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

Hydrogen bonding and π-π interactions in imidazolium-chloride ionic liquid clusters

Supplementary Information

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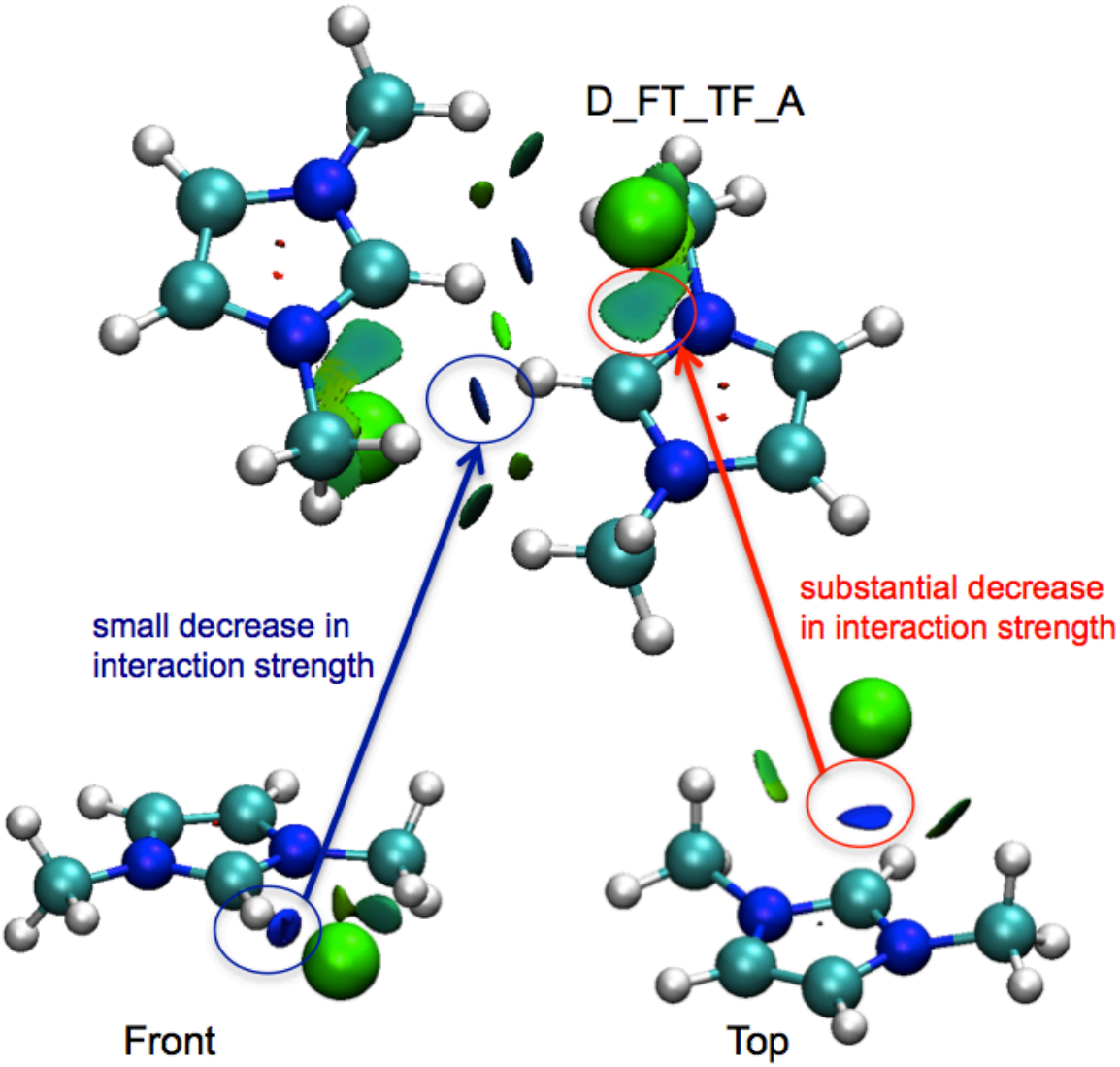

Figure S1. Decrease in interaction strength on moving from the IPs to the IP-dimers visualised using NCIPLOT for the D_FT_TF_A IP-dimer.

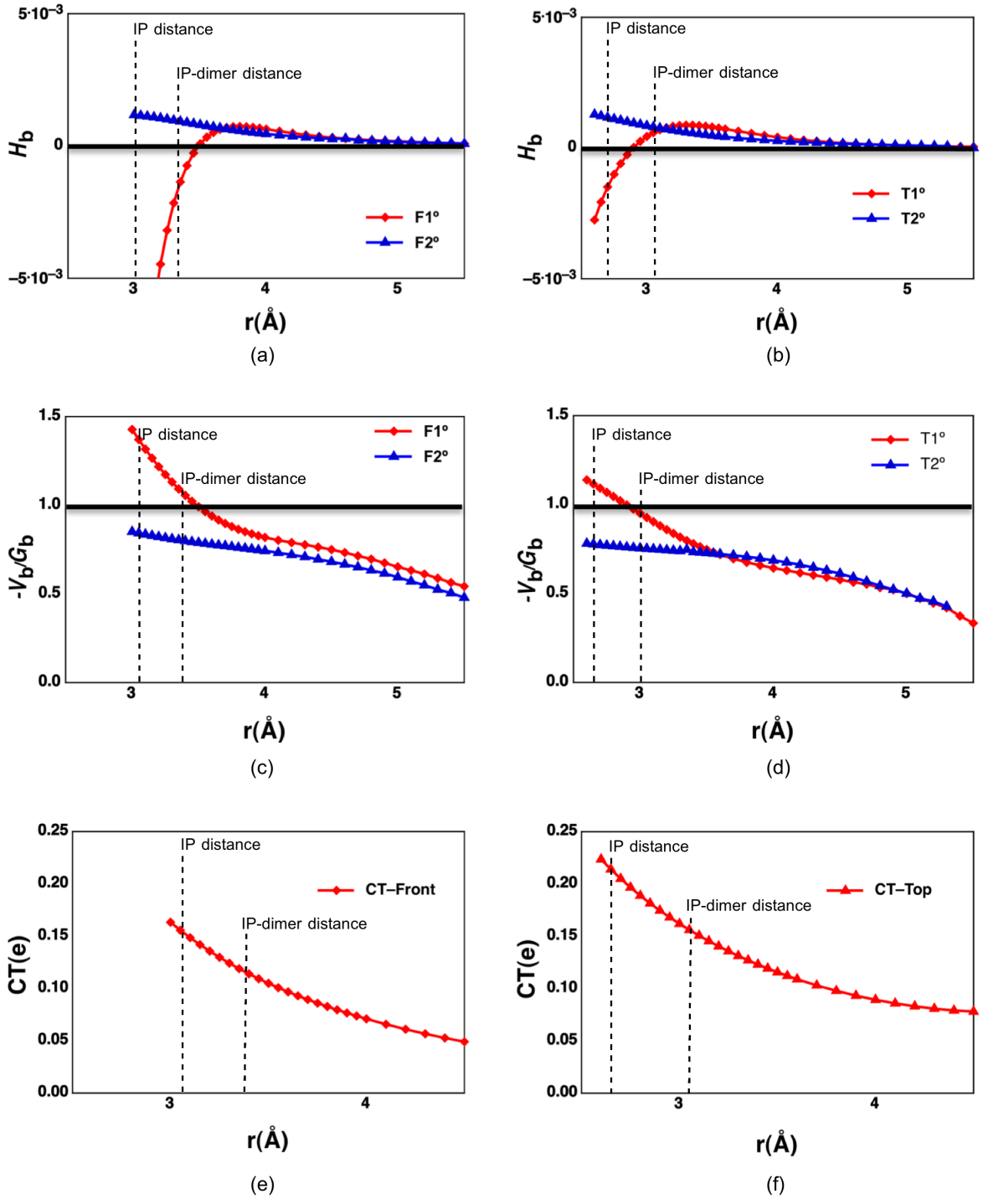

Figure S2. Plots of (a) H_b for F1º (red) and F2º (blue) H-bonding interactions, (b) H_b for T1º (red) and T2º (blue) top A-π⁺-D and H-bonding interactions, (c) $-V_b/G_b$ for F1º (red) and F2º (blue) H-bonding interactions, (d)) $-V_b/G_b$ for T1º (red) and T2º (blue), top A-π⁺-D and H-bonding interactions as a function of distance (r). CT (QTAIM) for the (e) front and (f) top IP conformers as a function of distance. Representative IP and IP-dimer positions are indicated.

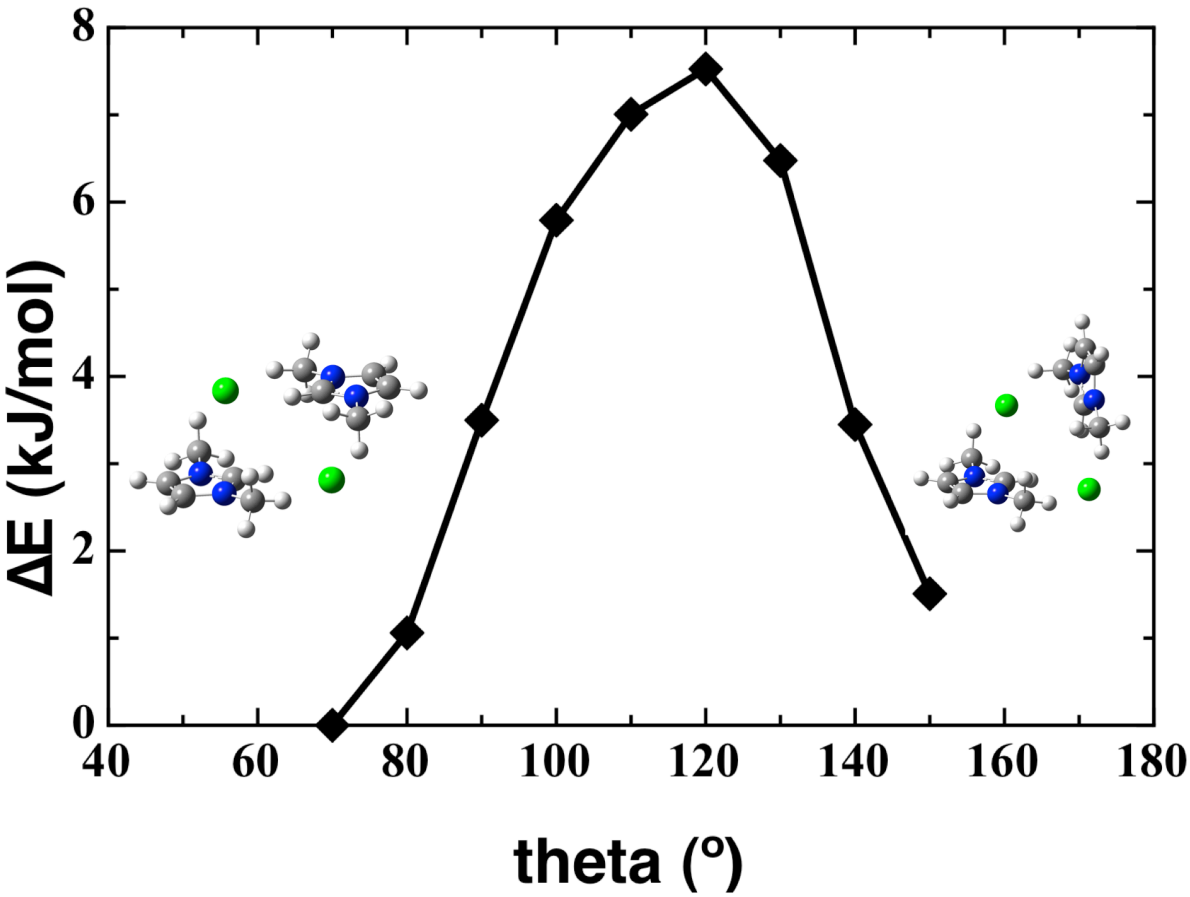

Figure S3. Potential energy profile on moving from D_FT_TF_A to D_FT_TF_T.

The potential energy profile has been computed using a relaxed scan of the angle between one of the Cl^- anions and the C^2–H moiety of a cation. Eight steps in 10.0º have been computed starting from D_FT_TF_A and moving to D_FT_TF_T. The calculations were performed at the B3LYP-D3/aug-cc-pVTZ level.

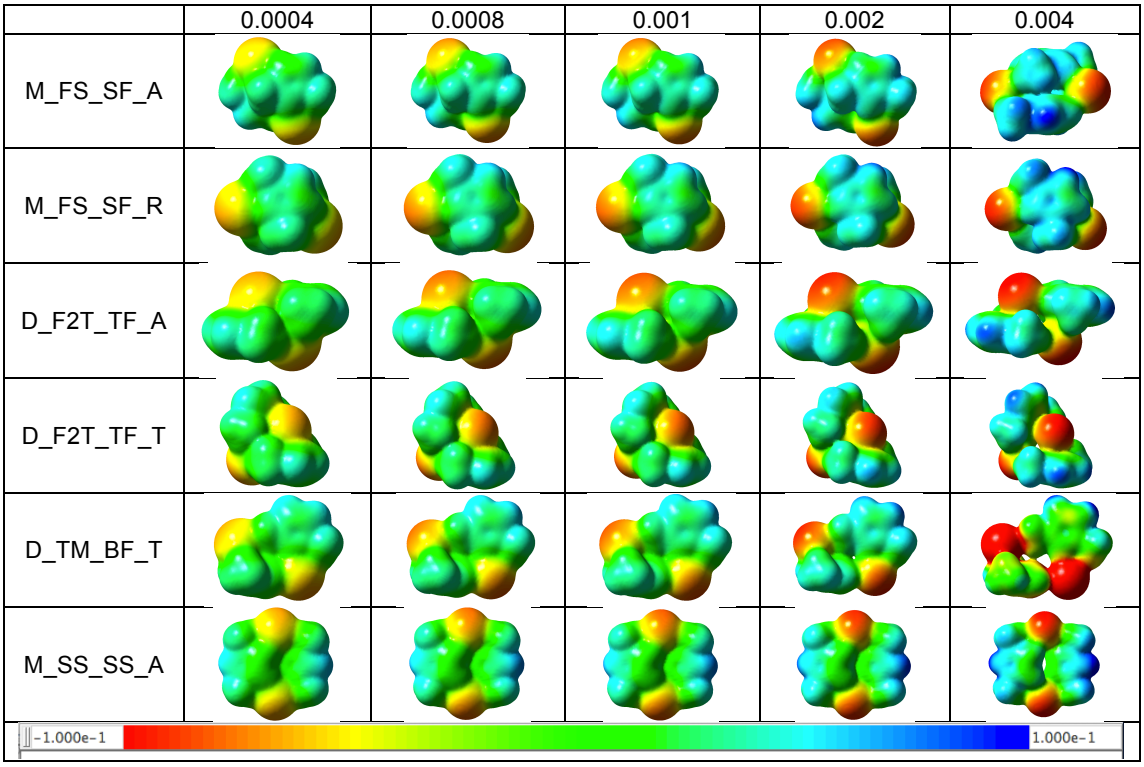

Figure S4. Electrostatic surface potentials (ESPs) of the $[C_1C_1im]_2Cl_2$ IP-dimers plotted on various isosurfaces contours in au (electrons/bohr^3). Scale provided below in eV.

Table S1: Partial atomic charges obtained using the NBO partitioning scheme for the $[C_1C_1im]Cl$ IP conformers. Associated figure showing atomic numbering is shown below..

Nr	Atom	front	side	back	top
1	C2	0.25413	0.23527	0.21527	0.32149
2	C4	-0.03987	-0.06379	-0.01704	-0.04118
3	C5	-0.0508	-0.01238	-0.01704	-0.04115
4	H2	0.28901	0.21932	0.21745	0.25199
5	H4	0.22838	0.23027	0.29629	0.22483
6	H5	0.22698	0.30781	0.29637	0.22483
7	N3	-0.32053	-0.3184	-0.3163	-0.34591
8	N1	-0.33184	-0.2986	-0.3163	-0.34591
9	C6	-0.38964	-0.36627	-0.36505	-0.37257
10	H61	0.2035	0.21697	0.22266	0.25111
11	H62	0.20349	0.21668	0.22256	0.20221
12	H63	0.28016	0.21361	0.20791	0.20609
13	C7	-0.36766	-0.40865	-0.36505	-0.3726
14	H71	0.23949	0.20383	0.20791	0.20606
15	H72	0.20886	0.29644	0.22259	0.20224
16	H73	0.20884	0.19995	0.22264	0.25114
17	Cl	-0.8425	-0.87207	-0.93486	-0.82265

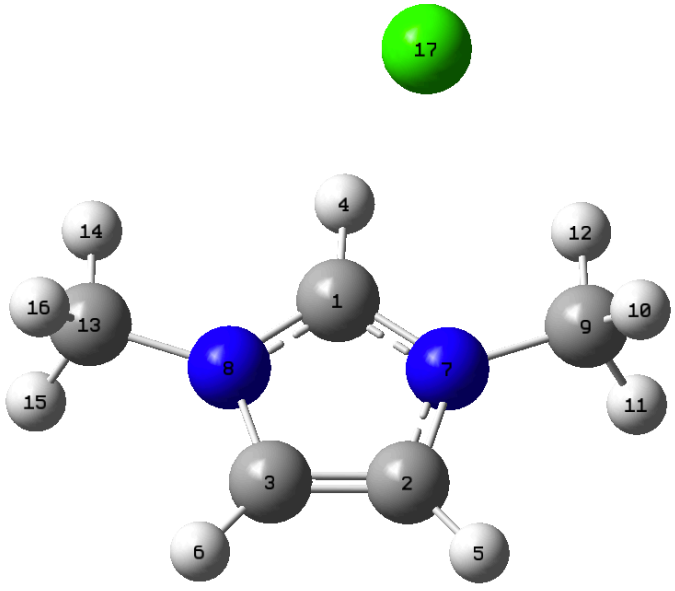

Table S2: Partial atomic charges obtained using the NBO partitioning scheme for each of the $[C_1C_1im]_2Cl_2$ IP-dimer conformers.

	Atom	M_FS_SF_A	M_FS_SF_R	D_F2T_TF_A	D_F2T_TF_T	M_SS_SS_A	D_TM_BF_T
	C2	0.2461	0.24001	0.29599	0.3013	0.23021	0.30209
	C4	-0.03024	-0.01853	-0.02906	-0.03044	-0.0386	-0.04142
	C5	-0.0624	-0.06799	-0.03704	-0.03903	-0.03862	-0.04154
	H2	0.28531	0.2861	0.28784	0.28734	0.21681	0.2505
	H4	0.28325	0.27359	0.22389	0.22337	0.2787	0.26027
	H5	0.22855	0.22442	0.22372	0.22329	0.27873	0.26025
	N3	-0.32334	-0.31883	-0.32262	-0.32322	-0.30612	-0.33219
	N1	-0.31927	-0.32105	-0.31807	-0.31964	-0.30614	-0.33221
Cat_1	C6	-0.3993	-0.39199	-0.37321	-0.37339	-0.39166	-0.37257
	H61	0.26534	0.20981	0.21367	0.19905	0.20563	0.20596
	H62	0.21009	0.26725	0.24594	0.21472	0.28062	0.24357
	H63	0.20821	0.2089	0.19984	0.24634	0.1987	0.20866
	C7	-0.38723	-0.3881	-0.38545	-0.3835	-0.39168	-0.37255
	H71	0.27001	0.27328	0.26335	0.26284	0.28062	0.20601
	H72	0.20472	0.20602	0.19798	0.19829	0.20562	0.20858
	H73	0.20546	0.19737	0.2106	0.20877	0.19871	0.24352
	C2	0.2461	0.23985	0.29599	0.30151	0.23021	0.24816
	C4	-0.03024	-0.02078	-0.03704	-0.03055	-0.0386	-0.04473
	C5	-0.0624	-0.06194	-0.02906	-0.03903	-0.03862	-0.0407
	H2	0.28531	0.28609	0.28784	0.28735	0.21681	0.28693
	H4	0.28325	0.27357	0.22372	0.22335	0.2787	0.22685
	H5	0.22855	0.22359	0.22389	0.22329	0.27873	0.23046
	N3	-0.32334	-0.31909	-0.31807	-0.32332	-0.30612	-0.31845
	N1	-0.31927	-0.32287	-0.32262	-0.31963	-0.30614	-0.3171
Cat_2	C6	-0.3993	-0.392	-0.38545	-0.37341	-0.39166	-0.38845
	H61	0.26534	0.20983	0.26335	0.21463	0.20563	0.27676
	H62	0.20821	0.26723	0.2106	0.19906	0.1987	0.20333
	H63	0.21009	0.20891	0.19798	0.24639	0.28062	0.20335
	C7	-0.38723	-0.38808	-0.37321	-0.38357	-0.39168	-0.37996
	H71	0.27001	0.27325	0.21367	0.2629	0.28062	0.24457
	H72	0.20546	0.20599	0.19984	0.20885	0.19871	0.22554
	H73	0.20472	0.19741	0.24594	0.19822	0.20562	0.22518
	Cl1	-0.88526	-0.88062	-0.89737	-0.87785	-0.90154	-0.89531
	Cl2	-0.88526	-0.88059	-0.89737	-0.91427	-0.90154	-0.88337

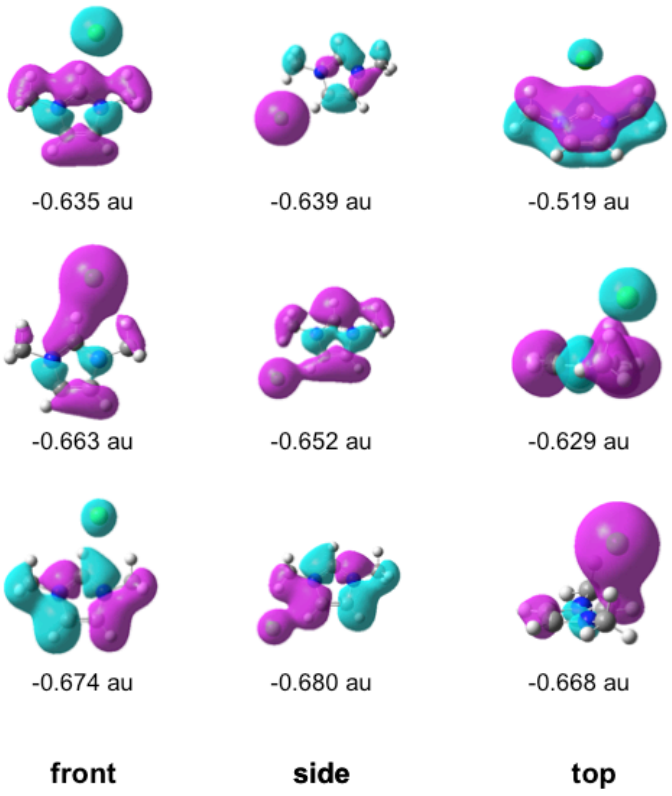

Figure S5. Comparison of lower energy MOs for the front, side and top $[C_1C_1im]Cl$ IPs.

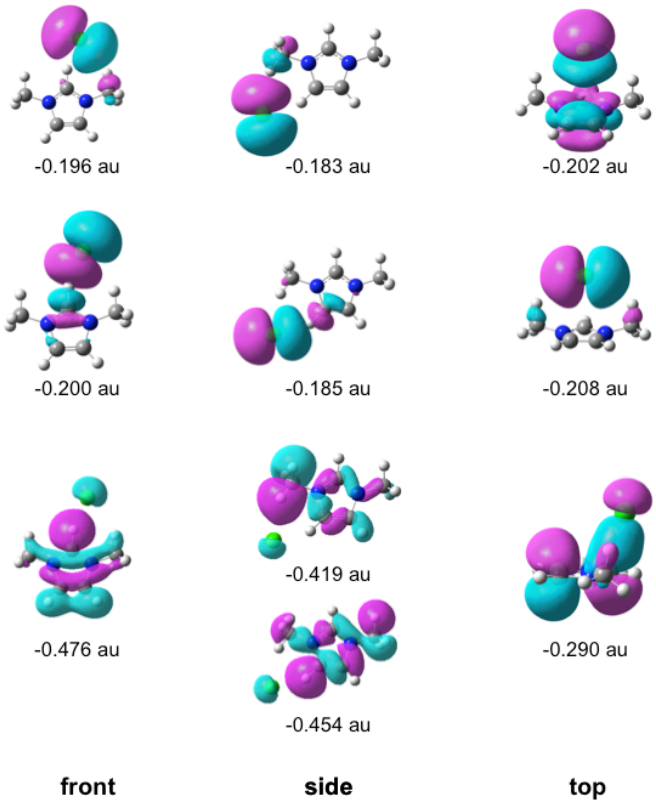

Figure S6. Comparison of higher energy MOs for the front, side and top $[C_1C_1im]Cl$ IPs.