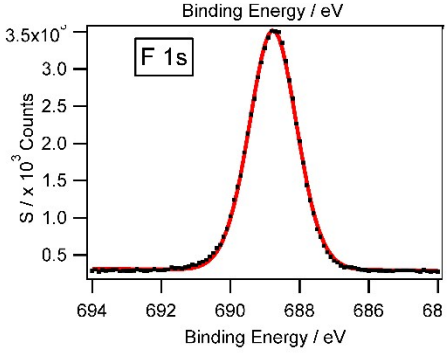


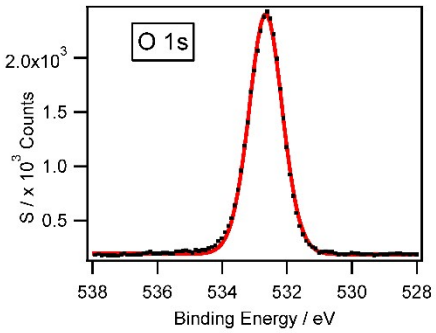
SI 2.3 Survey and high resolution scans of $[(C_2OC_2)C_1Im][Tf_2N]$

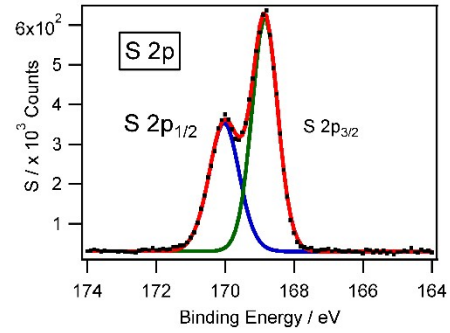


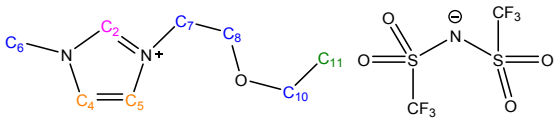




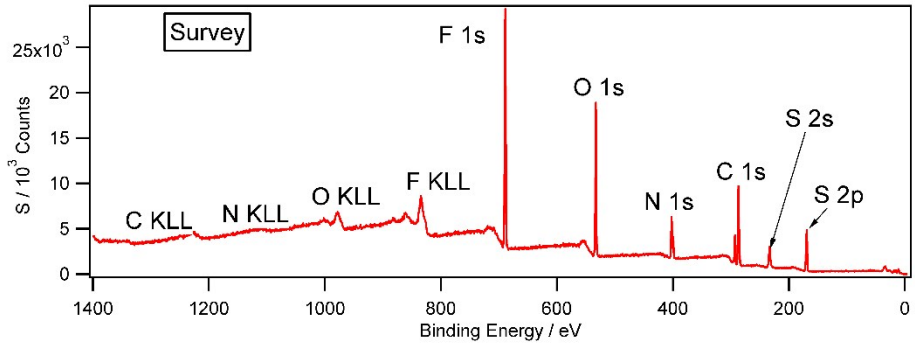


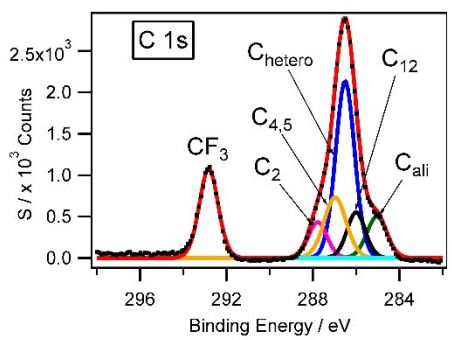


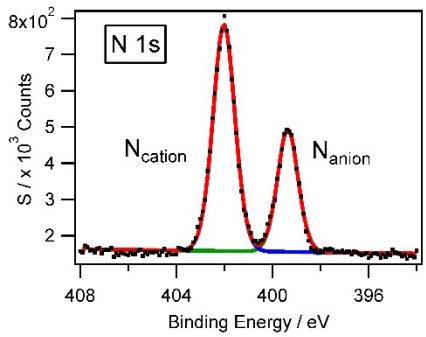


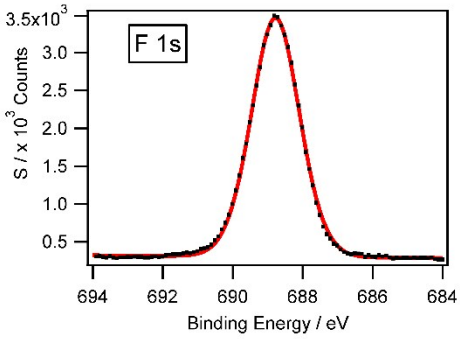


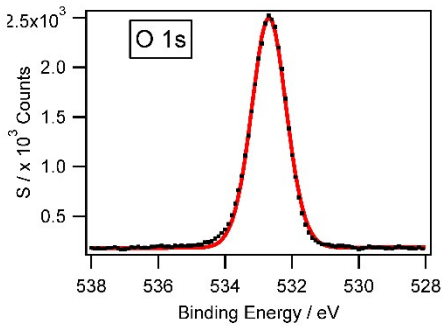
SI 2.4 Survey and high resolution scans of $[(C_2OC_2)C_1C_1Im][Tf_2N]$

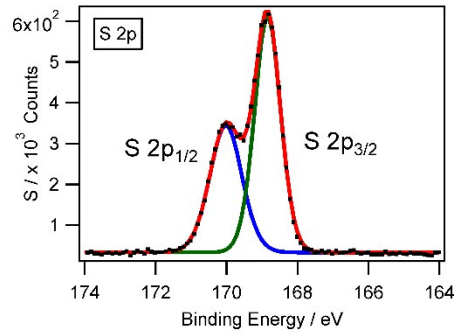


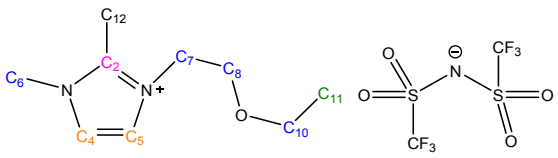




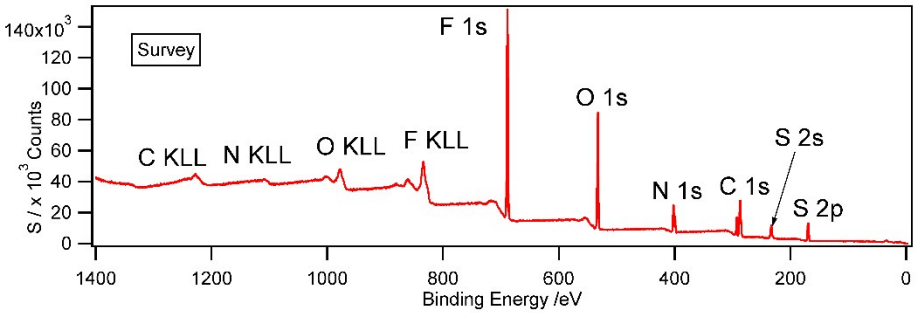


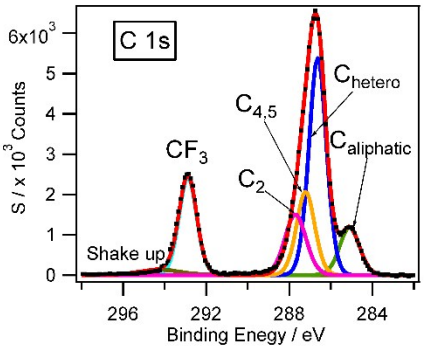


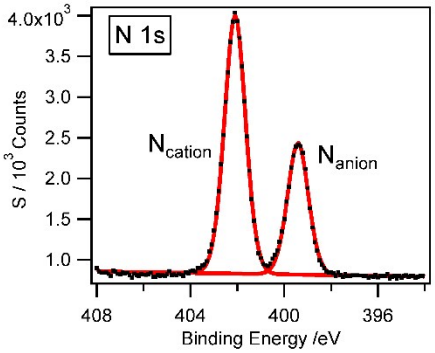


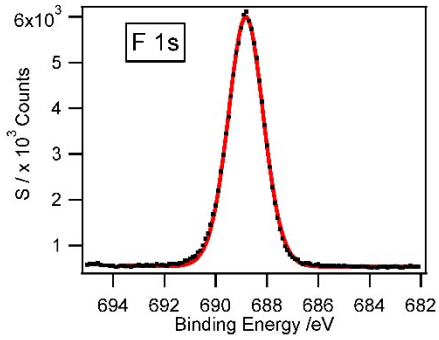


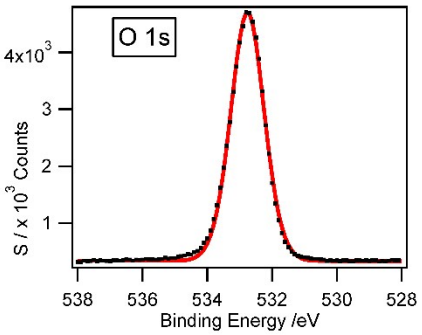
SI 2.5 Survey and high resolution scans of $[(C_2EG_1C_2)C_1Im][Tf_2N]$

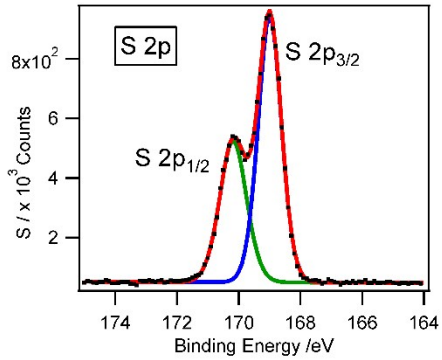


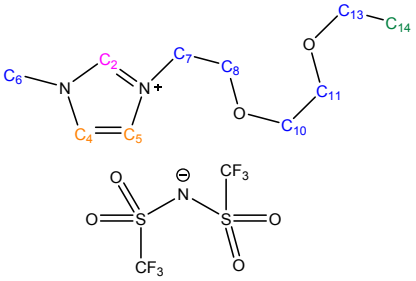




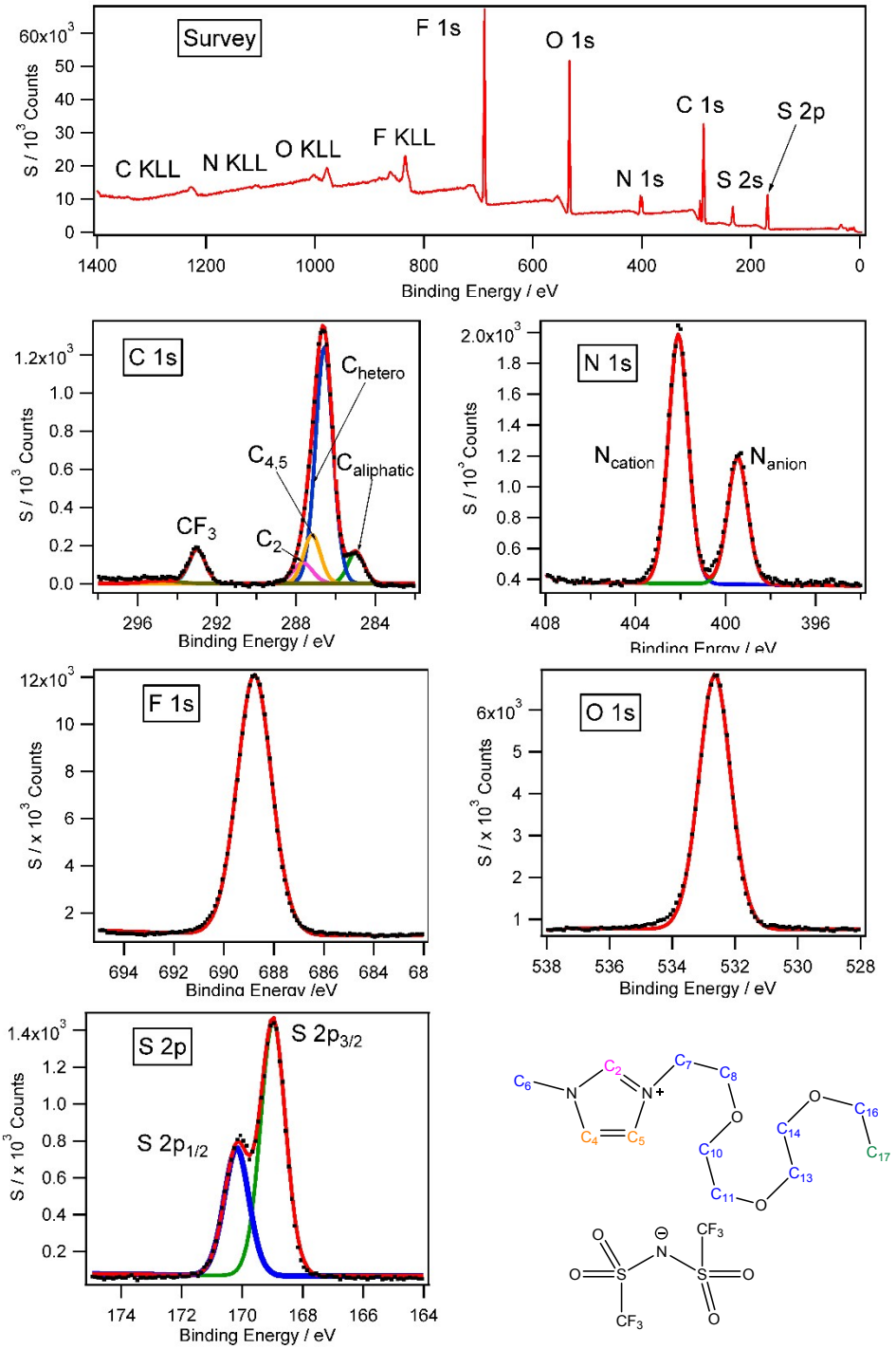




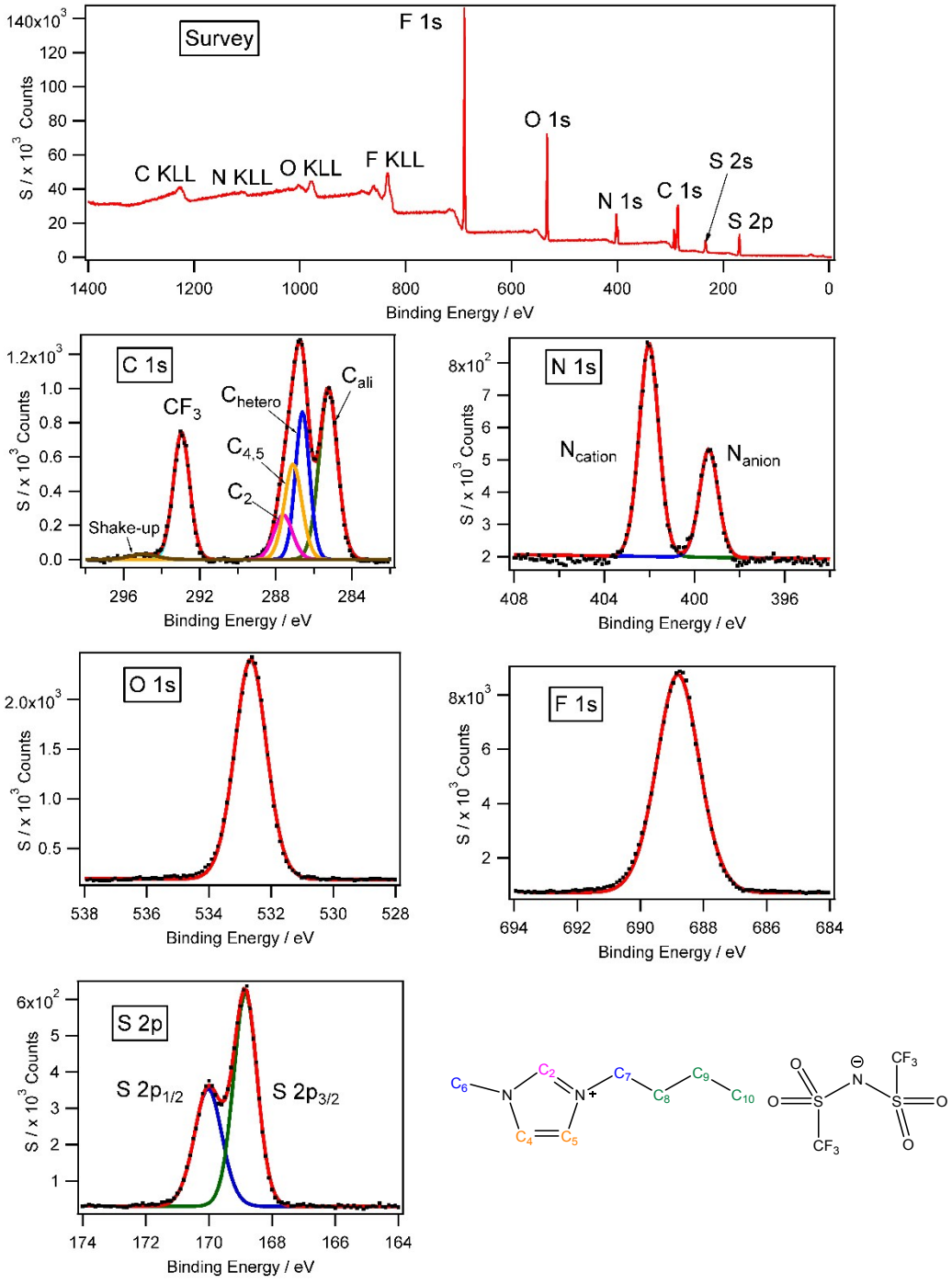




SI 2.6 Survey and high resolution scans of $[(C_2EG_2C_2)C_1Im][Tf_2N]$

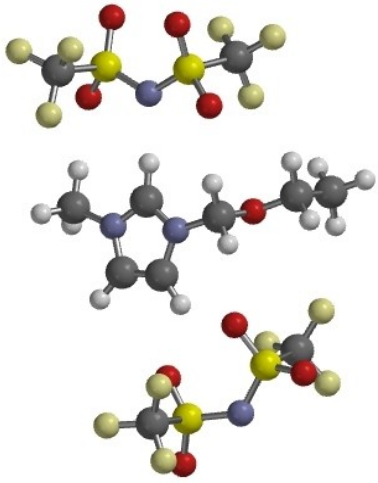


SI 2.7 Survey and high resolution scans of $[C_4C_1Im][Tf_2N]$

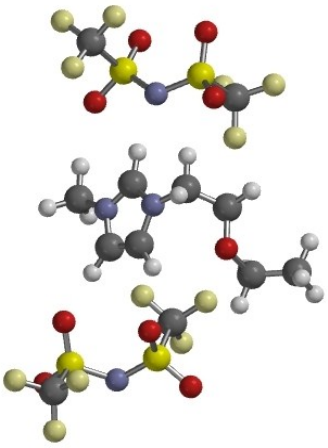


SI 3 DFT data

SI 3.1 Optimised DFT structures for non-methylated β and γ-ILs

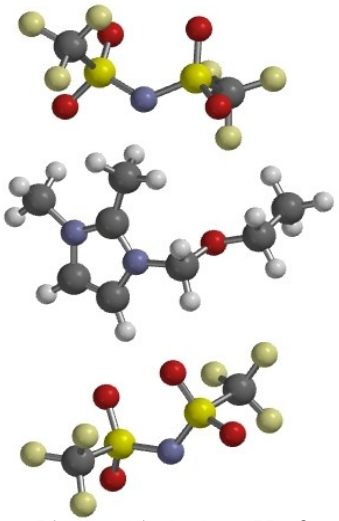


$[(C_1OC_2)C_1Im][Tf_2N]$, β-IL

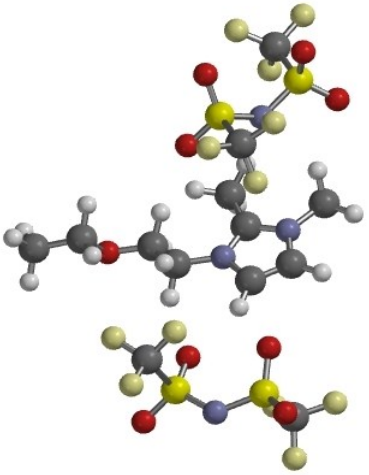


$[(C_2OC_2)C_1Im][Tf_2N]$, γ-IL

SI 3.2 Optimised DFT structure for methylated β and γ-ILs

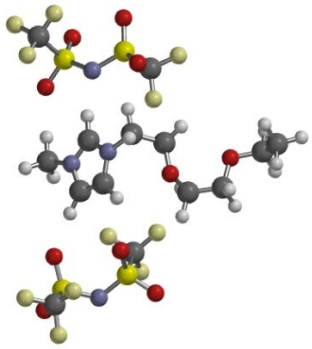


$[(C_1OC_2)C_1C_1Im][Tf_2N]$

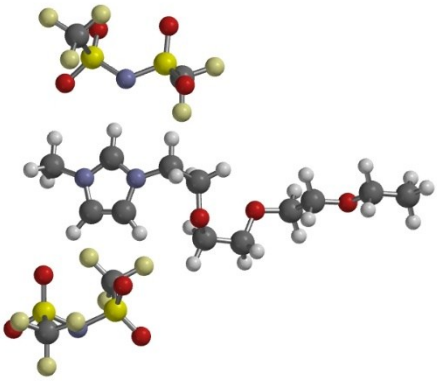


$[(C_2OC_2)C_1C_1Im][Tf_2N]$

SI 3.3 Optimised DFT Structures for $[(C_2EG_1C_2)C_1Im][Tf_2N]$ and $[(C_2EG_2C_2)C_1Im][Tf_2N]$

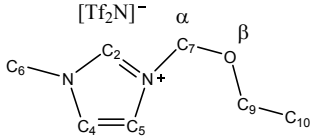


$[(C_2EG_1C_2)C_1Im][Tf_2N]$

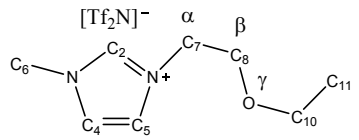


$[(C_2EG_2C_2)C_1Im][Tf_2N]$

Table SI.2 Comparison of XPS measurements and DFT core binding energy calculations for $[(C_1OC_2)C_1Im][Tf_2N]$[a] and $[(C_2OC_2)C_1Im][Tf_2N]$[b]



XPS Bulk / eV	Cationic component	DFT Model / eV
287.7	C_2	290.7
287.0	C_4 ($C_{4,5}$)	289.8
287.0	C_5 ($C_{4,5}$)	289.7
286.5	C_6 (C_{hetero})	290.0
288.3	C_7	291.4
-	C_8	-
286.5	C_9 (C_{hetero})	289.9
285.1	C_{10} ($C_{aliphatic}$)	288.3
-	C_{11}	-
533.5	O_{cation}	536.3
532.6	O_{anion}	536.0
402.0	N_{cation} (+)	405.4
402.0	N_{cation}	405.6

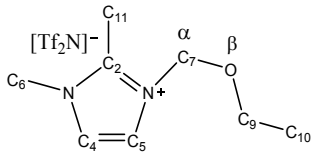


XPS Bulk / eV	Cationic component	DFT Model / eV
287.7	C_2	290.7
287.1	C_4 ($C_{4,5}$)	289.6
287.1	C_5 ($C_{4,5}$)	289.5
286.5	C_6 (C_{hetero})	289.9
286.5	C_7 (C_{hetero})	290.1
286.5	C_8 (C_{hetero})	290.1
-	C_9	-
286.5	C_{10} (C_{hetero})	289.8
285.1	C_{11} ($C_{aliphatic}$)	288.2
532.7	O_{cation}	536.0
c	O_{anion}	536.0
402.0	N_{cation} (+)	405.3
402.0	N_{cation}	405.4

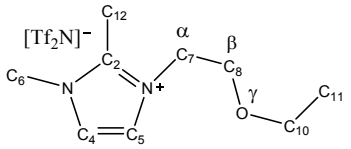
Note: XPS component fitting indicated in bracket
[a] = β-IL
[b] = γ-IL
c = Not distinguishable by XPS

Table SI 3: Comparison of XPS measurements and DFT core binding energy calculations for $[(C_1OC_2)C_1C_1Im][Tf_2N]$

and $[(C_2OC_2)C_1C_1Im][Tf_2N]$



XPS Bulk / eV	Cationic component	DFT Model / eV
287.9	C_2	291.1
286.9	C_4 ($C_{4,5}$)	289.7
286.9	C_5 ($C_{4,5}$)	289.7
286.5	C_6 (C_{hetero})	289.9
288.3	C_7	291.5
-	C_8	-
286.5	C_9 (C_{hetero})	290.0
285.2	C_{10} ($C_{aliphatic}$)	288.2
-	C_{11}	289.1
-	C_{12}	-
533.4	O_{cation}	536.3
532.6	O_{anion}	535.9
401.9	N_{cation} (+)	405.3
401.9	N_{cation}	405.4

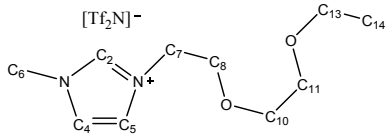


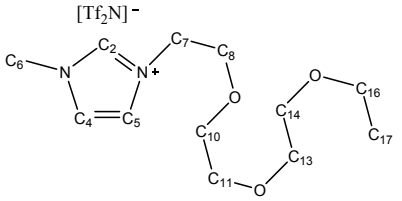
XPS Bulk / eV	Cationic component	DFT Model / eV
287.7	C_2	291.1
287.0	C_4 ($C_{4,5}$)	289.5
287.0	C_5 ($C_{4,5}$)	289.5
286.5	C_6 (C_{hetero})	289.9
286.5	C_7 (C_{hetero})	290.1
286.5	C_8 (C_{hetero})	290.0
-	C_9	-
286.5	C_{10} (C_{hetero})	289.8
285.0	C_{11} ($C_{aliphatic}$)	288.2
286.0	C_{12}	289.2
532.6	O_{cation}	536.0
a	O_{anion}	536.0
401.9	N_{cation} (+)	405.3
401.9	N_{cation}	405.3

Note: XPS component fitting indicated in bracket

[a] = Not distinguishable by XPS

Table SI 4: Comparison of XPS measurements and DFT core binding energy calculations for $[(C_2EG_1C_2)C_1Im][Tf_2N]$ and $[(C_2EG_2C_2)C_1Im][Tf_2N]$





XPS Bulk / eV	Cationic component	DFT Model / eV	XPS Bulk / eV	Cationic component	DFT Model / eV
287.7	C_2	290.7	287.7	C_2	290.7
287.1	C_4 ($C_{4,5}$)	289.5	286.9	C_4 ($C_{4,5}$)	289.5
287.1	C_5 ($C_{4,5}$)	289.6	286.9	C_5 ($C_{4,5}$)	289.6
286.5	C_6 (C_{hetero})	289.9	286.5	C_6 (C_{hetero})	289.9
286.5	C_7 (C_{hetero})	290.1	286.5	C_7 (C_{hetero})	290.1
286.5	C_8 (C_{hetero})	290.1	286.5	C_8 (C_{hetero})	290.1
286.5	C_{10} ($C_{aliphatic}$)	289.9	286.5	C_{10} (C_{hetero})	289.9
286.5	C_{11} (C_{hetero})	289.9	286.5	C_{11} ($C_{aliphatic}$)	289.8
286.5	C_{13} (C_{hetero})	289.8	286.5	C_{13} (C_{hetero})	289.8
285.0	C_{14} ($C_{aliphatic}$)	288.2	286.5	C_{14} (C_{hetero})	289.8
-	-	-	286.5	C_{16} (C_{hetero})	289.8
-	-	-	285.0	C_{17} ($C_{aliphatic}$)	288.2
532.7	O_{cation}	536.0	532.6	O_{cation}	536.0
a	O_{anion}	536.0	a	O_{anion}	536.0
402.0	N_{cation} (+)	405.4	401.8	N_{cation} (+)	405.4
402.0	N_{cation}	405.3	401.8	N_{cation}	405.3

Note: XPS component fitting indicated in bracket
a = Not distinguishable by XPS

Cartesian coordinates of the optimized $[(C_1OC_2)C_1Im][Tf_2N]$, β-IL structure

S	-4.2952217253	-1.0735297892	-1.0451492251
O	-5.5375941134	-1.0130129704	-1.8143233282
O	-3.0150095480	-1.3212192353	-1.7249641966
N	-4.0337783281	0.1375547772	0.0145000412
S	-5.1904716526	1.0842384207	0.6527746162
O	-6.5529979095	0.5545719533	0.6724830928
O	-4.6181284475	1.6898922605	1.8665583261
C	-4.4829441445	-2.5635282275	0.0999177903
F	-5.5069118244	-2.3991894172	0.9360843874
F	-4.6964008840	-3.6618227886	-0.6332083416
F	-3.3683665499	-2.7440401956	0.8167904327
C	-5.2237109813	2.5313647451	-0.5608513046
F	-5.5551923181	2.1344007765	-1.7865275917
F	-6.1081580777	3.4454288313	-0.1488549688
F	-4.0131323220	3.1128135221	-0.6133587657
H	-2.0979462396	0.6058782163	0.4221615728
C	-1.0682501940	0.9352795175	0.6009143050
N	-0.6926711763	1.9779908225	1.3484454986
N	0.0392230686	0.3686289405	0.1003153653
C	1.1529605981	1.0524492479	0.5502192080
H	2.1636418413	0.7675840380	0.2778446743
C	0.6923886449	2.0693535490	1.3282039077
H	1.2316126337	2.8389009910	1.8619219225
C	0.0601452749	-0.8666413091	-0.6797807378
H	-0.8193767183	-0.8668483794	-1.3390148856
H	0.9960037459	-0.8666510460	-1.2562173198
O	0.0129185654	-1.9214673177	0.2414045083
C	-0.0474674383	-3.1978164446	-0.3939903198
H	-0.9527096407	-3.2529558302	-1.0209993547
H	0.8344014606	-3.3290156731	-1.0435484109
C	-1.5957095973	2.8948588655	2.0437171741
H	-1.2728109685	2.9888832884	3.0855177505
H	-2.6151315429	2.4979336462	2.0082167540
H	-1.5643914601	3.8757243146	1.5567052680
C	-0.0723347416	-4.2557027223	0.6942612208
H	-0.9494099516	-4.1182743573	1.3379506145
H	-0.1200164343	-5.2566379881	0.2465022173
H	0.8329795263	-4.1889053115	1.3091821712
S	4.6238784693	-1.0878580591	-0.7485330189
O	3.3203472357	-0.4825094438	-1.0984325820
O	5.2565826495	-2.0031730284	-1.6966186197
N	5.7409946587	-0.0834471415	-0.1565011522
S	5.4390577976	1.3744613460	0.4798739674
O	4.0724167722	1.5978617995	0.9888915577
O	6.5785514912	1.7681487188	1.3073435274
C	4.2073104704	-2.1802787738	0.7350912266
F	3.6776431051	-1.4580958609	1.7266207723
F	3.3084202936	-3.1055494644	0.3613339639
F	5.2891073149	-2.8091910362	1.1958004439
C	5.5441149446	2.5100778075	-1.0259932496
F	4.6787961102	2.1320567629	-1.9714167995
F	5.2433242162	3.7642030996	-0.6576575390
F	6.7731591384	2.5076263329	-1.5457492549

Cartesian coordinates of the optimized $[(C_2OC_2)C_1Im][Tf_2N]$, γ-IL structure

S	4.8013309979	-1.4922346052	-0.0242238791
O	6.2529032881	-1.5999927909	-0.1659784939
O	4.1320137443	-2.0529873018	1.1604307075
N	4.1441503299	-0.0261723445	-0.2873380533
S	4.8371816775	1.1547233608	-1.1701843387
O	5.8278171909	0.7437894551	-2.1643072395
O	3.7567234590	2.0820081420	-1.5421333649
C	5.7981839643	2.1145241167	0.1412676410
F	6.6880284909	1.3339079582	0.7522049602
F	6.4420866699	3.1348012609	-0.4348836305
F	4.9589736350	2.6070357809	1.0590309699
C	4.0747869127	-2.5073801214	-1.4417679185
F	4.3897491605	-1.9871514082	-2.6253545928
F	4.5381804349	-3.7595432962	-1.3826469400
F	2.7362746230	-2.5487786688	-1.3373800734
H	2.1878647454	0.4845661184	0.1260780372
C	1.1349675928	0.5870667783	0.4016002924
N	0.2539340986	1.4697354556	-0.0863815653
N	0.4952118151	-0.1849168315	1.2925842646
C	-0.8284999354	0.2148114327	1.3656479248
H	-1.5533663489	-0.3007917385	1.9763721642
C	-0.9804193326	1.2552995408	0.5006468676
H	-1.8671606451	1.8226475421	0.2318706198
C	0.5262727361	2.4671210506	-1.1229981054
H	-0.0444353537	2.2096789321	-2.0212543736
H	1.5982593265	2.4717384187	-1.3402925338
H	0.2071667101	3.4497594773	-0.7628248965
C	1.0921645350	-1.3217058128	2.0059433238
H	0.9007285794	-1.1865025558	3.0768948567
H	2.1727963411	-1.3101864685	1.8281623074
C	0.5003517012	-2.6465262972	1.5405188835
H	1.0930397572	-3.4626145993	1.9869495828
H	0.5903553612	-2.7267208939	0.4441571970
O	-0.8522265266	-2.6973850863	1.9462581855
C	-1.7167224032	-3.4712159305	1.1179208734
H	-2.7304179071	-3.1377876980	1.3682120400
H	-1.5423645272	-3.2107251869	0.0611452264
C	-1.5648379985	-4.9726228178	1.3401365877
H	-1.7326827693	-5.2239027894	2.3955256925
H	-0.5651341960	-5.3285127462	1.0564417859
H	-2.2998704638	-5.5192117782	0.7341385789
S	-4.6384252588	-0.3137221521	-0.5169024876
O	-5.5587923513	-1.4511091336	-0.5417473543
O	-3.7250832117	-0.1546238477	0.6288664801
N	-5.4323536836	1.0103664195	-0.9953630245
S	-4.9783879456	2.5320594657	-0.6850249713
O	-3.5447442852	2.7525229777	-0.4043173015
O	-5.6548061779	3.4209731663	-1.6285530749
C	-5.8138823278	2.8916905185	0.9696679256
F	-5.4176440288	2.0263812927	1.9067163741
F	-5.4885798197	4.1282535369	1.3715998449
F	-7.1419578024	2.8203655914	0.8575796949
C	-3.4902389977	-0.6478195270	-1.9823916668
F	-2.6531505611	0.3781168390	-2.1910085649
F	-2.7490974522	-1.7413342345	-1.7346999243
F	-4.1853737502	-0.8595763597	-3.0993996534

Cartesian coordinates of the optimized $[(C_1OC_2)C_1C_1Im][Tf_2N]$ structure

S	-4.9816816071	-1.4970952258	0.1407409745
O	-6.4077204721	-1.6058501643	-0.1762517930
O	-3.9763625236	-1.9961705615	-0.8081399260
N	-4.4595109439	-0.0420760389	0.6557020394
S	-5.3894882371	1.1097730853	1.3139099417
O	-6.6147387676	0.6809049942	1.9889080340
O	-4.4830643389	2.0627354441	1.9762652006
C	-4.7352685932	-2.5763205456	1.6699120242
F	-5.4919931402	-2.1487608874	2.6799117659
F	-5.0808442150	-3.8366154398	1.3768771092
F	-3.4569829477	-2.5691348180	2.0582835827
C	-5.9745108716	2.0845680965	-0.1970077906
F	-6.6951462777	1.3301668607	-1.0231083444
F	-6.7196960113	3.1238787370	0.1964024934
F	-4.9181555967	2.5675851472	-0.8792984375
C	-0.6401020584	1.1208954034	-0.3539860949
N	-0.5022226279	2.1203572403	0.5329736891
N	0.5557454289	0.4996640018	-0.4378704336
C	1.4634272921	1.1057247725	0.4146450213
H	2.4961705577	0.7836244711	0.5046505432
C	0.7998649056	2.1269647458	1.0156002666
H	1.1399342758	2.8482167725	1.7443540667
C	0.7940521047	-0.7300685822	-1.1875959317
H	0.4580935236	-0.5779719039	-2.2281898904
H	1.8777090868	-0.9092430874	-1.1781342112
O	0.0528107268	-1.7282369634	-0.5511842073
C	-0.0216841827	-2.9489107401	-1.2864341474
H	-0.4297443167	-2.7445698146	-2.2933673859
H	0.9901079367	-3.3700441636	-1.4097367521
C	-1.5705282248	3.0367145604	0.9378647070
H	-1.1888218689	3.6587413125	1.7506012859
H	-2.4491017832	2.4819838532	1.2886465691
H	-1.8539181833	3.6789593655	0.0962246409
C	-0.9300334415	-3.8957491464	-0.5246822922
H	-1.9283497949	-3.4561681902	-0.4118667203
H	-1.0201470725	-4.8453936356	-1.0675504216
H	-0.5166450346	-4.1005983931	0.4703202759
S	5.1117152535	-1.1483891281	-0.4186415937
O	3.9711573852	-0.3646606194	-0.9426419311
O	5.9036094381	-1.9507227060	-1.3495153707
N	6.0967436030	-0.3788084280	0.5989225452
S	5.7248287581	0.9783708046	1.4027922296
O	4.2892319798	1.2897170745	1.5390554896
O	6.5898405756	1.0810348739	2.5766191732
C	4.2783522277	-2.4255504467	0.6965933699
F	3.6565648530	-1.8321934747	1.7196433791
F	3.3577694704	-3.1010972527	-0.0162213867
F	5.1595001701	-3.3002068499	1.1770755388
C	6.3666301919	2.3186323889	0.2373670292
F	5.8051729965	2.2156136930	-0.9716123795
F	6.0641195185	3.5244789786	0.7396368776
F	7.6911157559	2.2398097215	0.0998394076
C	-1.8801371688	0.7797121700	-1.0893209372
H	-1.6951218541	-0.0139625693	-1.8153815383
H	-2.2735532278	1.6631774708	-1.6084796634
H	-2.6614132325	0.4182418040	-0.4007471621

Cartesian coordinates of the optimized $[(C_2OC_2)C_1\ C_1Im][Tf_2N]$ structure

S	-4.0317694526	-0.2529115662	0.5804987186
O	-5.3168708913	-0.8729049776	0.9057999193
O	-3.1133874466	-0.9216172594	-0.3562632750
N	-4.0547464828	1.3237015118	0.1813341980
S	-5.2567106684	2.3544025349	0.5501439964
O	-6.0755236045	2.0387010878	1.7212538330
O	-4.7058763045	3.7082797284	0.3783079522
C	-3.0589895771	-0.2406917311	2.1991524939
F	-3.6752661449	0.4909082242	3.1261983104
F	-2.9346460563	-1.4933274395	2.6496600532
F	-1.8311728578	0.2624622333	2.0064189265
C	-6.4175770641	2.1739778401	-0.9289336136
F	-6.9183059608	0.9419238598	-1.0069130738
F	-7.4284402734	3.0426377925	-0.8124918034
F	-5.7657060438	2.4404633717	-2.0709303816
C	-0.8393857880	1.3848093284	-1.1857642067
N	-0.6464850466	2.4310625698	-0.3608307635
N	0.1290452028	0.4849238664	-0.9222840650
C	0.9437985508	0.9625155137	0.0884366343
H	1.8020230453	0.4083390831	0.4559158780
C	0.4547374211	2.1806084702	0.4387021266
H	0.7928765224	2.8837370765	1.1859380779
C	0.3194206751	-0.8198218759	-1.5704340435
H	-0.4051737688	-0.9093674964	-2.3830458329
H	1.3353638524	-0.8475490375	-1.9765633689
C	-1.4718781003	3.6382400294	-0.3064827272
H	-1.0782564898	4.2749858204	0.4891828147
H	-2.5135440697	3.3856825665	-0.0815168140
H	-1.4096453795	4.1793175022	-1.2573482403
S	4.7326551899	-1.1415733003	-1.0471219470
O	3.4271437336	-0.5014670657	-1.3032795844
O	5.7249766674	-1.1913496312	-2.1199530977
N	5.4734486313	-0.7226078573	0.3294669646
S	4.7236520282	-0.0903962458	1.6145193591
O	3.2688550445	-0.3253642604	1.7034274423
O	5.5530900715	-0.3019625073	2.7993349633
C	4.2945008853	-2.9556413877	-0.7465265923
F	3.4827344105	-3.0839462651	0.3102353031
F	3.6652496920	-3.4484390478	-1.8215142222
F	5.3911528984	-3.6832921181	-0.5289598429
C	4.8438917240	1.7707392889	1.2999769528
F	4.2847197135	2.0999828717	0.1284584068
F	4.1853565785	2.4262455447	2.2702935439
F	6.1105255860	2.1856484695	1.2972490343
C	-1.8865747546	1.3014164340	-2.2376249938
H	-2.1930107179	0.2639533231	-2.3875350509
H	-1.5164956225	1.7196179499	-3.1855049431
H	-2.7788144096	1.8447677533	-1.9146448883
C	0.1267455276	-1.9669384567	-0.5783743636
H	0.8777989378	-1.8991205951	0.2274977573
H	-0.8816143865	-1.9205560348	-0.1350622397
O	0.3076937533	-3.1497863674	-1.3266029524
C	0.2544225663	-4.3234387577	-0.5331793783
H	1.0206977439	-4.2738073444	0.2598821769
H	-0.7315160146	-4.3991534947	-0.0393428121
C	0.4996316579	-5.5197572237	-1.4363099832
H	1.4835666165	-5.4382342570	-1.9142374978
H	-0.2641030399	-5.5703725840	-2.2223662189
H	0.4665172043	-6.4504918969	-0.8552376348

Cartesian coordinates of the optimized $[(C_2EG_1C_2)C_1Im][Tf_2N]$ structure

S	4.8971300252	-0.6673417924	0.1006933067
O	6.3525276749	-0.6710255784	-0.0445600606
O	4.2687263578	-1.3227552860	1.2585737064
N	4.1414390372	0.7619875512	-0.0953639226
S	4.7431860525	2.0202784963	-0.9366164026
O	5.7488899642	1.7132833838	-1.9531373006
O	3.5998126669	2.8864908314	-1.2656971878
C	5.6544539021	2.9964461871	0.3992753528
F	6.5727494938	2.2434334526	1.0030526487
F	6.2597557097	4.0515146488	-0.1563894262
F	4.7914283299	3.4391601292	1.3199224012
C	4.2394342128	-1.6659425793	-1.3621177067
F	4.5562529399	-1.0960430831	-2.5224315440
F	4.7518356303	-2.8995037280	-1.3312047143
F	2.9021540387	-1.7638097354	-1.2875875662
H	2.1338821982	0.9998575932	0.3466848790
C	1.0630183855	0.9641586974	0.5676746940
N	0.1174929048	1.7728691260	0.0715866077
N	0.4656854718	0.0789186019	1.3788737266
C	-0.8960999267	0.3306364893	1.3930506746
H	-1.5943438785	-0.2847263694	1.9389762813
C	-1.1158233382	1.3951751042	0.5722393125
H	-2.0434022063	1.8851145080	0.2891221980
C	0.3443716490	2.8733658803	-0.8668125426
H	0.0433859921	3.8149887073	-0.3963548406
H	-0.2632037058	2.7055209704	-1.7615746226
H	1.4069567672	2.9065864634	-1.1251495862
C	1.1429888646	-1.0308063340	2.0648176069
H	2.2235863655	-0.8827817187	1.9663226169
H	0.8658783811	-0.9872426001	3.1246946091
C	0.7505404833	-2.3812672786	1.4781550725
H	1.3896346213	-3.1588496465	1.9226379238
H	0.9326770353	-2.3906652383	0.3933227024
O	-0.6175582530	-2.6167125109	1.7707743072
C	-1.3747845671	-3.2841065285	0.7720890193
H	-2.4228009133	-3.0174326032	0.9577919082
H	-1.1042065882	-2.9130398150	-0.2288255466
C	-1.2227689089	-4.7943367794	0.8126633144
H	-1.4169815399	-5.1487533325	1.8390575516
H	-1.9779037989	-5.2478232839	0.1428068409
O	0.0838953148	-5.1387621042	0.3851639327
C	0.3197522370	-6.5280653688	0.2407475877
H	1.2337765404	-6.6044941255	-0.3613064904
H	-0.4999076617	-6.9888990688	-0.3409903340
C	0.5079901150	-7.2622294713	1.5688863785
H	1.3187372477	-6.8010529070	2.1469455808
H	-0.4025150311	-7.2453712842	2.1808809016
H	0.7684162080	-8.3140116273	1.3864188254
S	-4.7383283037	-0.4509545034	-0.4012556040
O	-3.7707267727	-0.2814408013	0.6980343510
O	-5.5777120011	-1.6493753577	-0.4292038143
N	-5.6489500234	0.8330849427	-0.7644502510
S	-5.2769314863	2.3681056357	-0.4109795808
O	-3.8480500646	2.6701435835	-0.1922219637
O	-6.0571276492	3.2476999966	-1.2804863618
C	-6.0491759021	2.6065467537	1.2965420604
F	-5.5747741491	1.7162991689	2.1720976964
F	-5.7593652958	3.8359028748	1.7453558651
F	-7.3768149803	2.4817000853	1.2392890981

C	-3.6565070576	-0.6361377610	-1.9423032258
F	-2.8954097979	0.4482221473	-2.1394362102
F	-2.8404026998	-1.6933724125	-1.7904008964
F	-4.3982442256	-0.8360878826	-3.0315328046

Cartesian coordinates of the optimized $[(C_2EG_2C_2)C_1Im][Tf_2N]$ structure

S	-4.8385029681	-0.8578476180	0.3027862803
O	-6.2487492147	-1.2452201857	0.3049555323
O	-4.3208753201	0.0472965868	1.3411958411
N	-3.7489804492	-2.0566654005	0.1393241474
S	-4.0661256577	-3.5090535034	-0.5263395857
O	-5.1753981718	-3.5717782270	-1.4772980928
O	-2.7629464616	-4.0996144791	-0.8719081137
C	-4.6210071136	-4.5269221275	0.9646107644
F	-5.7169861837	-4.0118767904	1.5189800826
F	-4.8838286458	-5.7784581669	0.5740578230
F	-3.6527741016	-4.5653729446	1.8871205893
C	-4.5917074011	0.1324883834	-1.2879133721
F	-4.8114466620	-0.6134243407	-2.3678421914
F	-5.4344151502	1.1694486875	-1.2995320625
F	-3.3369382861	0.6068196455	-1.3462434882
H	-1.7196571054	-1.8047420619	0.4571221441
C	-0.6782028264	-1.5349885815	0.6556085756
N	0.4119755495	-2.2176696797	0.2812881767
N	-0.2729189720	-0.4387335729	1.3136637838
C	1.1112076014	-0.4241599125	1.3526107376
H	1.6701141843	0.3899550022	1.7873154962
C	1.5423948488	-1.5417940543	0.7046019272
H	2.5513397270	-1.8798777158	0.4851058893
C	0.4143343212	-3.4753427248	-0.4680409871
H	0.8582937874	-4.2623064362	0.1501453232
H	1.0143885424	-3.3454142771	-1.3741095094
H	-0.6160701708	-3.7368609076	-0.7252560221
C	-1.1562419070	0.6199469257	1.8226113842
H	-2.1890987039	0.2570546664	1.7799472000
H	-0.8846678470	0.8067189142	2.8681488568
C	-1.0166861889	1.9058045282	1.0152189946
H	-1.7926805640	2.6126901553	1.3464001351
H	-1.1904186869	1.7052600267	-0.0524407613
O	0.2804330274	2.4347815576	1.2341808502
C	0.9326612713	3.0200547807	0.1160438324
H	2.0088431536	2.9435812759	0.3150829768
H	0.7188052002	2.4459875535	-0.7990267477
C	0.5612609845	4.4752422347	-0.0957081639
H	0.6907026022	5.0236635717	0.8529860227
H	1.2454331337	4.9160249137	-0.8437403056
O	-0.7800075269	4.5497208767	-0.5567354794
C	-1.2727189103	5.8639930511	-0.7285237424
H	-2.0342969964	5.8231587130	-1.5169967899
H	-0.4767898775	6.5500780055	-1.0631545202
C	-1.9042729601	6.4024230732	0.5546940723
H	-2.7510484576	5.7561658902	0.8477063884
H	-1.1727107750	6.3884754884	1.3836221071
S	4.7526742656	0.8423969815	-0.6189955761
O	3.7758264109	0.6607686284	0.4708051370
O	5.3392725616	2.1667206293	-0.8289660155
N	5.9167092866	-0.2695946068	-0.7370369200
S	5.8375186138	-1.7771103223	-0.1547328642
O	4.4870053914	-2.3348517549	0.0577049491
O	6.8369309065	-2.5923310155	-0.8432398079
C	6.5213467264	-1.5940988516	1.5961519176
F	5.7651828723	-0.7707578640	2.3274754962
F	6.5318474211	-2.7958896019	2.1900538973
F	7.7698754526	-1.1227367260	1.5774093518
C	3.7403758292	0.5554898899	-2.1906211420

F	3.2004664000	-0.6696420118	-2.2060917852
F	2.7403027707	1.4523234809	-2.2456195232
F	4.4904549774	0.7019460491	-3.2821973088
O	-2.3394505374	7.7220837594	0.2972508952
C	-3.0025827375	8.3202019345	1.3942679426
H	-3.8865435934	7.7181798132	1.6753162817
H	-2.3330360988	8.3436029011	2.2745425360
C	-3.4167272515	9.7275723362	0.9998051089
H	-4.0857032695	9.6993788706	0.1309033114
H	-2.5363533937	10.3257809908	0.7342272735
H	-3.9396159573	10.2224541020	1.8281040474

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