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Supplementary Information

Anti-electrostatic hydrogen bonding between anions of ionic liquids: a density functional theory study

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Table of Contents

Table of Contents 2

Fig. S1 Potential energy curves at different calculation methods. 3

Fig. S2 Simulated infrared spectra of the dimers and ion pair. 4

Fig. S3 NBO 3d overlap diagrams and QTAIM molecular graphs. 5

Fig. S4 The lowest-energy and low-lying structures of ion clusters (No. 1-16) 6

Fig. S5 The low-lying structures of ion clusters (No. 17-32) 7

Fig. S6 The low-lying structures of ion clusters (No. 33-44) 8

Fig. S7 Potential energy curve of anionic dimer (OH···N). 9

Fig. S8 Simulated infrared spectrum of the anionic dimer (O–H□□□N). 10

Fig. S9 Simulated infrared spectra of ionic clusters in Fig. 6. 11

Table S1 Selected data calculated at different theoretical levels. 12

Table S2 SAPT interaction energy decomposition results. 12

Table S3 Calculated data for the OH···N hydrogen bonding between anions. 13

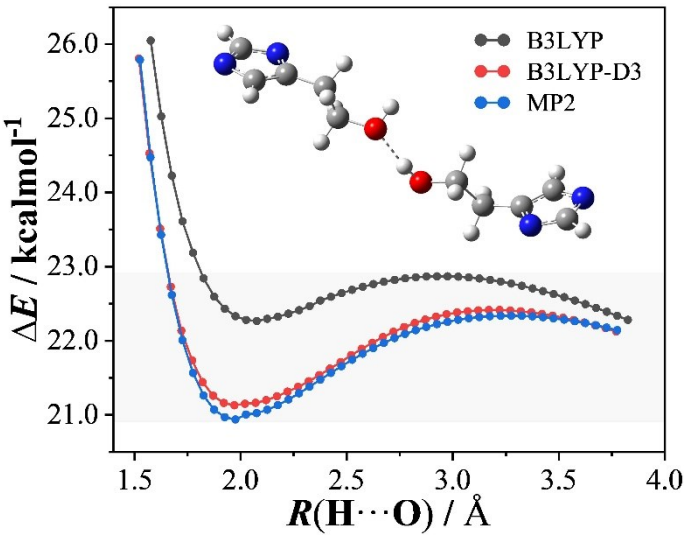

Fig. S1 Relaxed-scan potential energy curves for the anionic dimer, along the R(OH···O) hydrogen-bond stretching coordinate at different calculation methods.

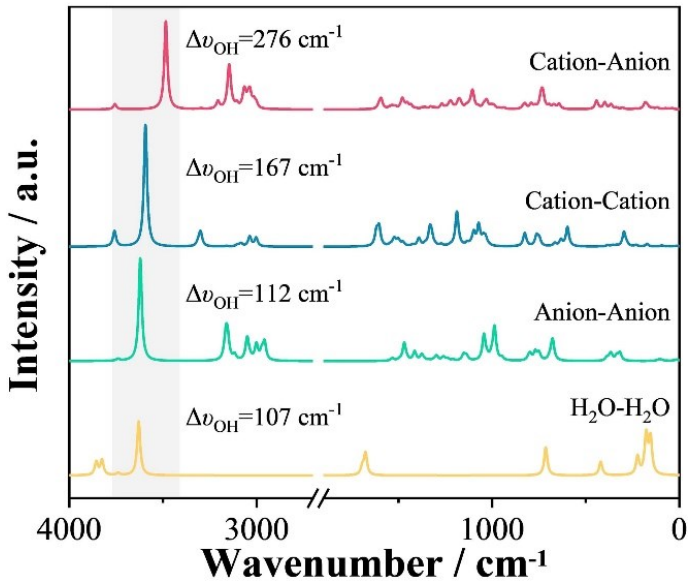

Fig. S2 Simulated infrared spectra of the dimers and ion pair at B3LYP-D3/6-31+G* level.

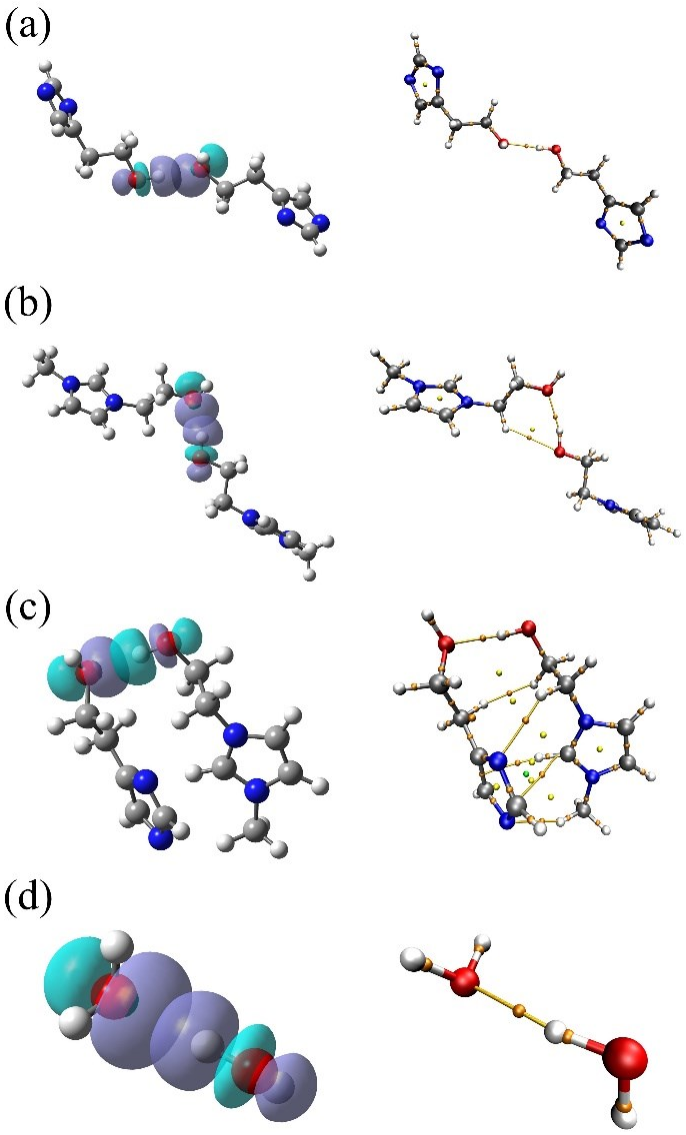

Fig. S3 NBO 3d overlap diagrams for n→σ* donor–acceptor interaction (left) and QTAIM molecular graphs (right) of the equilibrium geometries of anionic dimer (a), cationic dimer (b), cation-anion pair (c) and H_2O dimer (d). Larger spheres represent the atoms (C=gray, H=white, O=red, N=blue, S=yellow, Cr=mauve). Orange lines connecting the atoms are the bond paths traced within the electron density distribution. The small orange dots represent the bond critical points (BCPs), while the small yellow dots indicate the positions of ring critical points (RCPs).

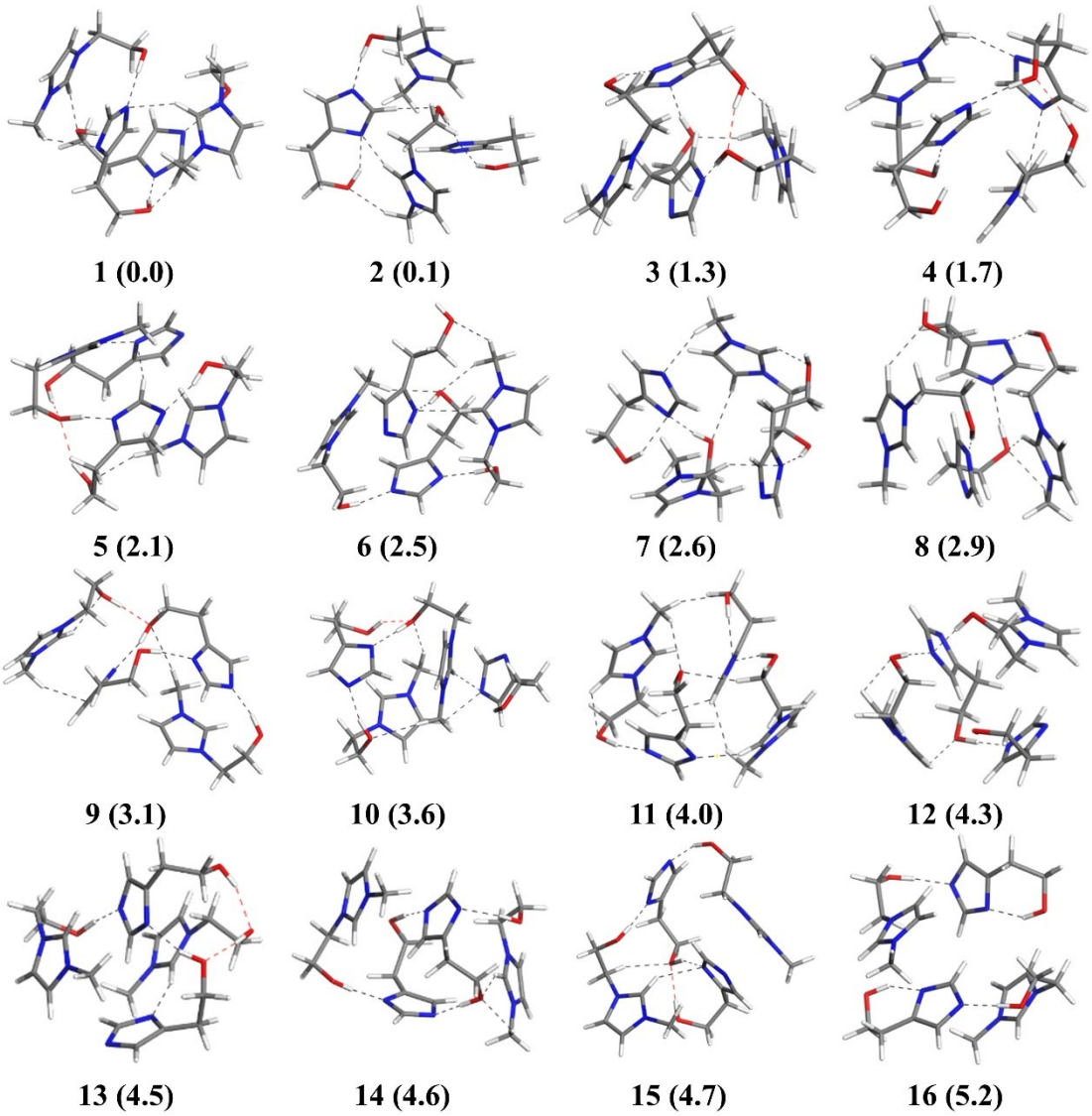

Fig. S4 The lowest-energy and low-lying structures of ion clusters $(HEMIm^{+})_2(HEIm^{-})_2$ at B3LYP-D3/6-31+G* level. The values in parentheses are the energy differences ($kcalmol^{-1}$) from the lowest-energy structure. Color legend: C grey, H white, O red, N blue. The red dashed lines represent the hydrogen bonds between hydroxyl groups and the black dashed lines represent other hydrogen bonds. (Note, too weak hydrogen bonds are ignored.)

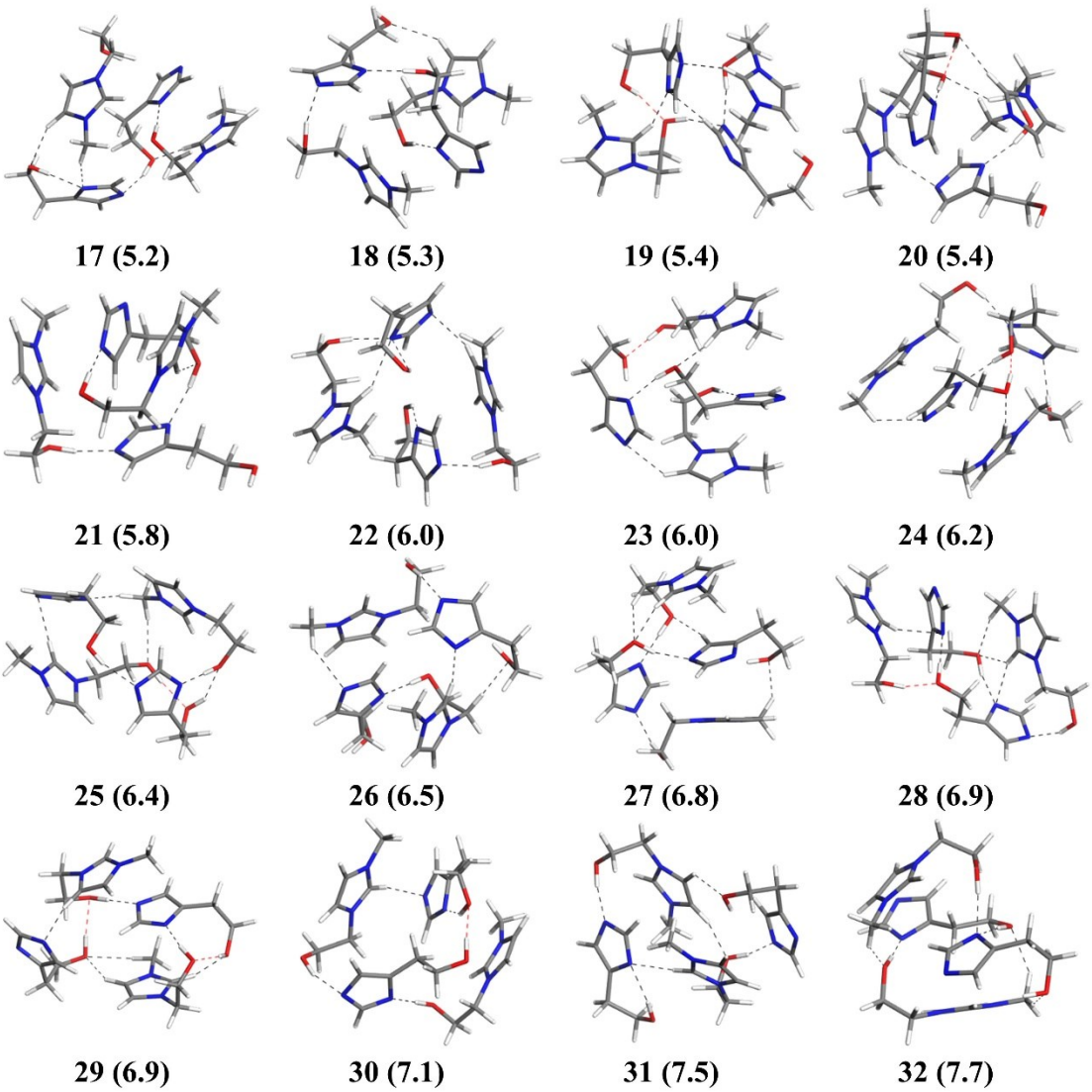

Fig. S5 The low-lying structures of ion clusters $(HEMIm^{+})_2(HEIm^{-})_2$ at B3LYP-D3/6-31+G* level. The values in parentheses are the energy differences ($kcalmol^{-1}$) from the lowest-energy structure. Color legend: C grey, H white, O red, N blue. The red dashed lines represent the hydrogen bonds between hydroxyl groups and the black dashed lines represent other hydrogen bonds. (Note, too weak hydrogen bonds are ignored.)

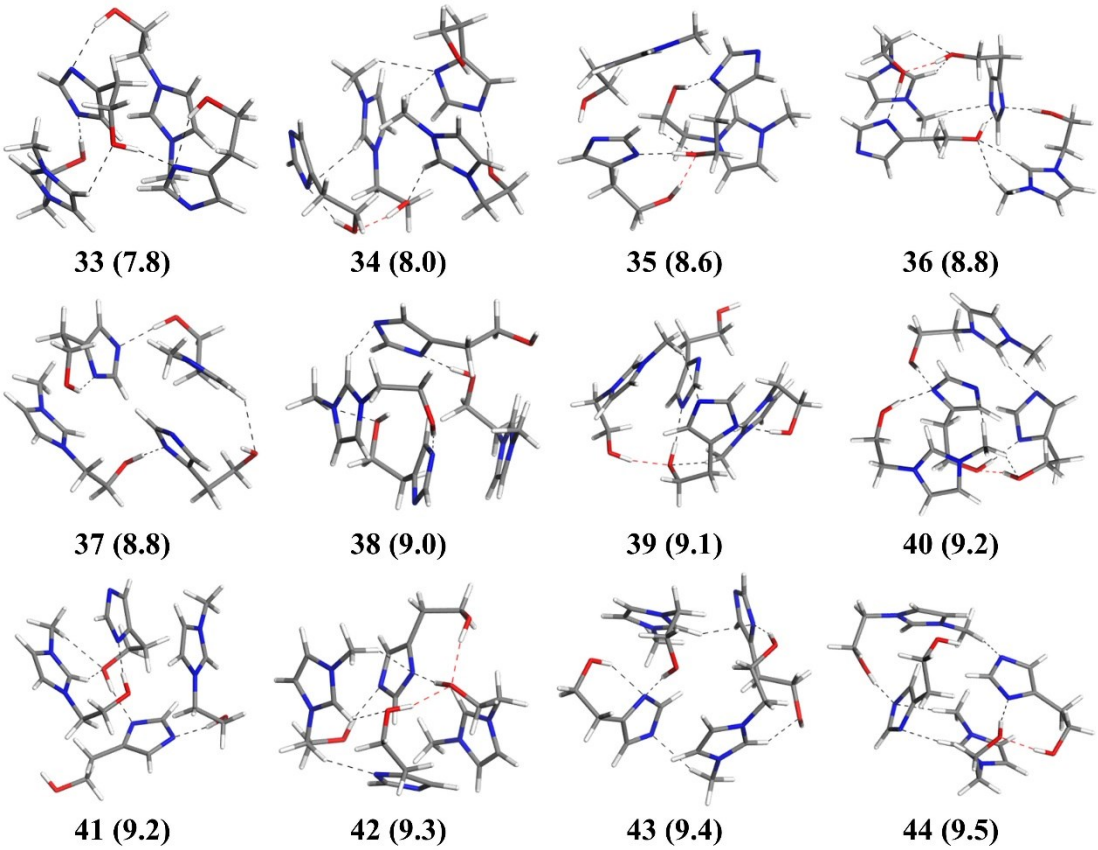

Fig. S6 The low-lying structures of ion clusters $(HEMIm^{+})_2(HEIm^{-})_2$ at B3LYP-D3/6-31+G* level. The values in parentheses are the energy differences ($kcalmol^{-1}$) from the lowest-energy structure. Color legend: C grey, H white, O red, N blue. The red dashed lines represent the hydrogen bonds between hydroxyl groups and the black dashed lines represent other hydrogen bonds. (Note, too weak hydrogen bonds are ignored.)

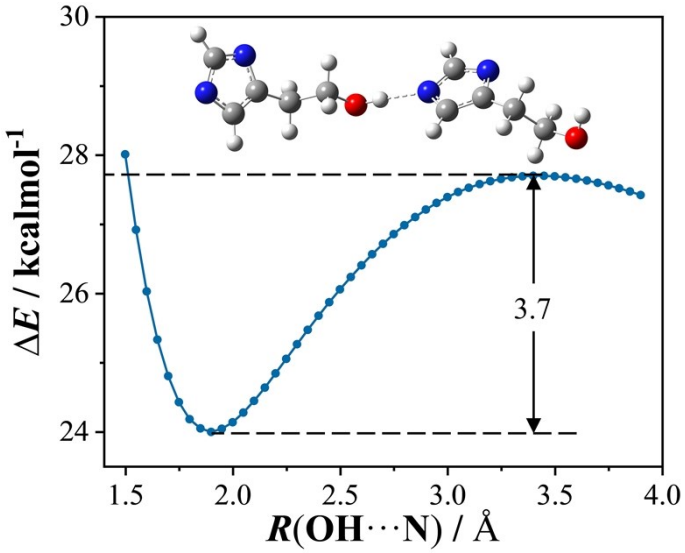

Fig. S7 Relaxed-scan potential energy curve (B3LYP-D3/6-31+G*) of anionic dimer, along the R(OH···N) hydrogen-bonding stretching coordinate.

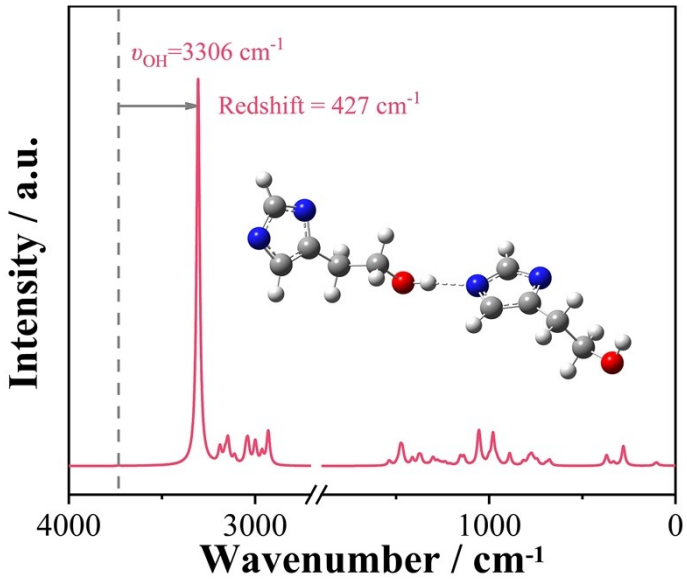

Fig. S8 Simulated infrared spectrum of the anionic dimer (O–H□□□N) at B3LYP-D3/6-31+G* level.

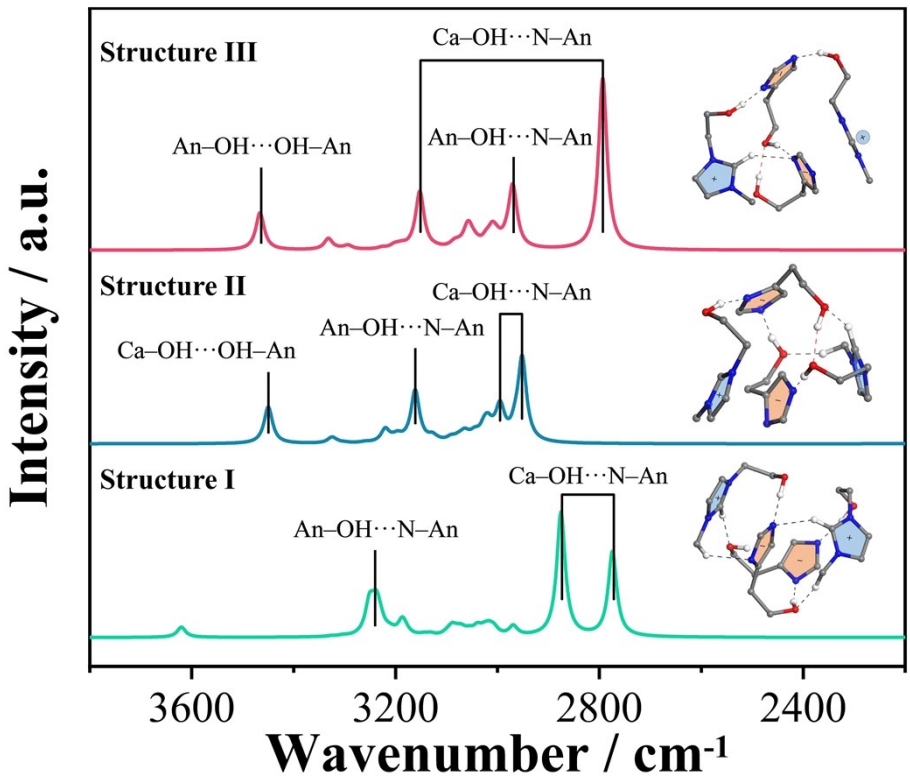

Fig. S9 Simulated infrared spectra of ionic clusters in Fig. 6. The stretching vibration absorption peaks of the associated hydroxyl groups are marked.

The results show that both inter-anionic HBs (An–OH···OH–An and An–OH···N–An) exhibit significant redshifts and appreciate intensities of absorption peaks. Thus, in the case of rational design of ionic liquids, inter-anionic HBs are expected to be experimentally detected through infrared spectroscopy.

Table S1 Selected data calculated at different theoretical levels for the hydrogen bonds in the anionic dimers.

Method	HB length (Å)	υ(OH) (cm^{-1})	HB well depths ($kcalmol^{-1}$)
B3LYP	2.08	3664	0.6
B3LYP-D3	1.97	3621	1.3
MP2	1.98	3656	1.4

Table S2 SAPT interaction energy decomposition results for the hydrogen bonding in the complexes at SAPT2+ level with aug-cc-pVDZ basis set.

	Electrostatics ($kcalmol^{-1}$)	Exchange ($kcalmol^{-1}$)	Induction ($kcalmol^{-1}$)	Dispersion ($kcalmol^{-1}$)	Total energy ($kcalmol^{-1}$)
Cation-Anion (OH···OH)	-110.6	48.6	-25.0	-21.2	-108.2
H_2O dimer (OH···OH)	-9.2	9.9	-2.9	-2.4	-4.7
Cation-Cation (OH···OH)	23.0	10.4	-4.5	-3.9	25.1
Anion-Anion (OH···OH)	21.7	9.0	-3.6	-3.3	23.8

Table S3 Calculated geometric parameters, harmonic frequencies, QTAIM and NBO data for the OH···N hydrogen bonding between anions.

HB length (Å)	1.90	ρ_{BCP} (a.u.)	0.034
υ(OH) (cm^{-1})	3306	$\nabla^2\rho_{BCP}$ (a.u.)	0.092
Redshift of υ(OH) (cm^{-1})	427	H_{BCP} (a.u.)	-0.0012
Charge transfer (e)	0.050	$E^{(2)}$ ($kcalmol^{-1}$)	21.8