Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Simulations of photoemission and equilibrium redox processes of ionic liquids: The role of ion pairing and long-range polarization

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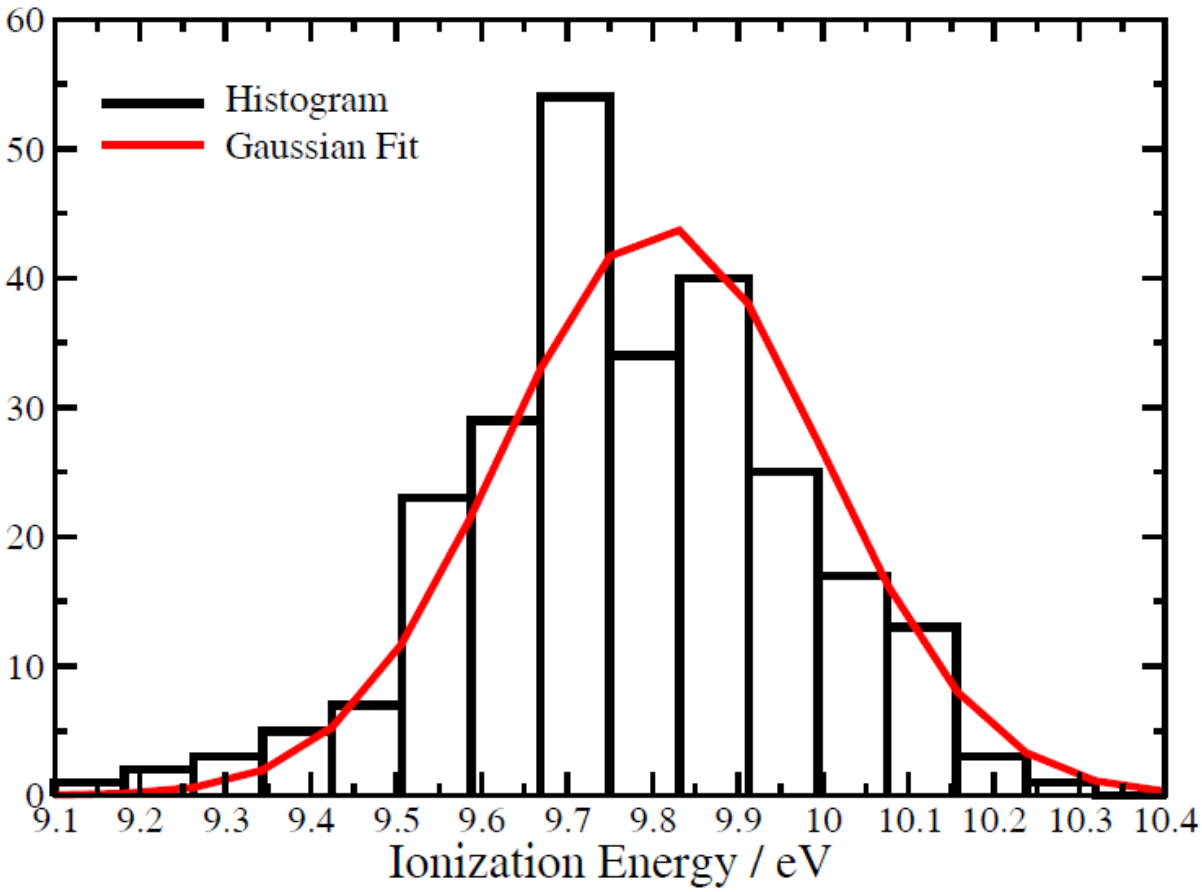
Supporting Information

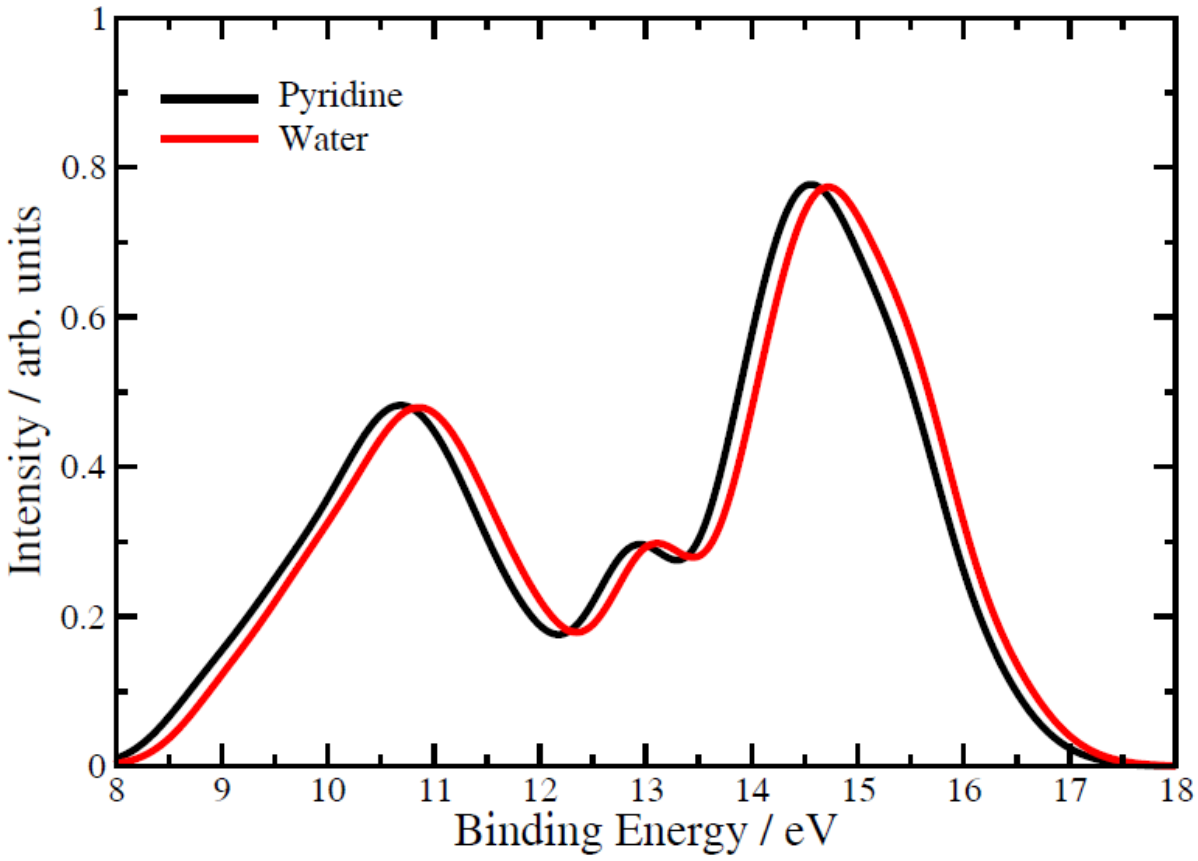
Distribution of first ionization energies

Figure S1: First ionization energy distribution from MD simulation of [bmim][Tf_2N] IL. The number of bins in histogram has been chosen as square-root of number of structures (i.e. $\sqrt{257}$). The distribution has been fitted on Gaussian function: $F(x) = A_0 e^{-A_1(A_2-x)^2}$, where coefficients was fitted as $A_0 = 43.95$, $A_1 = 14.23$ and $A_2 = 9.81$.



Effects of different solvents

Figure S2: Photoelectron spectra of [bmim][Tf_2N] in PCM solvent pyridine and water. Both spectra were calculated at combined MP2/PMP2/BMK/6-31+G* level using empirical broadening scheme.



Geometries of ionic liquids

Ground state structure of [emim][Tf_2N] optimized at MP2/6-31+G* level in xyz format (in Ångström).

C	-0.17168	-0.10675	0.174215
N	-0.05298	0.070912	1.498744
C	1.282207	0.119634	1.824057
C	1.985554	-0.01729	0.652091
N	1.060756	-0.15858	-0.35876
C	-1.1673	0.00569	2.447919
C	1.347987	-0.35303	-1.79537
C	2.281261	-1.5314	-2.02608
O	-1.44423	-2.10111	-1.55784
S	-1.06697	-3.32197	-0.81404
N	-0.80999	-2.93801	0.738814
S	0.526554	-3.35719	1.541181
O	0.483082	-2.63282	2.822126
O	-0.13422	-4.27001	-1.43066
C	-2.6748	-4.22431	-0.63309

F	-2.5166	-5.32388	0.121834
F	-3.60185	-3.43422	-0.05966
F	-3.11627	-4.59289	-1.84965
O	1.759717	-3.34031	0.74245
C	0.293124	-5.13017	2.043362
F	0.253507	-5.93471	0.971459
F	1.320859	-5.50163	2.830276
F	-0.8522	-5.26941	2.735735
H	-1.0925	-0.26234	-0.36952
H	-1.05672	0.809815	3.177303
H	0.379647	-0.52649	-2.26967
H	2.42313	-1.6541	-3.10436
H	-1.14718	-0.97238	2.930456
H	3.263783	-1.36724	-1.57463
H	-2.09666	0.135183	1.892884
H	1.768726	0.58461	-2.17305
H	1.86093	-2.45331	-1.6207
H	1.621081	0.197182	2.846631
H	3.049909	-0.04796	0.473373

Ground state structure of [bmim][Tf_2N] optimized at MP2/6-31+G* level in xyz format (in Ångström).

C	3.40472	-1.82745	-0.01088
C	3.676992	-0.50959	0.267364
N	2.830943	0.247506	-0.50687
C	2.051989	-0.57431	-1.23146
N	2.400113	-1.84054	-0.94685
C	2.71864	1.720573	-0.48313
C	2.328801	2.225743	0.900644
C	2.120279	3.739622	0.894796
C	1.667069	4.239169	2.264809
C	1.716891	-3.03312	-1.4558
O	-0.44815	0.949806	-1.91424
S	-1.09506	1.537759	-0.72226
N	-0.77183	0.782817	0.661733
S	-0.47716	-0.79417	0.795658
C	-1.78111	-1.25606	2.02671
F	-1.66516	-2.57016	2.309863
O	-0.96443	2.975852	-0.47949
C	-2.90648	1.271507	-1.02122
F	-3.16592	-0.03164	-1.21965
F	-3.62214	1.701628	0.031534
F	-3.28376	1.960824	-2.11399
O	0.792083	-1.01145	1.513966
O	-0.75071	-1.62781	-0.38994

F	-1.63854	-0.55674	3.163104
F	-3.00675	-1.03182	1.525468
H	1.245011	-0.25853	-1.88237
H	2.459975	-3.71736	-1.86934
H	3.681493	2.127905	-0.81208
H	3.110802	1.964574	1.627231
H	3.051334	4.244009	0.599258
H	2.403339	3.994625	3.038962
H	1.160355	-3.49538	-0.64034
H	1.527525	5.324757	2.261939
H	1.013992	-2.72168	-2.22715
H	1.960374	1.981655	-1.2268
H	1.407557	1.724663	1.214025
H	1.357724	3.991939	0.149123
H	0.713995	3.776299	2.539601
H	3.828282	-2.7367	0.39138
H	4.387494	-0.0669	0.94991

Structures of reactants and product on electrodes

Ground state structure of $[\mathrm{bmim\text{–}bmim}]$ complex optimized on MP2/6-31+G* level in PCM water solvent (xyz format in Ångström).

N	0.793346	0.491011	0.757566
C	1.050172	-0.9349	0.445481
N	2.508912	-1.04005	0.200974
C	3.00031	0.293568	0.219839
C	2.020041	1.163682	0.53498
C	2.872073	-1.81353	-0.99078
C	-0.39459	1.095227	0.126794
C	-0.32552	1.252319	-1.39219
C	-1.60362	1.870844	-1.95625
C	-1.54297	2.055766	-3.47138
H	2.542262	-2.847	-0.86216
H	3.960302	-1.79724	-1.10335
H	2.412178	-1.39846	-1.90347
H	4.06115	0.481064	0.092268
H	0.478467	-1.26874	-0.4408
H	2.094247	2.230814	0.718134
H	-0.53272	2.081145	0.591373
H	-1.25312	0.475724	0.408801
H	0.534838	1.883126	-1.65326
H	-0.15812	0.275023	-1.86543
H	-1.77898	2.841851	-1.47376
H	-2.45876	1.232196	-1.69697

H	-0.71041	2.711377	-3.74935
H	-1.3968	1.09336	-3.97419
H	-2.46644	2.500957	-3.85681
N	-0.81473	-1.70792	1.865484
C	0.644014	-1.81312	1.621025
N	0.900832	-3.23904	1.308979
C	-0.32595	-3.91165	1.531286
C	-1.3062	-3.04151	1.846383
H	-0.40019	-4.97876	1.348002
H	1.215708	-1.47925	2.5073
H	-2.36707	-3.22894	1.973795
C	-1.17791	-0.93461	3.057346
H	-0.84814	0.098893	2.928864
H	-2.26614	-0.95095	3.169906
H	-0.71801	-1.34978	3.969977
C	2.088622	-3.8433	1.93998
C	2.019268	-4.00031	3.458952
H	2.226791	-4.82924	1.475459
H	2.947237	-3.22385	1.658099
C	3.297203	-4.61894	4.023287
H	1.851899	-3.02297	3.932103
H	1.158797	-4.63101	3.719912
C	3.236275	-4.80372	5.538419
H	3.472536	-5.59	3.540899
H	4.152457	-3.98041	3.764089
H	4.159644	-5.24896	5.924043
H	3.090102	-3.84126	6.04112
H	2.403611	-5.45924	5.816302

Ground state structure of [bmim-H–bmim+H] complex optimized on MP2/6-31+G* level in PCM water solvent (xyz format in Ångström).

N	3.14832	0.471062	0.409356
C	1.9005	0.71331	0.930687
N	1.107259	0.637944	-0.18758
C	1.819754	0.36161	-1.3386
C	3.132335	0.255062	-0.95478
C	-0.35056	0.769568	-0.14848
C	-1.0518	-0.54314	-0.47925
C	-2.56482	-0.444	-0.30023
C	-3.26381	-1.75742	-0.64704
C	4.369371	0.472475	1.209181
C	0.96333	-2.56683	2.243183
N	1.150014	-3.014	0.860092
C	0.254738	-4.10662	0.75107

C	-0.69453	-4.00517	1.713634
N	-0.45515	-2.84532	2.493704
C	2.552806	-3.22698	0.505901
C	2.738963	-3.51283	-0.97792
C	4.214914	-3.59351	-1.36371
C	4.409323	-3.87328	-2.85264
C	-0.79109	-2.92817	3.91224
H	4.079693	0.580906	2.254114
H	5.012888	1.305746	0.916321
H	4.908315	-0.46801	1.071219
H	4.026643	0.066361	-1.53461
H	1.211416	-1.50869	2.361232
H	1.359728	0.264313	-2.31325
H	-0.64824	1.562812	-0.84534
H	-0.5928	1.095313	0.867231
H	-0.82662	-0.82791	-1.51668
H	-0.64644	-1.33022	0.166716
H	-2.9618	0.365566	-0.92802
H	-2.78654	-0.17285	0.740974
H	-3.08229	-2.02887	-1.69308
H	-2.88606	-2.56983	-0.01666
H	-4.34685	-1.68558	-0.5003
H	-0.62995	-1.95207	4.377836
H	-0.17222	-3.67881	4.433127
H	-1.84472	-3.19762	4.018115
H	-1.60963	-4.57572	1.829381
H	0.280541	-4.78125	-0.09625
H	2.986016	-4.04397	1.115886
H	3.083158	-2.30275	0.765673
H	2.247559	-4.45739	-1.2461
H	2.249468	-2.71466	-1.55093
H	4.704078	-4.37965	-0.77307
H	4.707538	-2.64811	-1.09945
H	3.939825	-4.82219	-3.13463
H	3.956045	-3.08017	-3.45784
H	5.471541	-3.93122	-3.11266
H	1.593834	-3.19152	2.931098

Ground state structure of $[\text{bmim–bmim}]^{+\cdot}$ complex optimized on MP2/6-31+G* level in PCM water solvent (xyz format in Ångström).

N	1.096725	0.45231	0.214376
C	1.33718	-0.97223	0.015594
N	2.766891	-1.01187	-0.26936
C	3.297662	0.219444	-0.09088

C	2.278763	1.113554	0.206261
C	3.421619	-2.11064	-0.97713
C	-0.21558	1.09473	0.097224
C	-0.62056	1.280667	-1.36412
C	-1.98278	1.963506	-1.47641
C	-2.4057	2.163862	-2.93034
H	3.20029	-3.05173	-0.47662
H	4.495671	-1.92022	-0.97785
H	3.051452	-2.14626	-2.00722
H	4.356315	0.413212	-0.20862
H	0.741887	-1.39497	-0.80717
H	2.343043	2.179331	0.387023
H	-0.13871	2.060255	0.608135
H	-0.93572	0.468746	0.627918
H	0.143416	1.880375	-1.87645
H	-0.65923	0.303014	-1.86245
H	-1.94434	2.934271	-0.9654
H	-2.73399	1.357969	-0.95284
H	-1.67829	2.784152	-3.46485
H	-2.47824	1.20241	-3.44998
H	-3.38126	2.656566	-2.99328
N	-0.42443	-1.66525	1.566754
C	1.02235	-1.75015	1.32737
N	1.364022	-3.16095	1.117624
C	0.108478	-3.81344	0.985747
C	-0.91037	-2.96299	1.228328
H	0.067262	-4.85223	0.675716
H	1.607648	-1.28882	2.135687
H	-1.97789	-3.14203	1.162957
C	-0.8424	-1.1807	2.892233
H	-0.45848	-0.16781	3.042717
H	-1.93509	-1.14736	2.915068
H	-0.48879	-1.82926	3.706398
C	2.325743	-3.77752	2.054172
C	1.87551	-3.84036	3.511338
H	2.515981	-4.79065	1.676748
H	3.266117	-3.2176	1.970798
C	2.885297	-4.58205	4.386151
H	1.739207	-2.82391	3.904963
H	0.900127	-4.34184	3.568105
C	2.452576	-4.6393	5.849884
H	3.016234	-5.60136	3.999649
H	3.862917	-4.08765	4.309877
H	3.185491	-5.17674	6.460653
H	2.34382	-3.63035	6.262456
H	1.489086	-5.15084	5.950108

Ground state structure of $[\text{bmim-H–bmim+H}]^{+\cdot}$ complex optimized on MP2/6-31+G* level in PCM water solvent (xyz format in Ångström).

N	3.202125	0.398357	0.502967
C	1.992435	0.179821	1.113948
N	1.108432	0.454572	0.098943
C	1.732764	0.815959	-1.07861
C	3.079502	0.782251	-0.81727
C	-0.33827	0.277935	0.23254
C	-0.81532	-0.99811	-0.45278
C	-2.31004	-1.23613	-0.25038
C	-2.80766	-2.45163	-1.03057
C	4.4856	0.201252	1.17191
C	1.247592	-2.86465	2.354521
N	1.464227	-3.78405	1.249471
C	0.33582	-4.48972	1.006198
C	-0.65563	-4.06405	1.880616
N	-0.1645	-3.06438	2.643771
C	2.687378	-3.80178	0.449981
C	2.537221	-3.00626	-0.84574
C	3.81077	-3.05778	-1.68792
C	3.61983	-2.39329	-3.05013
C	-0.81191	-2.4419	3.789434
H	5.009871	-0.65197	0.734753
H	4.283015	0.008443	2.225113
H	5.099979	1.098698	1.071753
H	3.929022	1.013989	-1.44648
H	1.46934	-1.81936	2.072878
H	1.193675	1.075312	-1.98055
H	-0.8352	1.157672	-0.19253
H	-0.54578	0.251182	1.306132
H	-0.59358	-0.93977	-1.52722
H	-0.24605	-1.84822	-0.05638
H	-2.86652	-0.34347	-0.56588
H	-2.51268	-1.37129	0.820729
H	-2.65255	-2.31061	-2.10584
H	-2.26962	-3.3568	-0.72856
H	-3.87628	-2.62202	-0.86295
H	-0.64185	-1.36402	3.755857
H	-0.40181	-2.84982	4.718555
H	-1.88132	-2.64681	3.735326
H	-1.67452	-4.41664	1.976123
H	0.277455	-5.24323	0.230971
H	2.928777	-4.84961	0.239096

H	3.486153	-3.3913	1.07657
H	1.699891	-3.42456	-1.42107
H	2.285891	-1.96554	-0.60991
H	4.111917	-4.1045	-1.82855
H	4.627128	-2.56508	-1.14345
H	2.838966	-2.9053	-3.6232
H	3.323767	-1.34594	-2.93286
H	4.543469	-2.42291	-3.63761
H	1.863077	-3.1472	3.227111