Efficient Prediction of the Local Electronic Structure of Ionic Liquids from Low-Cost Calculations

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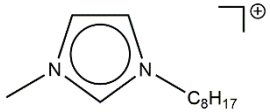
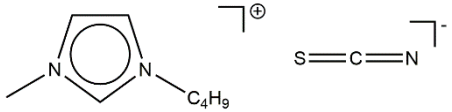
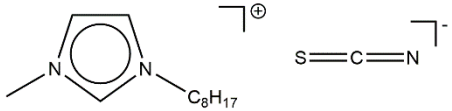
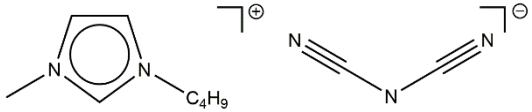
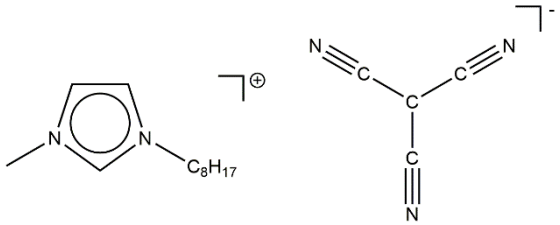
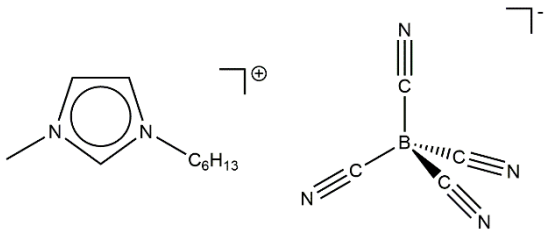
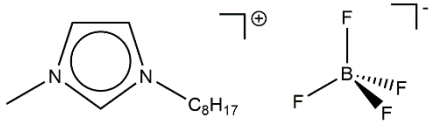
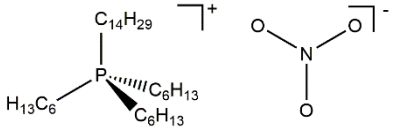
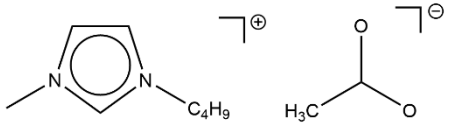
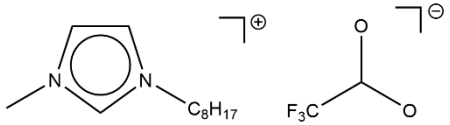
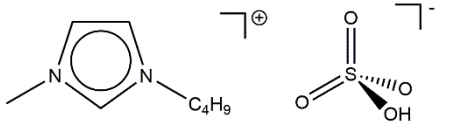
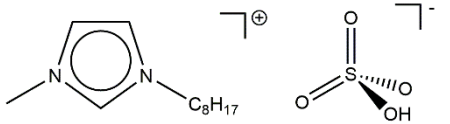
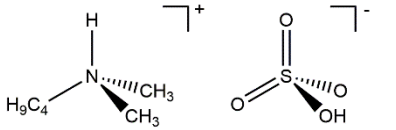
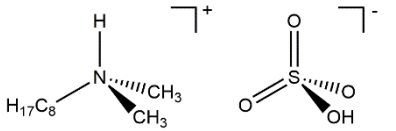
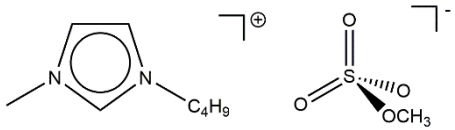
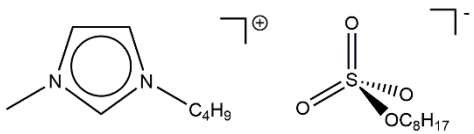
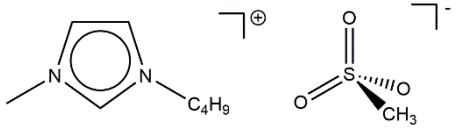
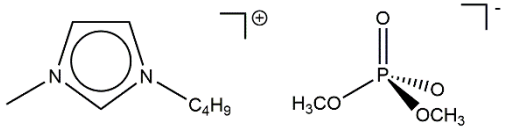
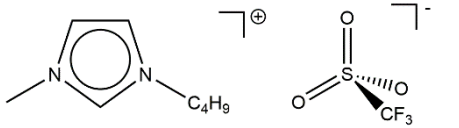
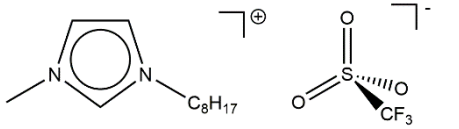
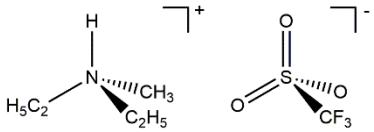
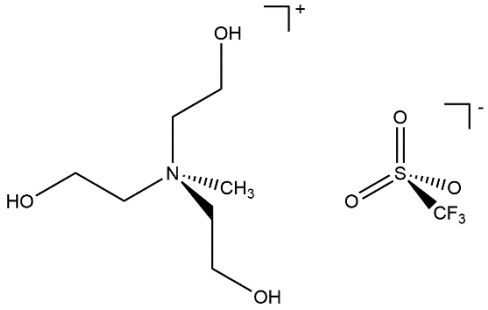
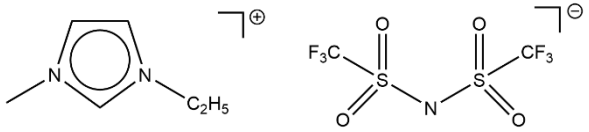
1. Ionic liquids studied

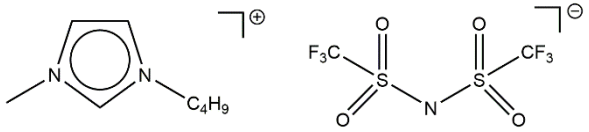
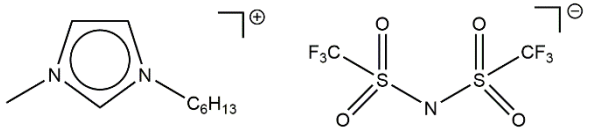
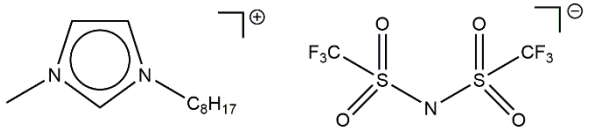
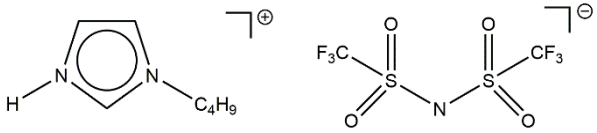
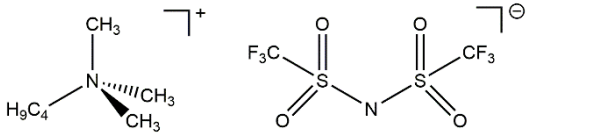
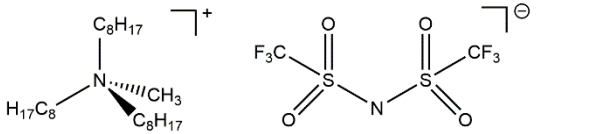
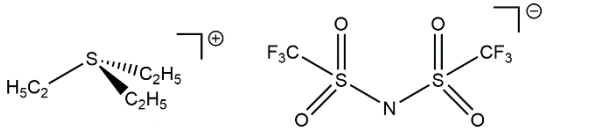
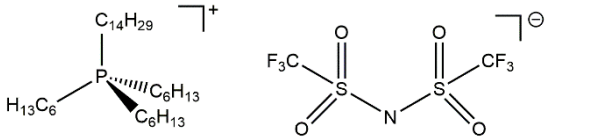
The five ionic liquids (ILs) that are newly studied here ($[C_4C_1Im][CH_3CO_2]$, $[C_2C_1Im][NTf_2]$, $[C_4C_1Im][NPf_2]$, $[C_4Py][NTf_2]$, $[C_2C_1Im][FAP]$) were purchased from Iolitec or Sigma (Table S1) and used as received. Sample purity for the five new ILs was confirmed by XP spectra (ESI Section 6) and in previous publications for the 39 other ILs.[1-5]

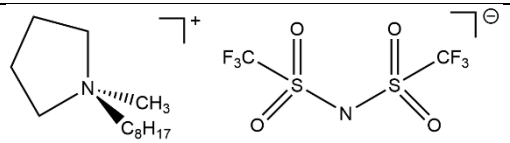
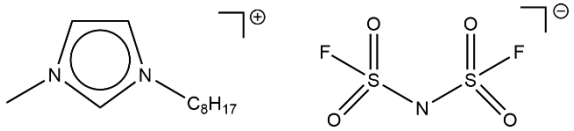
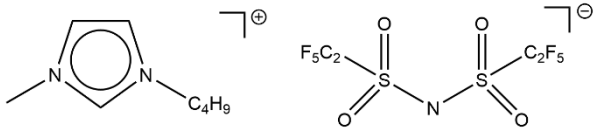
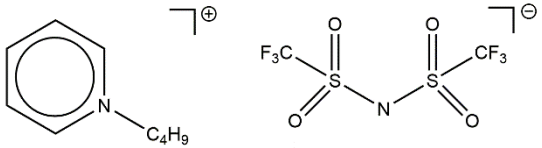
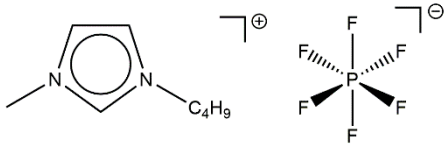
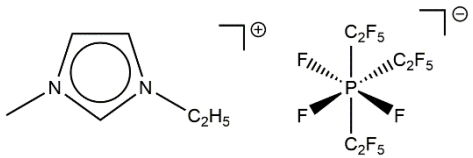
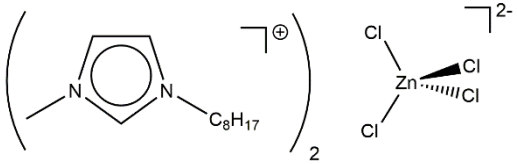
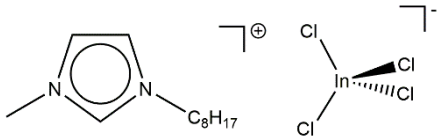
Table S1. ILs investigated in this work.

IL no.	Abbreviation	Structure	Name	Ref. or bought for this work
1	$[C_8C_1Im]Cl$		1–*n*–octyl–3–methylimidazolium chloride	[2]
2	$[C_4C_1Im][SCN]$		1–*n*–butyl–3–methylimidazolium thiocyanate	[1]
3	$[C_8C_1Im][SCN]$		1–*n*–octyl–3–methylimidazolium thiocyanate	[1]
4	$[C_4C_1Im][N(CN)_2]$		1–*n*–butyl–3–methylimidazolium dicyanamide	[1]
5	$[C_8C_1Im][C(CN)_3]$		1–*n*–octyl–3–methylimidazolium tricyanomethanide	[1]
6	$[C_6C_1Im][B(CN)_4]$		1–*n*–hexyl–3–methylimidazolium tetracyanoborate	[1]
7	$[C_8C_1Im][BF_4]$		1–*n*–octyl–3–methylimidazolium tetrafluoroborate	[1]

8	$[P_{6,6,6,14}][NO_3]$		*n*–tetradecyl(tri–*n*–hexyl)phosphonium nitrate	1
9	$[C_4C_1Im][CH_3CO_2]$		1–*n*–butyl–3–methylimidazolium acetate	Iolitec
10	$[C_8C_1Im][CF_3CO_2]$		1–*n*–octyl–3–methylimidazolium trifluoroacetate	3
11	$[C_4C_1Im][HSO_4]$		1–*n*–butyl–3–methylimidazolium hydrogensulfate	1
12	$[C_8C_1Im][HSO_4]$		1–*n*–octyl–3–methylimidazolium hydrogensulfate	1
13	$[N_{4,1,1,0}][HSO_4]$		*n*–butyl(dimethyl)ammonium hydrogensulfate	1
14	$[N_{8,1,1,0}][HSO_4]$		*n*–octyl(dimethyl)ammonium hydrogensulfate	1
15	$[C_4C_1Im][MeSO_4]$		1–*n*–butyl–3–methylimidazolium methylsulfate	1
16	$[C_4C_1Im][OcSO_4]$		1–*n*–butyl–3–methylimidazolium octylsulfate	1

17	$[C_2C_1Im][MeSO_3]$		1–ethyl–3–methylimidazolium methanesulfonate	1
18	$[C_4C_1Im][Me_2PO_4]$		1–*n*–butyl–3–methylimidazolium dimethylphosphate	1
19	$[C_4C_1Im][TfO]$		1–*n*–butyl–3–methylimidazolium trifluoromethylsulfonate	1
20	$[C_8C_1Im][TfO]$		1–*n*–octyl–3–methylimidazolium trifluoromethylsulfonate	1
21	$[N_{2,2,1,0}][TfO]$		diethyl(methyl)ammonium trifluoromethylsulfonate	1
22	$[N_{2OH,2OH,2OH,1}][TfO]$ or $[N_{(2OH)3,1}][TfO]$		triethanol(methyl)ammonium triflate	1
23	$[C_2C_1Im][NTf_2]$		1–ethyl–3–methylimidazolium bis[(trifluoromethane)sulfonyl]imide	Sigma

24	$[C_4C_1Im][NTf_2]$		1–*n*–butyl–3–methylimidazolium bis[(trifluoromethane)sulfonyl]imide	1
25	$[C_6C_1Im][NTf_2]$		1–*n*–hexyl–3–methylimidazolium bis[(trifluoromethane)sulfonyl]imide	1
26	$[C_8C_1Im][NTf_2]$		1–*n*–octyl–3–methylimidazolium bis[(trifluoromethane)sulfonyl]imide	1
27	$[C_4C_0Im][NTf_2]$		1–*n*–butyl–imidazolium bis[(trifluoromethane)sulfonyl]imide	1
28	$[N_{4,1,1,1}][NTf_2]$		*n*–butyl(trimethyl)ammonium bis[(trifluoromethane)sulfonyl]imide	1
29	$[N_{8,8,8,1}][NTf_2]$		tri–*n*–octyl(methyl)ammonium bis[(trifluoromethane)sulfonyl]imide	5
30	$[S_{2,2,2}][NTf_2]$		triethylsulfonium bis[(trifluoromethane)sulfonyl]imide	1
31	$[P_{6,6,6,14}][NTf_2]$		*n*–hexadecyl(tri–*n*–hexyl)phosphonium bis[(trifluoromethane)sulfonyl]imide	1

32	$[C_8C_1Pyrr][NTf_2]$		1-*n*-octyl-1-methylpyrridinium bis[(trifluoromethane)sulfonyl]imide	5
33	$[C_8C_1Im][FSI]$		1-*n*-octyl-3-methylimidazolium bis(fluorosulfonyl)imide	2
34	$[C_4C_1Im][NPf_2]$		1-*n*-butyl-3-methylimidazolium bis(pentafluoroethylsulfonyl)imide	Iolitec
35	$[C_4Py][NTf_2]$		1-*n*-butylpyridinium bis[(trifluoromethane)sulfonyl]imide	Iolitec
36	$[C_4C_1Im][PF_6]$		1-*n*-butyl-3-methylimidazolium hexafluorophosphate	2
37	$[C_2C_1Im][FAP]$		1-ethyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	Sigma
38	$[C_8C_1Im]_2[ZnCl_4]$		bis(1-*n*-octyl-3-methylimidazolium) tetrachlorozincate	2
39	$[C_8C_1Im][InCl_4]$		1-*n*-octyl-3-methylimidazolium tetrachloroindate	2

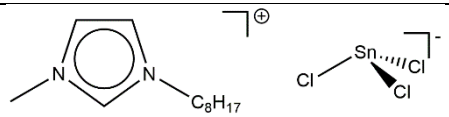
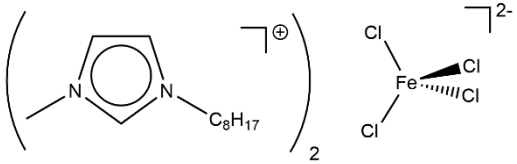
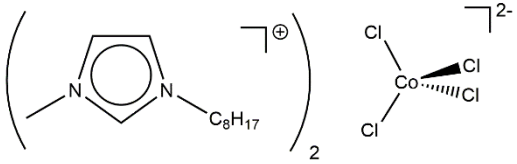
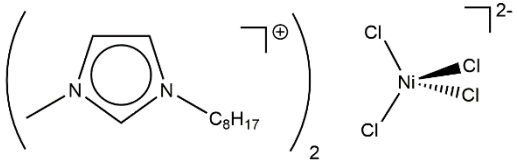
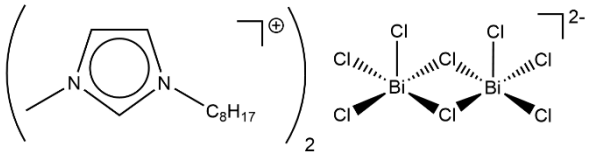
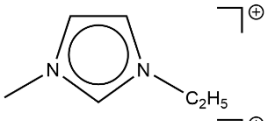
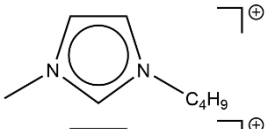
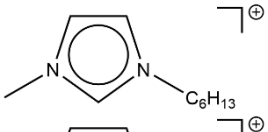
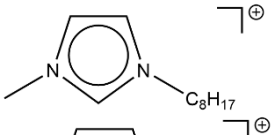
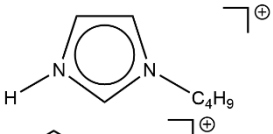
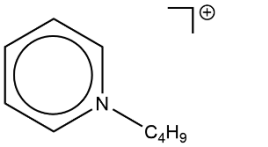
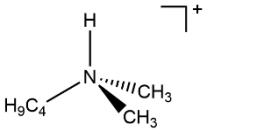
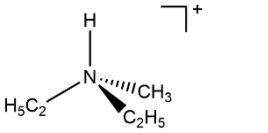
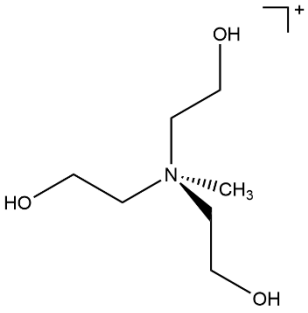
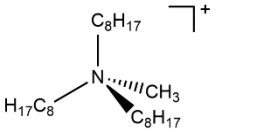
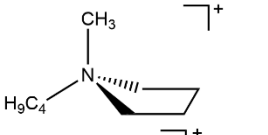
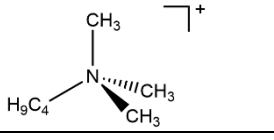
40	$[C_8C_1Im][SnCl_3]$		1-*n*-octyl-3-methylimidazolium trichlorostannate	2
41	$[C_8C_1Im]_2[FeCl_4]$		bis(1-*n*-octyl-3-methylimidazolium) tetrachloroferrate	2
42	$[C_8C_1Im]_2[CoCl_4]$		bis(1-*n*-octyl-3-methylimidazolium) tetrachlorocobaltate	2
43	$[C_8C_1Im]_2[NiCl_4]$		bis(1-*n*-octyl-3-methylimidazolium) tetrachloronickelate	2
44	$[C_8C_1Im]_2[Bi_2Cl_8]$		bis(1-*n*-octyl-3-methylimidazolium) octachlorodibismuthate	3

Table S2. Aqueous solution investigated in this work

Abbreviation	Name	Ref.
K[SCN] in water	*x* = 0.01 (0.5 M) potassium thiocyanate in water	6

2. Lone-ion-SMD DFT calculations: methods and ions studied

Table S3. Cations investigated using lone-ion-SMD DFT calculations in this work

Cation no.	Abbreviation	Structure	Name
1	$[C_2C_1Im]^+$		1–ethyl–3–methylimidazolium
2	$[C_4C_1Im]^+$		1–*n*–butyl–3–methylimidazolium
3	$[C_6C_1Im]^+$		1–*n*–hexyl–3–methylimidazolium
4	$[C_8C_1Im]^+$		1–*n*–octyl–3–methylimidazolium
5	$[C_4C_0Im]^+$		1–*n*–butyl–imidazolium
6	$[C_4Py]^+$		1–*n*–butylpyridinium
7	$[N_{4,1,1,0}]^+$		*n*–butyl(dimethyl)ammonium
8	$[N_{2,2,1,0}]^+$		diethyl(methyl)ammonium
9	$[N_{2OH,2OH,2OH,1}]^+$ or $[N_{(2OH)3,1}]^+$]		triethanol(methyl)ammonium
10	$[N_{8,8,8,1}]^+$		tri-*n*-octyl(methyl)ammonium
11	$[C_4C_1Pyrr]^+$		1-*n*-butyl-1-methylpyrrolidinium
12	$[N_{4,1,1,1}]^+$		*n*-butyl(trimethyl)ammonium

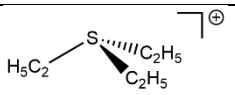
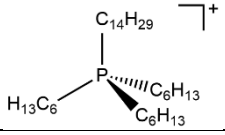
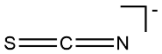
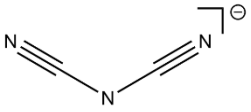
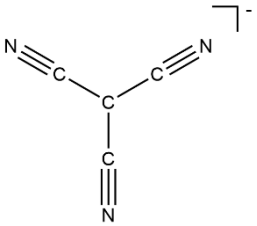
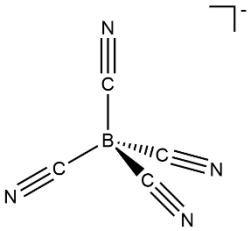
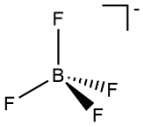
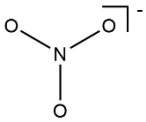
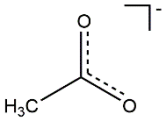
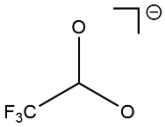
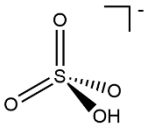
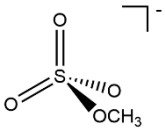
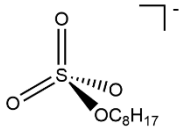
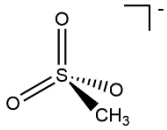
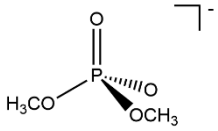
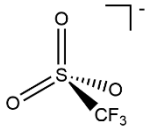
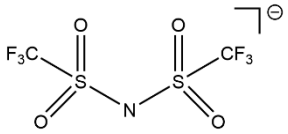
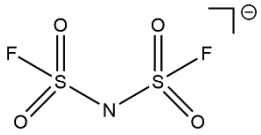
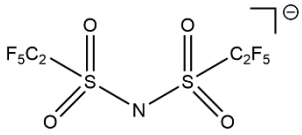
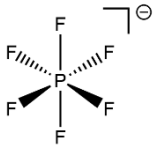
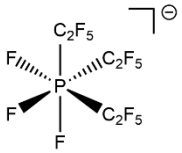
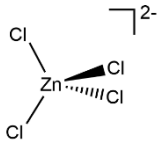
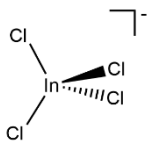
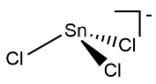
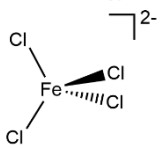
13	$[S_{2,2,2}]^+$		triethylsulfonium
14	$[P_{6,6,6,14}]^+$		*n*–hexadecyl(tri–*n*–hexyl)phosphonium

Table S4. Anions investigated using lone-ion-SMD DFT calculations in this work

Anion no.	Abbreviation	Structure	Name
1	Cl^-		chloride
2	$[SCN]^-$		thiocyanate
3	$[N(CN)_2]^-$		dicyanamide
4	$[C(CN)_3]^-$		tricyanomethanide
5	$[B(CN)_4]^-$		tetracyanoborate
6	$[BF_4]^-$		tetrafluoroborate
7	$[NO_3]^-$		nitrate
8	$[CH_3CO_2]^-$		acetate
9	$[CF_3CO_2]^-$		trifluoroacetate
10	$[HSO_4]^-$		hydrogensulfate
11	$[MeSO_4]^-$		methylsulfate

12	$[OcSO_4]^-$		*n*–octylsulfate
13	$[MeSO_3]^-$		methanesulfonate
14	$[Me_2PO_4]^-$		dimethylphosphate
15	$[TfO]^-$		trifluoromethylsulfonate
16	$[NTf_2]^-$		bis[(trifluoromethane)sulfonyl]imide
17	$[FSI]^-$		bis(fluorosulfonyl)imide
18	$[NPf_2]^-$		bis[(pentafluoroethyl)sulfonyl]imide
19	$[PF_6]^-$		hexafluorophosphate
20	$[FAP]^-$		*facial* tris(pentafluoroethyl)trifluorophosphate
21	$[ZnCl_4]^{2-}$		tetrachlorozincatesss
22	$[InCl_4]^-$		tetrachloroindate
23	$[SnCl_3]^-$		trichlorostannate
24	$[FeCl_4]^{2-}$		tetrachloroferrate

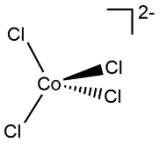
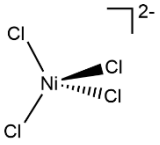
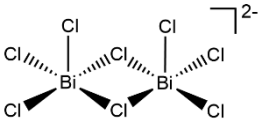
25	$[CoCl_4]^{2-}$		tetrachlorocobaltate
26	$[NiCl_4]^{2-}$		tetrachloronickelate
27	$[Bi_2Cl_8]^{2-}$		octachlorodibismuthate
28	$[Bi_3Cl_{12}]^{3-}$		dodecachlorotriibismuthate
29	$[Bi_2Cl_7]^{-}$		heptachlorodibismuthate
30	$[BiCl_4]^{-}$		tetrachlorobismuthate

Table S5. Parameters used in the SMD model and the references used to obtain the parameters.

Solvent	Relative permittivity, ε_r	Refractive index, n	Surface tension, γ / cal mol^{-1} Å^2)	Abraham acidity, α	Abraham basicity, β
$[C_4C_1Im][PF_6]$	11.40	1.4090	70.24	0.266	0.216

The spin-orbit coupling ΔE_B values for S 2p, Cl 2p and P 2p come from fitting experimental core-level XP spectra for many ILs and represent an average value of the ΔE_B values needed to obtain satisfactory fits when one electronic environment is present for the relevant element.

Table S6. Values used to produce calculated XP spectra

Orbital	*F* (FWHM) / eV	*m* (Gaussian-Lorentzian (GL) Product function)	Spin-orbit coupling ΔE_B / eV	E_B(calc.) with spin-orbit coupling correction	Spin-orbit coupling peak area ratio	Peak area ratio
F 1s	1.60	GL(30)	N/A	N/A	N/A	N/A
O 1s	1.35	GL(30)	N/A	N/A	N/A	N/A
N 1s	1.05	GL(30)	N/A	N/A	N/A	N/A
C 1s	1.10	GL(30)	N/A	N/A	N/A	N/A
S 2p	1.05	GL(30)	ΔE_B(S $2p_{3/2}$ - S $2p_{3/2}$) = 1.20 eV	E_B(S $2p_{3/2}$,calc.) = E_B(S 2p,calc.) – (1.20 × 2/3) E_B(S $2p_{1/2}$,calc.) = E_B(S 2p,calc.) + (1.20 × 1/3)	1:2 for $2p_{1/2}$:$2p_{3/2}$	Area(S $2p_{3/2}$,calc.) = Area(S 2p,calc.) × 2/3 Area(S $2p_{1/2}$,calc.) = Area(S 2p,calc.) × 1/3
Cl 2p	0.90	GL(30)	ΔE_B(Cl $2p_{3/2}$ - Cl $2p_{3/2}$) = 1.60 eV	E_B(Cl $2p_{3/2}$,calc.) = E_B(Cl 2p,calc.) – (1.60 × 2/3) E_B(Cl $2p_{1/2}$,calc.) = E_B(Cl 2p,calc.) + (1.60 × 1/3)	1:2 for $2p_{1/2}$:$2p_{3/2}$	Area(Cl $2p_{3/2}$,calc.) = Area(Cl 2p,calc.) × 2/3 Area(Cl $2p_{1/2}$,calc.) = Area(Cl 2p,calc.) × 1/3
P 2p	1.05	GL(30)	ΔE_B(P $2p_{3/2}$ - P $2p_{3/2}$) = 0.90 eV	E_B(P $2p_{3/2}$,calc.) = E_B(P 2p,calc.) – (0.90 × 2/3) E_B(P $2p_{1/2}$,calc.) = E_B(P 2p,calc.) + (0.90 × 1/3)	1:2 for $2p_{1/2}$:$2p_{3/2}$	Area(P $2p_{3/2}$,calc.) = Area(P 2p,calc.) × 2/3 Area(P $2p_{1/2}$,calc.) = Area(P 2p,calc.) × 1/3

3. Data analysis. Peak fitting core level XP spectra

Peak fitting core level XP spectra is important for charge referencing to obtain E_B(core) values (ESI Section 5.1) and demonstrating purity (ESI Section 6). All core-level XP spectra were fitted using CASAXPS™ software. Spectra were fitted with a GL30 lineshape (70% Gaussian, 30% Lorentzian) and a Shirley background. How the core level XP spectra were fitted is given in Table S7, along with any constraints used.

Table S7. Fitting constraints used for core level X-ray photoelectron spectroscopy (XPS) for each ionic liquid

IL no.	Abbreviation	Core level	Fitting constraints used
1	$[C_8C_1Im]Cl$	N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
2	$[C_4C_1Im][SCN]$	N 1s	none
		C 1s	area = 1:5:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
3	$[C_8C_1Im][SCN]$	N 1s	none
		C 1s	area = 1:5:7 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
4	$[C_4C_1Im][N(CN)_2]$	N 1s	none
		C 1s	area = 1:6:3 for C^2:C_{hetero}:C_{alkyl}
5	$[C_8C_1Im][C(CN)_3]$	N 1s	none
		C 1s	area = 1:8:7 for C^2:C_{hetero}:C_{alkyl}
6	$[C_6C_1Im][B(CN)_4]$	N 1s	none
		C 1s	area = 1:8:5 for C^2:C_{hetero}:C_{alkyl}
		B 1s	none
		F 1s	none
7	$[C_8C_1Im][BF_4]$	N 1s	none
		C 1s	area = 1:8:5 for C^2:C_{hetero}:C_{alkyl}
		B 1s	none
		O 1s	none
8	$[P_{6,6,6,14}][NO_3]$	N 1s	none
		C 1s	area = 4:28 for C_{hetero}:C_{alkyl}
		P 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	none
9	$[C_4C_1Im][CH_3CO_2]$	N 1s	none
		C 1s	area = 2:4:4 for C^2:C_{hetero}:C_{alkyl}
		F 1s	none
10	$[C_8C_1Im][CF_3CO_2]$	O 1s	none
		N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
11	$[C_4C_1Im][HSO_4]$	N 1s	none
		C 1s	area = 1:4:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
12	$[C_8C_1Im][HSO_4]$	N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
13	$[N_{4,1,1,0}][HSO_4]$	N 1s	none
		C 1s	area = 3:3 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
14	$[N_{8,1,1,0}][HSO_4]$	N 1s	none
		C 1s	area = 3:7 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
15	$[C_4C_1Im][MeSO_4]$	N 1s	none
		C 1s	area = 1:5:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$

		O 1s	area = 1:3 for O_{bridge}:$O_{terminal}$
16	$[C_4C_1Im][OcSO_4]$	N 1s	none
		C 1s	area = 1:5:10 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	none
17	$[C_2C_1Im][MeSO_3]$	N 1s	none
		C 1s	area = 1:5:1 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		O 1s	none
18	$[C_4C_1Im][Me_2PO_4]$	N 1s	none
		C 1s	area = 1:6:3 for C^2:C_{hetero}:C_{alkyl}
		P 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
19	$[C_4C_1Im][TfO]$	N 1s	none
		C 1s	area = 1:4:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
20	$[C_8C_1Im][TfO]$	N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
21	$[N_{2,2,1,0}][TfO]$	N 1s	none
		C 1s	area = 3:2 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
	$[N_{2OH,2OH,2OH,1}][TfO]$	F 1s	none
		O 1s	area = 1:1 for O_{cation}:O_{anion}
22	or	N 1s	none
		C 1s	area = 3:2 for C_{hetero}:C_{alkyl}
	$[N_{(2OH)3,1}][TfO]$	S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
23	$[C_2C_1Im][NTf_2]$	N 1s	none
		C 1s	area = 1:4:1 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
24	$[C_4C_1Im][NTf_2]$	N 1s	none
		C 1s	area = 1:4:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
25	$[C_6C_1Im][NTf_2]$	N 1s	none
		C 1s	area = 1:4:5 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
26	$[C_8C_1Im][NTf_2]$	N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
27	$[C_4C_0Im][NTf_2]$	N 1s	none
		C 1s	area = 1:3:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
28	$[N_{4,1,1,1}][NTf_2]$	N 1s	none
		C 1s	area = 4:3 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
29	$[N_{8,8,8,1}][NTf_2]$	F 1s	none

		O 1s	none
		N 1s	none
		C 1s	area = 4:21 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
30	$[S_{2,2,2}][NTf_2]$	N 1s	none
		C 1s	area = 3:3 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
		N 1s	none
31	$[P_{6,6,6,14}][NTf_2]$	C 1s	area = 4:21 for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		P 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
32	$[C_8C_1Pyrr][NTf_2]$	N 1s	none
		C 1s	area = 4: for C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
33	$[C_8C_1Im][FSI]$	N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
34	$[C_4C_1Im][NPf_2]$	N 1s	none
		C 1s	area = 1:4:3 for C^2:C_{hetero}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		O 1s	none
35	$[C_4Py][NTf_2]$	N 1s	none
		C 1s	area = 3:3:3 for C_{hetero}:C_{inter}:C_{alkyl}
		S 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		N 1s	none
36	$[C_4C_1Im][PF_6]$	C 1s	area = 1:4:3 for C^2:C_{hetero}:C_{alkyl}
		P 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		F 1s	none
		N 1s	none
37	$[C_2C_1Im][FAP]$	C 1s	area = 1:4:1 for C^2:C_{hetero}:C_{alkyl}
		P 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		Zn 2p	none
		N 1s	none
38	$[C_8C_1Im]_2[ZnCl_4]$	C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		In 4d	none
		N 1s	none
39	$[C_8C_1Im][InCl_4]$	C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		Sn 3d	none
		N 1s	none
40	$[C_8C_1Im][SnCl_3]$	C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		Fe 2p	none
		N 1s	none
41	$[C_8C_1Im]_2[FeCl_4]$	C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
		Co 2p	none
		N 1s	none
42	$[C_8C_1Im]_2[CoCl_4]$	C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$

43	$[C_8C_1Im]_2[NiCl_4]$	Ni 2p	none
		N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$
44	$[C_8C_1Im]_2[Bi_2Cl_8]$	Bi 4f	none
		N 1s	none
		C 1s	area = 1:4:7 for C^2:C_{hetero}:C_{alkyl}
		Cl 2p	area = 1:2 for $2p_{1/2}$:$2p_{3/2}$

4. Data analysis. Charge referencing, area normalisation and subtraction

4.1. Charge referencing

Table S8. Experimental X-ray photoelectron spectroscopy (XPS) details on the charge correction applied for each sample

IL no.	Abbreviation	Charge referencing method used from reference [2]	Core orbital used for charge referencing	E_B for core orbital used for charge referencing / eV	Rationale for choosing core orbital used for charge referencing
1	$[C_8C_1Im]Cl$	i	C_{alkyl} 1s	285.00	Long alkyl chain
2	$[C_4C_1Im][SCN]$	ii	N_{cation} 1s	401.9	N_{cation} 1s for $[C_8C_1Im][SCN]$
3	$[C_8C_1Im][SCN]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
4	$[C_4C_1Im][N(CN)_2]$	ii	N_{cation} 1s	402.0	N_{cation} 1s for $[C_8C_1Im][N(CN)_2]$ [7]
5	$[C_8C_1Im][C(CN)_3]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
6	$[C_6C_1Im][B(CN)_4]$	i	C_{alkyl} 1s	285.0	Long alkyl chain
7	$[C_8C_1Im][BF_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
8	$[P_{6,6,6,14}][NO_3]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
9	$[C_4C_1Im][CH_3CO_2]$	ii	N_{cation} 1s	401.70	N_{cation} 1s for $[C_8C_1Im][CH_3CO_2]$ [8]s
10	$[C_8C_1Im][CF_3CO_2]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
11	$[C_4C_1Im][HSO_4]$	ii	N_{cation} 1s	401.8	N_{cation} 1s for $[C_8C_1Im][HSO_4]$
12	$[C_8C_1Im][HSO_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
13	$[N_{4,1,1,0}][HSO_4]$	ii	S_{anion} $2p_{3/2}$	168.7	S_{anion} $2p_{3/2}$ for $[N_{8,1,1,0}][HSO_4]$
14	$[N_{8,1,1,0}][HSO_4]$	i	C_{alkyl} 1s	285.0	Long alkyl chain
15	$[C_4C_1Im][MeSO_4]$	iii	N_{cation} 1s	401.7	N_{cation} 1s for $[C_4C_1Im][OcSO_4]$
16	$[C_4C_1Im][OcSO_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
17	$[C_2C_1Im][MeSO_3]$	vi	N_{cation} 1s	401.9	Average N_{cation} 1s for $[C_8C_1Im][A]$ [7]
18	$[C_4C_1Im][Me_2PO_4]$	vi	N_{cation} 1s	401.9	Average N_{cation} 1s for $[C_8C_1Im][A]$ [7]
19	$[C_4C_1Im][TfO]$	ii	N_{cation} 1s	402.0	N_{cation} 1s for $[C_8C_1Im][TfO]$
20	$[C_8C_1Im][TfO]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
21	$[N_{2,2,1,0}][TfO]$	v	F_{anion} 1s	688.41	F_{anion} 1s for $[C_8C_1Im][TfO]$
22	$[N_{(2OH)3,1}][TfO]$	v	F_{anion} 1s	688.41	F_{anion} 1s for $[C_8C_1Im][TfO]$
23	$[C_2C_1Im][NTf_2]$	ii	N_{cation} 1s	402.10	N_{cation} 1s for $[C_8C_1Im][NTf_2]$
24	$[C_4C_1Im][NTf_2]$	ii	N_{cation} 1s	402.10	N_{cation} 1s for $[C_8C_1Im][NTf_2]$
25	$[C_6C_1Im][NTf_2]$	ii	N_{cation} 1s	402.10	N_{cation} 1s for $[C_8C_1Im][NTf_2]$
26	$[C_8C_1Im][NTf_2]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
27	$[C_4C_0Im][NTf_2]$	ii	C_{alkyl} 1s	285.22	C_{alkyl} 1s for $[C_4C_1Im][NTf_2]$
28	$[N_{4,1,1,1}][NTf_2]$	ii	N_{anion} 1s	399.46	N_{anion} 1s for $[C_nC_1Im][NTf_2]$
29	$[N_{8,8,8,1}][NTf_2]$	ii	N_{anion} 1s	399.46	N_{anion} 1s for $[C_nC_1Im][NTf_2]$
30	$[S_{2,2,2}][NTf_2]$	ii	N_{anion} 1s	399.46	N_{anion} 1s for $[C_nC_1Im][NTf_2]$
31	$[P_{6,6,6,14}][NTf_2]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
32	$[C_8C_1Pyrr][NTf_2]$	ii	N_{anion} 1s	399.46	N_{anion} 1s for $[C_nC_1Im][NTf_2]$
33	$[C_8C_1Im][FSI]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
34	$[C_4C_1Im][NPf_2]$	ii	C_{CF2} 1s	291.07	C_{CF2} 1s for $[C_8C_1Im][NPf_2]$ [9]
35	$[C_4Py][NTf_2]$	ii	N_{anion} 1s	399.46	N_{anion} 1s for $[C_nC_1Im][NTf_2]$
36	$[C_4C_1Im][PF_6]$	ii	N_{cation} 1s	402.1	N_{cation} 1s for $[C_8C_1Im][PF_6]$ [7]
37	$[C_2C_1Im][FAP]$	ii	C_{CF3} 1s	293.14	C_{CF3} 1s for $[C_8C_1Im][FAP]$ [9]
38	$[C_8C_1Im]_2[ZnCl_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
39	$[C_8C_1Im][InCl_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
40	$[C_8C_1Im][SnCl_3]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
41	$[C_8C_1Im]_2[FeCl_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
42	$[C_8C_1Im]_2[CoCl_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
43	$[C_8C_1Im]_2[NiCl_4]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
44	$[C_8C_1Im]_2[Bi_2Cl_8]$	i	C_{alkyl} 1s	285.00	Long alkyl chain
45	$[SCN]^-$ in water	N/A	N_{anion} 1s	397.79	N_{anion} 1s for $[C_nC_1Im][SCN]$ [6]

4.2. Area normalisation

Quantitative area normalisation is achieved using the same method as given in reference [1] for valence XPS.

4.3. Subtraction

For the subtraction method, both area normalisation and charge referencing must be used.

5. Results. XPS: demonstrating purity using XPS

The IL XPS measurements were made under ultrahigh vacuum (UHV) conditions. These UHV conditions mean that residual molecular solvents will have vaporized prior to XPS measurements, giving ultrapure samples from a molecular solvent contamination perspective. Furthermore, the element-specific nature of XPS means that a number of ionic impurities, *e.g*. Na^+, can be observed if present (see ESI Section 6). Therefore, we can have very high confidence in the purity of our ILs for the XPS measurements.

Relative sensitivity factors from ref [10] were used to ensure the experimental stoichiometries matched the nominal stoichiometries.

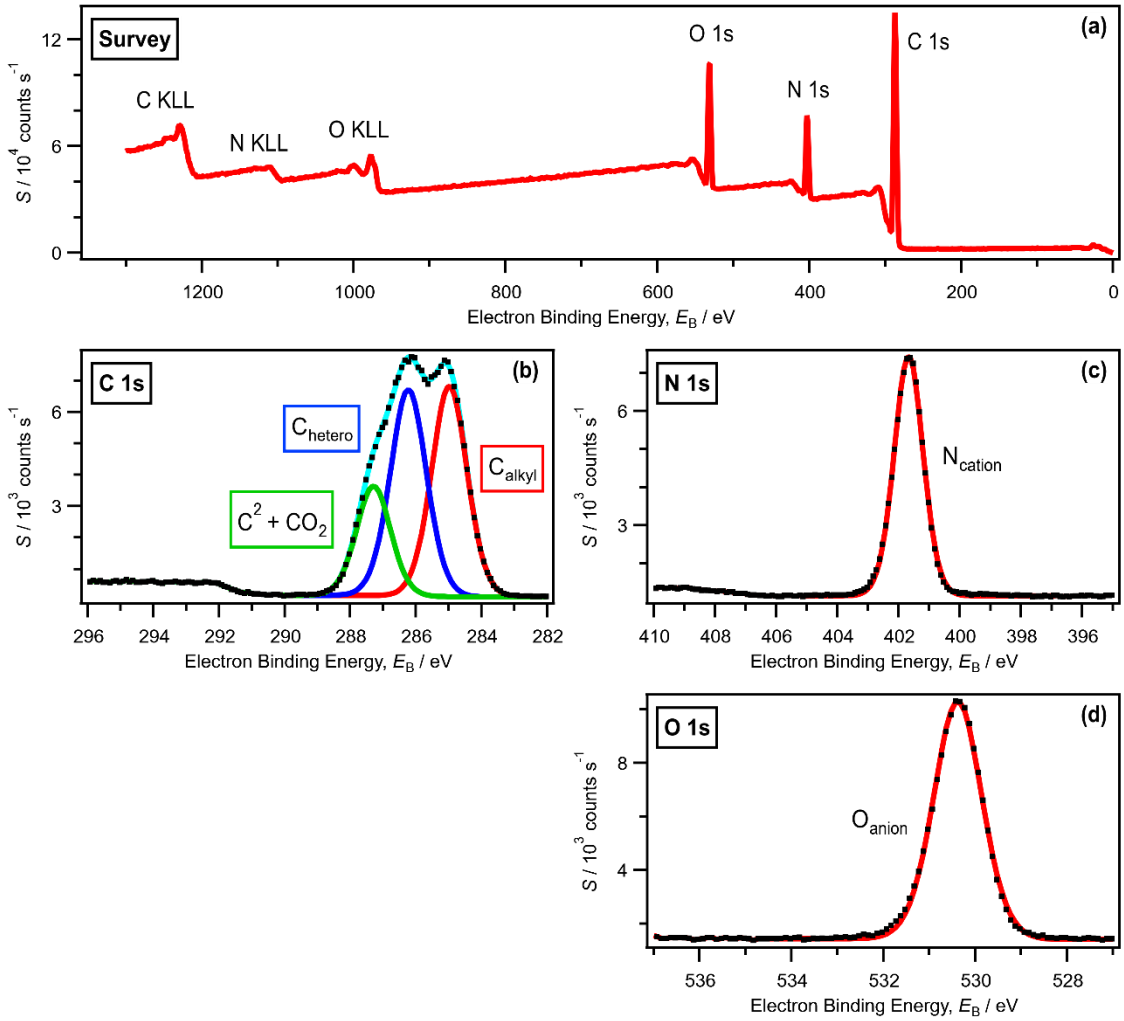


Figure S1. (a) Survey, (b-f) core XP spectra for $[C_4C_1Im][CH_3CO_2]$ recorded on laboratory–based XPS apparatus at $h\nu$ = 1486.6 eV. All XP spectra were charge referenced using the method outlined in ESI Section 5.1.

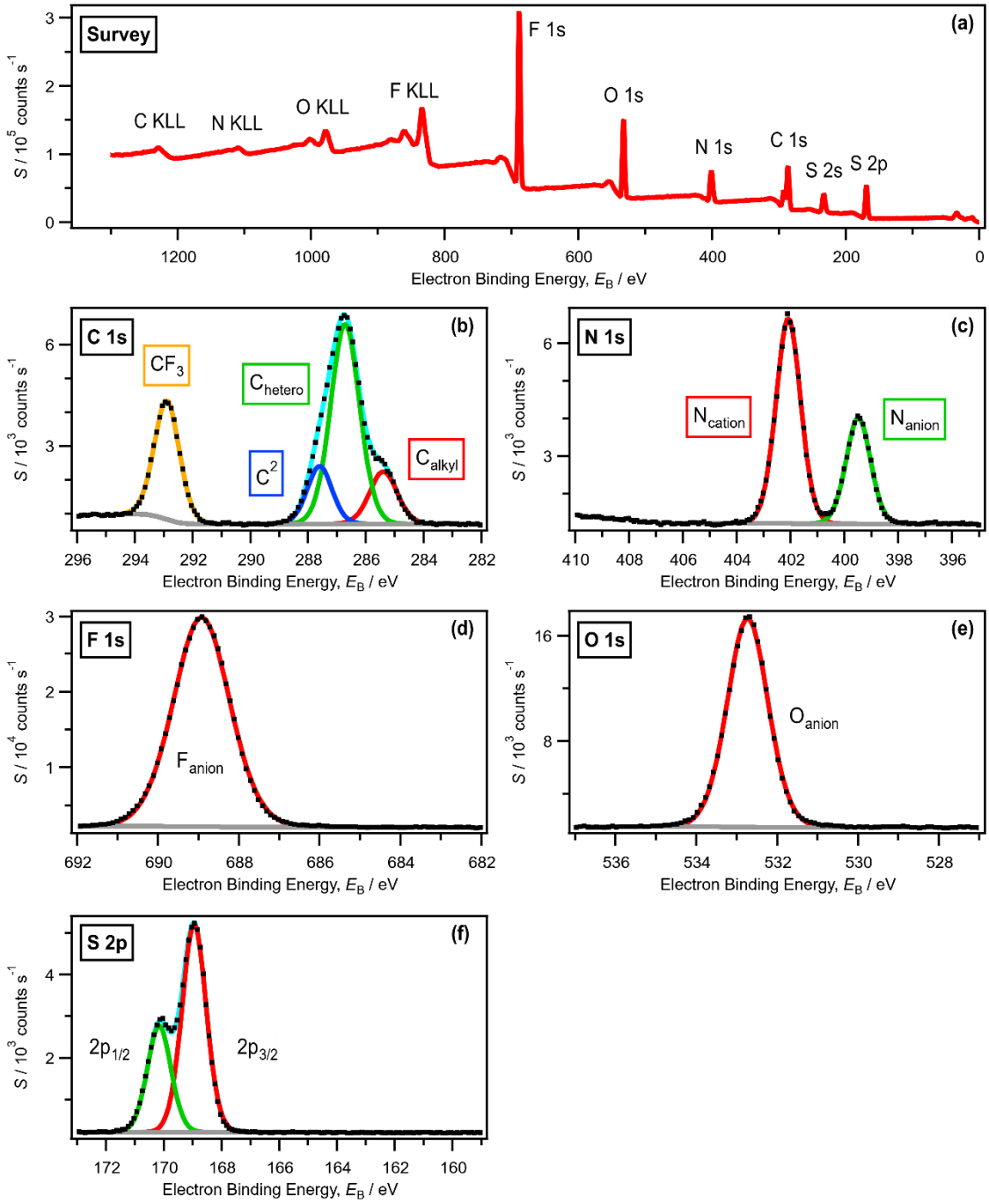


Figure S2. (a) Survey, (b-f) core XP spectra for $[C_2C_1Im][NTf_2]$ recorded on laboratory–based XPS apparatus at $h\nu$ = 1486.6 eV. All XP spectra were charge referenced using the method outlined in ESI Section 5.1.

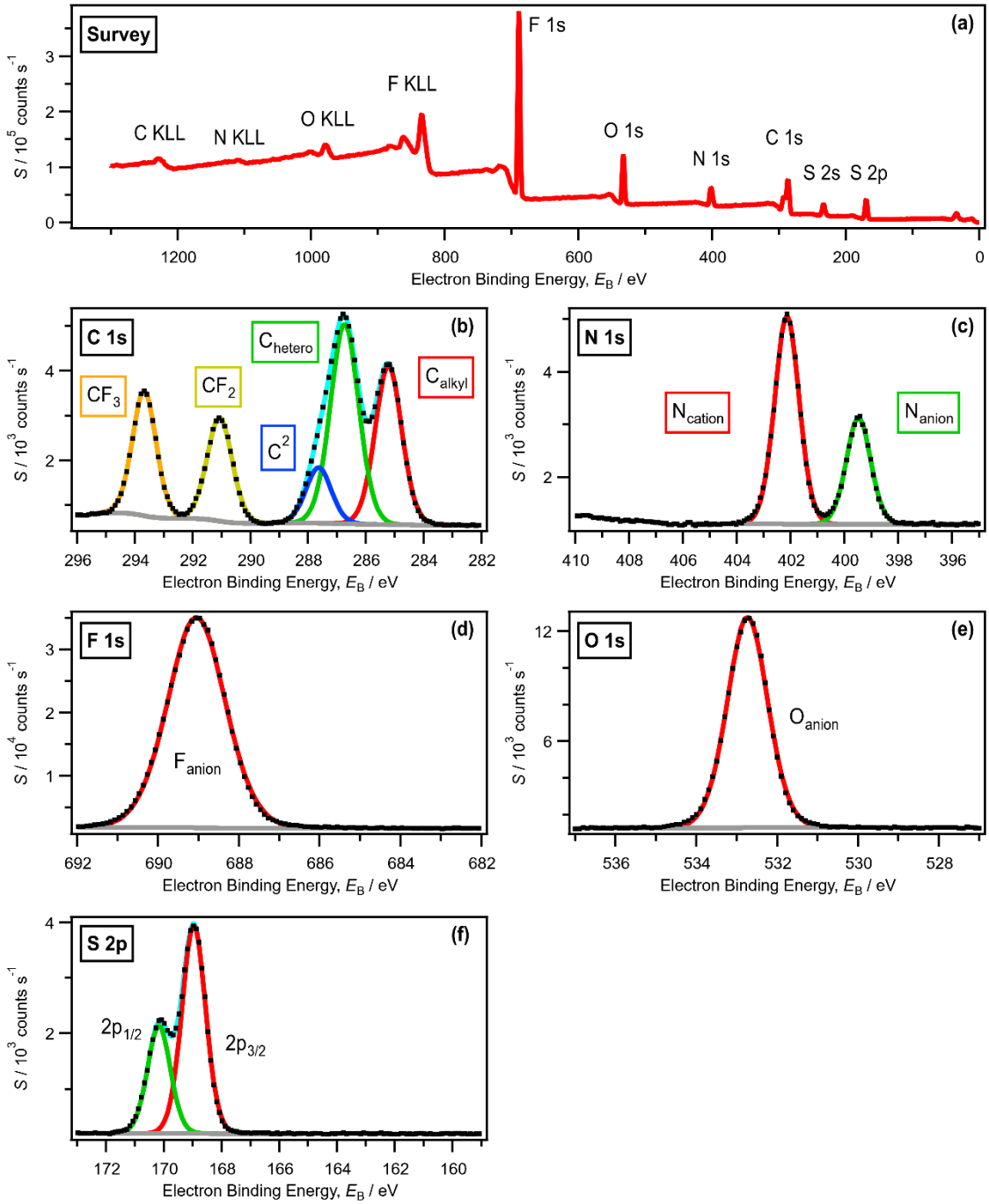


Figure S3. (a) Survey, (b-f) core XP spectra for $[C_4C_1Im][NPf_2]$ recorded on laboratory–based XPS apparatus at $h\nu$ = 1486.6 eV. All XP spectra were charge referenced using the method outlined in ESI Section 5.1.

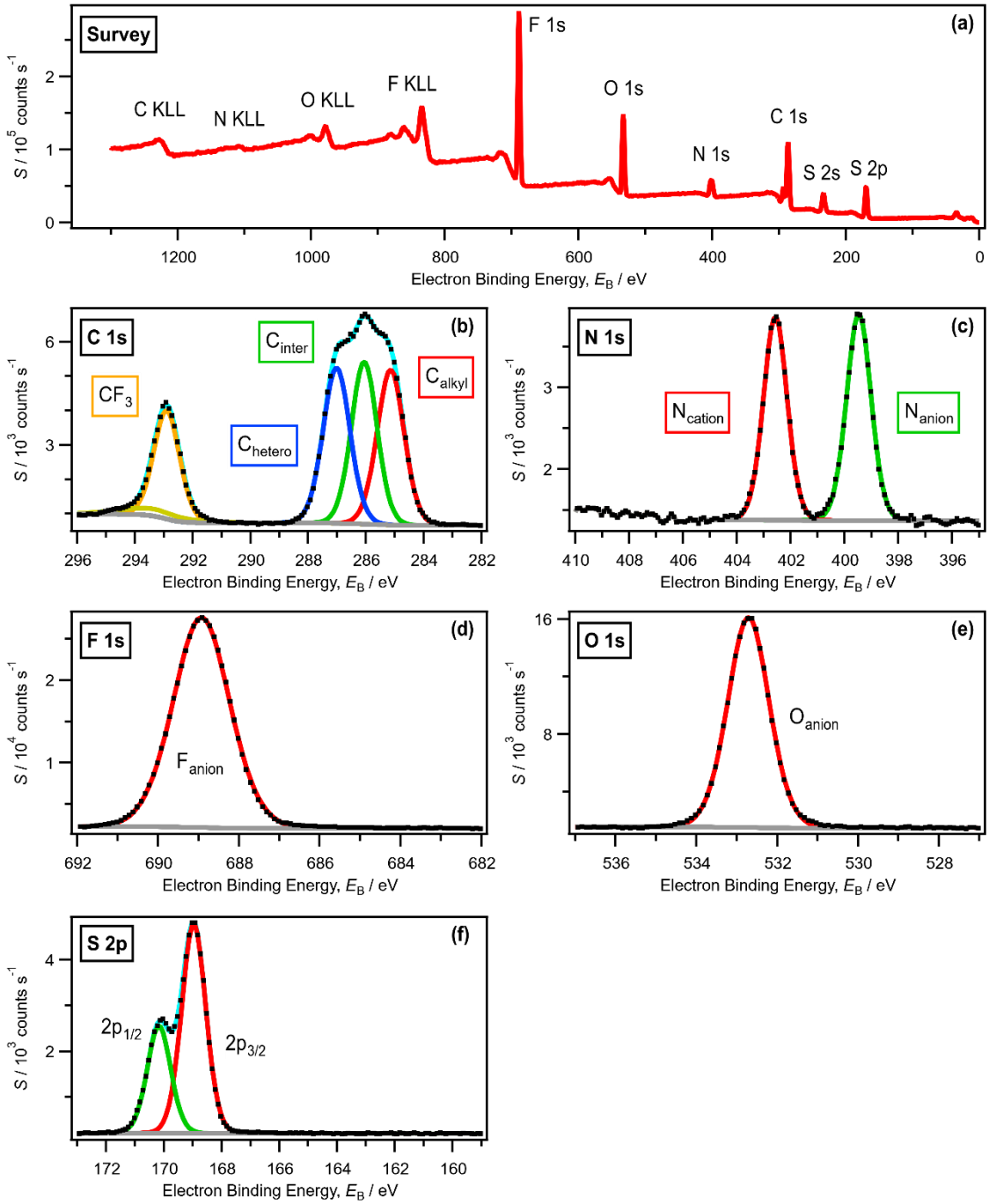


Figure S4. (a) Survey, (b-f) core XP spectra for $[C_4Py][NTf_2]$ recorded on laboratory–based XPS apparatus at $h\nu$ = 1486.6 eV. All XP spectra were charge referenced using the method outlined in ESI Section 5.1.

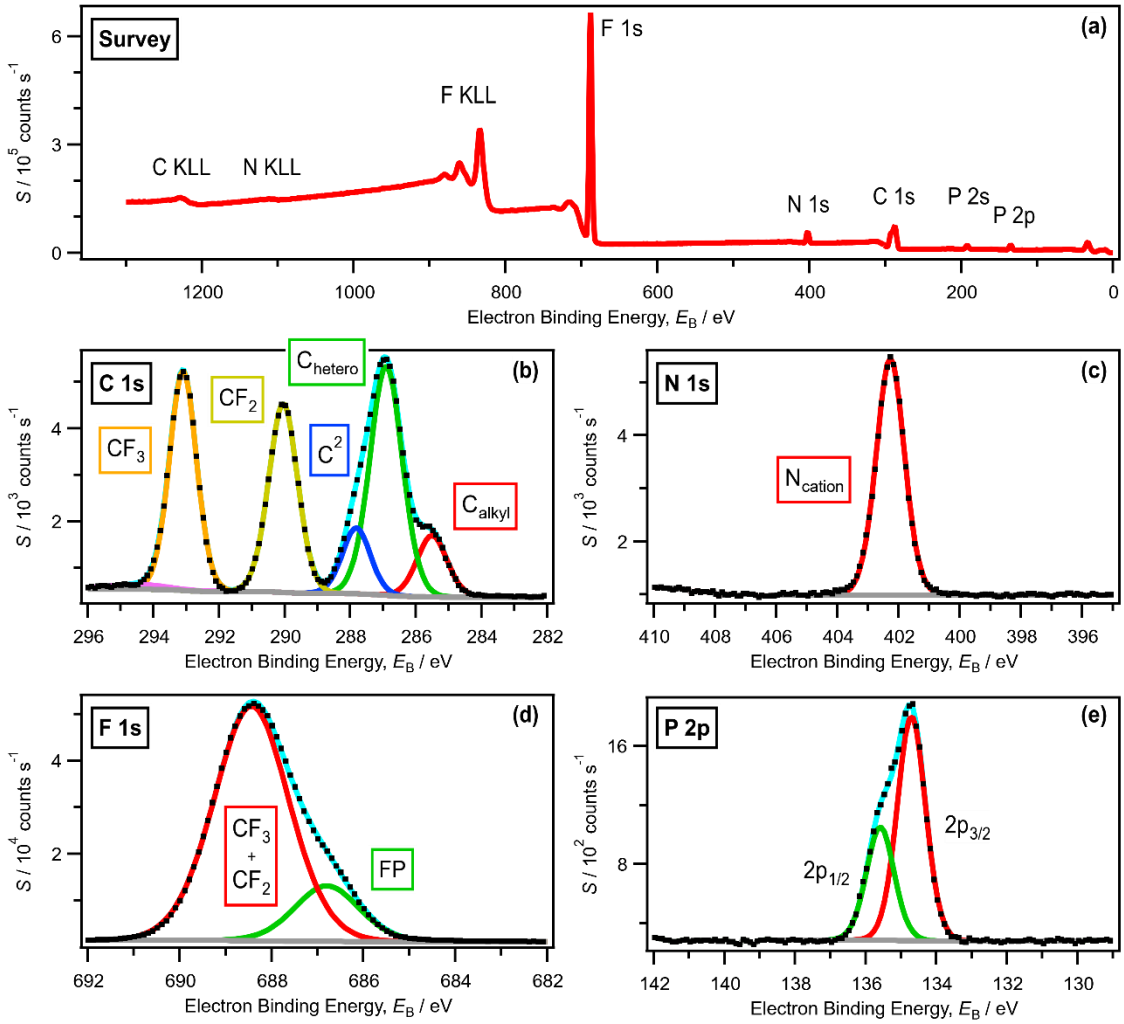


Figure S5. (a) Survey, (b-f) core XP spectra for $[C_2C_1Im][FAP]$ recorded on laboratory–based XPS apparatus at $h\nu$ = 1486.6 eV. All XP spectra were charge referenced using the method outlined in ESI Section 5.1.

The measured experimental and nominal stoichiometries (Table S9) match well for all four ILs newly investigated here using lab XPS. Differences, especially the larger carbon values relative to other elements, are likely due to differences in relative sensitivity factors (RSF) values, as these RSF values were not tuned specially to the Reading XPS apparatus (in references [10, 11] RSF values were tuned specially to the XPS apparatus used in those studies). All these matches, along with the high quality XP spectra given in ESI Figure S1 to ESI Figure S5, demonstrates the high purity of the IL samples newly presented here.

Table S9. Measured experimental and nominal (in brackets) stoichiometries for the ionic liquids studied in this work, recorded at $h\nu$ = 1486.6 eV.

			F 1s	O 1s	N 1s	C 1s	S $2p_{3/2}$	P $2p_{3/2}$
IL no.	Abbreviation	RSF [a]	1.000	0.580	0.350	0.205	0.267	0.200
	$[C_4C_1Im][CH_3CO_2]$	Measured (nominal)		1.9 (4)	2.0 (2)	10.2 (10)		
	$[C_2C_1Im][NTf_2]$	Measured (nominal)	5.5 (6)	3.9 (4)	3.0 (3)	8.3 (8)	2.2 (2)	
	$[C_4C_1Im][NPf_2]$	Measured (nominal)	9.3 (10)	3.9 (4)	3.0 (3)	12.5 (12)	2.3 (2)	
	$[C_4Py][NTf_2]$	Measured (nominal)	5.5 (6)	4.0 (4)	2.0 (2)	11.4 (11)	2.2 (2)	
	$[C_2C_1Im][FAP]$	Measured (nominal)	17.4 (18)		2.0 (2)	12.5 (12)		1.1 (1)

[a] RSF = relative sensitivity factors, taken from reference [11] for C 1s, N 1s, O 1s, F 1s, S $2p_{3/2}$, P $2p_{3/2}$

6. Results. Experimental and calculated E_B(core) data

Table S10. Experimental and calculated E_B(C 1s). The ion that corresponds to the data is shaded green; the counterion is shaded pink

Cation	Anion	Moiety	Calculated $-E_B$(C 1s) / eV	Average calculated E_B(C 1s) / eV	Experimental E_B(C 1s) / eV	ΔE_B(C 1s) / eV
$[C_2C_1Im]^+$	$[NTf_2]^-$	C^2	-279.91	279.91	287.61	7.71
			-278.64			
$[C_2C_1Im]^+$	$[NTf_2]^-$	C_{hetero}	-278.62	278.52	286.73	8.21
			-278.50			
			-278.32			
$[C_2C_1Im]^+$	$[NTf_2]^-$	C_{alkyl}	-276.90	276.90	285.41	8.51
$[C_4C_1Im]^+$	$[NTf_2]^-$	C^2	-279.87	279.87	287.68	7.81
			-278.64			
$[C_4C_1Im]^+$	$[NTf_2]^-$	C_{hetero}	-278.60	278.49	286.76	8.26
			-278.42			
			-278.31			
			-277.00			
$[C_4C_1Im]^+$	$[NTf_2]^-$	C_{alkyl}	-276.76	276.74	285.22	8.48
			-276.45			
$[C_6C_1Im]^+$	$[NTf_2]^-$	C^2	-279.89	279.89	287.73	7.85
			-278.64			
$[C_6C_1Im]^+$	$[NTf_2]^-$	C_{hetero}	-278.61	278.49	286.76	8.27
			-278.41			
			-278.31			
			-276.98			
			-276.71			
$[C_6C_1Im]^+$	$[NTf_2]^-$	C_{alkyl}	-276.54	276.61	285.09	8.48
			-276.52			
			-276.31			
$[C_8C_1Im]^+$	$[NTf_2]^-$	C^2	-279.89	279.89	287.68	7.79
			-278.64			
$[C_8C_1Im]^+$	$[NTf_2]^-$	C_{hetero}	-278.62	278.50	286.75	8.25
			-278.41			
			-278.32			
			-276.99			
			-276.71			
			-276.54			
$[C_8C_1Im]^+$	$[NTf_2]^-$	C_{alkyl}	-276.45	276.54	285.00	8.46
			-276.45			
			-276.41			
			-276.27			
			-279.36			
$[C_4Py]^+$	$[NTf_2]^-$	C_{hetero}	-279.36	279.08	287.05	7.97
			-278.52			
			-278.43			
$[C_4Py]^+$	$[NTf_2]^-$	C_{hetero}	-278.18	278.27	286.10	7.83
			-278.18			
			-277.10			
$[C_4Py]^+$	$[NTf_2]^-$	C_{alkyl}	-276.84	276.80	285.19	8.39
			-276.47			
			-278.44			
$[N_{4,1,1,0}]^+$	$[HSO_4]^-$	C_{hetero}	-278.28	278.33	286.45	8.12
			-278.27			
			-277.10			
$[N_{4,1,1,0}]^+$	$[HSO_4]^-$	C_{alkyl}	-276.90	276.83	285.08	8.24
			-276.51			
			-278.41			
$[N_{8,1,1,0}]^+$	$[HSO_4]^-$	C_{hetero}	-278.28	278.32	286.45	8.13
			-278.26			
			-277.09			
$[N_{8,1,1,0}]^+$	$[HSO_4]^-$	C_{alkyl}	-276.77	276.58	285.00	8.42

			-276.56 -276.46 -276.46 -276.42 -276.28			
$[N_{2,2,1,0}]^+$	$[TfO]^-$	C_{hetero}	-278.47 -278.46 -278.24	278.39	286.63	8.23
$[N_{2,2,1,0}]^+$	$[TfO]^-$	C_{alkyl}	-276.98 -276.96	276.97	285.33	8.35
$[S_{2,2,2}]^+$	$[NTf_2]^-$	C_{hetero}	-278.56 -278.56 -278.56	278.56	286.53	7.97
$[S_{2,2,2}]^+$	$[NTf_2]^-$	C_{alkyl}	-277.15 -277.15 -277.15	277.15	285.65	8.50
$[C_4C_0Im]^+$	$[NTf_2]^-$	C^2	-280.05	280.05	287.76	7.71
$[C_4C_0Im]^+$	$[NTf_2]^-$	C_{hetero}	-277.03 -276.78 -276.46	278.65	286.67	8.02
$[C_4C_0Im]^+$	$[NTf_2]^-$	C_{alkyl}	-278.78 -278.71 -278.46	276.75	285.16	8.40
$[P_{6,6,6,14}]^+$	$[NO_3]^-$	C_{hetero}	-277.48 -277.48 -277.48	277.48	285.87	8.39
$[P_{6,6,6,14}]^+$	$[NO_3]^-$	C_{alkyl}	-277.48 -277.04 -277.04 -277.04 -277.03 -276.66 -276.66 -276.66 -276.66 -276.52 -276.52 -276.52 -276.52 -276.52 -276.51 -276.44 -276.39 -276.39 -276.36 -276.35 -276.34 -276.33 -276.32 -276.32 -276.31 -276.31 -276.31 -276.22	276.53	285.00	8.47
$[N_{4,1,1,1}]^+$	$[NTf_2]^-$	C_{hetero}	-278.37 -278.21 -278.20 -278.20	278.24	286.80	8.56
$[N_{4,1,1,1}]^+$	$[NTf_2]^-$	C_{alkyl}	-277.05 -276.84 -276.47	276.79	285.28	8.49
$[N_{8,8,8,1}]^+$	$[NTf_2]^-$	C_{hetero}	-278.28	278.23	286.70	8.47

$[N_{8,8,8,1}]^+$	$[NTf_2]^-$	C_{alkyl}	-278.28 -278.25 -278.10 -277.01 -277.01 -277.00 -276.74 -276.74 -276.74 -276.55 -276.55 -276.54 -276.45 -276.45 -276.45 -276.45 -276.45 -276.45 -276.41 -276.41 -276.41 -276.27 -276.27 -276.27	276.55	285.07	8.52
$[N_{(2OH)3,1}]^+$	$[TfO]^-$	C_{hetero}	-278.74 -278.65 -278.55 -278.50 -278.43 -278.27 -278.21	278.48	286.58	8.10
$[C_8C_1Im]^+$	$[NTf_2]^-$	CF_3	-284.41 -284.41	284.41	292.93	8.52
$[C_8C_1Im]^+$	$[TfO]^-$	CF_3	-283.88	283.88	292.50	8.63
$[C_2C_1Im]^+$	$[FAP]^-$	CF_3	-284.26 -284.22 -284.22	284.23	293.11	8.88
$[C_2C_1Im]^+$	$[FAP]^-$	CF_2	-282.03 -281.98 -281.98	282.00	290.05	8.05
$[C_8C_1Im]^+$	$[CF_3CO_2]^-$	CF_3	-283.13	283.13	292.24	9.11
$[C_8C_1Im]^+$	$[CF_3CO_2]^-$	CO_2	-279.47	279.47	288.46	8.99
$[C_4C_1Im]^+$	$[NPf_2]^-$	CF_3	-284.70 -284.70	284.70	293.68	8.98
$[C_4C_1Im]^+$	$[NPf_2]^-$	CF_2	-282.98 -282.98	282.98	291.07	8.09
water/K^+	$[SCN]^-$	cyano	-277.26	277.26	285.90 (ref. [6])	8.64
subtracted	$[N(CN)_2]^-$	cyano	-278.09 -278.08	278.08	286.80	8.72
subtracted	$[C(CN)_3]^-$	cyano + central C	-277.84 -277.83 -277.83 -277.81	277.83	286.50	8.67
subtracted	$[B(CN)_4]^-$	cyano	-277.48 -277.48 -277.48 -277.48	277.48	286.40	8.92
subtracted	$[MeSO_4]^-$	C-O	-277.65	277.65	286.50	8.85
subtracted	$[OcSO_4]^-$	C_{alkyl}	-276.28 -276.24 -276.23 -276.16	276.18	285.00	8.82

		-276.15			
		-276.14			
		-276.07			
				average	8.37

Table S11. Experimental and calculated E_B(N 1s). The ion that corresponds to the data is shaded green; the counterion is shaded pink

Cation	Anion	Moiety	Calculated $-E_B$(N 1s) / eV	Average calculated E_B(N 1s) / eV	Experimental E_B(N 1s) / eV	ΔE_B(N 1s) / eV
$[N_{8,1,1,0}]^+$	$[HSO_4]^-$	cation	-393.07	393.07	402.23	9.16
$[N_{4,1,1,1}]^+$	$[NTf_2]^-$	cation	-393.21	393.21	402.98	9.76
$[N_{8,8,8,1}]^+$	$[NTf_2]^-$	cation	-393.01	393.01	402.73	9.72
$[C_8C_1Im]^+$	$[NTf_2]^-$	cation	-392.49 -392.40	392.45	402.10	9.65
$[C_4Py]^+$	$[NTf_2]^-$	cation	-393.03	393.03	402.60	9.57
$[C_8C_1Pyrr]^+$	$[NTf_2]^-$	cation	-392.96	392.96	402.70	9.74
$[C_8C_1Im]^+$	$[NTf_2]^-$	S-N-S	-389.93	389.93	399.46	9.53
$[C_8C_1Im]^+$	$[SCN]^-$	C≡N	-388.03	388.03	397.79	9.75
$[C_4C_1Im]^+$	$[N(CN)_2]^-$	C-N-C	-389.55	389.55	399.65	10.10
$[C_4C_1Im]^+$	$[N(CN)_2]^-$	C≡N	-388.39 -388.39	388.39	398.36	9.96
$[C_8C_1Im]^+$	$[C(CN)_3]^-$	C≡N	-389.05 -389.05 -389.05	389.05	398.84	9.79
$[C_6C_1Im]^+$	$[B(CN)_4]^-$	C≡N	-389.45 -389.45 -389.45 -389.45	389.45	399.75	10.30
$[P_{6,6,6,14}]^+$	$[NO_3]^-$	N-O	-395.85	395.85	406.16	10.31
$[C_8C_1Im]^+$	$[FSI]^-$	S-N-S	-390.32	390.32	399.79	9.47
$[C_4C_1Im]^+$	$[NPf_2]^-$	S-N-S	-389.98	389.98	399.49	9.50
					average	9.76

Table S12. Experimental and calculated E_B(S 2p). The ion that corresponds to the data is shaded green; the counterion is shaded pink

Cation	Anion	Moiety	Calculated $-E_B$(S 2p) / eV	Average calculated E_B(S $2p_{3/2}$) / eV	Experimental E_B(S $2p_{3/2}$) / eV	ΔE_B(S $2p_{3/2}$) / eV
$[S_{2,2,2}]^+$	$[NTf_2]^-$	cation	-163.21 -163.21 -163.07	162.37	166.31	3.95
$[C_8C_1Im]^+$	$[HSO_4]^-$	anion	-165.64 -165.58 -165.58	164.80	168.58	3.78
$[C_8C_1Im]^+$	$[NTf_2]^-$	anion	-166.18 -166.18 -166.16 -166.16 -166.16 -166.16	165.36	168.98	3.61
$[C_8C_1Im]^+$	$[TfO]^-$	anion	-165.44 -165.43 -165.43	164.63	168.47	3.84
$[C_4C_1Im]^+$	$[OcSO_4]^-$	anion	-165.47 -165.42 -165.41	164.63	168.29	3.65
$[C_4C_1Im]^+$	$[MeSO_4]^-$	anion	-165.50 -165.45 -165.45	164.67	168.28	3.61
$[C_2C_1Im]^+$	$[MeSO_3]^-$	anion	-164.62 -164.62 -164.59	163.81	167.70	3.89
$[C_8C_1Im]^+$	$[SCN]^-$	anion	-158.90 -158.67 -158.67	157.95	162.33	4.39
$[C_8C_1Im]^+$	$[FSI]^-$	anion	-167.08 -167.08	166.23	169.90	3.68

			-167.00 -167.00 -166.99 -166.99			
$[C_4C_1Im]^+$	$[NPf_2]^-$	anion	-166.20 -166.20 -166.18 -166.18 -166.18 -166.18	165.39	168.97	3.58
					average	3.80

Table S13. Experimental and calculated E_B(O 1s). The ion that corresponds to the data is shaded green; the counterion is shaded pink

Cation	Anion	Moiety	Experimental - E_B(O 1s) / eV	Average calculated E_B(O 1s) / eV	Experimental E_B(O 1s) / eV	ΔE_B(O 1s) / eV
$[N_{(2OH)3,1}]^+$	$[TfO]^-$	cation	-521.14 -520.93 -520.53	520.87	532.84	11.98
$[C_8C_1Im]^+$	$[HSO_4]^-$	anion	-520.85	520.85	533.04	12.18
$[C_8C_1Im]^+$	$[HSO_4]^-$	anion	-519.50 -519.48 -519.48	519.48	531.63	12.15
$[C_8C_1Im]^+$	$[NTf_2]^-$	anion	-520.64 -520.64 -520.60 -520.60	520.62	532.66	12.04
$[C_8C_1Im]^+$	$[TfO]^-$	anion	-519.81 -519.81 -519.81	519.81	531.91	12.11
$[C_4C_1Im]^+$	$[OcSO_4]^-$	anion	-520.70	520.70	532.86	12.16
$[C_4C_1Im]^+$	$[OcSO_4]^-$	anion	-519.40 -519.37 -519.37	519.38	531.43	12.05
$[C_2C_1Im]^+$	$[MeSO_3]^-$	anion		518.99	531.20	12.22
$[C_4C_1Im]^+$	$[Me_2PO_4]^-$	anion	-520.21 -520.10	520.15	532.62	12.46
$[C_4C_1Im]^+$	$[Me_2PO_4]^-$	anion	-518.30 -518.30	518.30	530.40	12.10
$[C_4C_1Im]^+$	$[MeSO_4]^-$	anion	-520.79	520.79	533.02	12.23
$[C_4C_1Im]^+$	$[MeSO_4]^-$	anion	-519.45 -519.42 -519.42	519.43	531.47	12.04
$[P_{6,6,6,14}]^+$	$[NO_3]^-$	anion	-519.95 -519.95 -519.94	519.94	531.66	11.72
$[C_8C_1Im]^+$	$[FSI]^-$	anion	-521.00 -521.00 -520.98 -520.98	520.99	533.03	12.04
$[C_4C_1Im]^+$	$[NPf_2]^-$	anion	-520.66 -520.66 -520.63 -520.63	520.64	532.74	12.09
$[C_4C_1Im]^+$	$[CH_3CO_2]^-$	anion	-518.21 -518.16	518.18	530.39	12.21
$[C_8C_1Im]^+$	$[CF_3CO_2]^-$	CO_2	-519.03 -518.99	519.01	531.29	12.28
					average	12.12

Table S14. Experimental and calculated $E_B(F_{anion}\ 1s)$. The anion that corresponds to the data is shaded green; the countercation is shaded pink

Cation	Anion	Moiety	Calculated $-E_B(F_{anion}\ 1s)$ / eV	Average calculated $E_B(F_{anion}\ 1s)$ / eV	Experimental $E_B(F_{anion}\ 1s)$ / eV	$\Delta E_B(F_{anion}\ 1s)$ / eV
$[C_4C_1Im]^+$	$[PF_6]^-$	PF	-670.93 -670.93 -670.93 -670.92 -670.92 -670.92	670.93	686.79	15.87
$[C_8C_1Im]^+$	$[BF_4]^-$	BF	-669.91 -669.91 -669.91 -669.91	669.91	685.91	16.00
$[C_8C_1Im]^+$	$[NTf_2]^-$	CF_3	-673.13 -673.13 -673.12 -673.12 -673.11 -673.11	673.12	688.87	15.75
$[C_8C_1Im]^+$	$[TfO]^-$	CF_3	-672.75 -672.75 -672.75	672.75	688.41	15.66
$[C_2C_1Im]^+$	$[FAP]^-$	CF_x	-672.87 -672.87 -672.86 -672.86 -672.86 -672.86 -672.80 -672.79 -672.79 -672.41 -672.41 -672.39 -672.39 -672.29 -672.29	672.65	688.44	15.79
$[C_2C_1Im]^+$	$[FAP]^-$	PF	-671.16 -671.12 -670.89	671.06	686.79	15.73
$[C_8C_1Im]^+$	$[FSI]^-$	F	-672.01 -672.00	672.00	687.82	15.81
$[C_4C_1Im]^+$	$[NPf_2]^-$	CF_x	-673.23 -673.23 -673.20 -673.20 -673.18 -673.18 -673.12 -673.12 -673.09 -673.09	673.16	689.05	15.89
$[C_8C_1Im]^+$	$[CF_3CO_2]^-$	CF_3	-672.18 -672.18 -672.18	672.18	688.24	16.06
					average	15.84

Table S15. Experimental and calculated E_B(Cl $2p_{3/2}$). The anion that corresponds to the data is shaded green; the countercation is shaded pink

Cation	Anion	Moiety	Calculated -E_B(Cl 2p) / eV	Average calculated E_B(Cl $2p_{3/2}$) / eV	Experimental E_B(Cl $2p_{3/2}$) / eV	ΔE_B(Cl $2p_{3/2}$) / eV
$[C_8C_1Im]^+$	Cl^-	anion	-192.88 -192.88 -192.88	191.81	196.96	5.15
$[C_8C_1Im]^+$	$[ZnCl_4]^{2-}$	anion	-193.90 -193.90 -193.90 -193.90 -193.82 -193.82 -193.82 -193.82 -193.82 -193.82 -193.82 -193.82	192.78	198.16	5.38
$[C_8C_1Im]^+$	$[NiCl_4]^{2-}$	anion	-193.95 -193.95 -193.95 -193.95 -193.86 -193.86 -193.86 -193.86 -193.85 -193.85 -193.85 -193.85	192.81	198.16	5.35
$[C_8C_1Im]^+$	$[CoCl_4]^{2-}$	anion	-193.92 -193.92 -193.91 -193.91 -193.84 -193.84 -193.83 -193.83 -193.83 -193.83 -193.83 -193.83	192.78	198.18	5.40
$[C_8C_1Im]^+$	$[FeCl_4]^{2-}$	anion	-193.90 -193.90 -193.90 -193.90 -193.84 -193.84 -193.84 -193.83 -193.83 -193.83 -193.83 -193.83	192.78	198.20	5.42
$[C_8C_1Im]^+$	$[SnCl_3]^-$	anion	-194.80 -194.80 -194.80 -194.70 -194.70 -194.70 -194.70 -194.70	193.67	198.58	4.91

			-194.70			
$[C_8C_1Im]^+$	$[InCl_4]^-$	anion	-195.44 -195.44 -195.44 -195.44 -195.31 -195.31 -195.31 -195.31 -195.31 -195.31 -195.30 -195.30	194.28	199.38	5.10
$[C_8C_1Im]^+$	$[Bi_2Cl_8]^{2-}$	anion	-195.28 -195.28 -195.12 -195.12 -195.12 -195.12 -194.83 -194.83 -194.82 -194.82 -194.77 -194.77 -194.76 -194.76 -194.76 -194.76 -194.65 -194.65 -194.65 -194.65 -194.65 -194.65 -194.65 -194.65	193.77	198.47	4.70
					average	5.18

Table S16. Experimental and calculated E_B(P $2p_{3/2}$). The ion that corresponds to the data is shaded green; the counterion is shaded pink

Cation	Anion	Moiety	Calculated $-E_B$(P 2p) / eV	Calculated E_B(P $2p_{3/2}$) / eV	Experimental E_B(P $2p_{3/2}$) / eV	ΔE_B(P $2p_{3/2}$) / eV
$[C_4C_1Im]^+$	$[PF_6]^-$	anion	-133.77 -133.77 -133.77	133.17	136.68	3.51
$[C_2C_1Im]^+$	$[FAP]^-$	anion	-132.49 -132.41 -132.33	131.81	134.71	2.90
$[C_4C_1Im]^+$	$[Me_2PO_4]^-$	anion	-130.05 -130.03 -129.97	129.42	132.82	3.41
$[P_{6,6,6,14}]^+$	$[NO_3]^-$	cation	-130.00 -130.00 -130.00	129.40	132.50	3.10
					average	3.23

Table S17. Calculated E_B(Cl $2p_{3/2}$) for chlorobismuthate anions that do not form in the liquid-phase

Cation	Anion	Moiety	Calculated $-E_B$(Cl 2p) / eV	Average calculated E_B(Cl $2p_{3/2}$) / eV
N/A	$[BiCl_4]^-$	anion	-195.53 -195.53 -195.39 -195.39 -195.38 -195.38 -194.61 -194.61 -194.53 -194.53 -194.53 -194.53	193.93
N/A	$[Bi_2Cl_7]^-$	anion	-196.07 -196.07 -195.96 -195.96 -195.92 -195.92 -195.65 -195.65 -195.52 -195.52 -195.51 -195.51 -195.32 -195.32 -195.21 -195.21 -195.21 -195.21 -195.20 -195.20 -195.14	194.47
N/A	$[Bi_3Cl_{12}]^{2-}$	anion	-194.89 -194.88 -194.88 -194.87 -194.87 -194.87 -194.85 -194.85 -194.84 -194.84 -194.81 -194.81 -194.80 -194.80 -194.80 -194.79 -194.79 -194.79 -194.76 -194.76 -194.76 -194.76 -194.75 -194.75 -194.75 -194.75 -194.68	193.70

		-194.67
		-194.67
		-194.67
		-194.67
		-194.67
		-194.64
		-194.64
		-194.64
		-194.64

Table S18. Average E_B(correction) = E_B(core,exp.) - E_B(core,calc.) where E_B(core,calc.) comes from lone-ion-SMD calculations, and E_B ranges for E_B(core,exp.) for each core-level

Core-level	Average E_B(correction) from lone-ion-SMD / eV	Standard deviation of E_B(correction) from lone-ion-SMD / eV	Number of datapoints, *n*	Standard error of the sample mean / eV	Average E_B(core,exp) / eV
F 1s	15.84	0.13	9	0.04	687.81
O 1s	12.12	0.16	17	0.04	532.01
N 1s	9.76	0.31	15	0.08	400.97
C 1s	8.37	0.36	47	0.05	287.15
Cl $2p_{3/2}$	5.18	0.26	8	0.09	198.26
S $2p_{3/2}$	3.80	0.24	10	0.08	167.78
P $2p_{3/2}$	3.23	0.28	4	0.14	134.18

7. Results. Experimental versus DFT calculated XP spectra for ions

7.1. Carbon: cations

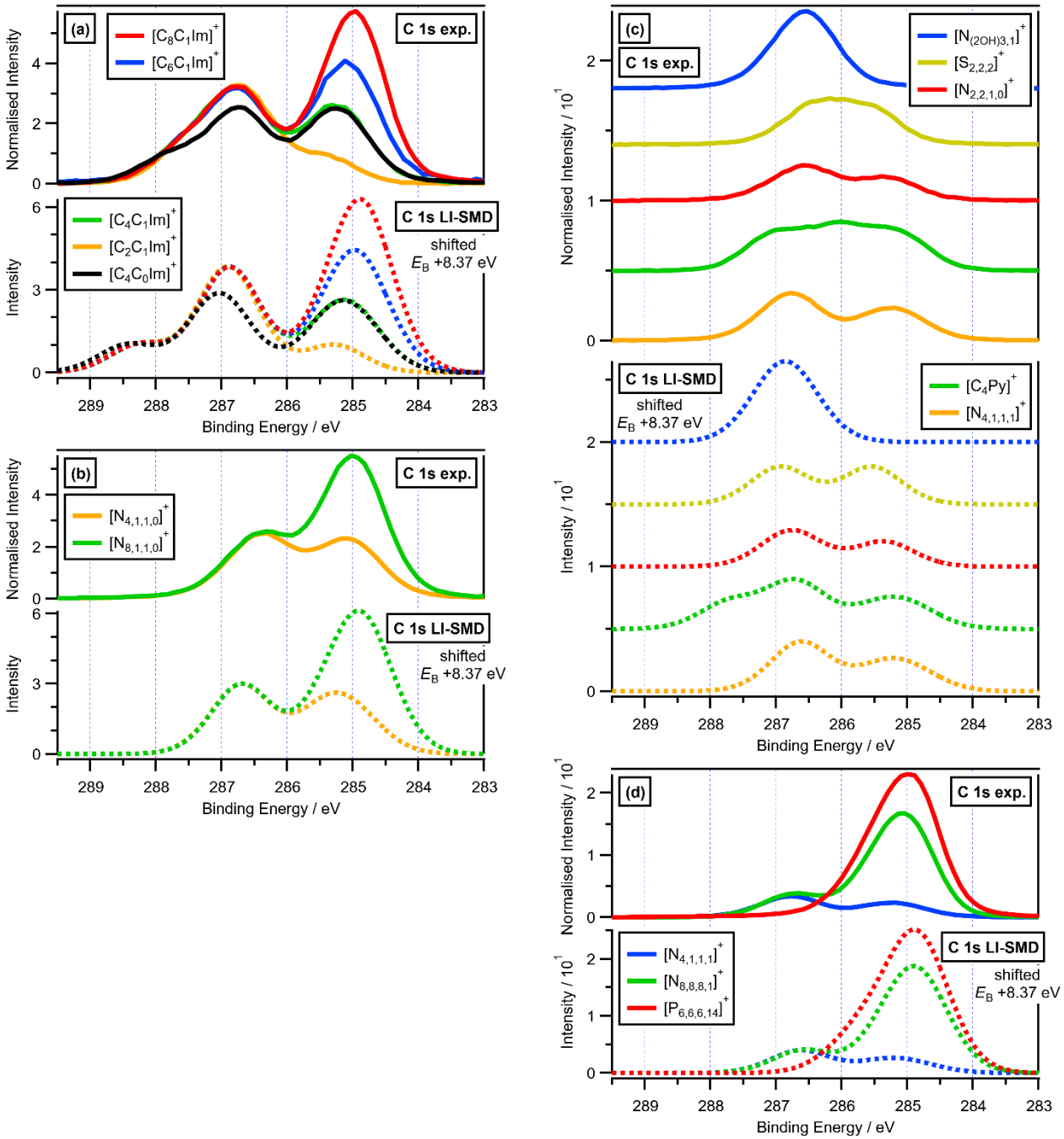


Figure S6. Experimental and calculated C 1s XPS and C-containing lone cations. (a) (top) experimental C 1s XPS for four $[C_nC_1Im][NTf_2]$ ILs (where n = 2, 4, 6, 8); (bottom) calculated C 1s XPS for lone-ion-SMD of four $[C_nC_1Im]^+$ cations (where n = 2, 4, 6, 8) (E_B(correction) = +8.37 eV). (b) (top) experimental C 1s XPS for two $[N_{n,1,1,0}][HSO_4]$ ILs (where n = 4, 8); (bottom) calculated C 1s XPS for lone-ion-SMD of two $[N_{n,1,1,0}]^+$ cations (where n = 4, 8) (E_B(correction) = +8.37 eV). (c) (top) experimental C 1s XPS of the ILs $[N_{(2OH)3,1}][TfO]$, $[S_{2,2,2}][NTf_2]$, $[N_{2,2,1,0}][TfO]$, $[C_4Py][NTf_2]$ and $[N_{4,1,1,1}][NTf_2]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the cations $[N_{(2OH)3,1}]^+$, $[S_{2,2,2}]^+$, $[N_{2,2,1,0}]^+$, $[C_4Py]^+$ and $[N_{4,1,1,1}]^+$ (E_B(correction) = +8.37 eV). (d) (top) experimental C 1s XPS of the ILs $[N_{4,1,1,1}][NTf_2]$, $[N_{8,8,8,1}][NTf_2]$ and $[P_{6,6,6,14}][NTf_2]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the cations $[N_{4,1,1,1}]^+$, $[N_{8,8,8,1}]^+$ and $[P_{6,6,6,14}]^+$ (E_B(correction) = +8.37 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

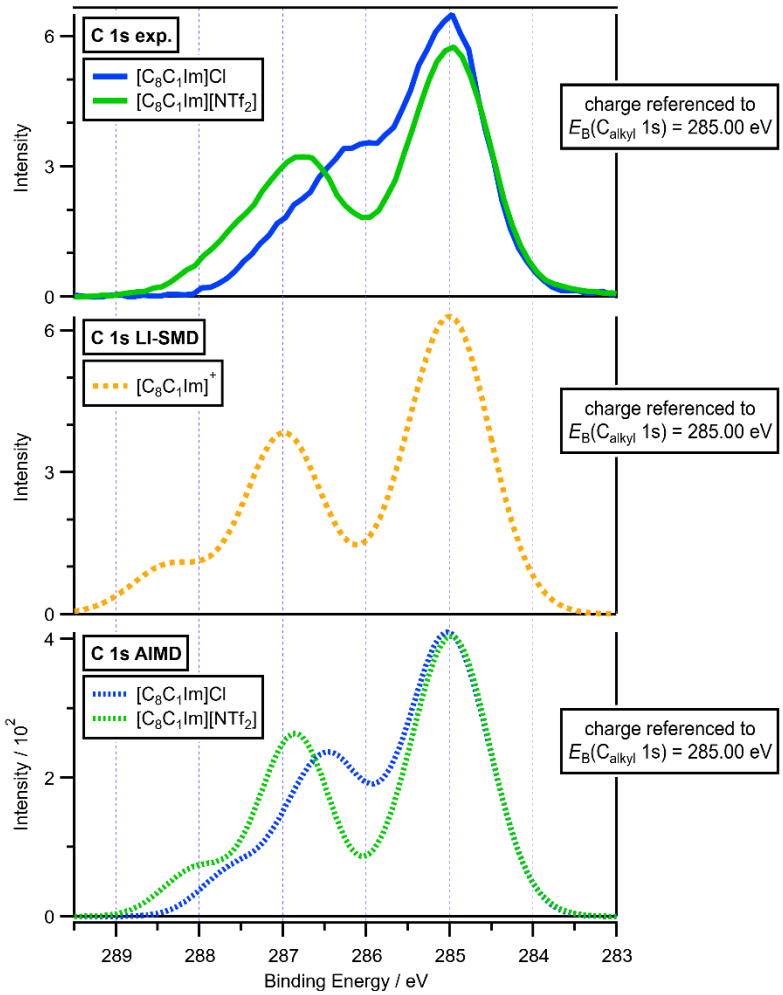


Figure S7. Experimental and calculated C 1s XPS for $[C_8C_1Im]^+$-containing ILs. (top) experimental C 1s XPS for $[C_8C_1Im]Cl$ and $[C_8C_1Im][NTf_2]$ ILs; (middle) calculated C 1s XPS for lone-ion-SMD of $[C_8C_1Im]^+$ cation (E_B(correction) = +8.48 eV); (bottom) calculated C 1s XPS for AIMD of $[C_8C_1Im]Cl$ and $[C_8C_1Im][NTf_2]$ (E_B corrections taken from reference [3]). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5.

7.2. Carbon: anions

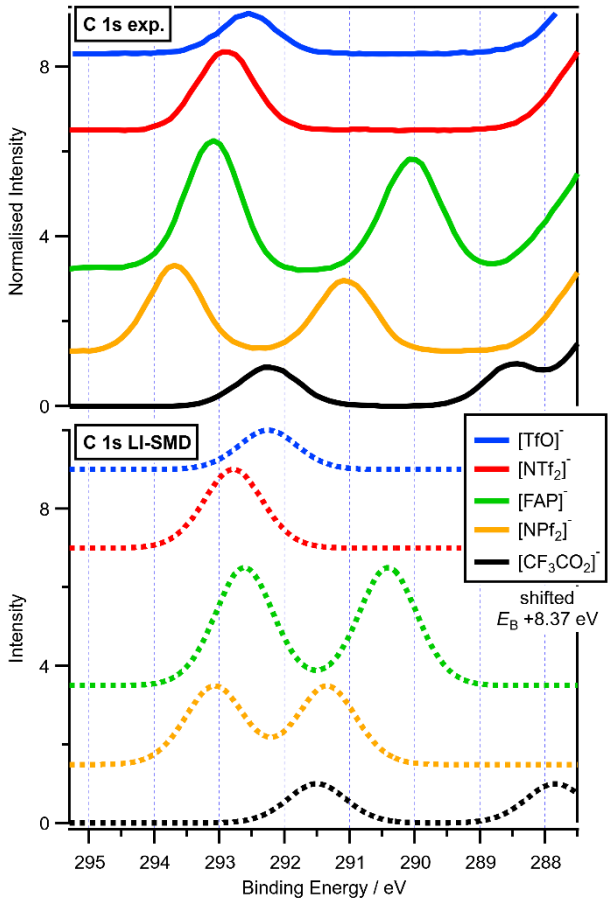


Figure S8. Experimental and calculated C 1s XPS and C-containing lone anions with large E_B and V_n. (top) experimental C 1s XPS of the ILs $[C_8C_1Im][TfO]$, $[C_8C_1Im][NTf_2]$, $[C_2C_1Im][FAP]$, $[C_8C_1Im][NPf_2]$ and $[C_8C_1Im][CF_3CO_2]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the cations $[TfO]^-$, $[NTf_2]^-$, $[FAP]^-$, $[NPf_2]^-$ and $[CF_3CO_2]^-$ (E_B(correction) = +8.37 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

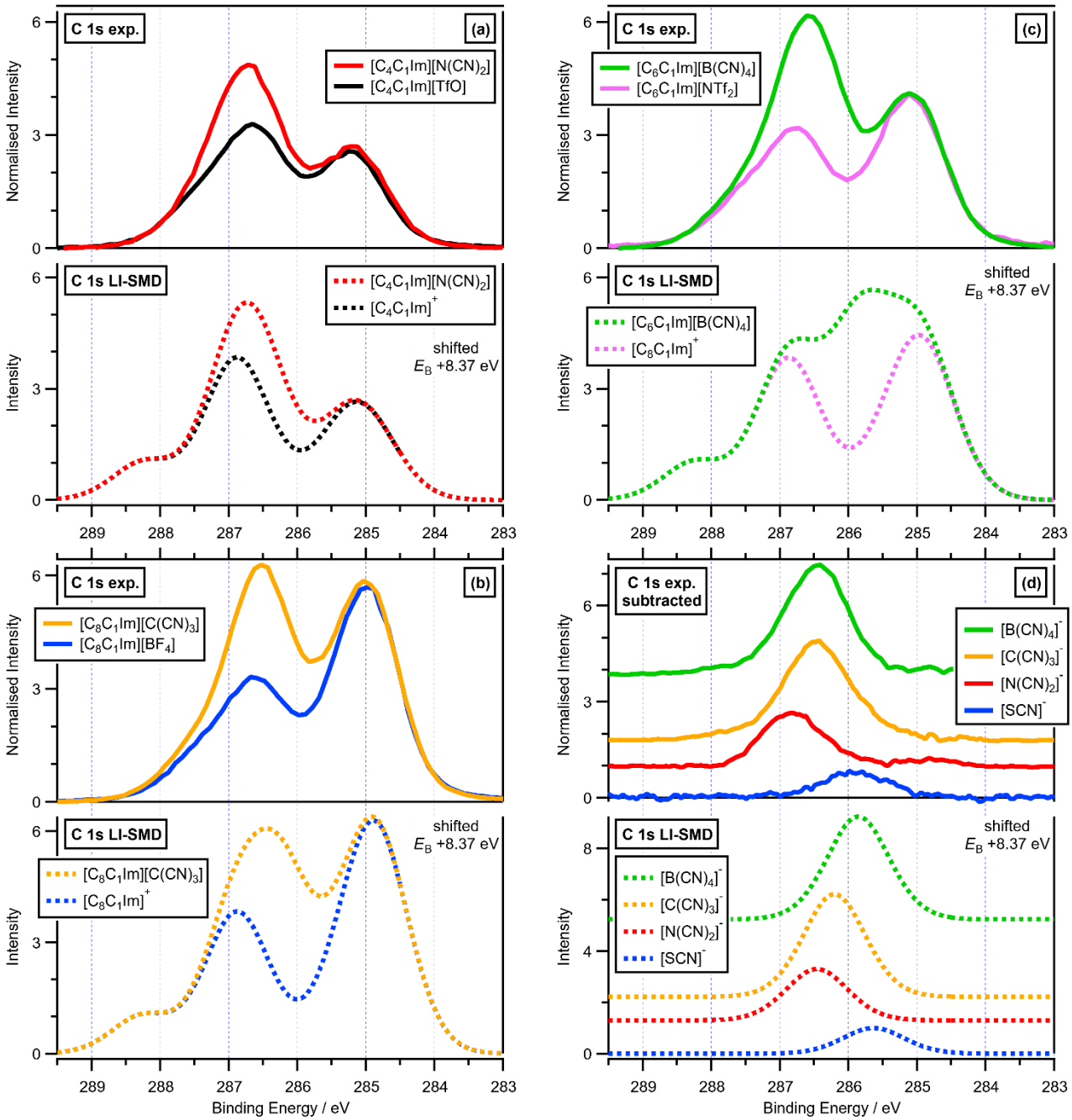


Figure S9. (a) (top) experimental C 1s XPS of the ILs $[C_4C_1Im][N(CN)_2]$ and $[C_4C_1Im][TfO]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_4C_1Im]^+ + [N(CN)_2]^-$ and $[C_4C_1Im]^+$ (E_B(correction) = +8.37 eV). (b) (top) experimental C 1s XPS of the ILs $[C_8C_1Im][C(CN)_3]$ and $[C_8C_1Im][BF_4]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_8C_1Im]^+ + [C(CN)_3]^-$ and $[C_8C_1Im]^+$ (E_B(correction) = +8.37 eV). (c) (top) experimental C 1s XPS of the ILs $[C_6C_1Im][B(CN)_4]$ and $[C_6C_1Im][NTf_2]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_6C_1Im]^+ + [B(CN)_4]^-$ and $[C_6C_1Im]^+$ (E_B(correction) = +8.37 eV). (d) lone-anions: (top) subtracted experimental C 1s XPS of the anions $[B(CN)_4]^-$, $[C(CN)_3]^-$, $[N(CN)_2]^-$ and $[SCN]^-$; (bottom) calculated C 1s XPS for lone-ion-SMD of the anions $[B(CN)_4]^-$, $[C(CN)_3]^-$, $[N(CN)_2]^-$ and $[SCN]^-$ (E_B(correction) = +8.37 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

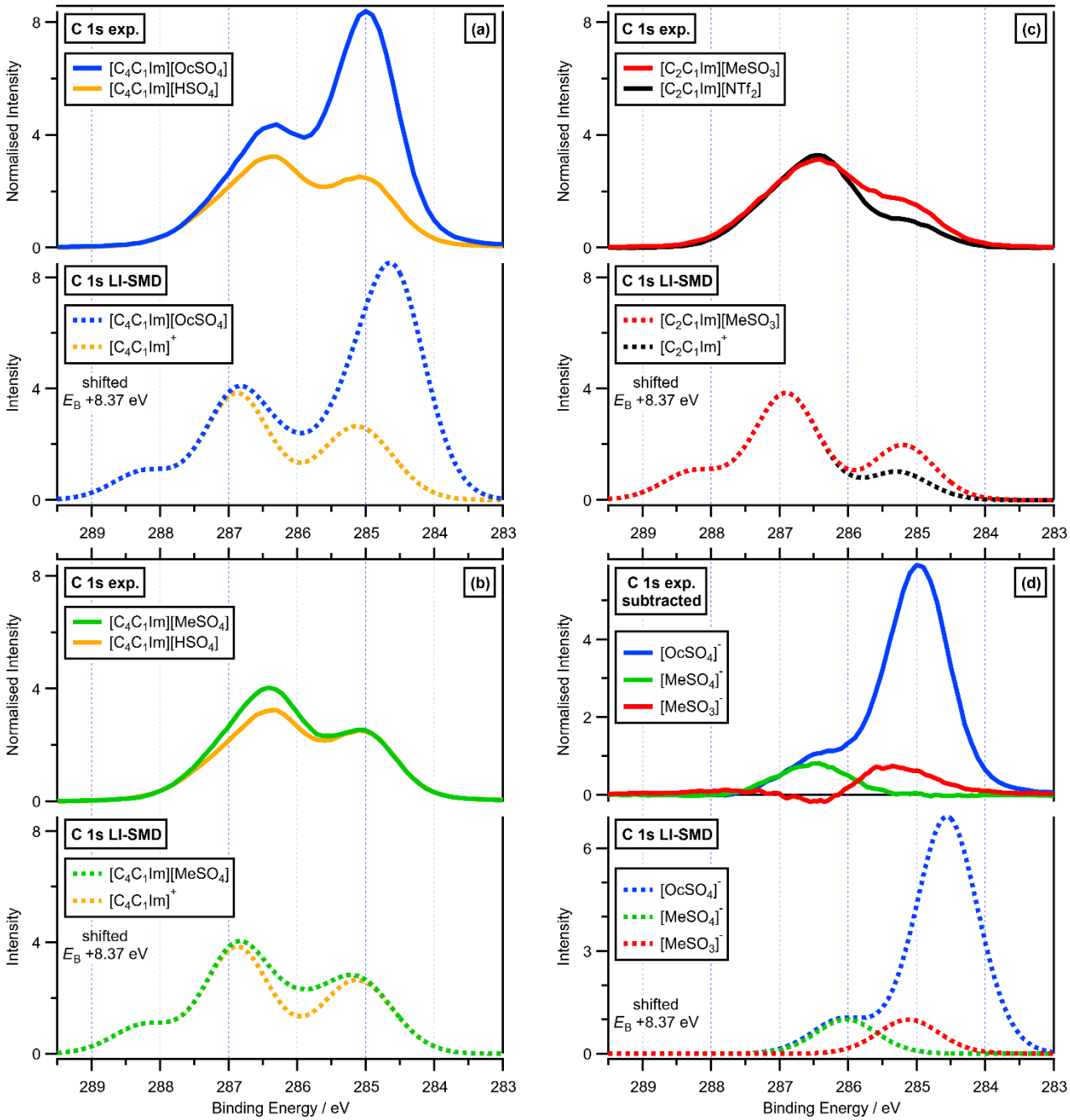


Figure S10. Experimental and calculated C 1s XPS for alkyl-SO_x-containing lone-ions. (a) (top) experimental C 1s XPS of the ILs $[C_4C_1Im][OcSO_4]$ and $[C_4C_1Im][HSO_4]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_4C_1Im]^+$ + $[OcSO_4]^-$ and $[C_4C_1Im]^+$ (E_B(correction) = +8.37 eV). (b) (top) experimental C 1s XPS of the ILs $[C_4C_1Im][MeSO_4]$ and $[C_4C_1Im][HSO_4]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_4C_1Im]^+$ + $[MeSO_4]^-$ and $[C_4C_1Im]^+$ (E_B(correction) = +8.37 eV). (c) (top) experimental C 1s XPS of the ILs $[C_2C_1Im][MeSO_3]$ and $[C_2C_1Im][NTf_2]$; (bottom) calculated C 1s XPS for lone-ion-SMD of the ions $[C_2C_1Im]^+$ + $[MeSO_3]^-$ and $[C_2C_1Im]^+$ (E_B(correction) = +8.37 eV). (d) anions; (top) subtracted experimental C 1s XPS of the anions $[OcSO_4]^-$, $[MeSO_4]^-$ and $[MeSO_3]^-$; (bottom) calculated C 1s XPS for lone-ion-SMD of the anions $[OcSO_4]^-$, $[MeSO_4]^-$ and $[MeSO_3]^-$ (E_B(correction) = +8.37 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

7.3. Nitrogen

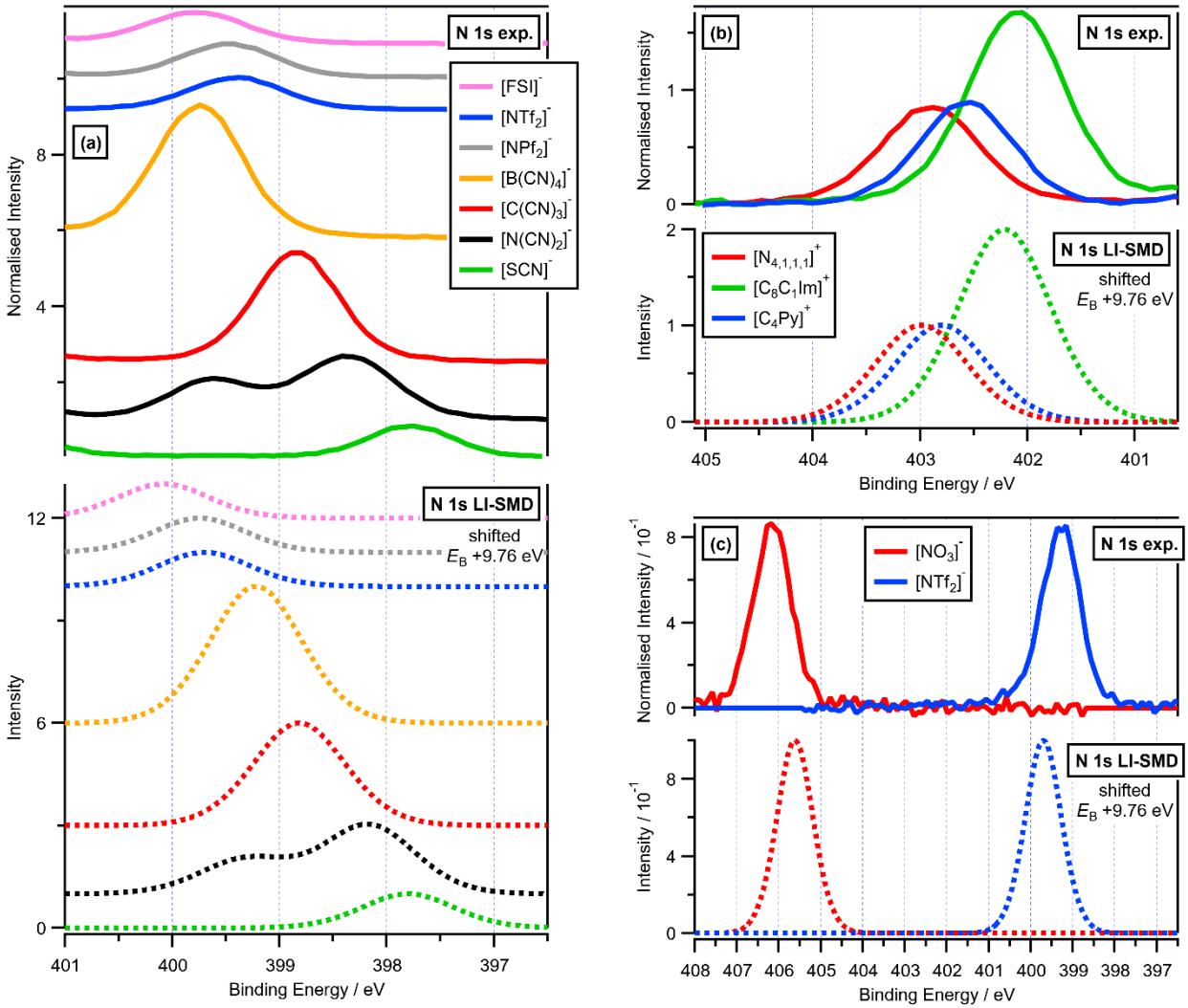


Figure S11. Experimental and calculated N 1s XPS for ILs and N-containing lone ions. (a) anions with small E_B and V_n; (top) experimental N 1s XPS of the ILs $[C_8C_1Im][FSI]$, $[C_8C_1Im][NTf_2]$, $[C_4C_1Im][NPf_2]$, $[C_6C_1Im][B(CN)_4]$, $[C_8C_1Im][C(CN)_3]$, $[C_4C_1Im][N(CN)_2]$ and $[C_8C_1Im][SCN]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the anions $[FSI]^-$, $[NTf_2]^-$, $[NPf_2]^-$, $[B(CN)_4]^-$, $[C(CN)_3]^-$, $[N(CN)_2]^-$ and $[SCN]^-$ (E_B(correction) = +9.76 eV). (b) cations; (top) experimental N 1s XPS of the ILs $[N_{4,1,1,1}][NTf_2]$, $[C_8C_1Im][NTf_2]$ and $[C_4Py][NTf_2]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the cations $[N_{4,1,1,1}]^+$, $[C_8C_1Im]^+$ and $[C_4Py]^{+\cdot}$ (E_B(correction) = +9.76 eV). (c) an anion with large E_B and V_n; (top) experimental N 1s XPS of the ILs $[P_{6,6,6,14}][NO_3]$ and $[C_8C_1Im][NTf_2]$; (bottom) calculated N 1s XPS for lone-ion-SMD of the anions $[NO_3]^-$ and $[NTf_2]^-$ (E_B(correction) = +9.76 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

7.4. Sulfur

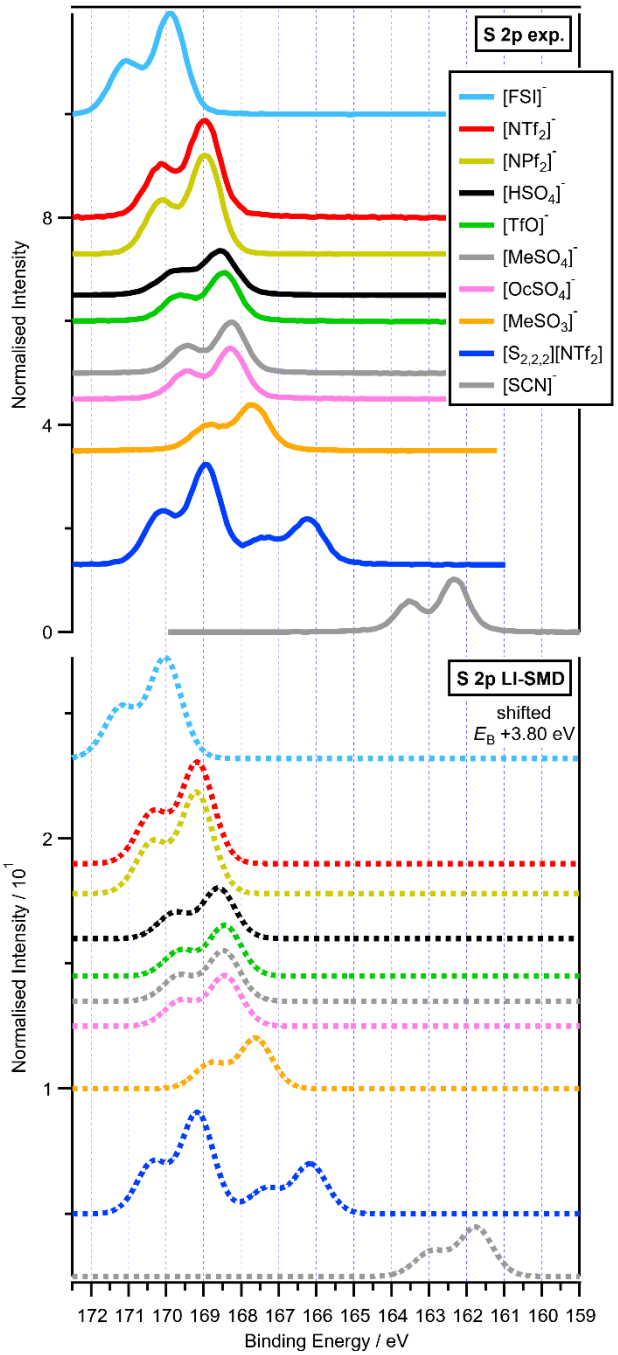


Figure S12. Experimental and calculated S 2p XPS for 10 ILs and the matching S-containing lone ions: (top) experimental S 2p XPS of the ILs $[C_8C_1Im][FSI]$, $[C_8C_1Im][NTf_2]$, $[C_4C_1Im][NPf_2]$, $[C_8C_1Im][HSO_4]$, $[C_8C_1Im][TfO]$, $[C_4C_1Im][MeSO_4]$, $[C_4C_1Im][OcSO_4]$, $[C_2C_1Im][MeSO_3]$, $[S_{2,2,2}][NTf_2]$ and $[C_8C_1Im][SCN]$; (bottom) calculated S 2p XPS for lone-ion-SMD of the ions $[FSI]^-$, $[NTf_2]^-$, $[NPf_2]^-$, $[HSO_4]^-$, $[TfO]^-$, $[MeSO_4]^-$, $[OcSO_4]^-$, $[MeSO_3]^-$, sum of $[S_{2,2,2}]^+$ and $[NTf_2]^-$ and $[SCN]^-$ (E_B(correction) = +3.80 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

7.5. Oxygen

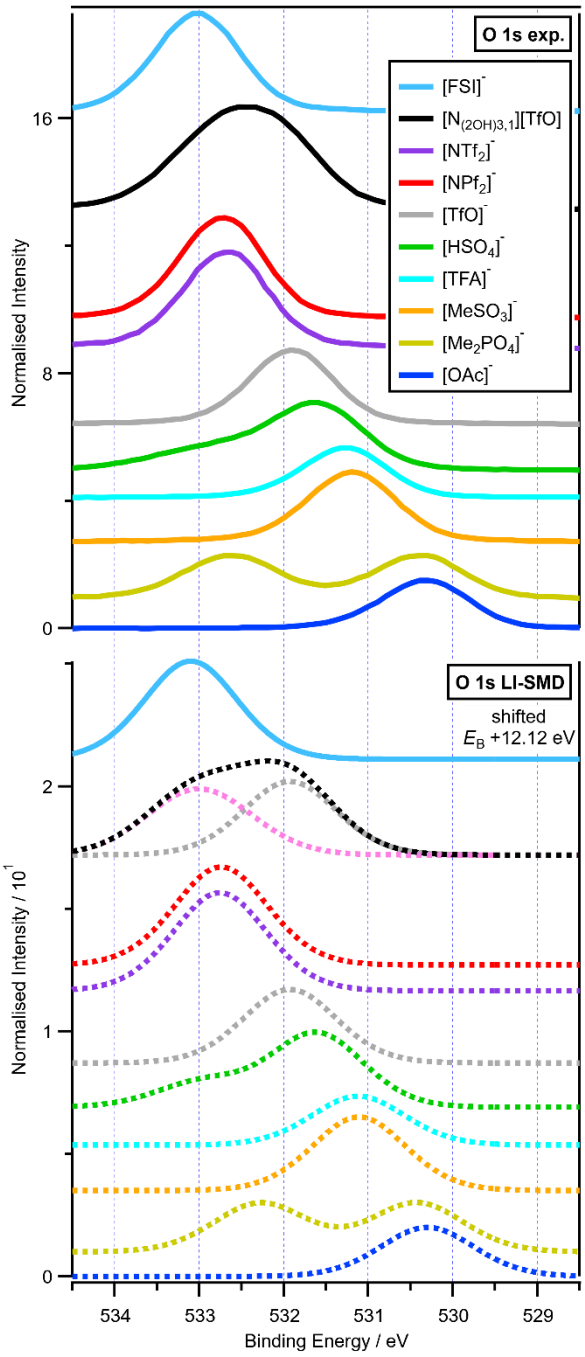


Figure S13. Experimental and calculated O 1s XPS for 10 ILs and the matching O-containing lone ions: (top) experimental O 1s XPS of the ILs $[C_8C_1Im][FSI]$, $[N_{(2OH)3,1}][TfO]$, $[C_8C_1Im][NTf_2]$, $[C_4C_1Im][NPf_2]$, $[C_8C_1Im][TfO]$, $[C_8C_1Im][HSO_4]$, $[C_8C_1Im][CF_3CO_2]$, $[C_2C_1Im][MeSO_3]$, $[C_4C_1Im][Me_2PO_4]$ and $[C_8C_1Im][CH_3CO_2]$; (bottom) calculated O 1s XPS for lone-ion-SMD of the ions $[FSI]^-$, $[N_{(2OH)3,1}]^+$ and $[TfO]^-$ (also including their sum), $[NTf_2]^-$, $[NPf_2]^-$, $[TfO]^-$, $[HSO_4]^-$, $[CF_3CO_2]^-$, $[MeSO_3]^-$, $[Me_2PO_4]^-$ and $[CH_3CO_2]^-$ (E_B(correction) = +12.12 eV). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5. Traces are vertically offset for clarity.

7.6. Fluorine

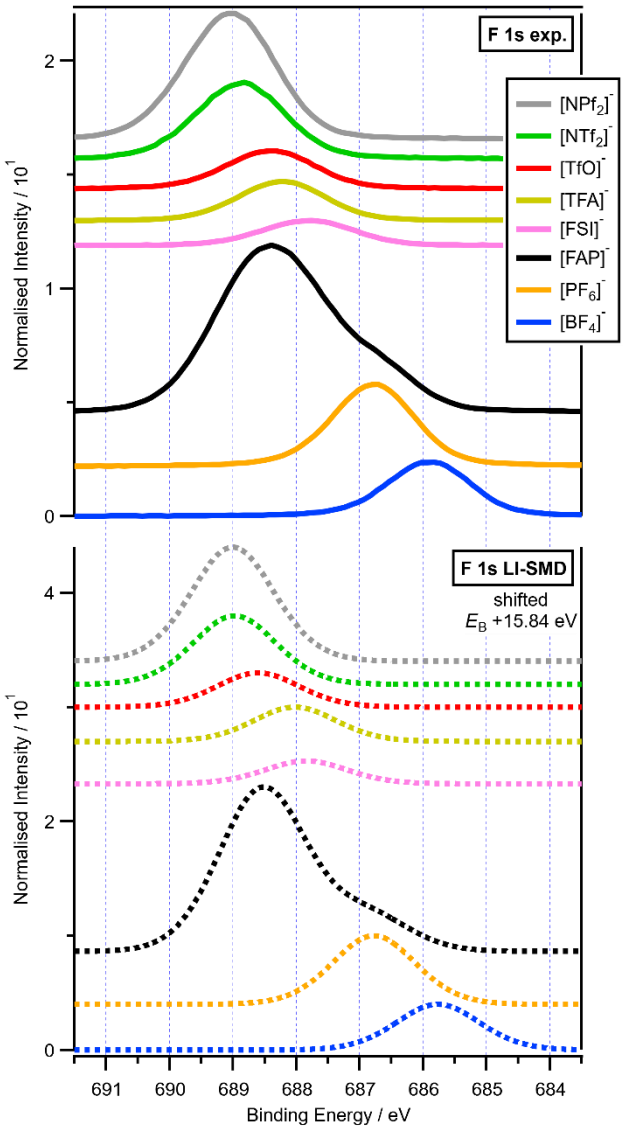


Figure S14. Experimental and calculated F 1s XPS for $[C_nC_1Im][A]$ where $[A]^-$ = $[BF_4]^-$, $[PF_6]^-$, $[FAP]^-$, $[FSI]^-$, $[CF_3CO_2]^-$, $[TfO]^-$, $[NTf_2]^-$ and $[NPf_2]^-$: (top) experimental F 1s XPS (vertically offset for clarity); (bottom) calculated F 1s XPS for lone-ion-SMD of the anions (E_B(correction) = +15.84 eV, vertically offset for clarity). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5.

7.7. Chlorine

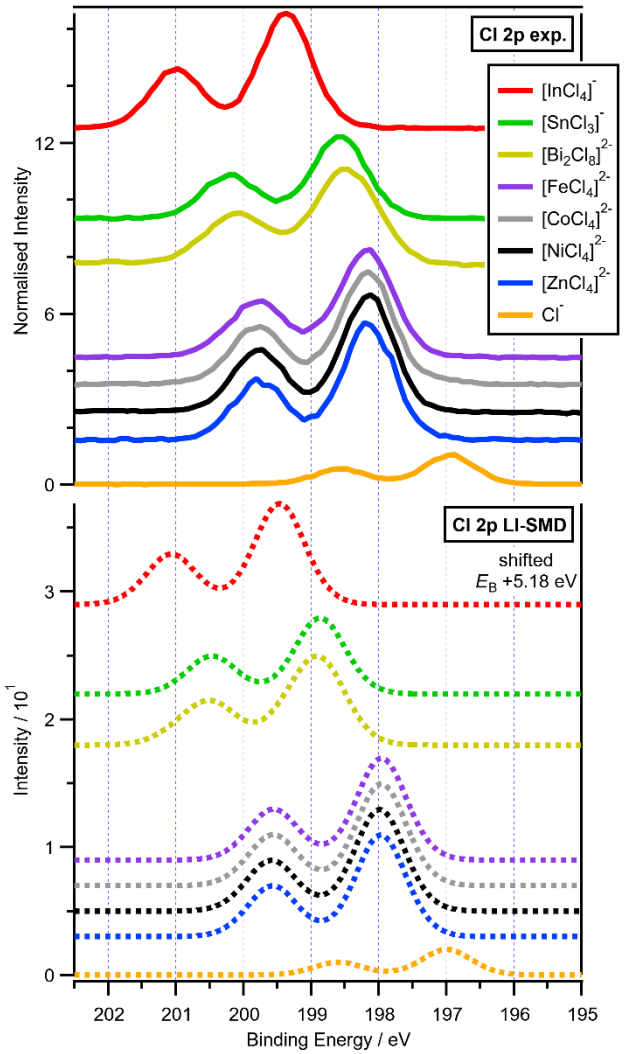


Figure S15. Experimental and calculated Cl 2p XPS for $[C_8C_1Im][A]$ where A = Cl^-, $[ZnCl_4]^{2-}$, $[NiCl_4]^{2-}$, $[CoCl_4]^{2-}$, $[FeCl_4]^{2-}$, $[Bi_2Cl_8]^{2-}$, $[SnCl_3]^-$ and $[InCl_4]^-$: (top) experimental Cl 2p XPS (vertically offset for clarity); (bottom) calculated Cl 2p XPS for lone-ion-SMD of the anions (E_B(correction) = +5.18 eV, vertically offset for clarity). Experimental XP spectra are area normalised and charge referenced using methods given in ESI Section 5.

8. Results: Experimental versus DFT calculated XP spectra for a chlorobismuthate IL

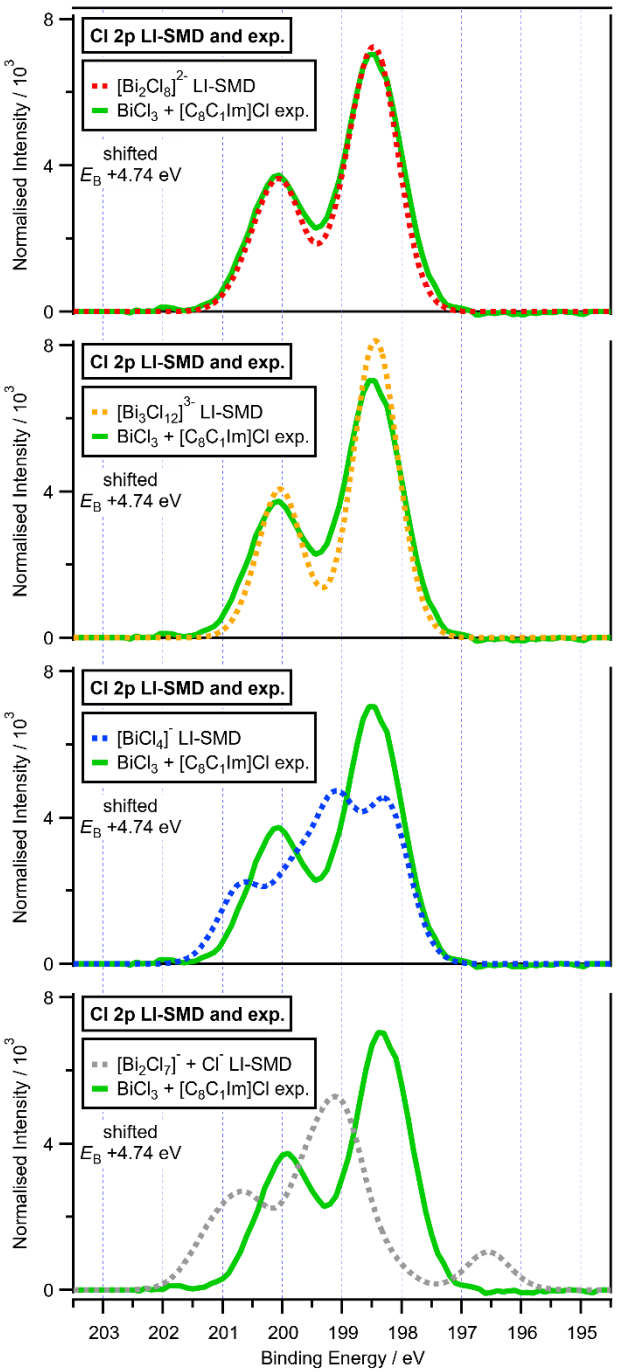


Figure S16. Experimental Cl 2p XPS for x = 0.5 $BiCl_3$ dissolved in $[C_8C_1Im]Cl$ (all four graphs) and calculated Cl 2p XPS for lone-ion-SMD of the anions (E_B(correction) = +4.74 eV): (top) $[Bi_2Cl_8]^{2-}$; (upper middle) $[Bi_3Cl_{12}]^{3-}$; (lower middle) $[BiCl_4]^-$, (bottom) $[Bi_2Cl_7]^-$ + Cl^-. The experimental XP spectrum is charge referenced using methods given in ESI Section 5.

9. Results. Effect of basis set choice

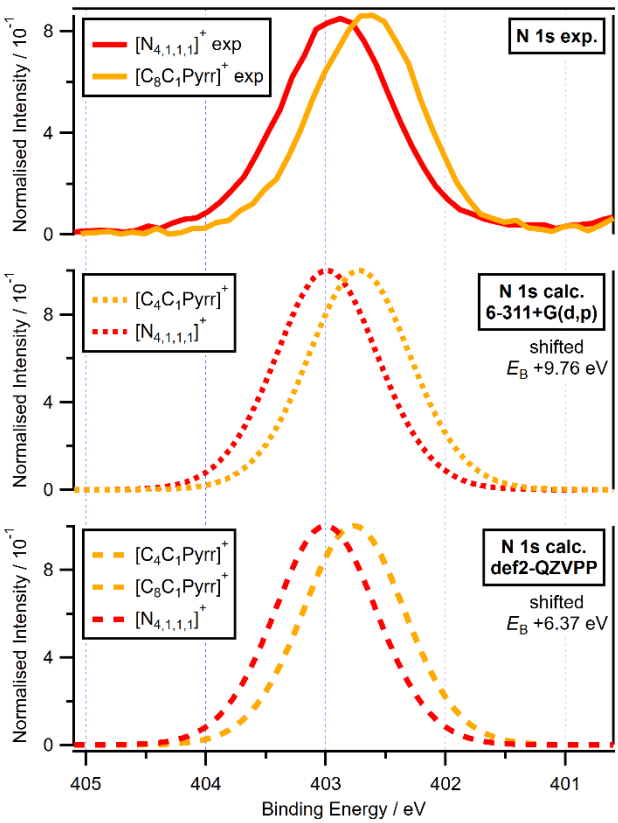


Figure S17. (top) Experimental N 1s XPS for $[N_{4,1,1,1}][NTf_2]$ and $[C_8C_1Pyrr][NTf_2]$. (middle) Calculated N 1s XPS for lone-ion-SMD of the cations: $[N_{4,1,1,1}]^+$ and $[C_8C_1Pyrr]^+$ with the 6-311+G(d,p) basis set (E_B(correction) = +9.76 eV). (bottom) Calculated N 1s XPS for lone-ion-SMD of the cations: $[N_{4,1,1,1}]^+$, $[C_4C_1Pyrr]^+$ and $[C_8C_1Pyrr]^+$ with the def2-QZVPP basis set taken from reference [5] (E_B(correction) = +6.37 eV). The experimental XP spectra are charge referenced using methods given in ESI Section 5.

10. References

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