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

Supplementary Material to:

Complexes of carborane acids linked by strong hydrogen bonds; acidity scales

by

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Fig. 1SI The molecular graphs of the $HAlF_4$, HPF_6 and HBF_4 acids which could be rather treated as complexes of HF with AlF_3, PF_5 and BF_3, respectively. Big circles correspond to attractors, small green ones to the bond critical points, the bond paths are indicated (solid and broken lines). The CCl_4 solvent results are presented; however those for the gas phase and the water solvent are very similar.

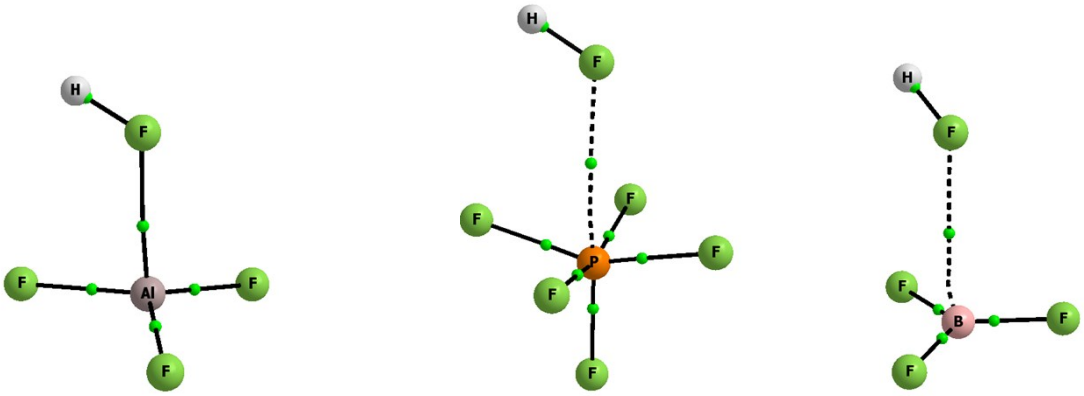
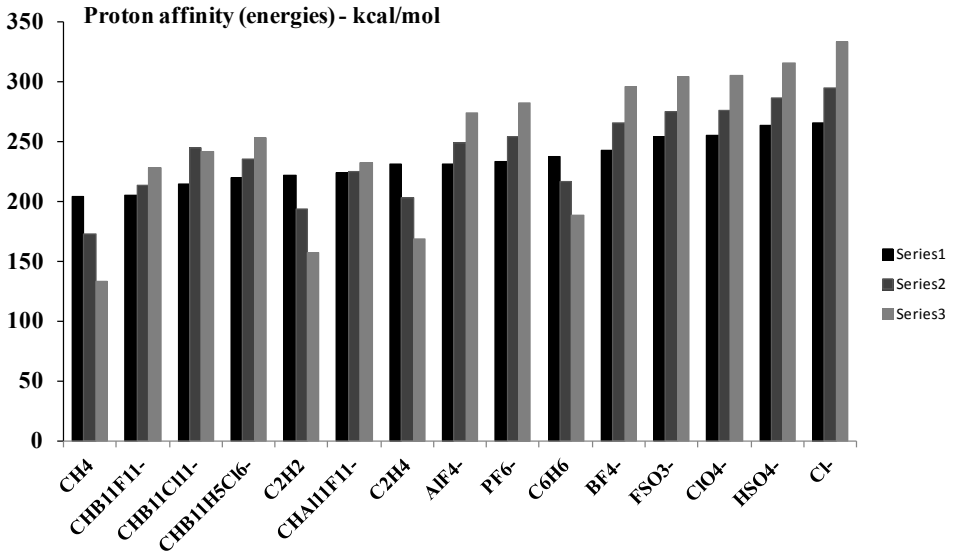
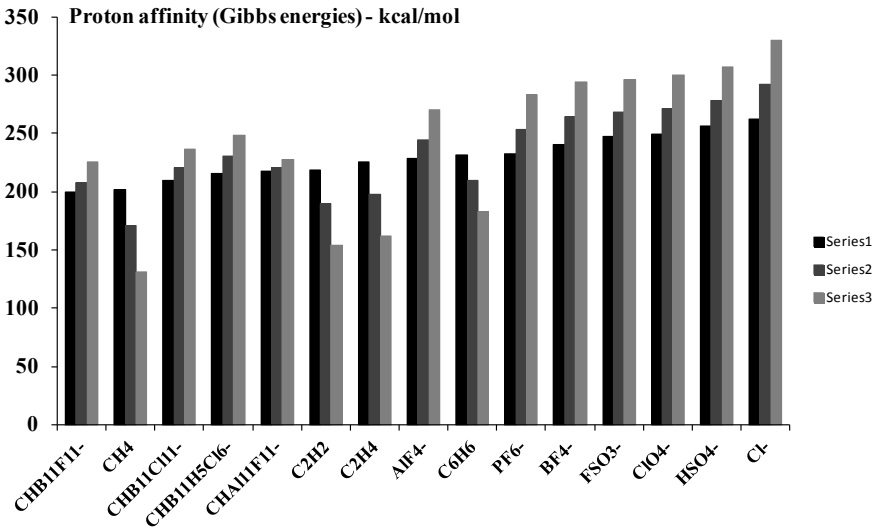


Fig. 2SI The histograms of the proton affinity values are presented based on the energies (Fig. 2SIa) and on the Gibbs free energies (Fig. 2SIb) where the water and CCl_4 solvents and the gas phase are considered. The bases conjugate of the acids considered are indicated in the horizontal lines of figure; and the order (from left side to the right one) shows the lowering of the acidity of acids if the water solvent is taken into account (Series 1). Series 2 and 3 correspond to CCl_4 solvent and to the gas phase, respectively.



(a)



(b)

Fig. 3SI The relationships between the NH stretching frequency (cm^{-1}) and the corresponding N-H bond length (Å).

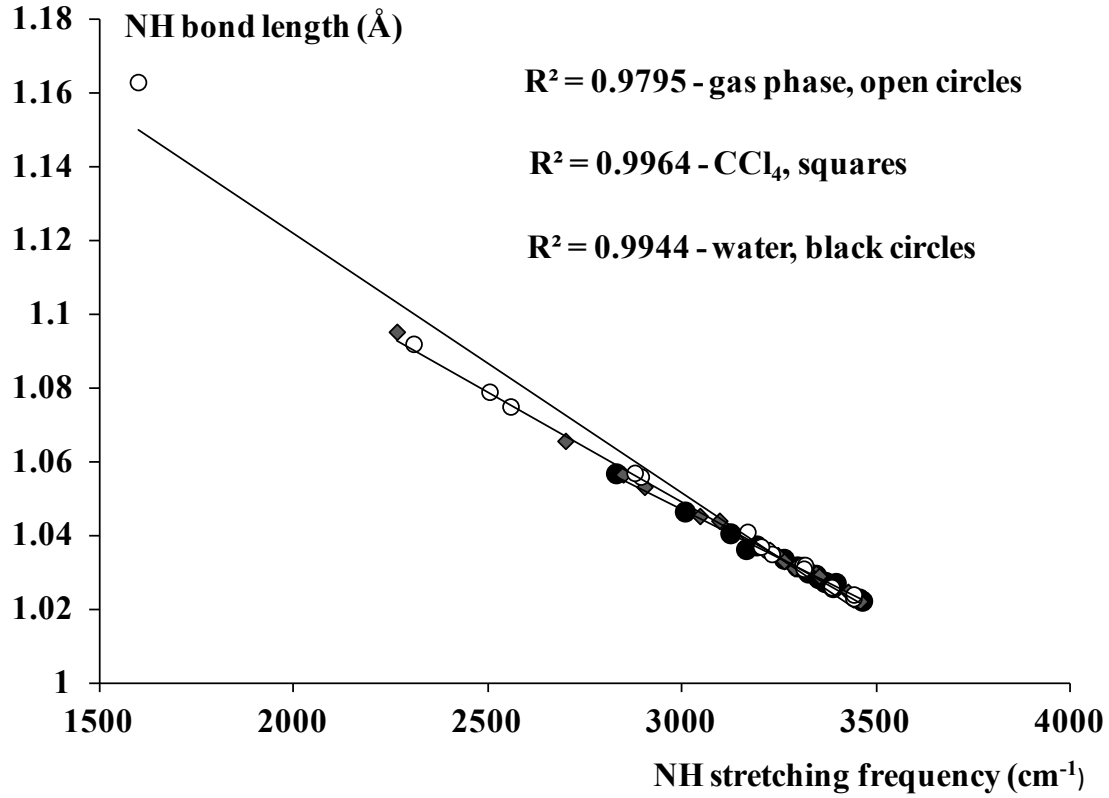


Fig. 4SI The molecular graph of the $HCHB_{11}F_{11}\ldots C_6H_7^+$ complex. Big circles correspond to attractors, small green ones to the bond critical points, the bond paths are indicated (solid and broken lines).

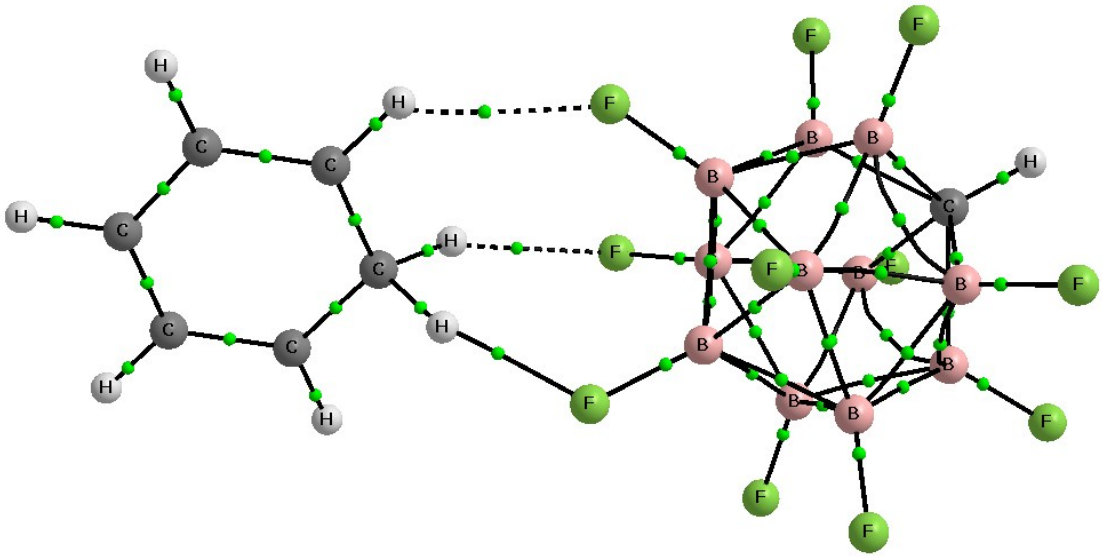


Fig. 5SI The histograms of the electron density at the F…H BCP (in au) are presented where the water or CCl_4 solvents and the gas phase are considered. The bases conjugate of the acids considered are indicated in the horizontal lines of figure; and the order (from left side to the right one) shows the lowering of the acidity of acids if the water solvent is taken into account (Series 1). Series 2 and 3 correspond to CCl_4 solvent and to the gas phase, respectively.

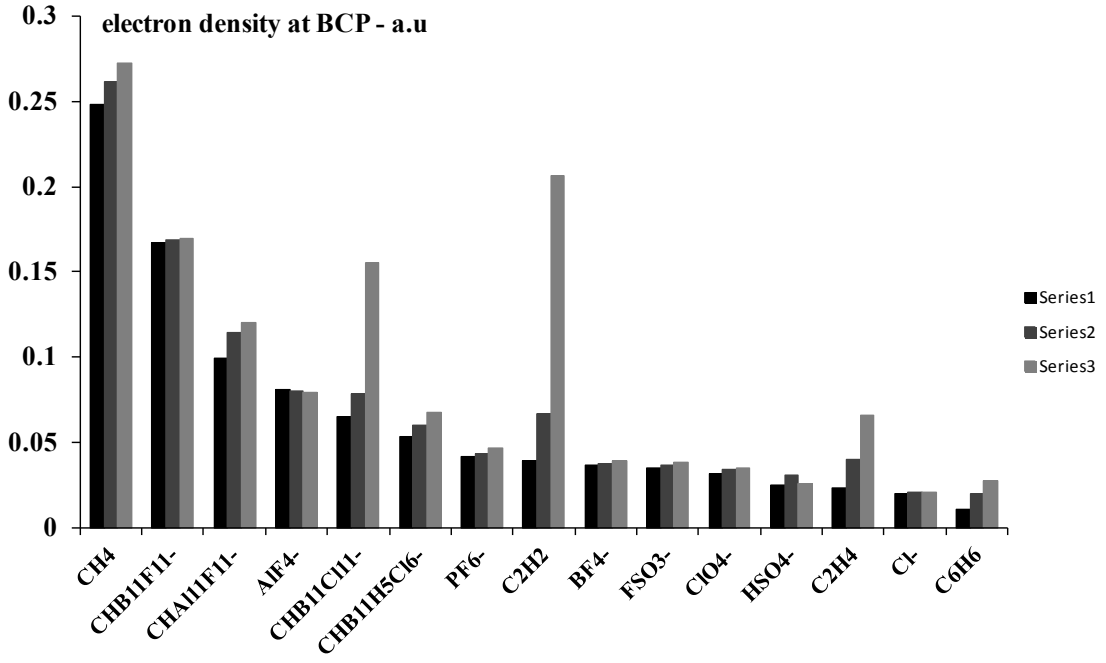


Fig. 6SI The histograms of the $-V_{BCP}/G_{BCP}$ parameter at the F…H BCP (in au) are presented where the water or CCl_4 solvents and the gas phase are considered. The bases conjugate of the acids considered are indicated in the horizontal lines of figure; and the order (from left side to the right one) shows the lowering of the acidity of acids if the water solvent is taken into account (Series 1). Series 2 and 3 correspond to CCl_4 solvent and to the gas phase, respectively.

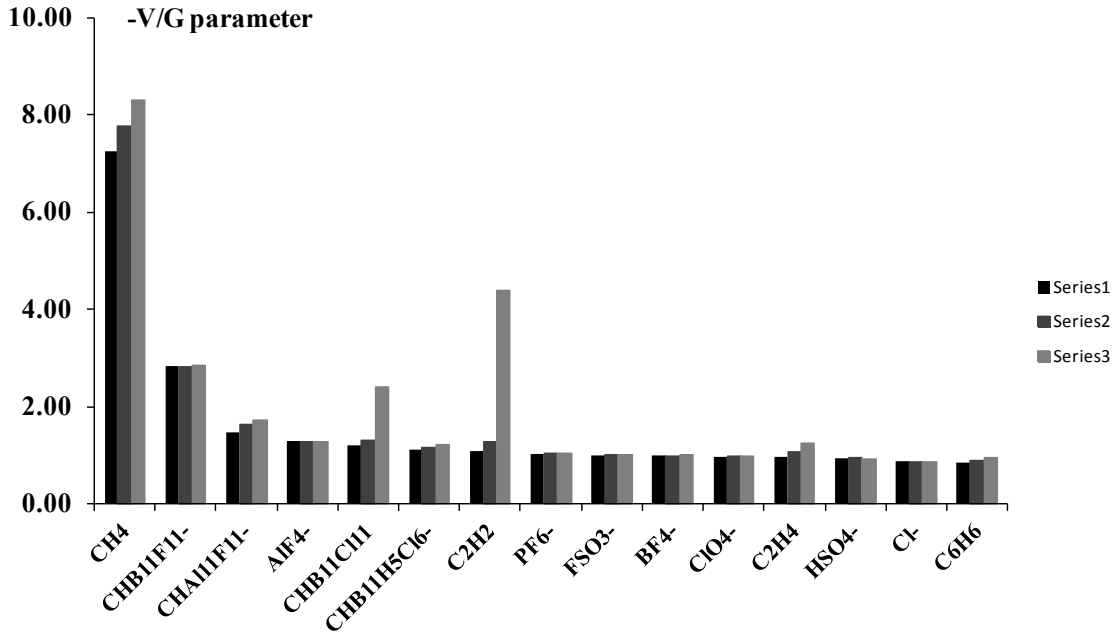


Table 1SI The NH bond lengths (in Å) for the trimethylammonium cation complexes with conjugate bases; gas phase, water solvent and CCl_4 solvent results presented.

Base	NH gas	NH CCl_4	NH H_2O
$CHB_{11}H_5Cl_6^-$	1.032	1.030	1.027
$CHB_{11}Cl_{11}^-$	1.032	1.029	1.026
$CHB_{11}F_{11}^-$	1.024	1.030	1.027
$CHAl_{11}F_{11}^-$	1.036	1.035	1.032
BF_4^-	1.056	1.044	1.034
AlF_4^-	1.057	1.045	1.036
C_6H_6	1.031	1.030	1.027
C_2H_2	1.035	1.031	1.028
C_2H_4	1.037	1.033	1.030
CH_4	1.026	1.025	1.023
ClO_4^-	1.075	1.053	1.037
Cl^-	1.163	1.095	1.057
FSO_3^-	1.079	1.057	1.041
HSO_4^-	1.092	1.066	1.047
PF_6^-	1.041	1.036	1.029

The N-H bond length for $NH(CH_3)_3^+$ not involved in any interaction is equal 1.023, 1.022 and 1.022 Å for gas phase, CCl_4 and water, respectively.

Table 2SI The interaction energies (in kcal/mol), E_1 and E_2 (defined in the main text and also explained in Scheme 1); for the gas phase, water solvent and CCl_4 solvent.

Base	E_1 gas	E_2 gas	E_1 CCl_4	E_2 CCl_4	E_1 H_2O	E_2 H_2O
$CHB_{11}H_5Cl_6^-$	-15.0	-39.8	-9.2	-30.5	-5.2	-19.7
$CHB_{11}Cl_{11}^-$	-17.3	-30.0	-10.7	-42.2	-4.4	-13.3
$CHB_{11}F_{11}^-$	-33.5	-33.5	-24.8	-24.8	-15.5	-15.5
$CHAl_{11}F_{11}^-$	-35.4	-39.0	-22.0	-33.1	-9.9	-27.8
BF_4^-	-12.1	-79.3	-8.2	-60.1	-4.8	-41.4
AlF_4^-	-23.1	-68.7	-16.8	-52.1	-10.2	-36.2
C_6H_6	-65.9	-25.6	-28.4	-30.9	-2.0	-34.0
C_2H_2	-89.2	-18.2	-39.1	-19.0	-4.7	-20.7
C_2H_4	-81.8	-21.4	-35.5	-25.4	-3.0	-28.8
CH_4	-101.8	-6.5	-46.8	-5.9	-5.5	-4.0
ClO_4^-	-12.3	-88.7	-8.1	-70.8	-4.3	-53.3
Cl^-	-6.5	-110.7	-4.2	-85.7	-2.1	-61.7
FSO_3^-	-13.6	-88.7	-9.1	-70.9	-4.8	-53.5
HSO_4^-	-15.1	-101.8	-7.5	-80.2	-4.0	-62.2
PF_6^-	-13.1	-67.0	-9.3	-50.1	-5.6	-33.5

Table 3SI QTAIM parameters (au), gas phase, for BCP1 and BCP2 (shown in Scheme 1 of the main text); the F…H distances corresponding to BCP1 included (Å).

Base	BCP1						BCP2				
	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$	F…H	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$
$CHB_{11}H_5Cl_6^-$	0.0676	0.0576	-0.0698	-0.0122	0.1814	1.477	0.1986	0.0375	-0.2067	-0.1692	-0.5271
$CHB_{11}Cl_{11}^-$	0.1549	0.0970	-0.2326	-0.1356	-0.1544	1.178	0.1262	0.0413	-0.1207	-0.0794	-0.1524
$CHB_{11}F_{11}^-$	0.1694	0.1069	-0.3029	-0.1960	-0.3562	1.133	0.1694	0.1069	-0.3029	-0.1960	-0.3562
$CHAl_{11}F_{11}^-$	0.1203	0.0997	-0.1709	-0.0711	0.1142	1.256	0.2235	0.2235	-0.4822	-0.2587	-0.1407
BF_4^-	0.0388	0.0408	-0.0405	0.0003	0.1645	1.632	0.3324	0.0750	-0.7769	-0.7019	-2.5074
AlF_4^-	0.0797	0.0767	-0.0979	-0.0212	0.2219	1.388	0.2720	0.0811	-0.6118	-0.5307	-1.7982
C_6H_6	0.0274	0.0236	-0.0222	0.0015	0.1005	1.869	0.2446	0.0359	-0.2614	-0.2254	-0.7580
C_2H_2	0.2067	0.0912	-0.4001	-0.3089	-0.8705	1.086	0.0793	0.0332	-0.0666	-0.0334	-0.0007
C_2H_4	0.0660	0.0535	-0.0668	-0.0133	0.1605	1.510	0.1590	0.0436	-0.1441	-0.1005	-0.2273
CH_4	0.2722	0.0724	-0.6014	-0.5289	-1.8260	0.997	0.0448	0.0271	-0.0359	-0.0089	0.0729
ClO_4^-	0.0351	0.0349	-0.0343	0.0007	0.1425	1.699	0.3289	0.0597	-0.7000	-0.6403	-2.3221
Cl^-	0.0208	0.0186	-0.0159	0.0027	0.0851	1.919	0.2357	0.0462	-0.2587	-0.2125	-0.6653
FSO_3^-	0.0384	0.0383	-0.0386	-0.0003	0.1517	1.660	0.3226	0.0588	-0.6899	-0.6311	-2.2890
HSO_4^-	0.0259	0.0249	-0.0232	0.0018	0.1068	1.831	0.3403	0.0625	-0.7272	-0.6646	-2.4085
PF_6^-	0.0464	0.0480	-0.0503	-0.0023	0.1826	1.570	0.3194	0.0741	-0.7410	-0.6669	-2.3714

Table 4SI QTAIM parameters (au), CCl_4 solvent, for BCP1 and BCP2 (shown in Scheme 1 of the main text); the F…H distances corresponding to BCP1 included (Å).

Base	BCP1						BCP2				
	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$	F…H	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$
$CHB_{11}H_5Cl_6^-$	0.0601	0.0521	-0.0605	-0.0084	0.1745	1.516	0.2046	0.0371	-0.2146	-0.1775	-0.5616
$CHB_{11}Cl_{11}^-$	0.0787	0.0641	-0.0834	-0.0193	0.1793	1.421	0.1850	0.0373	-0.1894	-0.1522	-0.4597
$CHB_{11}F_{11}^-$	0.1686	0.1065	-0.3007	-0.1942	-0.3510	1.141	0.1686	0.1065	-0.3007	-0.1942	-0.3510
$CHAl_{11}F_{11}^-$	0.1144	0.0966	-0.1582	-0.0616	0.1399	1.271	0.2287	0.0949	-0.4972	-0.4023	-1.2293
BF_4^-	0.0372	0.0390	-0.0383	0.0007	0.1590	1.648	0.3346	0.0752	-0.7826	-0.7073	-2.5284
AlF_4^-	0.0805	0.0774	-0.0992	-0.0218	0.2223	1.383	0.2706	0.0812	-0.6080	-0.5268	-1.7823
C_6H_6	0.0197	0.0161	-0.0144	0.0017	0.0712	2.013	0.2513	0.0361	-0.2717	-0.2356	-0.7983
C_2H_2	0.0671	0.0532	-0.0680	-0.0148	0.1539	1.494	0.1673	0.0482	-0.1604	-0.1122	-0.2561
C_2H_4	0.0400	0.0323	-0.0346	-0.0023	0.1198	1.712	0.1738	0.0515	-0.1648	-0.1133	-0.2472
CH_4	0.2614	0.0735	-0.5704	-0.4969	-1.6935	1.009	0.0494	0.0293	-0.0410	-0.0117	0.0702
ClO_4^-	0.0338	0.0336	-0.0327	0.0009	0.1382	1.712	0.3299	0.0597	-0.7022	-0.6425	-2.3311
Cl^-	0.0204	0.0180	-0.0155	0.0025	0.0823	1.931	0.2362	0.0464	-0.2596	-0.2132	-0.6672
FSO_3^-	0.0368	0.0366	-0.0366	0.0001	0.1467	1.676	0.3243	0.0587	-0.6939	-0.6351	-2.3056
HSO_4^-	0.0312	0.0311	-0.0296	0.0015	0.1302	1.738	0.3324	0.0600	-0.7111	-0.6512	-2.3649
PF_6^-	0.0436	0.0450	-0.0463	-0.0014	0.1745	1.593	0.3229	0.0738	-0.7507	-0.6768	-2.4119

Table 5SI QTAIM parameters (au), water solvent, for BCP1 and BCP2 (shown in Scheme 1 of the main text); the F…H distances corresponding to BCP1 included (Å).

Base	BCP1						BCP2				
	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$	F…H	ρ_{BCP}	G_{BCP}	V_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$
$CHB_{11}H_5Cl_6^-$	0.0536	0.0466	-0.0522	-0.0056	0.1638	1.558	0.2089	0.0367	-0.2200	-0.1833	-0.5862
$CHB_{11}Cl_{11}^-$	0.0649	0.0546	-0.0657	-0.0111	0.1737	1.487	0.1953	0.0360	-0.2025	-0.1665	-0.5218
$CHB_{11}F_{11}^-$	0.1672	0.1054	-0.2973	-0.1919	-0.3461	1.142	0.1672	0.1054	-0.2973	-0.1919	-0.3461
$CHAl_{11}F_{11}^-$	0.0997	0.0882	-0.1300	-0.0418	0.1860	1.314	0.2423	0.0886	-0.5347	-0.4461	-1.4300
BF_4^-	0.0369	0.0381	-0.0375	0.0006	0.1550	1.658	0.3359	0.0761	-0.7850	-0.7088	-2.5310
AlF_4^-	0.0810	0.0775	-0.0998	-0.0223	0.2208	1.381	0.2688	0.0811	-0.6028	-0.5217	-1.7622
C_6H_6	0.0105	0.0080	-0.0067	0.0012	0.0369	2.303	0.2570	0.0363	-0.2803	-0.2440	-0.8310
C_2H_2	0.0392	0.0320	-0.0343	-0.0023	0.1190	1.695	0.1856	0.0556	-0.1847	-0.1292	-0.2944
C_2H_4	0.0234	0.0178	-0.0170	0.0008	0.0743	1.902	0.1801	0.0561	-0.1748	-0.1188	-0.2509
CH_4	0.2484	0.0737	-0.5338	-0.4600	-1.5451	1.024	0.0533	0.0305	-0.0448	-0.0143	0.0650
ClO_4^-	0.0321	0.0317	-0.0304	0.0013	0.1316	1.733	0.3311	0.0596	-0.7050	-0.6453	-2.3428
Cl^-	0.0202	0.0176	-0.0152	0.0024	0.0804	1.939	0.2364	0.0465	-0.2599	-0.2135	-0.6679
FSO_3^-	0.0351	0.0346	-0.0342	0.0004	0.1398	1.696	0.3253	0.0586	-0.6961	-0.6375	-2.3158
HSO_4^-	0.0250	0.0240	-0.0221	0.0018	0.1032	1.753	0.3390	0.0617	-0.7228	-0.6612	-2.3981
PF_6^-	0.0421	0.0437	-0.0445	-0.0008	0.1714	1.605	0.3259	0.0740	-0.7591	-0.6850	-2.4439

Table 6SI QTAIM parameters (au), gas phase, CCl_4 solvent and water solvent, for BCP corresponding to intermolecular contact (specified in the second left column) for complexes of HF with BF_3, AlF_3 and PF_5 species (or for HBF_4, $HAlF_4$ and HPF_6 acids, respectively).

Acid	Contact	gas phase			CCl_4			water		
		ρ_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$	ρ_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$	ρ_{BCP}	H_{BCP}	$\nabla^2\rho_{BCP}$
HBF_4	F…B	0.013	0.000	0.047	0.013	0.001	0.050	0.014	0.001	0.054
$HAlF_4$	F…Al	0.036	0.003	0.224	0.038	0.005	0.259	0.041	0.008	0.310
HPF_6	F…P	0.006	0.001	0.031	0.018	0.000	0.059	0.020	0.000	0.063