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

Mutual solubilities between water and non-aromatic sulfonium-, ammonium- and phosphonium- hydrophobic ionic liquids†

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Electronic Supporting Information

Table S1a. Experimental mole fraction solubility of water, x_w, in the studied ILs as a function of temperature along with its standard deviation, σ.

T/K	$[S_{221}][NTf_2]$	$[S_{222}][NTf_2]$	$[N_{4111}][NTf_2]$	$[N_{4441}][NTf_2]$	$[N_{8881}][NTf_2]$	$[P_{8881}][NTf_2]$
	$x_w \pm \sigma$					
288.15	0.2284 ± 0.0003	0.1841 ± 0.0001	0.2104 ± 0.0005	0.0979 ± 0.0009	0.0169 ± 0.0005	0.0132 ± 0.0004
293.15	0.2420 ± 0.0003	0.1936 ± 0.0008	0.2243 ± 0.0003	0.1023 ± 0.0005	0.0215 ± 0.0006	0.0163 ± 0.0003
298.15	0.2561 ± 0.0005	0.2065 ± 0.0006	0.2396 ± 0.0001	0.1089 ± 0.0002	0.0272 ± 0.0006	0.0195 ± 0.0004
303.15	0.2705 ± 0.0001	0.2177 ± 0.0004	0.2513 ± 0.0009	0.1179 ± 0.0001	0.0354 ± 0.0004	0.0240 ± 0.0008
308.15	0.2854 ± 0.0008	0.2324 ± 0.0001	0.2723 ± 0.0003	0.1252 ± 0.0003	0.0426 ± 0.0006	0.0316 ± 0.0004
313.15	0.3007 ± 0.0006	0.2455 ± 0.0008	0.2857 ± 0.0003	0.1329 ± 0.0007	0.0508 ± 0.0002	0.0416 ± 0.0005
318.15	0.3163 ± 0.0004	0.2559 ± 0.0003	0.2995 ± 0.0008	0.1399 ± 0.0005	0.0597 ± 0.0002	0.0474 ± 0.0004

Table S1b. Experimental mass fraction solubility of water, w_w, in the studied ILs as a function of temperature along with its standard deviation, σ.

T/K	$[S_{221}][NTf_2]$	$[S_{222}][NTf_2]$	$[N_{4111}][NTf_2]$	$[N_{4441}][NTf_2]$	$[N_{1888}][NTf_2]$	$[P_{1888}][NTf_2]$
	$w_w \pm \sigma$					
288.15	0.0137 ± 0.00001	0.0101 ± 0.00001	0.0120 ± 0.00002	0.0041 ± 0.00003	0.0005 ± 0.00001	0.0004 ± 0.00001
293.15	0.0147 ± 0.00001	0.0107 ± 0.00004	0.0130 ± 0.00001	0.0043 ± 0.00002	0.0006 ± 0.00002	0.0004 ± 0.00001
298.15	0.0158 ± 0.00002	0.0116 ± 0.00003	0.0141 ± 0.00001	0.0046 ± 0.00001	0.0008 ± 0.00002	0.0005 ± 0.00001
303.15	0.0170 ± 0.00001	0.0124 ± 0.00002	0.0150 ± 0.00004	0.0050 ± 0.00001	0.0010 ± 0.00001	0.0007 ± 0.00002
308.15	0.0183 ± 0.00004	0.0135 ± 0.00001	0.0167 ± 0.00001	0.0053 ± 0.00001	0.0012 ± 0.00002	0.0009 ± 0.00001
313.15	0.0197 ± 0.00003	0.0145 ± 0.00004	0.0179 ± 0.00001	0.0057 ± 0.00003	0.0015 ± 0.00001	0.0012 ± 0.00001
318.15	0.0212 ± 0.00002	0.0153 ± 0.00001	0.0191 ± 0.00004	0.0061 ± 0.00002	0.0018 ± 0.00001	0.0013 ± 0.00001

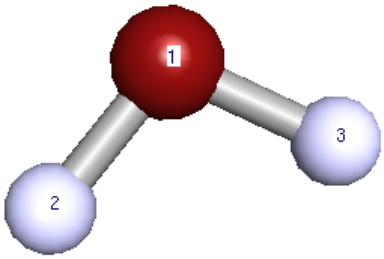
Table S2a. Experimental mole fraction solubility of the studied ILs, x_{IL}, in water as a function of temperature along with its standard deviation, σ.

T/K	$[S_{221}][NTf_2]$	$[S_{222}][NTf_2]$	$[N_{4111}][NTf_2]$	$[N_{4441}][NTf_2]$
	$10^2 \cdot (x_{IL} \pm \sigma)$	$10^3 \cdot (x_{IL} \pm \sigma)$	$10^3 \cdot (x_{IL} \pm \sigma)$	$10^3 \cdot (x_{IL} \pm \sigma)$
288.15	0.1194 ± 0.0001	0.6436 ± 0.0008	0.9250 ± 0.0001	0.1190 ± 0.0001
293.15	0.1228 ± 0.0001	0.6596 ± 0.0009	0.9353 ± 0.0004	0.1286 ± 0.0002
298.15	0.1266 ± 0.0001	0.6778 ± 0.0008	0.9491 ± 0.0005	0.1395 ± 0.0002
303.15	0.1308 ± 0.0009	0.6983 ± 0.0006	0.9664 ± 0.0005	0.1518 ± 0.0001
308.15	0.1354 ± 0.0002	0.7211 ± 0.0004	0.9872 ± 0.0006	0.1656 ± 0.0007
313.15	0.1405 ± 0.0003	0.7466 ± 0.0008	1.0116 ± 0.0006	0.1810 ± 0.0005
318.15	0.1461 ± 0.0004	0.7747 ± 0.0003	1.0399 ± 0.0009	0.1981 ± 0.0006

Table S2b. Experimental mass fraction solubility of the studied ILs, w_{IL}, in water as a function of temperature along with its standard deviation, σ.

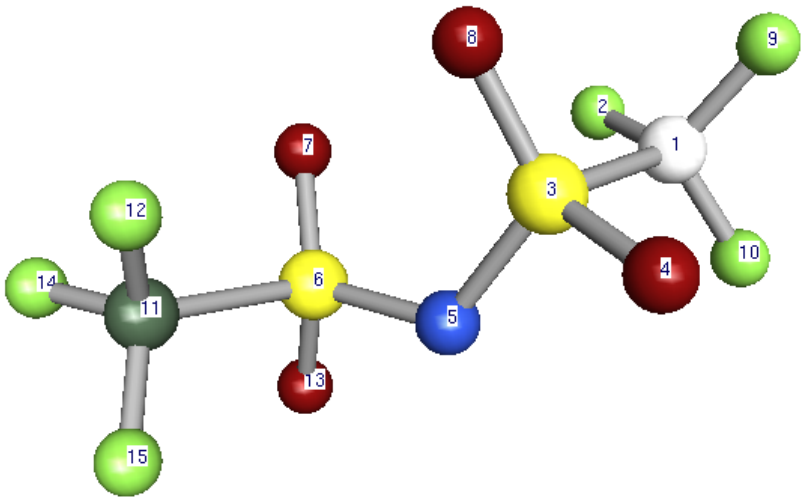
T/K	$[S_{221}][NTf_2]$	$[S_{222}][NTf_2]$	$[N_{4111}][NTf_2]$	$[N_{4441}][NTf_2]$
			$w_{IL} \pm \sigma$	
288.15	0.0249 ± 0.00002	0.0141 ± 0.00018	0.0200 ± 0.00002	0.0032 ± 0.00003
293.15	0.0256 ± 0.00002	0.0144 ± 0.00020	0.0202 ± 0.00009	0.0034 ± 0.00005
298.15	0.0264 ± 0.00002	0.0148 ± 0.00018	0.0205 ± 0.00011	0.0037 ± 0.00005
303.15	0.0272 ± 0.00019	0.0153 ± 0.00013	0.0208 ± 0.00011	0.0040 ± 0.00003
308.15	0.0282 ± 0.00004	0.0157 ± 0.00009	0.0213 ± 0.00013	0.0044 ± 0.00019
313.15	0.0292 ± 0.00006	0.0163 ± 0.00018	0.0218 ± 0.00020	0.0048 ± 0.00013
318.15	0.0304 ± 0.00009	0.0169 ± 0.00007	0.0224 ± 0.00002	0.0053 ± 0.00016

Table S3. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for H_2O.



Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	8	O	0.6391	-0.0279	0.4947	-0.948	5.6933	0
2	1	H	0.1598	0.0324	-0.3698	0.474	0	1.9255
3	1	H	-0.7990	-0.0045	-0.1249	0.474	0	1.9252
Total							5.6933	3.8506

Table S4. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[NTf_2]$- anion.



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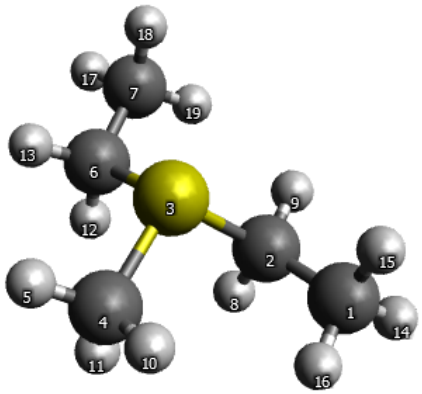
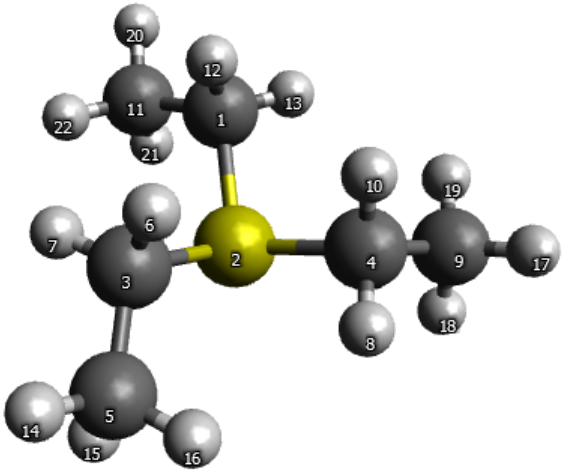
Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	6	C	-0.3638	-0.0445	2.6363	0.867	0	0
2	9	F	-1.4434	-0.7669	2.2879	-0.353	0	0
3	16	S	0.8690	0.0948	1.1568	2.195	0	0
4	8	O	1.8978	1.0554	1.6514	-0.944	0.5086	0
5	7	N	-0.0011	0.8858	0.0003	-1.219	0.6511	0
6	16	S	-0.8696	0.0948	-1.1573	2.195	0	0
7	8	O	-1.2738	-1.3118	-0.8670	-0.937	0.2948	0
8	8	O	1.2734	-1.3116	0.8663	-0.937	0.3072	0
9	9	F	0.2600	-0.6546	3.6631	-0.361	0	0
10	9	F	-0.7620	1.1790	3.0295	-0.356	0	0
11	12	C	0.3643	-0.0445	-2.6359	0.867	0	0
12	9	F	1.4455	-0.7635	-2.2855	-0.353	0	0
13	8	O	-1.8983	1.0550	-1.6525	-0.944	0.5305	0
14	9	F	-0.2575	-0.6581	-3.6618	-0.361	0	0
15	9	F	0.7596	1.1792	-3.0314	-0.356	0	0
Total						1.000	2.2922	0

Table S5. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[S_{221}]^+$ cation.



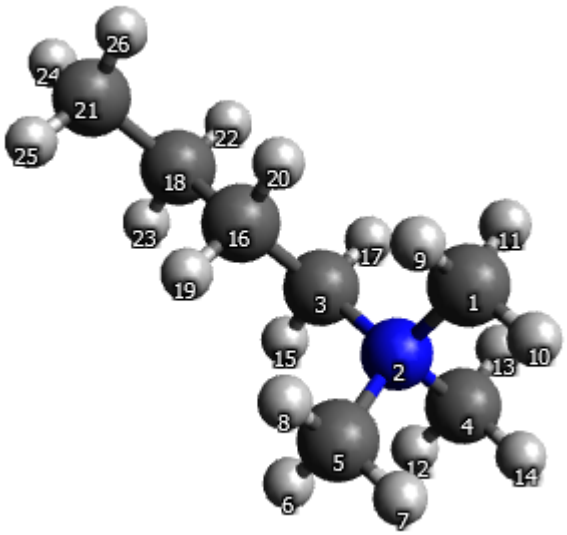
Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	6	C	-0.0342	0.9937	2.4073	-0.711	0	0
2	6	C	0.4013	0.9776	0.9491	-0.587	0	0
3	16	S	-0.4653	-0.3527	-0.0014	0.881	0	0
4	6	C	0.2704	-1.8716	0.6878	-0.834	0	0
5	1	H	-0.0668	-2.6985	0.0534	0.290	0	0.1681
6	6	C	0.3670	-0.2673	-1.6530	-0.586	0	0
7	6	C	-0.0494	0.9736	-2.4284	-0.712	0	0
8	1	H	1.4783	0.8085	0.8223	0.268	0	0.0692
9	1	H	0.1122	1.9013	0.4322	0.284	0	0.0641
10	1	H	-0.1262	-1.9990	1.7001	0.291	0	0.0723
11	1	H	1.3622	-1.7878	0.6901	0.271	0	0.0873
12	1	H	1.4474	-0.3187	-1.4677	0.269	0	0.0452
13	1	H	0.0389	-1.1899	-2.1490	0.285	0	0.1363
14	1	H	0.4452	1.8549	2.8929	0.285	0	0
15	1	H	-1.1216	1.1112	2.5069	0.262	0	0
16	1	H	0.2803	0.0909	2.9463	0.249	0	0
17	1	H	0.4043	0.9146	-3.4274	0.286	0	0
18	1	H	-1.1388	1.0296	-2.5545	0.262	0	0
19	1	H	0.3060	1.8994	-1.9580	0.249	0	0
Total						1.000	0	0.6425

Table S6. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[S_{222}]^+$ cation.



Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	6	C	-1.5907	-0.4510	0.4745	-0.585	0	0
2	16	S	0.0001	0.3713	0.0000	0.861	0	0
3	6	C	0.3848	-0.4512	-1.6148	-0.585	0	0
4	6	C	1.2071	-0.4501	1.1407	-0.585	0	0
5	6	C	1.5855	0.1897	-2.2946	-0.709	0	0
6	1	H	0.5281	-1.5172	-1.3963	0.268	0	0.0459
7	1	H	-0.5324	-0.3233	-2.2040	0.281	0	0.0191
8	1	H	2.1760	-0.3197	0.6422	0.281	0	0.0140
9	6	C	1.1927	0.1893	2.5210	-0.709	0	0
10	1	H	0.9489	-1.5168	1.1543	0.268	0	0.0456
11	6	C	-2.7796	0.1897	-0.2268	-0.709	0	0
12	1	H	-1.4731	-1.5170	0.2414	0.268	0	0.0450
13	1	H	-1.6430	-0.3231	1.5633	0.281	0	0.0172
14	1	H	1.7428	-0.3196	-3.2557	0.283	0	0
15	1	H	1.4156	1.2551	-2.4976	0.262	0	0
16	1	H	2.5065	0.0802	-1.7068	0.247	0	0
17	1	H	1.9473	-0.3189	3.1376	0.283	0	0
18	1	H	1.4507	1.2554	2.4766	0.262	0	0
19	1	H	0.2232	0.0766	3.0238	0.247	0	0
20	1	H	-3.6908	-0.3197	0.1171	0.283	0	0
21	1	H	-2.8706	1.2551	0.0215	0.262	0	0
22	1	H	-2.7305	0.0795	-1.3183	0.247	0	0
Total						1.000	0.0000	0.1868

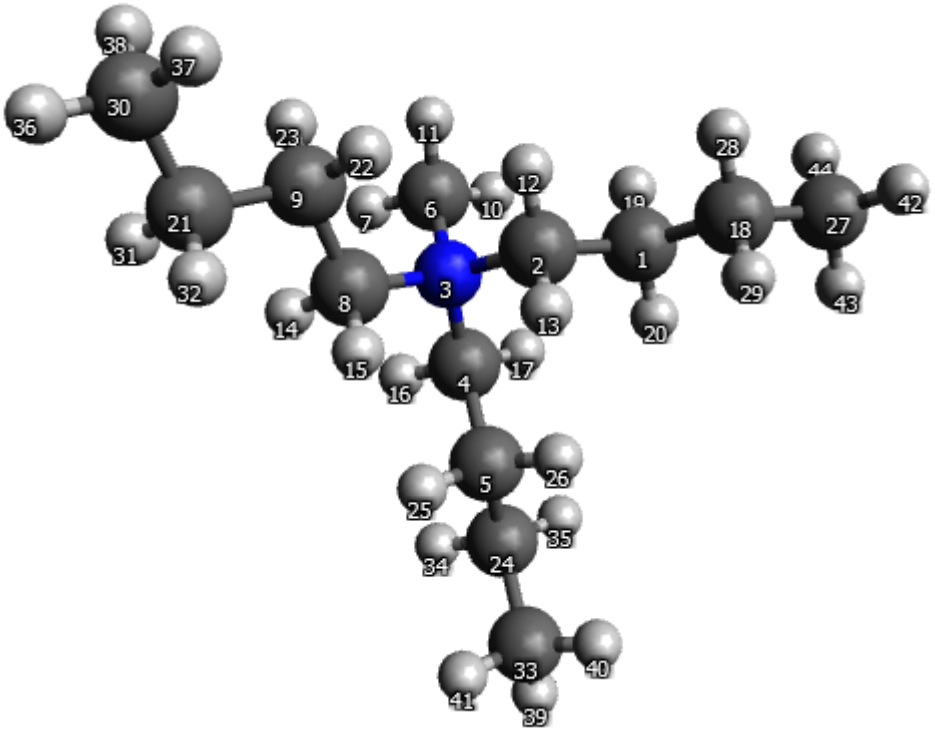
Table S7. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[N_{4111}]^+$ cation.



Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	6	C	-0.6065	-0.0152	-1.4247	-0.474	0	0
2	7	N	-0.0856	0.0649	-0.0141	-0.295	0	0
3	6	C	1.1129	-0.8678	0.1811	-0.252	0	0
4	6	C	0.3819	1.4735	0.2511	-0.472	0	0
5	6	C	-1.1910	-0.2679	0.9523	-0.474	0	0
6	1	H	-0.7874	-0.2339	1.9695	0.263	0	0.0269
7	1	H	-1.9852	0.4765	0.8336	0.264	0	0.0273
8	1	H	-1.5804	-1.2645	0.7275	0.265	0	0.0033
9	1	H	-1.0062	-1.0166	-1.6060	0.265	0	0.0036
10	1	H	-1.4015	0.7287	-1.5391	0.264	0	0.0309
11	1	H	0.2168	0.2000	-2.1137	0.263	0	0.0247
12	1	H	0.7532	1.5307	1.2795	0.264	0	0.0300
13	1	H	1.1809	1.7159	-0.4569	0.264	0	0.0285
14	1	H	-0.4658	2.1529	0.1146	0.263	0	0.0258
15	1	H	1.4573	-0.6844	1.2078	0.260	0	0.0152
16	6	C	0.8471	-2.3510	-0.0439	-0.489	0	0
17	1	H	1.8813	-0.4993	-0.5118	0.260	0	0.0223
18	6	C	2.1353	-3.1596	0.1927	-0.457	0	0
19	1	H	0.0674	-2.7155	0.6420	0.245	0	0
20	1	H	0.4967	-2.5321	-1.0714	0.245	0	0
21	6	C	1.9277	-4.6624	-0.0213	-0.681	0	0
22	1	H	2.9234	-2.7938	-0.4857	0.241	0	0
23	1	H	2.4950	-2.9774	1.2187	0.241	0	0
24	1	H	2.8606	-5.2173	0.1540	0.257	0	0
25	1	H	1.1654	-5.0602	0.6661	0.235	0	0
26	1	H	1.5979	-4.8755	-1.0495	0.235	0	0

Total	1.000	0.0000	0.2385

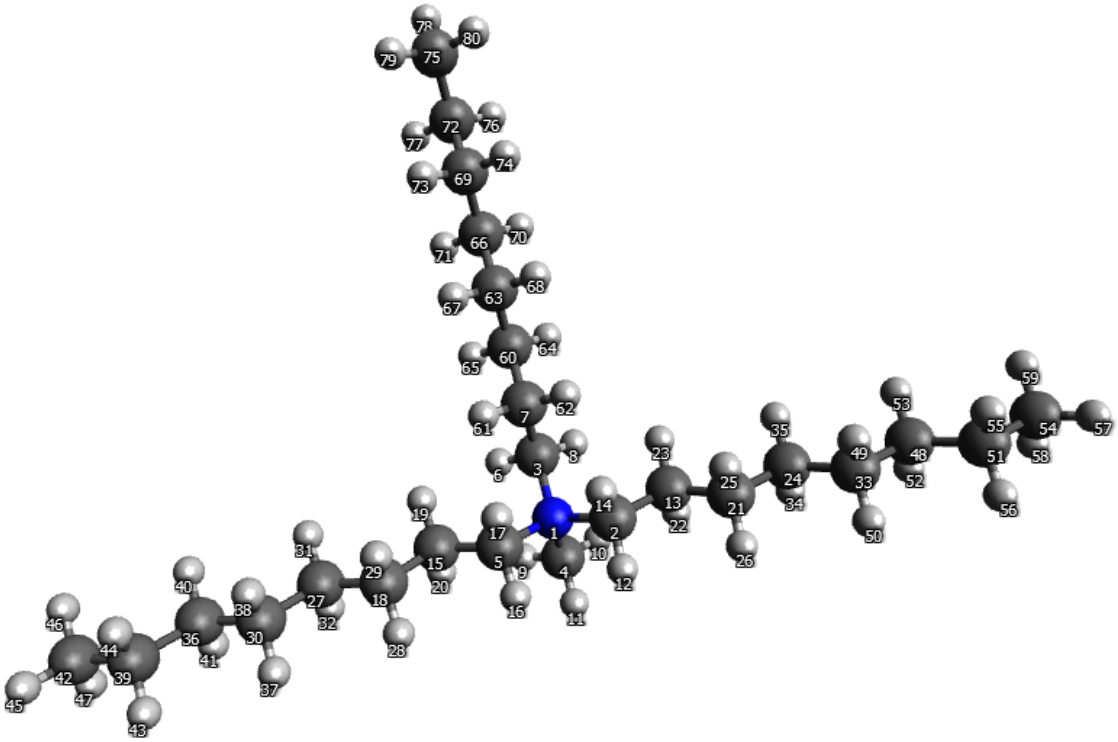
Table S8. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[N_{4441}]^+$ cation.



Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	6	C	3.5856	-0.5121	-1.2998	-0.486	0	0
2	6	C	2.9721	-1.0713	-0.0204	-0.255	0	0
3	7	N	1.4459	-1.1490	0.0062	-0.288	0	0
4	6	C	0.8949	-1.9236	-1.1964	-0.254	0	0
5	6	C	1.4033	-3.3501	-1.3688	-0.486	0	0
6	6	C	0.8507	0.2344	-0.0467	-0.475	0	0
7	1	H	-0.2292	0.1525	0.1162	0.260	0	0.0158
8	6	C	0.9936	-1.8550	1.2894	-0.252	0	0
9	6	C	1.3072	-1.1410	2.6005	-0.485	0	0
10	1	H	1.0431	0.6678	-1.0323	0.261	0	0.0080
11	1	H	1.3075	0.8550	0.7288	0.262	0	0.0040
12	1	H	3.2512	-0.4466	0.8362	0.258	0	0.0004
13	1	H	3.3314	-2.0899	0.1738	0.259	0	0.0017
14	1	H	-0.0904	-1.9917	1.1756	0.256	0	0.0163
15	1	H	1.4702	-2.8417	1.2728	0.258	0	0.0005
16	1	H	-0.1960	-1.9091	-1.0702	0.258	0	0.0166
17	1	H	1.1363	-1.3175	-2.0781	0.259	0	0.0010
18	6	C	5.1155	-0.4257	-1.1595	-0.456	0	0
19	1	H	3.1898	0.4923	-1.5151	0.243	0	0
20	1	H	3.3428	-1.1514	-2.1620	0.242	0	0

21	6	C	0.8087	-1.9846	3.7874	-0.456	0	0
22	1	H	2.3900	-0.9790	2.7111	0.243	0	0
23	1	H	0.8195	-0.1560	2.6353	0.243	0	0
24	6	C	0.7923	-3.9788	-2.6337	-0.456	0	0
25	1	H	1.1382	-3.9703	-0.5001	0.244	0	0
26	1	H	2.5007	-3.3646	-1.4583	0.242	0	0
27	6	C	5.7871	0.1226	-2.4228	-0.680	0	0
28	1	H	5.3652	0.2154	-0.2983	0.239	0	0
29	1	H	5.5169	-1.4269	-0.9312	0.239	0	0
30	6	C	1.0938	-1.3177	5.1366	-0.680	0	0
31	1	H	-0.2750	-2.1566	3.6808	0.239	0	0
32	1	H	1.2882	-2.9764	3.7556	0.239	0	0
33	6	C	1.2672	-5.4182	-2.8564	-0.680	0	0
34	1	H	-0.3070	-3.9588	-2.5542	0.240	0	0
35	1	H	1.0537	-3.3621	-3.5093	0.238	0	0
36	1	H	0.7268	-1.9371	5.9676	0.255	0	0
37	1	H	2.1739	-1.1640	5.2836	0.234	0	0
38	1	H	0.6017	-0.3356	5.2062	0.234	0	0
39	1	H	0.8199	-5.8441	-3.7660	0.255	0	0
40	1	H	2.3616	-5.4628	-2.9669	0.233	0	0
41	1	H	0.9880	-6.0642	-2.0099	0.234	0	0
42	1	H	6.8784	0.1729	-2.2983	0.255	0	0
43	1	H	5.5769	-0.5167	-3.2937	0.234	0	0
44	1	H	5.4278	1.1368	-2.6554	0.234	0	0
Total						1.000	0.0000	0.0643

Table S9. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[N_{1888}]^+$ cation.

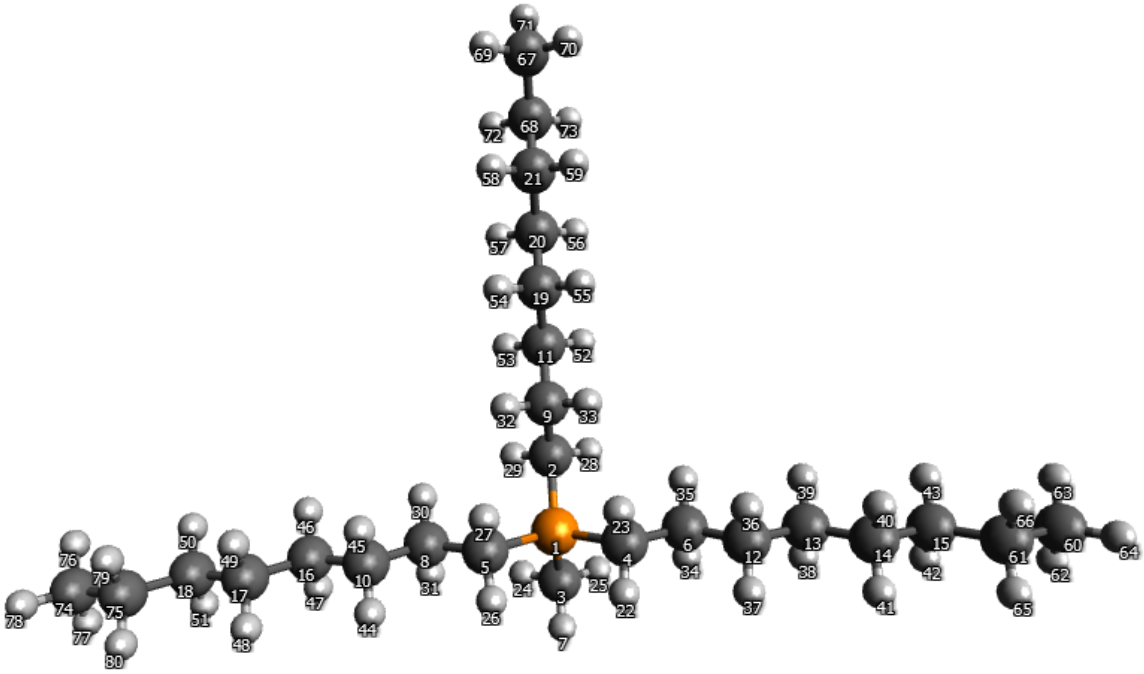


Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	7	N	-0.0022	-1.5530	0.8441	-0.288	0	0
2	6	C	-1.2289	-1.8449	-0.0297	-0.253	0	0
3	6	C	-0.0017	-0.1158	1.3610	-0.256	0	0
4	6	C	-0.0030	-2.4774	2.0336	-0.471	0	0
5	6	C	1.2242	-1.8454	-0.0296	-0.253	0	0
6	1	H	0.8819	-0.0322	2.0057	0.260	0	0.0008
7	6	C	-0.0017	0.9701	0.2932	-0.482	0	0
8	1	H	-0.8847	-0.0318	2.0063	0.260	0	0.0007
9	1	H	0.8870	-2.2827	2.6378	0.260	0	0.0036
10	1	H	-0.8970	-2.2866	2.6332	0.260	0	0.0030
11	1	H	0.0001	-3.5108	1.6716	0.258	0	0.0208
12	1	H	-1.1433	-2.9079	-0.2917	0.257	0	0.0159
13	6	C	-2.5875	-1.5505	0.5948	-0.482	0	0
14	1	H	-1.0908	-1.2609	-0.9482	0.259	0	0.0011
15	6	C	2.5831	-1.5590	0.5980	-0.482	0	0
16	1	H	1.1350	-2.9071	-0.2959	0.257	0	0.0169
17	1	H	1.0893	-1.2574	-0.9459	0.259	0	0.0010
18	6	C	3.7056	-1.9629	-0.3747	-0.450	0	0
19	1	H	2.6850	-0.4887	0.8337	0.243	0	0
20	1	H	2.7079	-2.1171	1.5380	0.242	0	0

21	6	C	-3.7103	-1.9548	-0.3772	-0.450	0	0
22	1	H	-2.7155	-2.1036	1.5373	0.242	0	0
23	1	H	-2.6860	-0.4789	0.8260	0.243	0	0
24	6	C	-5.1097	-1.6865	0.1910	-0.451	0	0
25	1	H	-3.5887	-1.4041	-1.3256	0.236	0	0
26	1	H	-3.6129	-3.0262	-0.6216	0.237	0	0
27	6	C	5.1052	-1.6924	0.1916	-0.451	0	0
28	1	H	3.6089	-3.0346	-0.6181	0.237	0	0
29	1	H	3.5827	-1.4131	-1.3235	0.236	0	0
30	6	C	6.2332	-2.0738	-0.7763	-0.452	0	0
31	1	H	5.1932	-0.6224	0.4496	0.231	0	0
32	1	H	5.2294	-2.2512	1.1358	0.231	0	0
33	6	C	-6.2384	-2.0668	-0.7766	-0.452	0	0
34	1	H	-5.2323	-2.2473	1.1341	0.231	0	0
35	1	H	-5.1983	-0.6171	0.4509	0.231	0	0
36	6	C	7.6365	-1.8201	-0.2111	-0.454	0	0
37	1	H	6.1369	-3.1409	-1.0446	0.230	0	0
38	1	H	6.1120	-1.5067	-1.7163	0.229	0	0
39	6	C	8.7666	-2.1854	-1.1832	-0.454	0	0
40	1	H	7.7299	-0.7553	0.0687	0.227	0	0
41	1	H	7.7617	-2.3958	0.7235	0.227	0	0
42	6	C	10.1651	-1.9382	-0.6065	-0.676	0	0
43	1	H	8.6686	-3.2472	-1.4684	0.229	0	0
44	1	H	8.6443	-1.6047	-2.1138	0.229	0	0
45	1	H	10.9523	-2.2055	-1.3273	0.240	0	0
46	1	H	10.3028	-0.8786	-0.3391	0.227	0	0
47	1	H	10.3293	-2.5346	0.3048	0.227	0	0
48	6	C	-7.6411	-1.8109	-0.2112	-0.454	0	0
49	1	H	-6.1167	-1.5005	-1.7171	0.229	0	0
50	1	H	-6.1434	-3.1341	-1.0450	0.230	0	0
51	6	C	-8.7721	-2.1782	-1.1815	-0.454	0	0
52	1	H	-7.7662	-2.3837	0.7252	0.227	0	0
53	1	H	-7.7335	-0.7452	0.0654	0.227	0	0
54	6	C	-10.1699	-1.9222	-0.6070	-0.676	0	0
55	1	H	-8.6473	-1.6036	-2.1156	0.229	0	0
56	1	H	-8.6778	-3.2419	-1.4602	0.229	0	0
57	1	H	-10.9580	-2.1928	-1.3256	0.240	0	0
58	1	H	-10.3363	-2.5108	0.3090	0.227	0	0
59	1	H	-10.3044	-0.8600	-0.3480	0.227	0	0
60	6	C	-0.0013	2.3611	0.9506	-0.451	0	0
61	1	H	0.8841	0.8786	-0.3538	0.242	0	0
62	1	H	-0.8875	0.8788	-0.3539	0.242	0	0
63	6	C	0.0010	3.5025	-0.0740	-0.451	0	0
64	1	H	-0.8858	2.4566	1.6032	0.236	0	0
65	1	H	0.8823	2.4550	1.6048	0.236	0	0
66	6	C	0.0042	4.8940	0.5725	-0.452	0	0
67	1	H	0.8846	3.4018	-0.7283	0.231	0	0
68	1	H	-0.8829	3.4056	-0.7285	0.231	0	0

69	6	C	0.0082	6.0422	-0.4446	-0.454	0	0
70	1	H	-0.8794	4.9923	1.2279	0.229	0	0
71	1	H	0.8872	4.9873	1.2294	0.229	0	0
72	6	C	0.0142	7.4346	0.2006	-0.454	0	0
73	1	H	0.8908	5.9434	-1.1017	0.227	0	0
74	1	H	-0.8755	5.9505	-1.1012	0.227	0	0
75	6	C	0.0190	8.5761	-0.8224	-0.676	0	0
76	1	H	-0.8679	7.5325	0.8566	0.229	0	0
77	1	H	0.8970	7.5249	0.8569	0.229	0	0
78	1	H	0.0246	9.5601	-0.3301	0.240	0	0
79	1	H	0.9067	8.5225	-1.4722	0.227	0	0
80	1	H	-0.8705	8.5317	-1.4705	0.227	0	0
Total						1.000	0.0000	0.0638

Table S10. Atom coordinates, charges from Natural Population Analysis (NPA), and σ-moment calculated at the BP-TZVP level of theory for $[P_{1888}]^+$ cation.



Centre number	Atomic Number	Atom	Coordinates/Å			NPA	σ-moment	
			x	y	z		Hb_acc3	Hb_don3
1	15	P	0.0318	-1.5349	0.7073	1.689	0	0
2	6	C	0.0113	0.1720	1.3813	-0.805	0	0
3	6	C	0.0459	-2.7043	2.1028	-1.044	0	0
4	6	C	-1.4466	-1.8377	-0.3372	-0.800	0	0
5	6	C	1.5168	-1.8023	-0.3376	-0.800	0	0
6	6	C	-2.7969	-1.6521	0.3729	-0.461	0	0
7	1	H	0.0623	-3.7305	1.7145	0.287	0	0.0127
8	6	C	2.8631	-1.6016	0.3760	-0.461	0	0
9	6	C	-0.0143	1.2852	0.3221	-0.461	0	0
10	6	C	4.0443	-1.8689	-0.5688	-0.451	0	0
11	6	C	-0.0304	2.6783	0.9693	-0.451	0	0
12	6	C	-3.9728	-1.9567	-0.5672	-0.451	0	0
13	6	C	-5.3384	-1.8031	0.1145	-0.452	0	0
14	6	C	-6.5188	-2.1125	-0.8151	-0.452	0	0
15	6	C	-7.8866	-1.9844	-0.1320	-0.454	0	0
16	6	C	5.4072	-1.7143	0.1181	-0.452	0	0
17	6	C	6.5918	-1.9799	-0.8198	-0.452	0	0
18	6	C	7.9577	-1.8641	-0.1307	-0.454	0	0
19	6	C	-0.0679	3.8156	-0.0594	-0.452	0	0
20	6	C	-0.0838	5.2106	0.5793	-0.452	0	0
21	6	C	-0.1318	6.3525	-0.4442	-0.454	0	0
22	1	H	-1.3371	-2.8669	-0.7146	0.280	0	0.0120

23	1	H	-1.3575	-1.1677	-1.2064	0.282	0	0.0004
24	1	H	0.9352	-2.5287	2.7206	0.289	0	0.0021
25	1	H	-0.8518	-2.5558	2.7156	0.289	0	0.0019
26	1	H	1.4253	-2.8292	-0.7256	0.280	0	0.0137
27	1	H	1.4176	-1.1253	-1.2003	0.282	0	0.0008
28	1	H	-0.8668	0.2313	2.0430	0.281	0	0.0015
29	1	H	0.8974	0.2581	2.0293	0.281	0	0.0009
30	1	H	2.9365	-0.5739	0.7666	0.239	0	0
31	1	H	2.9335	-2.2784	1.2421	0.238	0	0
32	1	H	0.8654	1.2018	-0.3357	0.239	0	0
33	1	H	-0.9019	1.1744	-0.3207	0.239	0	0
34	1	H	-2.8549	-2.3160	1.2499	0.238	0	0
35	1	H	-2.8898	-0.6199	0.7470	0.239	0	0
36	1	H	-3.9203	-1.2876	-1.4433	0.236	0	0
37	1	H	-3.8689	-2.9858	-0.9524	0.235	0	0
38	1	H	-5.3823	-2.4709	0.9930	0.230	0	0
39	1	H	-5.4396	-0.7739	0.5022	0.230	0	0
40	1	H	-6.4822	-1.4360	-1.6876	0.229	0	0
41	1	H	-6.4070	-3.1366	-1.2142	0.229	0	0
42	1	H	-7.9231	-2.6634	0.7388	0.227	0	0
43	1	H	-7.9992	-0.9617	0.2709	0.227	0	0
44	1	H	3.9541	-2.8898	-0.9786	0.235	0	0
45	1	H	3.9843	-1.1801	-1.4290	0.236	0	0
46	1	H	5.4933	-0.6953	0.5352	0.230	0	0
47	1	H	5.4606	-2.4064	0.9769	0.230	0	0
48	1	H	6.4900	-2.9900	-1.2555	0.229	0	0
49	1	H	6.5503	-1.2731	-1.6676	0.229	0	0
50	1	H	8.0592	-0.8573	0.3133	0.227	0	0
51	1	H	8.0005	-2.5772	0.7122	0.227	0	0
52	1	H	-0.9061	2.7569	1.6362	0.235	0	0
53	1	H	0.8612	2.7902	1.6096	0.236	0	0
54	1	H	0.8066	3.7310	-0.7280	0.230	0	0
55	1	H	-0.9599	3.6979	-0.6994	0.230	0	0
56	1	H	-0.9542	5.2907	1.2544	0.229	0	0
57	1	H	0.8113	5.3292	1.2153	0.229	0	0
58	1	H	0.7372	6.2720	-1.1214	0.227	0	0
59	1	H	-1.0280	6.2345	-1.0794	0.227	0	0
60	6	C	-10.4307	-2.1744	-0.3645	-0.676	0	0
61	6	C	-9.0692	-2.2918	-1.0596	-0.454	0	0
62	1	H	-10.5054	-2.8759	0.4814	0.227	0	0
63	1	H	-10.5883	-1.1585	0.0306	0.227	0	0
64	1	H	-11.2575	-2.3955	-1.0561	0.239	0	0
65	1	H	-8.9516	-3.3104	-1.4687	0.229	0	0
66	1	H	-9.0371	-1.6079	-1.9253	0.229	0	0
67	6	C	-0.1997	8.8827	-0.8392	-0.676	0	0
68	6	C	-0.1463	7.7490	0.1914	-0.454	0	0
69	1	H	0.6715	8.8484	-1.5119	0.227	0	0
70	1	H	-1.1044	8.8094	-1.4626	0.227	0	0

71	1	H	-0.2079	9.8699	-0.3529	0.240	0	0
72	1	H	0.7506	7.8676	0.8235	0.229	0	0
73	1	H	-1.0127	7.8275	0.8704	0.229	0	0
74	6	C	10.5032	-2.0276	-0.3662	-0.676	0	0
75	6	C	9.1440	-2.1222	-1.0688	-0.454	0	0
76	1	H	10.6525	-1.0304	0.0769	0.227	0	0
77	1	H	10.5815	-2.7677	0.4456	0.227	0	0
78	1	H	11.3328	-2.2094	-1.0659	0.239	0	0
79	1	H	9.1092	-1.3998	-1.9027	0.229	0	0
80	1	H	9.0336	-3.1217	-1.5241	0.229	0	0
Total						1.000	0.0000	0.0460

Table S11. Partial molar excess enthalpy of binary mixtures (water + IL) at equilibrium concentration predicted using COSMO-RS.[a]

T/K	x_{IL}	x_{H2O}	H_{MF}/kJ·mol^{-1}[b]	H_{HB}/kJ·mol^{-1}[c]	H_{VdW}/kJ·mol^{-1}[d]	H_{INT}/kJ·mol^{-1}[e]
$[S_{221}][NTf_2]$						
288.15	0.2284	0.7716	0.0577	1.6020	-0.0989	1.5607
293.15	0.2420	0.7580	0.0688	1.7253	-0.1056	1.6885
298.15	0.2561	0.7439	0.0809	1.8486	-0.1121	1.8175
303.15	0.2705	0.7295	0.0942	1.9712	-0.1184	1.9470
308.15	0.2854	0.7146	0.1086	2.0925	-0.1247	2.0764
313.15	0.3007	0.6993	0.1246	2.2315	-0.1331	2.2230
318.15	0.3163	0.6837	0.1406	2.3278	-0.1367	2.3318
$[N_{4111}][NTf_2]$						
288.15	0.2104	0.7896	0.0735	1.5724	-0.1038	1.5421
293.15	0.2243	0.7757	0.0865	1.6997	-0.1115	1.6747
298.15	0.2396	0.7604	0.1007	1.8273	-0.1192	1.8089
303.15	0.2513	0.7487	0.1154	1.9317	-0.1240	1.9232
308.15	0.2723	0.7277	0.1339	2.1024	-0.1368	2.0994
313.15	0.2857	0.7143	0.1520	2.2261	-0.1441	2.2340
318.15	0.2995	0.7005	0.1702	2.3258	-0.1486	2.3475
$[S_{222}][NTf_2]$						
288.15	0.1841	0.8159	0.0809	1.4201	-0.0784	1.4226
293.15	0.1936	0.8064	0.0935	1.5220	-0.0829	1.5326
298.15	0.2065	0.7935	0.1070	1.6243	-0.0873	1.6440
303.15	0.2177	0.7823	0.1229	1.7514	-0.0940	1.7802
308.15	0.2324	0.7676	0.1387	1.8529	-0.0982	1.8934
313.15	0.2455	0.7545	0.1569	1.9782	-0.1047	2.0303
318.15	0.2559	0.7441	0.1765	2.1013	-0.1112	2.1666
$[N_{4441}][NTf_2]$						
288.15	0.0979	0.9021	0.0927	0.9069	-0.0484	0.9511
293.15	0.1023	0.8977	0.1093	1.0100	-0.0542	1.0652
298.15	0.1089	0.8911	0.1236	1.0776	-0.0571	1.1440
303.15	0.1179	0.8821	0.1388	1.1452	-0.0601	1.2238
308.15	0.1252	0.8748	0.1597	1.2510	-0.0658	1.3448
313.15	0.1329	0.8671	0.1822	1.3569	-0.0715	1.4675
318.15	0.1399	0.8601	0.2009	1.4236	-0.0744	1.5501
$[N_{1888}][NTf_2]$						
288.15	0.0179	0.9821	0.0308	0.1959	-0.0079	0.2188
293.15	0.0215	0.9785	0.0506	0.3182	-0.0136	0.3552
298.15	0.0272	0.9728	0.0640	0.3831	-0.0166	0.4305
303.15	0.0354	0.9646	0.0787	0.4487	-0.0197	0.5077
308.15	0.0426	0.9574	0.1054	0.5723	-0.0257	0.6520
313.15	0.0508	0.9492	0.1231	0.6388	-0.0289	0.7330
318.15	0.0597	0.9403	0.1537	0.7621	-0.0352	0.8806
$[P_{1888}][NTf_2]$						
288.15	0.0112	0.9888	0.0293	0.1942	-0.0079	0.2155

293.15	0.0153	0.9847	0.0506	0.3182	-0.0136	0.3552
298.15	0.0195	0.9805	0.0640	0.3831	-0.0166	0.4305
303.15	0.0240	0.9760	0.0787	0.4487	-0.0197	0.5077
308.15	0.0316	0.9684	0.1054	0.5723	-0.0257	0.6520
313.15	0.0416	0.9584	0.1231	0.6388	-0.0289	0.7330
318.15	0.0474	0.9526	0.1537	0.7621	-0.0352	0.8806

[a]The partial excess molar enthalpy was estimated using the method describe in reference 1.
[b]Partial excess molar enthalpy as contribution of electrostatic-misfit interaction, H_{MF}.
[c]Partial excess molar enthalpy as contribution of hydrogen-bond interaction, H_{HB}.
[d]Partial excess molar enthalpy as contribution of Van der Waals forces, H_{VdW}.
[e]Total Partial excess molar enthalpy as contribution of electrostatic-misfit interaction, $H_{INT} = H_{MF} + H_{HB} + H_{VdW}$

Table S12. Parameters for the mole fraction solubility correlations as a function of temperature along with the respective standard deviation, σ.

IL	$A \pm \sigma$	$B \pm \sigma$	$C \pm \sigma$	$D \pm \sigma$	$E \pm \sigma$
$[S_{221}][NTf_2]$	1.98 ± 0.01	-995 ± 3	-87 ± 1	3081 ± 44	12 ± 1
$[S_{222}][NTf_2]$	1.90 ± 0.07	-1036 ± 20	-92 ± 1	3331 ± 32	13 ± 1
$[N_{4111}][NTf_2]$	2.24 ± 0.09	-1096 ± 26	-103 ± 1	4016 ± 36	14 ± 1
$[N_{4441}][NTf_2]$	1.60 ± 0.11	-1135 ± 34	-135 ± 2	4361 ± 90	20 ± 1
$[N_{1888}][NTf_2]$	9.51 ± 0.35	-3911 ± 107			
$[P_{1888}][NTf_2]$	9.67 ± 0.54	-4044 ± 162			

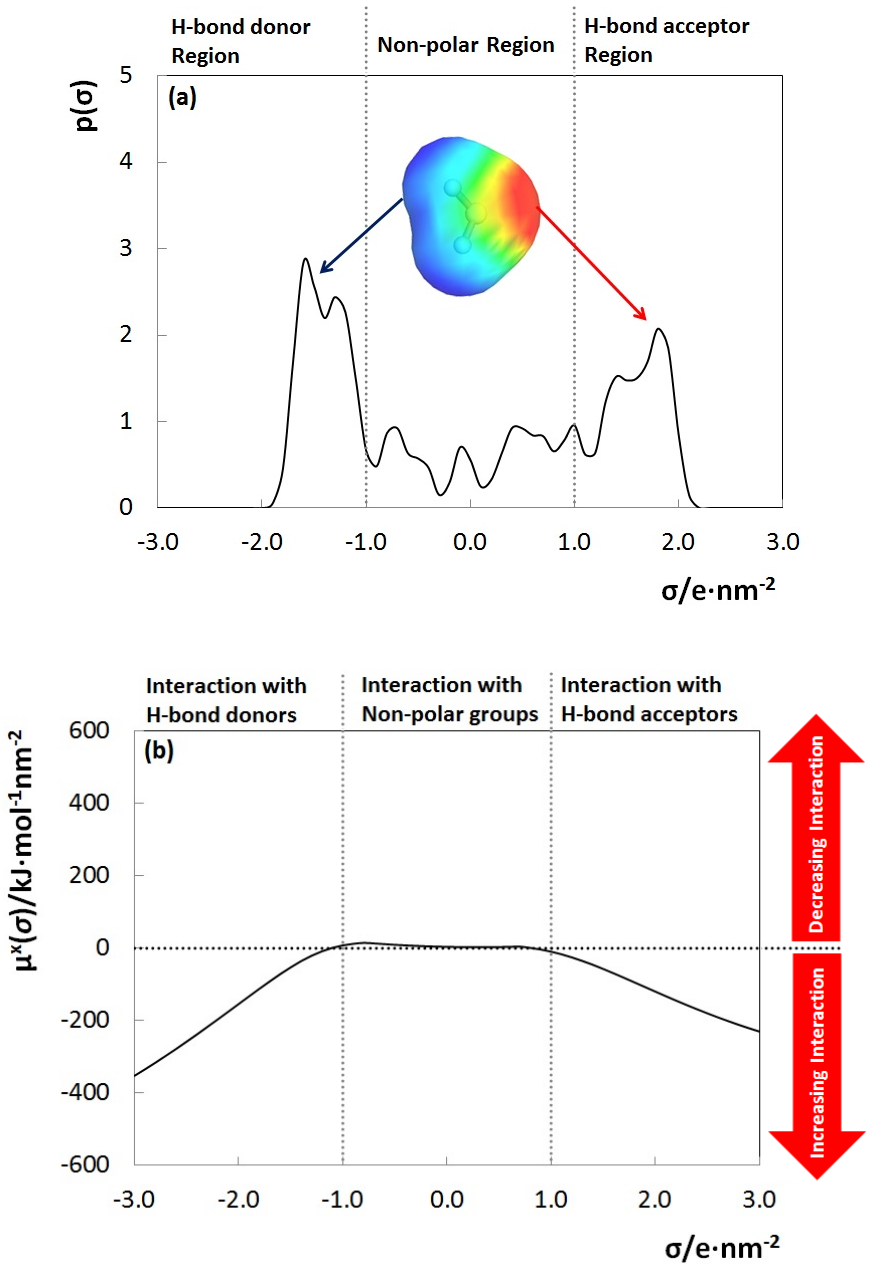


Figure S1. Sigma profile (a) and sigma-potential (b) of H_2O computed by COSMO-RS.

Reference

1 Kurnia, K. A.; Coutinho, J. A. P. *Ind. Eng. Chem. Res.* 2013, ***52***, 13862.