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Cooperatively enhanced hydrogen bonds in ionic liquids: closing the loop with molecular mimics of hydroxyl-functionalized cations

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The authors declare no conflict of interest.

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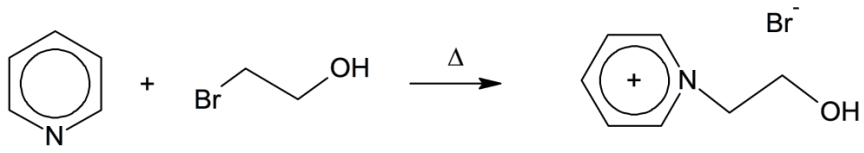
Contents

Synthesis

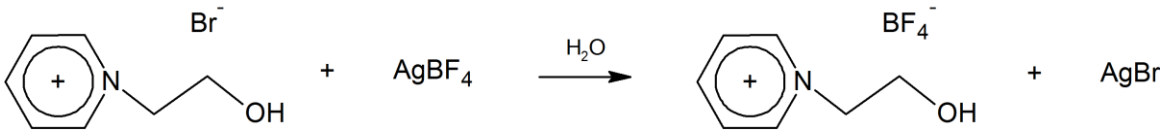
Apart from the reactions in aqueous solutions all reactions were performed in a moisture-guarded assembly and reflux condenser was used while heating. The used solvents were dried with molecular sieves to a water content less than 50 ppm and distilled freshly. All starting materials used in the synthesis were purchased from Sigma Aldrich and dried by conventional methods for the use in moisture-free reactions. All water contends were determined by KARL-FISCHER-titration.

1-(2-Hydroxyethyl)pyridinium-bromide [HEPy][Br]



At room temperature equimolar amounts of pyridine (8.977 g; 113 mmol; 9.6 ml) and 2-bromoethanol (14.929 g; 113 mmol; 14.9 ml) were mixed and heated slowly up to 110 °C. When the reaction begins, the solution turns brown and starts to crystallize. The mixture was cooled to room temperature. The crude product was recrystallized from about 330 ml acetonitrile. The product (**[HEPy][Br]**) was obtained as rod-shaped colorless crystals. Yield 89 %.
EA % cal. (exp.): C 41.20 (41.22); H 4.94 (4.92); N 6.86 (6.76). ^{1}**H-NMR**(298.2 K, DMSO-d6, 300.13 MHz, [ppm]): δ = 3.86 (dd, 2H, CH2−C*H*2−OH); 4.67-4.74 (m, 2H, C*H*2−CH2−OH); 5.25(t, 1H, O*H*); 8.14-8.21 (m, 2H, *m*-C*H*); 8.60-8.67 (m, 1H, *p*-C*H*); 9.03-9.09 (m, 2H, *o*-C*H*).^{13}**C-NMR**(298 K, DMSO-d6, 75.46 MHz, [ppm]): δ = 59.98 (s, CH2−*C*H2−OH); 63.04 (s, *C*H2−CH2−OH); 127.67 (s, *m*-*C*H); 145.15 (s, *p*-*C*H); 145.53 (s, *o*-*C*H).

1-(2-Hydroxyethyl)pyridinium- tetrafluoroborate [HEPy][BF_4]



10.804 g (**[HEPy][Br]**) (53 mmol) and 10.318 g silver tetrafluoroborate $AgBF_4$ (53 mmol) were stirred in 100 ml H_2O for 2 h. To remove the precipitate AgBr, the suspension was then filtered. The water in the obtained colorless solution was then evaporated in vacuum at 60 °C by a rotary evaporator. The obtained colorless liquid of [HEPy][BF_4] was dried for 6 h in vacuum at 60 °C.

Yield 95 %.

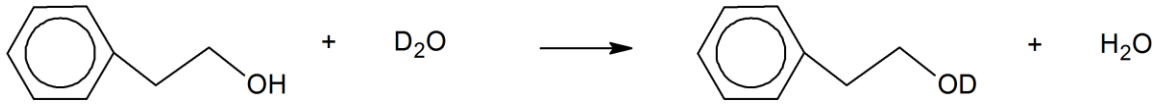
EA % cal. (exp.): C 39.85 (39.48); H 4.78 (4.74); N 6.64 (6.52). ^{1}**H-NMR**(298.2 K, DMSO-d6, 298.2 MHz, [ppm]): δ = 3.86 (dd, 2H, CH2−C*H*2−OH); 4.65- 4.74 (m, 2H, C*H*2−CH2−OH); 5.25(t, 1H, O*H*); 8.14-8.21 (m, 2H, *m*-C*H*); 8.60-8.67 (m, 1H, *p*-C*H*); 9.03- 9.09 (m, 2H, *o*-C*H*). ^{11}**B-NMR**(298 K, DMSO-d$_6$, 96.29 MHz, [ppm]): δ = −1.28 (s, BF_4^-). ^{13}**C-NMR**(298 K, DMSO-d6, 75.46 MHz, [ppm]): δ = 59.98 (s, CH2−*C*H2−OH); 63.04 (s, *C*H2−CH2−OH); 127.67 (s, *m*-*C*H); 145.15 (s, *p*-*C*H); 145.53 (s, *o*-*C*H). ^{19}**F-NMR**(298 K, DMSO-d6, 282.40 MHz, [ppm]): δ = −148.30 (s, B*F*$_4$). **IR** (Transm., CaF_2-Window, 12 μm Spacer, 20 °C, 128 Scans, [cm^{-1}]): 3545 (w); 3142 (w); 3098 (w); 3074 (w); 2972 (vw); 2946 (vw); 2890 (vw); 1941 (vw); 1848 (vw); 1637 (w); 1584 (vw); 1491 (m); 1450 (vw); 1310 (vw); 1288 (vw); 1255 (vw); 1176 (w); 1063 (w).

Deuteration

1-(2-Hydroxyethyl)pyridinium- tetrafluoroborate [HEPy][BF$_4$]-d$_1$

10 g (**[HEPy][BF$_4$]**) (47 mmol) were mixed with 3 g D_2O (150 mmol) at 50 °C. After addition of the water and a short mixing period, the water was then evaporated in vacuum. The D_2O-treatment procedure was repeated three more times. The degree of deuteration was verified by ATR measurements to make sure that the OH contributions in the spectra disappeared completely to the benefit of the OD contributions. The obtained colorless liquid of [HEPy][BF$_4$]-d$_1$ was dried for 6 h in vacuum at 60 °C.

2-Phenylethanol-d$_1$



20 g 2-Phenylethanol (164 mmol) were mixed with 10 g D_2O (500 mmol). After addition of the water and a short mixing period, approximately 90 % of the water was then removed by distillation. The D_2O-treatment procedure was repeated three more times. The degree of deuteration was verified by ATR measurements to make sure, that the OH contributions in the spectra disappeared completely to the benefit of the OD contributions. The obtained colorless liquid of 2-Phenylethanol-d$_1$ was then distilled by vacuum distillation and dried consecutively with molecular sieves 4 Å and 3 Å and distilled freshly to reach a water contend below 10 ppm.

FT-IR Spectroscopy of the liquid phase

IR experiments for the condensed phase were performed on a TENSOR II FTIR spectrometer from BRUKER. The spectrometer uses a Globar® source, a KBr beam splitter and a DTGS room temperature detector. To reach temperatures down to -80 °C an evacuatable variable temperature cell was used under moisture free conditions. The sample cell was a demountable liquid cell with CaF_2-windows and a 12 µm Mylar®-spacer. For data collection analyses the OPUS 7.5 software was used. Every spectrum was accumulated for 128 scans with a resolution of 1 cm^{-1} and a 3 mm aperture. To avoid interference fringes, CCl_4 was used as background. The pure IL was dried in vacuum to a water contend below 10 ppm. 2-Phenylethanol was dried consecutively over molecular sieves 4 Å and 3 Å and distilled freshly to reach a water contend below 10 ppm. The IL/alcohol mixtures were prepared under SCHLENK-conditions in a 5 ml SCHLENK-tube in 2 g portions. Every concentration was mesured as fully protonated as well as fully hydroxyl-deuterated sample to investigate exclusively OH vibrations by subtracting the OD spectrum from the OH spectrum (see below).

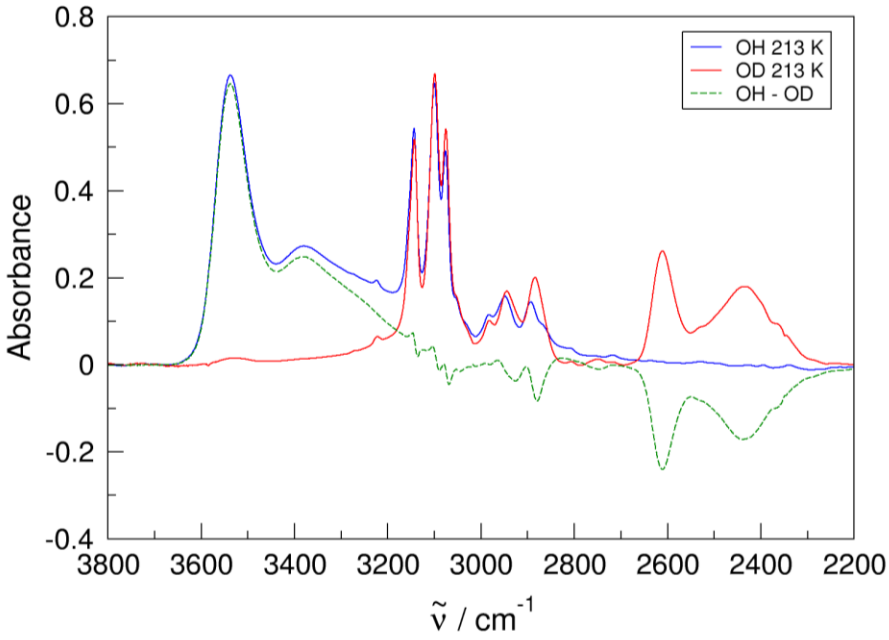


Fig. S0. The infrared spectra of [HEPy][NTf2] for the protonated OH (blue line) and the deuterated OD (red line) hydroxyl groups. The frequency range between 2800 and 3200 cm^{-1} shows the C-H stretch vibrational modes, which are present in both ILs. It is shown that these intensities are almost equal and only have to be corrected slightly for the different densities in the systems. Subtracting the OD spectrum from the OH spectrum leads to the spectra (green line) as shown in **Figures 1 and 3** of the manuscript. These spectra can be nicely deconvoluted without disturbing C-H stretch contributions.

Cryogenic ion vibrational predissociation spectroscopy of cold gas-phase cluster ions

Pure ionic liquids were diluted to millimolar concentrations in acetonitrile and were introduced into the evaporation chamber of a mass spectrometer via electrospray ionization. In case of the mixed complexes the evaporation chamber was saturated with the neutral alcohol by adding a few milliliters of the alcohol (2-Phenylethanol) directly into the chamber. The resulting ions were then transported through differential pumping regions by RF-only octopole guides and electrostatic ion optics into a three-dimensional quadrupole ion trap (R.M. Jordan) mounted to a closed-cycle helium cryostat held at a temperature of ~35 K.[1-3] He buffer gas with a trace amount (~10%) of N_2 was pulsed into the trap to collisionally cool the ions and facilitate the attachment of N_2 adducts for messenger spectroscopy.[4-5] The ions were stored for ~90 ms before being ejected into the time-of-flight region of the photofragmentation mass spectrometer. A particular *m/z* target was intersected with the output of a 10 Hz pulsed OPO/OPA tunable infrared light source (Laservision). Resonant absorption of a single photon caused the evaporation of the weakly bound[6-7] (~800 cm^{-1}) N_2 "tag" and the resulting photofragment was separated by a second stage of mass selection. Spectra were generated by monitoring the photofragment yield as a function of continuously scanned photon energy and normalized to fluctuations in laser pulse energy over the scan range.

Computational Details

Harmonic frequency calculations were performed at the B3LYP-D3/6-31+G(d) level of theory using the Gaussian 09 package[8] for all of the ionic constituents. All calculated vibrational spectra were scaled by a factor of 0.97 based on the OH stretch of $HEPy^+$. Optimized structures were identified for $HPPy^+$, $(HPPy^+)_3(BF_4^-)_2$ amongst the many calculated structures, and their charge states, multiplicities and XYZ coordinates are provided in Tables of Charge State, Multiplicity, Energy and XYZ Coordinates of $(HEPy^+)_2(BF_4^-)_2(PhenEtOH)_2$ (c-c-m-m), $(HEPy^+)_2(BF_4^-)_2(PhenEtOH)_2$ (c-m-c-m), $(HEPy^+)(PhenEtOH)_2$, $(HEPy^+)(PhenEtOH)_3$, and $(PhenEtOH)_4$.

Calculated geometries of neutral and ionic complexes

$(HEPy^+)_2(BF_4^-)_2(PhenEtOH)_2$ (c-c-m-m) (Fig. 3)

0 1, E(RB3LYP) = -2426.80122087

6	0	-5.405368	0.089761	-0.216038
7	0	-4.509697	1.068282	0.061212
6	0	-4.791464	2.372439	-0.175726
6	0	-6.021919	2.734161	-0.702663
6	0	-6.963301	1.743871	-0.995618
6	0	-6.645389	0.407083	-0.748912
6	0	-3.162331	0.683337	0.559573
6	0	-2.261963	0.323226	-0.624415
8	0	-1.031502	-0.106568	-0.055949
8	0	0.480857	0.068378	2.150197
6	0	0.899115	1.417472	1.982379
6	0	1.137116	1.771585	0.490556
7	0	2.296534	2.695289	0.361226
6	0	3.539801	2.160137	0.280128
6	0	4.652361	2.982373	0.213979
6	0	4.478765	4.369122	0.235085
6	0	3.188678	4.895041	0.320259
6	0	2.100590	4.034373	0.381676
8	0	2.540494	-1.013600	0.764602
6	0	3.562296	-1.919071	1.194840
6	0	4.328856	-2.396869	-0.040844
6	0	4.948594	-1.263609	-0.830798
6	0	4.258312	-0.661780	-1.895170

6	0	4.828622	0.394412	-2.611736
6	0	6.101224	0.868386	-2.277483
6	0	6.795512	0.283311	-1.213517
6	0	6.219782	-0.770997	-0.496988
8	0	0.877226	-1.465951	-1.424579
6	0	0.712322	-2.763418	-2.021383
6	0	-0.206880	-3.686323	-1.212723
6	0	0.309866	-3.958623	0.181798
6	0	-0.221848	-3.276354	1.285657
6	0	0.267343	-3.513752	2.574017
6	0	1.286536	-4.448661	2.781019
6	0	1.821976	-5.138874	1.687435
6	0	1.341436	-4.886093	0.399874
9	0	-1.604532	3.404094	1.549724
5	0	-1.639492	4.276115	0.428668
9	0	-2.925557	4.820233	0.294204
9	0	-0.667730	5.286182	0.595804
9	0	-1.320678	3.511786	-0.726384
9	0	-3.548368	-4.429843	-0.486533
5	0	-3.918267	-3.097234	-0.575374
9	0	-3.369575	-2.497720	-1.743403
9	0	-3.420316	-2.363276	0.553558
9	0	-5.327209	-2.934823	-0.599225
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1	0	4.279300	0.841409	-3.436778
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1	0	1.850907	-0.879749	1.459446
1	0	5.105938	-3.096159	0.293245
1	0	3.638527	-2.968281	-0.672187
1	0	3.116540	-2.774579	1.710877
1	0	4.244817	-1.401611	1.886847
1	0	1.467480	-1.525698	-0.638836
1	0	1.702400	-3.224057	-2.159810
1	0	0.282088	-2.582424	-3.011174
1	0	-1.206444	-3.247523	-1.172299
1	0	-0.306957	-4.628169	-1.769392
1	0	-0.511015	-0.661931	-0.687348
1	0	-2.716990	-0.483630	-1.205871
1	0	-2.105127	1.210021	-1.252993
1	0	-2.754809	1.525365	1.120600

1	0	-3.279243	-0.188769	1.202325
1	0	-0.270323	-0.095132	1.530769
1	0	1.839340	1.511231	2.537499
1	0	0.167342	2.112241	2.407779
1	0	0.270451	2.249457	0.038962
1	0	1.383545	0.879985	-0.080237
1	0	1.753055	-5.435244	-0.445885
1	0	1.653159	-4.646455	3.785534
1	0	-0.161099	-2.977159	3.416758
1	0	-4.023206	3.100742	0.061560
1	0	-6.221433	3.785492	-0.878303
1	0	-7.332259	-0.403340	-0.966122
1	0	1.073667	4.386513	0.444639
1	0	5.338920	5.030107	0.181189
1	0	3.589418	1.075465	0.267083
1	0	7.791635	0.633628	-0.952136
1	0	6.550228	1.679680	-2.845298
1	0	3.264814	-1.014605	-2.159187
1	0	5.630279	2.523951	0.128928
1	0	6.772149	-1.229943	0.321120
1	0	-5.102875	-0.932012	-0.018367
1	0	2.606296	-5.877381	1.838261
1	0	-1.048552	-2.588045	1.132574

$(HEPy^{+})_2(BF_4^{-})_2(PhenEtOH)_2$ (c-m-c-m) (Fig. 3)

0 1, E(RB3LYP) = -2426.80952789

6	0	-3.191657	-3.302391	0.894082
6	0	-2.694523	-3.179302	-0.416555
6	0	-1.613178	-3.986373	-0.796963
6	0	-1.054966	-4.908837	0.098390
6	0	-1.567913	-5.035809	1.391885
6	0	-2.639694	-4.223532	1.786243
6	0	-3.381469	-2.196193	-1.348425
6	0	-2.818372	-2.062428	-2.756836
8	0	-1.542406	-1.396340	-2.804426
8	0	-0.088777	-0.897907	-0.480995
6	0	-0.580156	-0.554302	0.817836
6	0	-0.123564	-1.598451	1.837448

7	0	1.351894	-1.766820	1.806262
6	0	1.883334	-2.601568	0.879587
6	0	3.255565	-2.701534	0.730059
6	0	4.091894	-1.923436	1.535970
6	0	3.524543	-1.072830	2.483550
6	0	2.144821	-1.004363	2.592349
8	0	1.030794	1.184997	-1.865848
6	0	2.458509	1.307580	-1.993603
6	0	3.134132	-0.045994	-1.729758
6	0	4.618581	0.053682	-1.457646
6	0	5.075980	0.705752	-0.298140
6	0	6.441842	0.785641	-0.018939
6	0	7.376022	0.212847	-0.890191
6	0	6.932360	-0.435677	-2.045748
6	0	5.563058	-0.510820	-2.325342
8	0	-0.943552	1.094103	-3.723758
6	0	-1.722607	2.072058	-3.039288
6	0	-2.180823	1.562875	-1.656904
7	0	-2.232937	2.634929	-0.632253
6	0	-1.074147	3.031395	-0.043823
6	0	-1.090990	3.967783	0.975160
6	0	-2.316550	4.498449	1.389975
6	0	-3.493275	4.079884	0.769718
6	0	-3.426421	3.136673	-0.244004
9	0	0.890450	1.866892	2.753690
5	0	2.000003	2.121236	1.908361
9	0	1.960121	1.152981	0.855441
9	0	1.907250	3.402653	1.348898
9	0	3.198424	1.952070	2.620314
9	0	-5.539288	-0.805959	0.908718
5	0	-5.001933	0.422147	0.527524
9	0	-3.598110	0.439944	0.828063
9	0	-5.615072	1.505590	1.168769
9	0	-5.120489	0.595983	-0.890093
1	0	7.649244	-0.880210	-2.731985
1	0	3.657949	-3.361696	-0.030096
1	0	-2.351089	5.216941	2.203593
1	0	0.452144	-0.152830	-0.843512
1	0	-0.415251	-1.294182	2.844829
1	0	-0.565008	-2.570485	1.621125

1	0	-1.673079	-0.553102	0.819924
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1	0	-1.103483	-1.404454	-1.924084
1	0	-2.721092	-3.042596	-3.244093
1	0	-3.507183	-1.461263	-3.360453
1	0	-3.398829	-1.209437	-0.878068
1	0	-4.439589	-2.477597	-1.431265
1	0	-1.289679	0.183070	-3.543400
1	0	-2.590335	2.363931	-3.646563
1	0	-1.079053	2.950579	-2.922982
1	0	-1.474488	0.824581	-1.290936
1	0	-3.163534	1.096026	-1.686350
1	0	0.579847	1.085134	-2.735283
1	0	2.773973	2.037389	-1.246481
1	0	2.714786	1.691395	-2.989110
1	0	2.938068	-0.725081	-2.569611
1	0	2.643886	-0.470107	-0.849160
1	0	-1.196848	-3.905742	-1.797456
1	0	-1.143713	-5.760390	2.082751
1	0	-3.048475	-4.309770	2.790136
1	0	-0.162099	2.564781	-0.405656
1	0	-0.149197	4.230867	1.441370
1	0	-4.468458	4.433649	1.083501
1	0	5.224447	-1.016343	-3.228023
1	0	8.439273	0.276564	-0.672432
1	0	4.357095	1.141874	0.390013
1	0	4.123747	-0.410995	3.096375
1	0	5.168534	-1.961270	1.406291
1	0	1.171730	-3.153785	0.279538
1	0	6.775308	1.299423	0.879660
1	0	1.644461	-0.313816	3.259856
1	0	-4.304932	2.724814	-0.723004
1	0	-0.229207	-5.539730	-0.225030
1	0	-4.020583	-2.667465	1.200399

($HEPy^{+}$)$(PhenEthOH)_2$ (Fig. 4,5)

1 1, E(RB3LYP) = -1174.80177108

6	0	-2.555363	-4.219927	0.244339

6	0	-2.450811	-2.823581	0.314001
6	0	-3.602057	-2.051060	0.097911
6	0	-4.828716	-2.658967	-0.180387
6	0	-4.920595	-4.052267	-0.248771
6	0	-3.780351	-4.832052	-0.034503
6	0	-1.114222	-2.157727	0.559619
6	0	-0.351088	-1.927600	-0.752326
8	0	0.856209	-1.163480	-0.543624
8	0	1.962827	-0.387751	1.817720
6	0	3.332587	-0.410772	1.503209
6	0	3.585214	0.281756	0.142975
7	0	5.037738	0.284543	-0.179079
6	0	5.824855	1.290049	0.274983
6	0	7.191406	1.281280	0.045351
6	0	7.758436	0.216479	-0.660857
6	0	6.933080	-0.814111	-1.118727
6	0	5.572026	-0.756896	-0.862382
8	0	0.683040	1.537642	0.084072
6	0	-0.495816	2.359587	-0.058054
6	0	-1.781736	1.574897	0.228492
6	0	-3.020583	2.416255	0.013947
6	0	-3.664968	2.430338	-1.231387
6	0	-4.785316	3.237260	-1.446459
6	0	-5.275928	4.043127	-0.415015
6	0	-4.642079	4.035598	0.831158
6	0	-3.522395	3.227023	1.042077
1	0	0.811304	1.288064	1.018433
1	0	-0.421023	3.236695	0.597171
1	0	-0.482876	2.710396	-1.093527
1	0	0.634938	-0.204258	-0.554595
1	0	-0.988543	-1.413661	-1.482960
1	0	-0.046015	-2.881310	-1.192766
1	0	1.487061	-0.931179	1.142600
1	0	3.727629	-1.438473	1.466403
1	0	3.860031	0.124959	2.300365
1	0	-1.804891	0.698170	-0.429946
1	0	-1.748223	1.203118	1.261952
1	0	-0.492191	-2.767936	1.227281
1	0	-1.260556	-1.190483	1.054910
1	0	3.062784	-0.247239	-0.655998

1	0	3.227536	1.312760	0.154670
1	0	4.876166	-1.520272	-1.191498
1	0	7.331688	-1.656640	-1.673237
1	0	8.826559	0.192010	-0.853701
1	0	7.795274	2.102773	0.415109
1	0	5.322132	2.085558	0.813089
1	0	-3.544589	-0.965870	0.158383
1	0	-5.711890	-2.045002	-0.336492
1	0	-5.874756	-4.526945	-0.460862
1	0	-3.845253	-5.916110	-0.078027
1	0	-1.673563	-4.833917	0.419077
1	0	-3.040159	3.217811	2.018045
1	0	-5.022747	4.653354	1.640198
1	0	-6.149662	4.667838	-0.579088
1	0	-5.277383	3.231801	-2.415485
1	0	-3.293036	1.798776	-2.036452

$(HEPy^{+})(PhenEthOH)_3$ (Fig. 4,5)

1 1, E(RB3LYP) = -1560.95208579

6	0	-4.376943	-1.244917	-2.723111
7	0	-3.200947	-1.404974	-2.072377
6	0	-3.051515	-2.361262	-1.119308
6	0	-4.110474	-3.194322	-0.794698
6	0	-5.334160	-3.043001	-1.452971
6	0	-5.464259	-2.053845	-2.431188
6	0	-2.032883	-0.536043	-2.382605
6	0	-0.903073	-1.296572	-3.134269
8	0	0.366190	-0.916100	-2.640126
8	0	0.272881	1.702249	-1.648479
6	0	1.478141	2.495929	-1.596390
6	0	2.603734	1.777074	-0.839978
6	0	3.857907	2.620821	-0.775637
6	0	4.049120	3.537950	0.267786
6	0	5.183281	4.353174	0.304150
6	0	6.144217	4.261594	-0.707132
6	0	5.964555	3.350290	-1.751735
6	0	4.828533	2.537474	-1.784034

8	0	-0.527849	0.571685	0.675353
6	0	-1.578641	1.201999	1.417414
6	0	-2.938782	1.073824	0.712709
6	0	-4.064901	1.681233	1.518554
6	0	-4.422947	3.026107	1.347410
6	0	-5.431122	3.601219	2.125556
6	0	-6.096237	2.836180	3.088155
6	0	-5.747346	1.494320	3.268175
6	0	-4.738325	0.923683	2.488094
8	0	-0.051709	-1.936726	-0.143671
6	0	0.995666	-2.642325	0.561430
6	0	2.325852	-1.880076	0.516966
6	0	3.416053	-2.634493	1.246366
6	0	3.643131	-2.418696	2.613026
6	0	4.617057	-3.148747	3.299396
6	0	5.377932	-4.107837	2.624725
6	0	5.161100	-4.330300	1.261643
6	0	4.186114	-3.598151	0.579429
1	0	0.458583	0.875670	-2.146670
1	0	1.795809	2.748591	-2.615808
1	0	1.203281	3.425329	-1.089758
1	0	-0.246519	1.125533	-0.098484
1	0	-1.336737	2.258871	1.586731
1	0	-1.611644	0.707756	2.393144
1	0	-0.215411	-1.067276	0.307335
1	0	0.685231	-2.813678	1.599889
1	0	1.089757	-3.615512	0.070661
1	0	0.448226	-1.330379	-1.743377
1	0	-1.051778	-2.380345	-3.029131
1	0	-0.921683	-1.056439	-4.200480
1	0	2.247796	1.536044	0.169537
1	0	2.813517	0.823594	-1.343280
1	0	2.606571	-1.721187	-0.532546
1	0	2.178583	-0.889428	0.964845
1	0	-2.869988	1.559893	-0.269797
1	0	-3.131181	0.005034	0.541966
1	0	-1.653697	-0.173705	-1.427854
1	0	-2.398056	0.326153	-2.942415
1	0	-2.070150	-2.417020	-0.648331
1	0	-3.969218	-3.948387	-0.027962

1	0	-6.174576	-3.684825	-1.206794
1	0	-6.395858	-1.901038	-2.964857
1	0	-4.414280	-0.456478	-3.465761
1	0	-3.910014	3.627958	0.599236
1	0	-5.697401	4.644625	1.979336
1	0	-6.880665	3.282105	3.693334
1	0	-6.259482	0.893464	4.015134
1	0	-4.469256	-0.121361	2.635731
1	0	3.060795	-1.665989	3.141604
1	0	4.786115	-2.963766	4.356940
1	0	6.139299	-4.672913	3.155485
1	0	5.755099	-5.067994	0.728507
1	0	4.029383	-3.769253	-0.484294
1	0	4.698561	1.825235	-2.597012
1	0	6.710309	3.268483	-2.538161
1	0	7.028864	4.891916	-0.678385
1	0	5.319082	5.054289	1.123494
1	0	3.308526	3.608684	1.062702

$(PhenEthOH)_4$ (Fig. 4,5)

0 1, E(RB3LYP) = -1544.532669290

6	0	-4.376943	-1.244917	-2.723111
7	0	-3.200947	-1.404974	-2.072377
6	0	-3.051515	-2.361262	-1.119308
6	0	-4.110474	-3.194322	-0.794698
6	0	-5.334160	-3.043001	-1.452971
6	0	-5.464259	-2.053845	-2.431188
6	0	-2.032883	-0.536043	-2.382605
6	0	-0.903073	-1.296572	-3.134269
8	0	0.366190	-0.916100	-2.640126
8	0	0.272881	1.702249	-1.648479
6	0	1.478141	2.495929	-1.596390
6	0	2.603734	1.777074	-0.839978
6	0	3.857907	2.620821	-0.775637
6	0	4.049120	3.537950	0.267786
6	0	5.183281	4.353174	0.304150
6	0	6.144217	4.261594	-0.707132
6	0	5.964555	3.350290	-1.751735

6	0	4.828533	2.537474	-1.784034
8	0	-0.527849	0.571685	0.675353
6	0	-1.578641	1.201999	1.417414
6	0	-2.938782	1.073824	0.712709
6	0	-4.064901	1.681233	1.518554
6	0	-4.422947	3.026107	1.347410
6	0	-5.431122	3.601219	2.125556
6	0	-6.096237	2.836180	3.088155
6	0	-5.747346	1.494320	3.268175
6	0	-4.738325	0.923683	2.488094
8	0	-0.051709	-1.936726	-0.143671
6	0	0.995666	-2.642325	0.561430
6	0	2.325852	-1.880076	0.516966
6	0	3.416053	-2.634493	1.246366
6	0	3.643131	-2.418696	2.613026
6	0	4.617057	-3.148747	3.299396
6	0	5.377932	-4.107837	2.624725
6	0	5.161100	-4.330300	1.261643
6	0	4.186114	-3.598151	0.579429
1	0	0.458583	0.875670	-2.146670
1	0	1.795809	2.748591	-2.615808
1	0	1.203281	3.425329	-1.089758
1	0	-0.246519	1.125533	-0.098484
1	0	-1.336737	2.258871	1.586731
1	0	-1.611644	0.707756	2.393144
1	0	-0.215411	-1.067276	0.307335
1	0	0.685231	-2.813678	1.599889
1	0	1.089757	-3.615512	0.070661
1	0	0.448226	-1.330379	-1.743377
1	0	-1.051778	-2.380345	-3.029131
1	0	-0.921683	-1.056439	-4.200480
1	0	2.247796	1.536044	0.169537
1	0	2.813517	0.823594	-1.343280
1	0	2.606571	-1.721187	-0.532546
1	0	2.178583	-0.889428	0.964845
1	0	-2.869988	1.559893	-0.269797
1	0	-3.131181	0.005034	0.541966
1	0	-1.653697	-0.173705	-1.427854
1	0	-2.398056	0.326153	-2.942415
1	0	-2.070150	-2.417020	-0.648331

1	0	-3.969218	-3.948387	-0.027962
1	0	-6.174576	-3.684825	-1.206794
1	0	-6.395858	-1.901038	-2.964857
1	0	-4.414280	-0.456478	-3.465761
1	0	-3.910014	3.627958	0.599236
1	0	-5.697401	4.644625	1.979336
1	0	-6.880665	3.282105	3.693334
1	0	-6.259482	0.893464	4.015134
1	0	-4.469256	-0.121361	2.635731
1	0	3.060795	-1.665989	3.141604
1	0	4.786115	-2.963766	4.356940
1	0	6.139299	-4.672913	3.155485
1	0	5.755099	-5.067994	0.728507
1	0	4.029383	-3.769253	-0.484294
1	0	4.698561	1.825235	-2.597012
1	0	6.710309	3.268483	-2.538161
1	0	7.028864	4.891916	-0.678385
1	0	5.319082	5.054289	1.123494
1	0	3.308526	3.608684	1.062702

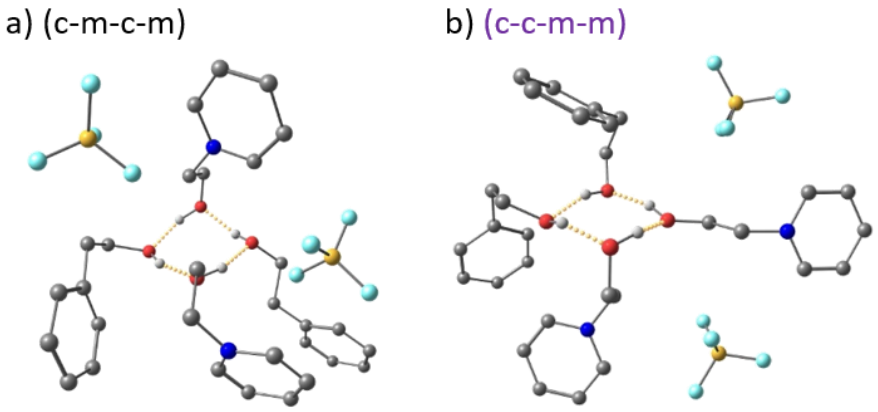

Fig. S1. Calculated cyclic tetramer neutral clusters formed in the IL/ML bulk, with their calculated frequencies shown in **Fig. 3**. H-atoms connected to carbon atoms are omitted for clarity.

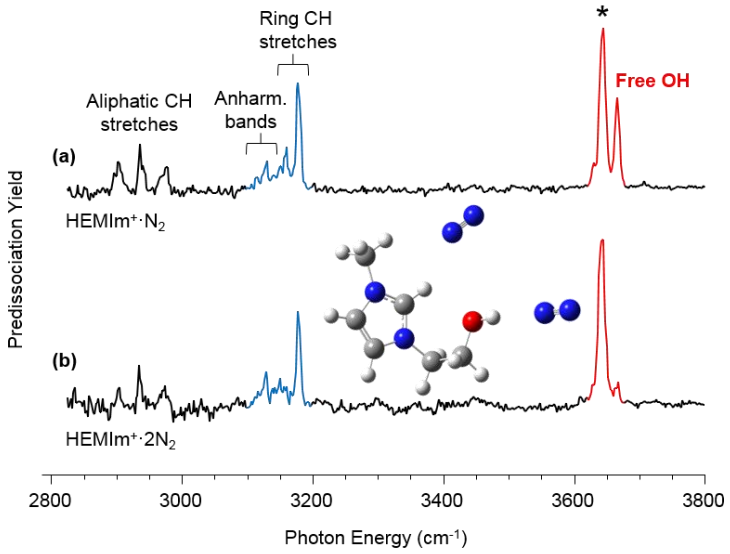

Fig. S2. Vibrational predissociation spectra of previously studied (a) $HEMIm^{+}\cdot N_2$ and (b) $HEMIm^{+}\cdot 2N_2$.[28] The OH stretches are colored red and the ring CH bands are blue. The asymmetric doublet in trace (a) represents two types of binding motifs for the N_2 adduct, one in which it is attached remotely (resulting in the free OH band) and another where it is bound to the OH, which result in the redshifted OH band (*). With the attachment of a second N_2 tag, the free OH band is significantly reduced in trace (b) while * feature still remains with increased intensity.

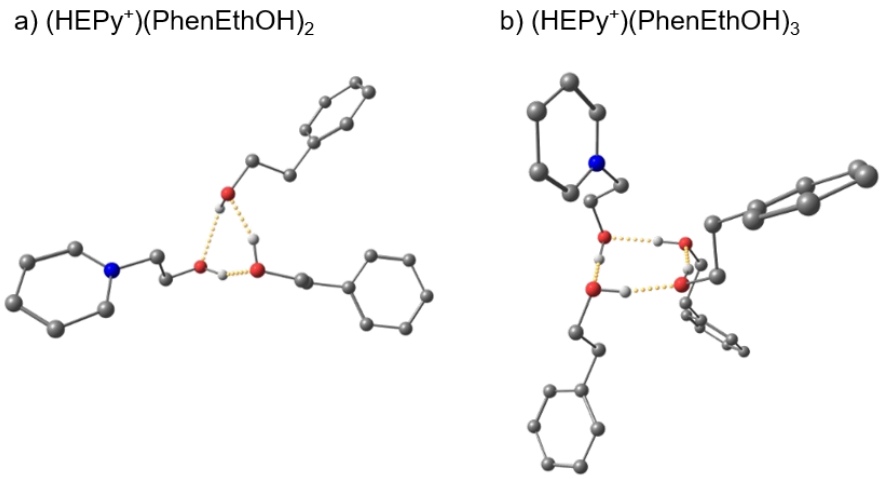

Fig. S3. Calculated cyclic trimer and tetramer ionic clusters formed in the gas phase, with their calculated frequencies shown in **Fig. 4**. H-atoms connected to carbon atoms are omitted for clarity.

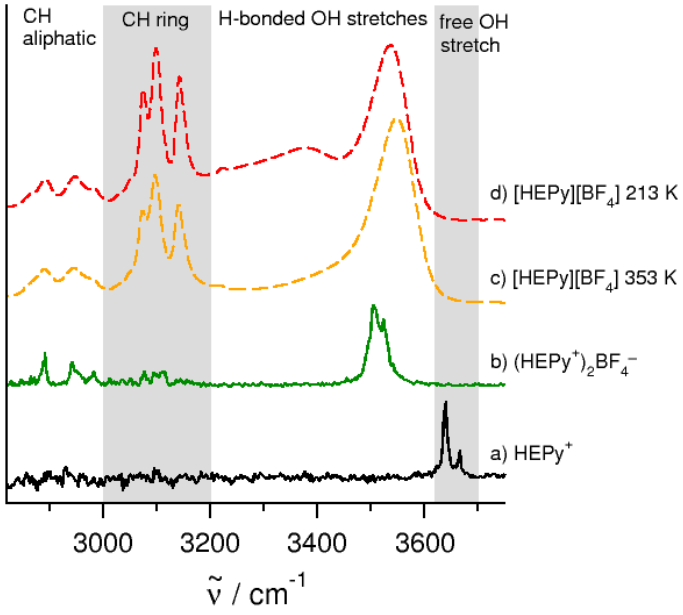

Fig. S4. Vibrational predissociation spectra of N_2-tagged (a) $HEPy^+$ (black line) and (b) $(HEPy^+)_2BF_4^-$ (green line). The OH doublet observed in the cationic (2,1) cluster correspond to the (c-a) bands of the bulk liquid IR spectra of [HEPy][BF_4] at 213 K (red dashed line) and 353 K (orange dashed line).

Experimental Frequencies

Table S1. Experimental frequencies (cm^{-1}, ±4 cm^{-1}) for the ionic species obtained by N_2 predissociation displayed in Fig. 4. The Free OH frequencies marked by an asterisk is a red-shifted value caused by the binding of the N_2 tagging molecule.

Complex	X_4	X_3	X_2	X_1	ν_{OH}^{free}
$HPPy^+$	-	-	-	-	3640*, 3666
$(HPPy^+)(PhenEthOH)_2$				3401	3639*, 3659
$(HPPy^+)(PhenEthOH)_2$		3289	3369	3525	-
$(HPPy^+)(PhenEthOH)_3$	3223	3285	3341	3467	-

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