Hydrogen Bonding in the Crystal Structures of Hydrophobic and Hydrophilic COOH-functionalized Imidazolium Ionic Liquids

Xiao-Peng Xuan,* Liang-Liang Chang, Heng Zhang, Na Wang and Yang Zhao

Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xinxiang, Henan 453007, P. R. China

* Corresponding author, E-mail: xpxuan@henannu.edu.cn

1.1. Synthesis

Compounds 1-3 were synthesized similarly. The typical synthesis route for **1** is reported in literature. 1H NMR(400 MHz, D_2O): δ =8.72 (s, 1H), 7.43 (s, 2H), 5.03 (s, 2H), 3.87 ppm (s, 3H).

Compounds 4-6 were synthesized similarly. The typical synthesis route for **4** is: A mixture of 1-carboxyethyl-3-methylimidazolium bromide (0.01 mol) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (0.01 mol) in 10 mL water was stirred for 24 h at room temperature and the aqueous phase separated from the ionic liquid. The ionic liquid phase was washed by (3 ×10 ml) with distilled water, and dried in vacuum to give the product. Single crystals were grown in an ethanol + dichloromethane mixture (1:1). NMR (400 MHz, DMSO-d_6): δ=9.11 (s,1H), 7.71 (d,2H), 4.35 (t,2H), 3.85 (s,3H), 2.89 ppm (t,2H).

1.2. Measurements and computational method

FT-IR spectra were collected using a Nicolet Nexus FT-IR spectrometer with a KBr pellet for data collection. The FT-Raman spectra were recorded on a Raman module of the Nexus spectrometer with 1064 nm excitation from a Nd:YAG laser. Both IR and Raman spectra are obtained with a resolution of 2 cm^{-1} at room

temperature. Differential scanning calorimetric (DSC) measurements were carried out in a nitrogen stream at a rate of 10 °C min^{-1} on a Netzsch STA 449 C system using α-Al_2O_3 as a reference material. NMR spectra were measured in D_2O or DMSO-d6 on a Bruker AV-400 NMR Spectrometer at room temperature. Solubility was determined.

A single crystal with appropriate dimensions was mounted on a Bruker APEX-II CCD diffractometer with graphite-monochromated *MoKα* radiation with λ = 0.71073 Å at room temperature. Absorption corrections were applied using the SADABSprogram. Crystal structure was solved by direct methods using SHELXL97 software, and subsequently refined by full-matrix least-squares. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

Density functional calculations of the geometric optimization and the electrostatic potential were carried out using Gaussian 09 program. The optimized structures were used for the vibrational frequency calculations at the same level to confirm their stability. All of calculations were used at ωB97XD/6-311++G(d,p) and B3LYP/6-311++G(d,p) levels

1.3. Figures

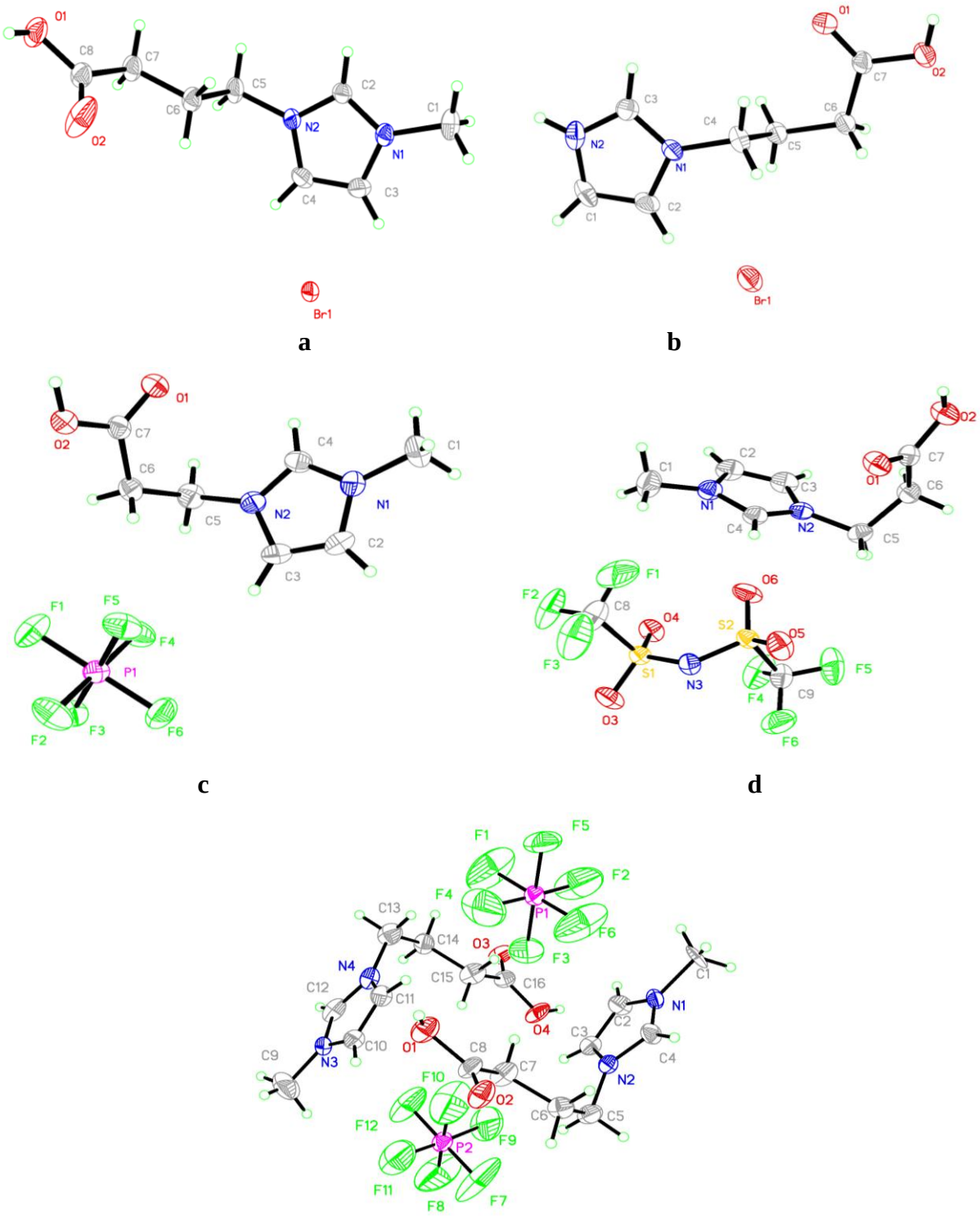


Fig.S1 ORTEP drawings for 1-carboxypropyl-3-methylimidazolium bromide (a), 1-carboxypropyl-imidazolium bromide (b), 1-carboxyethyl-3-methylimidazolium hexafluorophosphate (c), 1-carboxypropyl-3-methylimidazolium bistrifluoromethanesulfonimide (d), and 1-carboxyethy-3-methylimidazolium hexafluorophosphate (e) (50% thermal ellipsoids).

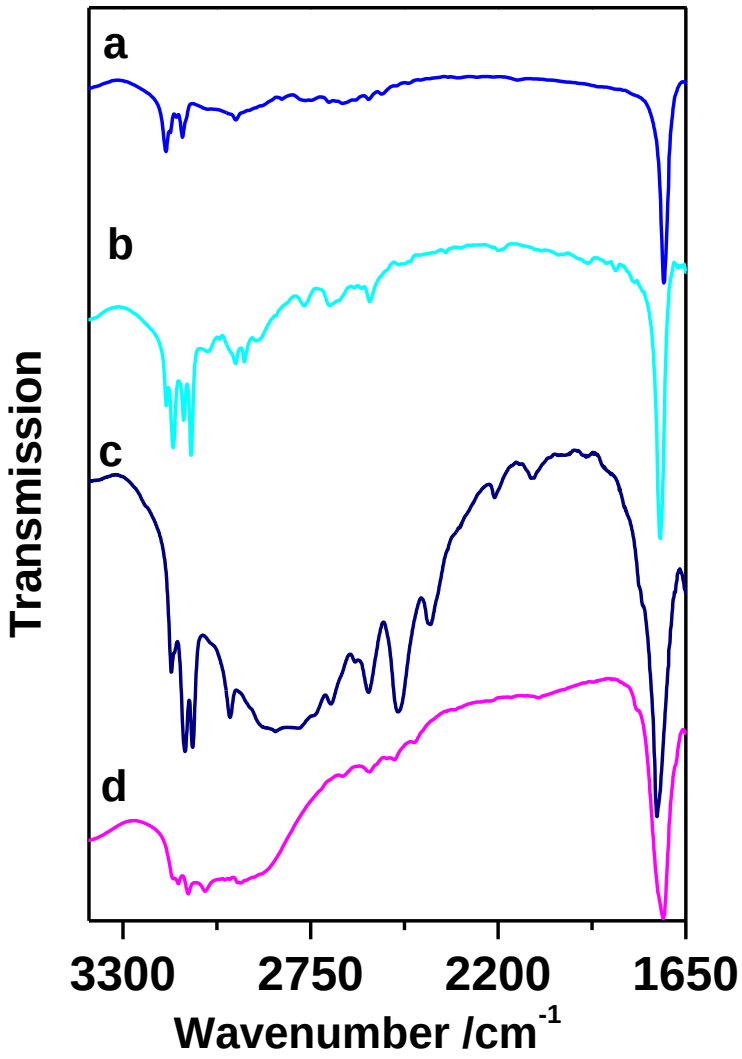
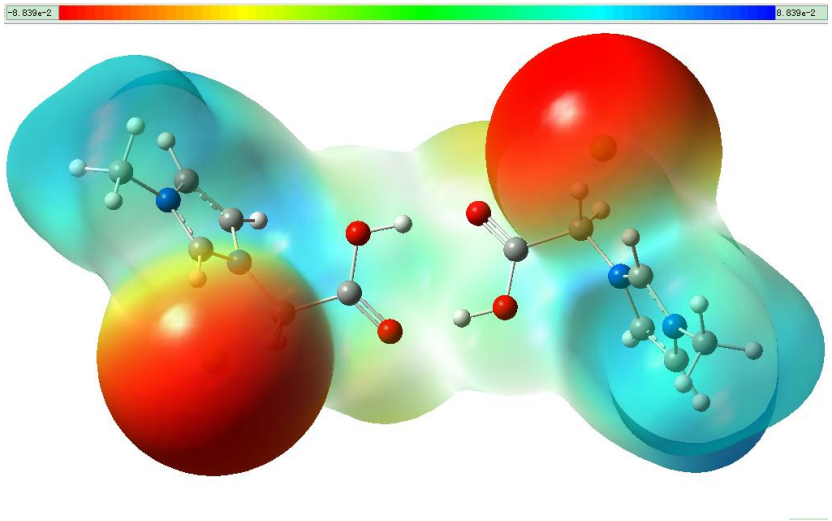
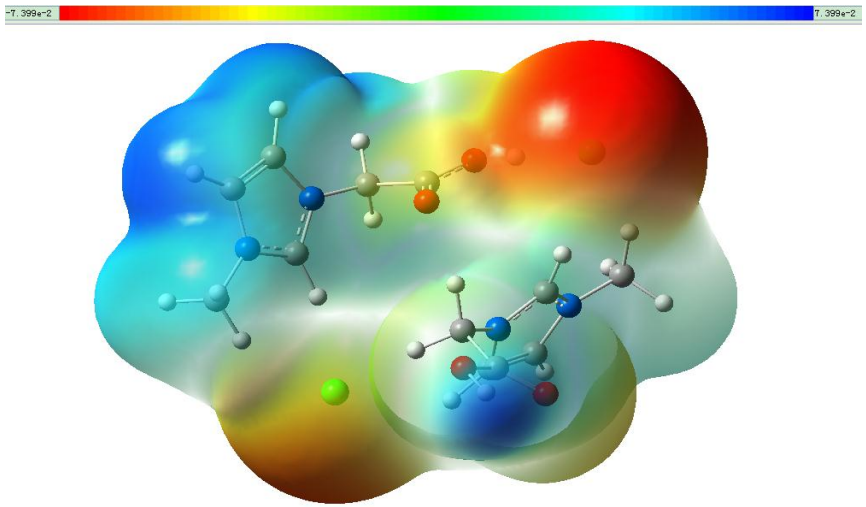


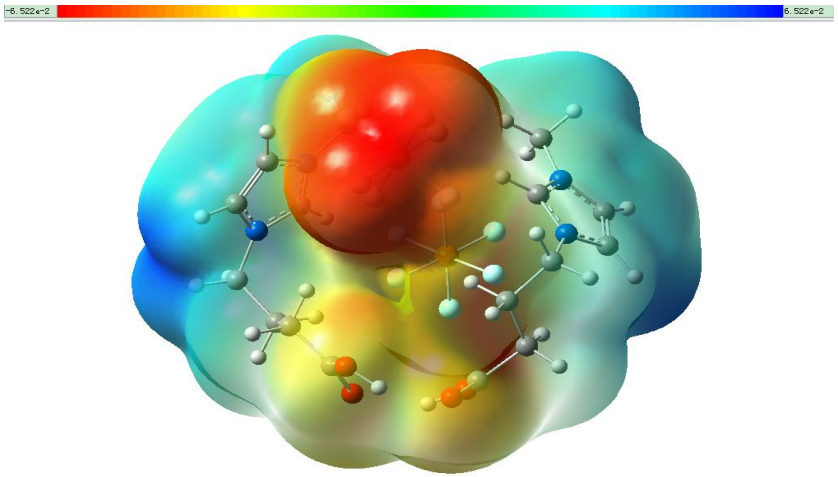
Fig S2 Infrared spectra of 1-carboxypropyl-3-methylimidazolium hexafluorophosphate (a), 1-carboxyethy-3-methylimidazolium bistrifluoromethanesulfonimide (b), 1-carboxymethyl-3-methylimidazolium bromide (c), and 1-carboxypropyl-3-methylimidazolium bromide (d).



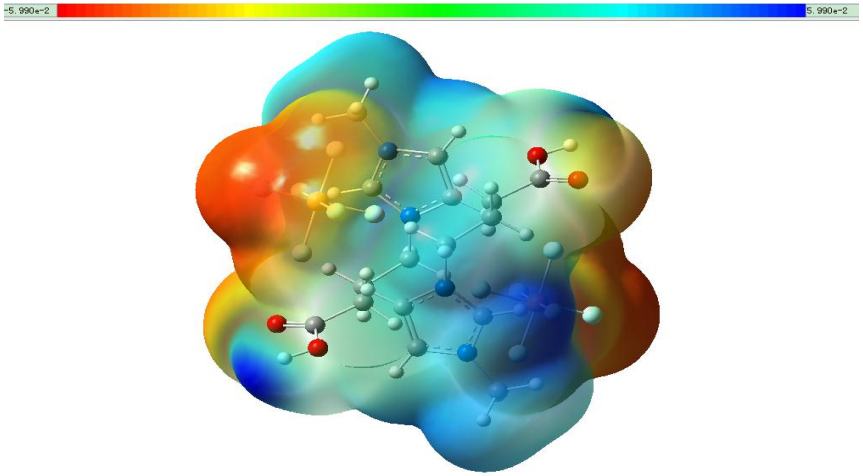
a



b



c



d

Fig. S3 Electrostatic potential diagrams for structures ***a-d*** calculated at wb98xd/6-311G++(d,p) level

1.4 Tables

Table S1 Atom Coordinates Calculated at the wb97xd/6-311++G(d,p) level of theory

Structure a

7	-0.943408000	5.702912000	-0.395224000
7	0.170763000	4.204719000	0.677183000
6	-1.363364000	6.602663000	-1.462130000
1	-0.628151000	6.549755000	-2.263002000
1	-1.411494000	7.622488000	-1.080959000
1	-2.339039000	6.298003000	-1.841186000
6	-1.532575000	5.576944000	0.849169000
1	-2.390201000	6.158894000	1.139962000
6	-0.831903000	4.634187000	1.520994000
1	-0.969885000	4.222238000	2.505377000
6	0.082385000	4.861705000	-0.479405000
1	0.821247000	4.716319000	-1.298087000
6	1.176041000	3.182390000	0.934676000
1	1.708031000	3.406159000	1.860621000
1	1.902702000	3.224440000	0.100755000
6	0.616429000	1.784248000	1.020682000
8	-0.681588000	1.694167000	0.875303000
8	1.363364000	0.844324000	1.219910000
1	0.974474000	-0.747946000	0.980003000
7	0.943408000	-5.702912000	-0.395224000
7	-0.170763000	-4.204719000	0.677183000
6	1.363364000	-6.602663000	-1.462130000
1	0.628151000	-6.549755000	-2.263002000
1	1.411494000	-7.622488000	-1.080959000
1	2.339039000	-6.298003000	-1.841186000
6	1.532575000	-5.576944000	0.849169000
1	2.390201000	-6.158894000	1.139962000
6	0.831903000	-4.634187000	1.520994000
1	0.969885000	-4.222238000	2.505377000
6	-0.082385000	-4.861705000	-0.479405000
1	-0.821247000	-4.716319000	-1.298087000
6	-1.176041000	-3.182390000	0.934676000
1	-1.708031000	-3.406159000	1.860621000
1	-1.902702000	-3.224440000	0.100755000
6	-0.616429000	-1.784248000	1.020682000
8	0.681588000	-1.694167000	0.875303000
8	-1.363364000	-0.844324000	1.219910000

1	-0.974474000	0.747946000	0.980003000
17	-2.649250000	-4.038761000	-1.949578000
17	2.649250000	4.038761000	-1.949578000

Structure b

17	3.712379000	6.070623000	5.712936000
7	9.284507000	-4.328115000	7.361019000
7	7.976379000	-3.794908000	8.987590000
6	9.981431000	-4.246229000	6.077447000
1	9.750849000	-3.276733000	5.632305000
1	9.643013000	-5.050378000	5.424370000
1	11.053957000	-4.326884000	6.249810000
6	9.444108000	-5.290810000	8.336929000
1	10.121796000	-6.119208000	8.221617000
6	8.626485000	-4.951751000	9.363102000
1	8.455741000	-5.425088000	10.314628000
6	8.395832000	-3.435160000	7.773393000
1	8.135362000	-2.516897000	7.215281000
6	7.053715000	-2.989958000	9.774463000
1	6.965675000	-3.429092000	10.768934000
1	6.070857000	-2.979377000	9.305309000
6	7.595532000	-1.565461000	9.895400000
8	8.784170000	-1.350784000	9.991119000
8	6.644305000	-0.677347000	9.865548000
1	7.036359000	0.225132000	9.711820000
17	8.350433000	-0.792000000	6.059369000
7	6.119646000	3.235885000	5.723348000
7	8.043488000	2.986848000	6.662145000
6	4.897249000	2.960415000	4.960401000
1	4.420717000	2.068741000	5.366602000
1	5.152781000	2.809302000	3.911706000
1	4.242124000	3.834388000	5.067092000
6	6.420156000	4.441744000	6.324946000
1	5.700432000	5.268016000	6.257803000
6	7.626980000	4.279518000	6.921125000
1	8.222519000	4.962060000	7.502283000
6	7.102265000	2.372256000	5.941310000
1	7.156607000	1.334007000	5.633489000
6	9.219607000	2.336102000	7.190912000
1	9.973610000	3.086057000	7.434292000
1	9.630107000	1.649310000	6.448325000
6	8.895113000	1.507772000	8.417433000
8	7.793592000	1.473989000	8.924178000

8	9.945432000	0.846001000	8.843990000

Structure c

8	-1.428303000	-3.754716000	-0.873333000
1	-0.557333000	-4.182362000	-1.007118000
8	-1.195207000	-3.227301000	-3.032932000
7	-3.281765000	1.496979000	1.440088000
7	-3.587950000	0.716236000	-0.548642000
6	-2.690657000	2.225235000	2.556689000
1	-1.835810000	2.782266000	2.180432000
1	-2.353099000	1.507560000	3.302181000
1	-3.430274000	2.910158000	2.972266000
6	-4.370500000	0.659471000	1.503311000
1	-4.890929000	0.470429000	2.425740000
6	-4.563379000	0.170189000	0.254603000
1	-5.295245000	-0.520406000	-0.126682000
6	-2.816534000	1.501865000	0.196759000
1	-1.943446000	2.040999000	-0.142624000
6	-3.343644000	0.416349000	-1.965492000
1	-2.964142000	1.329079000	-2.421855000
1	-4.312365000	0.180214000	-2.411936000
6	-2.338206000	-0.708846000	-2.158174000
1	-1.432563000	-0.465941000	-1.596609000
1	-2.058093000	-0.724360000	-3.213791000
6	-2.864207000	-2.090836000	-1.752442000
1	-3.168171000	-2.113693000	-0.706304000
1	-3.709812000	-2.373429000	-2.388469000
6	-1.759361000	-3.093902000	-1.961381000
8	1.285370000	-3.990299000	-1.123623000
8	1.417593000	-2.613294000	-2.883294000
1	0.573520000	-3.047875000	-3.133440000
7	2.873035000	1.475049000	1.451185000
7	3.941208000	-0.332475000	0.948139000
6	1.955965000	2.398172000	2.114149000
1	1.140961000	1.820138000	2.541323000
1	2.495317000	2.946290000	2.887856000
1	1.554879000	3.079402000	1.368423000
6	3.772705000	1.806523000	0.467235000
1	3.804561000	2.794249000	0.041933000
6	4.445021000	0.673666000	0.151407000
1	5.212942000	0.490509000	-0.579758000
6	2.980400000	0.179165000	1.716351000
1	2.359858000	-0.369583000	2.410941000
6	4.343120000	-1.744454000	0.914611000

1	5.276031000	-1.780103000	0.348186000
1	4.564464000	-2.053960000	1.937358000
6	3.280117000	-2.642047000	0.295562000
1	3.665929000	-3.664785000	0.296228000
1	2.384005000	-2.644302000	0.918695000
6	2.906157000	-2.213560000	-1.114737000
1	3.758841000	-2.259852000	-1.801888000
1	2.548806000	-1.178539000	-1.136169000
6	1.793127000	-3.046329000	-1.693267000
15	0.545923000	2.875017000	-1.534336000
9	-0.030084000	4.256272000	-2.134228000
9	1.352268000	2.567847000	-2.892802000
9	1.835492000	3.665122000	-0.897794000
9	-0.285172000	3.163160000	-0.120234000
9	-0.777492000	2.069927000	-2.090052000
9	1.094374000	1.482526000	-0.875830000
15	-0.631405000	-1.104212000	2.090733000
9	-0.456304000	0.510635000	1.814081000
9	0.611117000	-1.007931000	3.173772000
9	-1.696017000	-0.753081000	3.276691000
9	-1.844757000	-1.139461000	1.001909000
9	0.452477000	-1.392507000	0.901377000
9	-0.781976000	-2.676263000	2.377341000

Structure d

8	-3.227567000	0.032190000	2.552343000
1	-3.628783000	-0.036373000	3.427125000
8	-3.439015000	-2.183066000	2.723181000
7	1.881272000	-3.200348000	0.167941000
7	-0.028149000	-2.738096000	-0.734756000
6	2.882902000	-3.736618000	1.082160000
1	3.395043000	-2.909758000	1.569634000
1	3.580190000	-4.362501000	0.524935000
1	2.379008000	-4.322248000	1.847410000
6	2.125314000	-2.339454000	-0.875947000
1	3.110622000	-1.981146000	-1.115289000
6	0.929361000	-2.049004000	-1.444784000
1	0.682172000	-1.401751000	-2.270164000
6	0.574059000	-3.417553000	0.237675000
1	0.086809000	-4.016619000	0.986441000
6	-1.464472000	-2.789070000	-1.054956000
1	-1.653923000	-3.739973000	-1.557913000
1	-1.643551000	-1.988562000	-1.769759000
6	-2.352283000	-2.647265000	0.170938000
1	-2.138260000	-3.424630000	0.909328000

1	-3.379002000	-2.830601000	-0.157436000
6	-2.256586000	-1.276537000	0.827592000
1	-1.220647000	-1.022475000	1.074096000
1	-2.601670000	-0.489528000	0.152867000
6	-3.029327000	-1.231288000	2.115962000
8	3.439015000	2.183066000	-2.723181000
8	3.227567000	-0.032190000	-2.552343000
1	3.628783000	0.036373000	-3.427125000
7	-1.881272000	3.200348000	-0.167941000
7	0.028149000	2.738096000	0.734756000
6	-2.882902000	3.736618000	-1.082160000
1	-3.395043000	2.909758000	-1.569634000
1	-2.379008000	4.322248000	-1.847410000
1	-3.580190000	4.362501000	-0.524935000
6	-2.125314000	2.339454000	0.875947000
1	-3.110622000	1.981146000	1.115289000
6	-0.929361000	2.049004000	1.444784000
1	-0.682172000	1.401751000	2.270164000
6	-0.574059000	3.417553000	-0.237675000
1	-0.086809000	4.016619000	-0.986441000
6	1.464472000	2.789070000	1.054956000
1	1.643551000	1.988562000	1.769759000
1	1.653923000	3.739973000	1.557913000
6	2.352283000	2.647265000	-0.170938000
1	3.379002000	2.830601000	0.157436000
1	2.138260000	3.424630000	-0.909328000
6	2.256586000	1.276537000	-0.827592000
1	2.601670000	0.489528000	-0.152867000
1	1.220647000	1.022475000	-1.074096000
6	3.029327000	1.231288000	-2.115962000
15	-1.196065000	0.880374000	-3.168498000
9	-0.817245000	2.448113000	-2.878517000
9	-1.428182000	1.195780000	-4.723935000
9	-2.762027000	1.188622000	-2.832347000
9	-0.954395000	0.559121000	-1.557617000
9	0.382975000	0.548683000	-3.427234000
9	-1.551982000	-0.699039000	-3.399034000
15	1.196065000	-0.880374000	3.168498000
9	0.817245000	-2.448113000	2.878517000
9	-0.382975000	-0.548683000	3.427234000
9	0.954395000	-0.559121000	1.557617000
9	2.762027000	-1.188622000	2.832347000
9	1.428182000	-1.195780000	4.723935000
9	1.551982000	0.699039000	3.399034000

Table S2 The energies of structures ***a-d***

Structure	energies [a,b]	
	B3LYP	WBX97D
a	-1908.485189	-1908.123154
b	-1908.514692	-1908.159868
c	-3026.805753	-3026.090352
d	-3026.799851	-3026.090258

[a] Sum. of electronic and zero-point Energies; [b] unite: a.u.

Table S3 AIM parameters at the BCP of hydrogen bond in the local minimum of strucutres ***a-d***[a.b]

Structure	*Hydrogen bond*[c]	*Type*	$\rho_{(r)}$	$\nabla^2\rho_{(r)}$	*G(r)*	*V(r)*	*H(r)*
a	O17-H38⋯O37	(3,-1)	0.04793	0.1382	0.03549	-0.03643	-0.0009376
	O36-H19⋯O18	(3,-1)	0.04793	0.1382	0.03549	-0.03643	-0.0009376
b	O19-H20⋯Cl1	(3,-1)	0.06214	0.06273	0.03125	-0.04683	-0.01557
c	O27-H28… O3	(3,-1)	0.03502	0.01091	0.02685	-0.02643	0.0004204
	O50-H26…O2	(3,-1)	0.02972	0.09074	0.02254	-0.02240	0.0001397
d	C41-H42…F64	(3,-1)	0.01824	0.06005	0.01554	-0.01607	-0.0005300
	C16-H17…F57	(3,-1)	0.01824	0.06005	0.01554	-0.01607	-0.0005300

[a] AIM parameters are in atomic units.

[b] Electron densities, ρ(r); Laplacian of the electron density, $\nabla^2\rho_{(r)}$; kinetic energy density, G(r); potential energy density, V(r); energy density, H(r).

[c] Atom numbering see Table S1.