Electronic Supplementary Information for

Determinants for proton location and electron coupled proton transfer in hydrogen bonded pentafluorophenol-anion clusters

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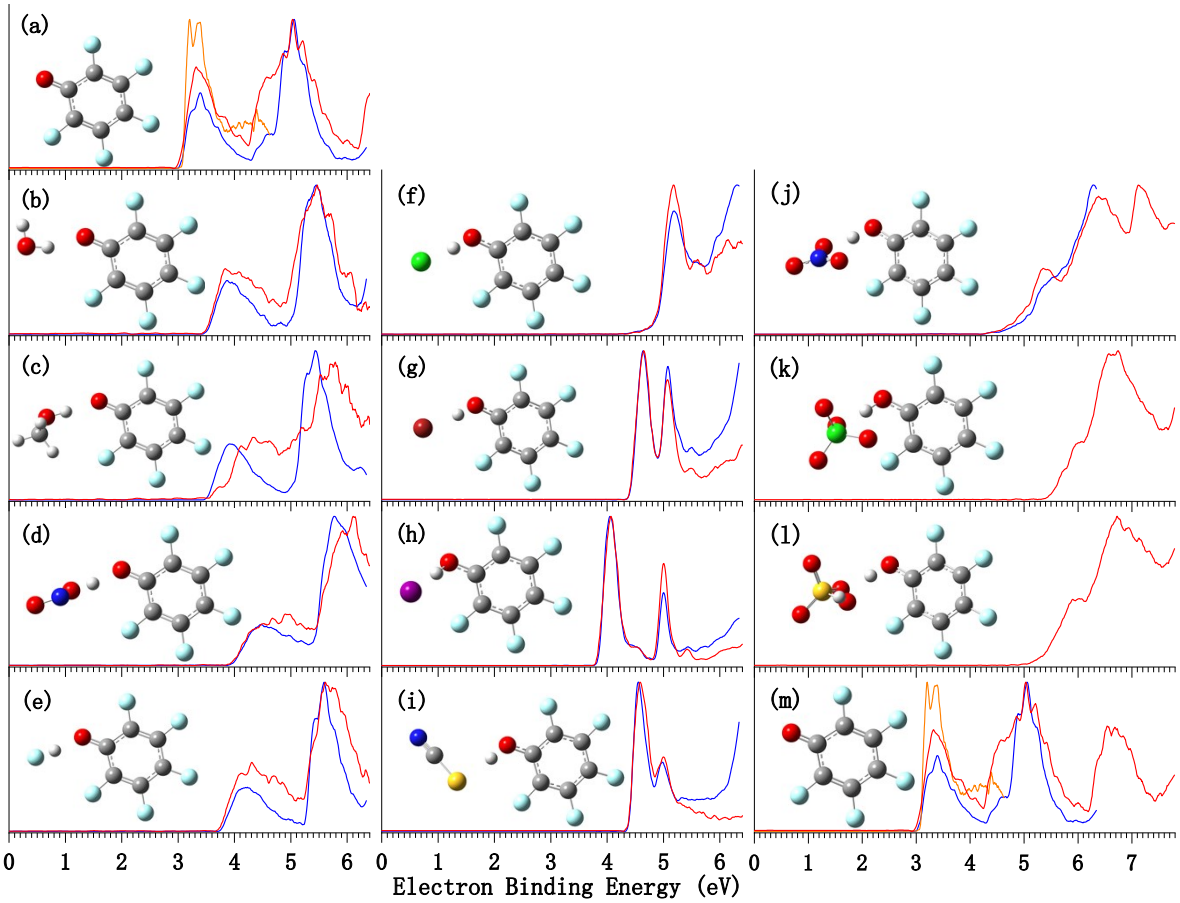

Figure S1 Comparison of NIPE spectra of $C_6F_5O^-$ (a), $[C_6F_5O^-•H^+•A^-]^-$ A = OH (b), CH_3O (c), NO_2 (d), F (e), Cl (f), Br (g), I (h), SCN (i), NO_3 (j), ClO_4 (k), HSO_4 (l), and $C_6F_5O^-$ (m) at 266 (4.661 eV, orange), 193 (6.424 eV, blue), and 157 nm (7.867 eV, red). The B3LYP/6-311++g(df,pd) (LANL2DZ for I) optimized anion complex structures are shown as inset. Note the157 nm spectra of (a)-(i) are only plotted out to 6.4 eV for better view of the onset region of the spectra.

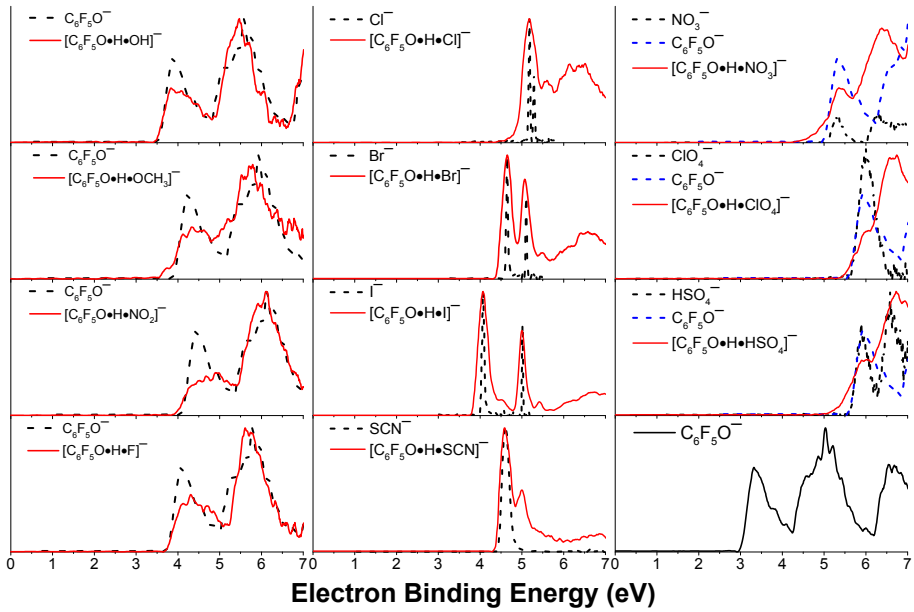

Figure S2 Comparison of the NIPE spectra of $[C_6F_5O^-•H^+•A^-]^-$ with the spectra of the isolated anions A^- (ref. 1-5) and $C_6F_5O^-$ that are shifted in EBE to match the complex spectra.

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2 X. B. Wang and L. S. Wang, *J. Chem. Phys*. 2000, **113**, 10928-10933.
3 G. L. Hou, W. Lin, S. H. M. Deng, J. Zhang, W. Zheng, F. Paesani, and X.-B. Wang, J. *Phys. Chem. Lett.* 2013, **4**, 779-785.
4 M. Valiev, S. H. M. Deng, and X. B. Wang, *J. Phys Chem. B*, 2016, **120**, 1518-1525.
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Table S1. NPA charge distributions of the $[C_6F_5O•H•A]^-$ complexes and the corresponding unrelaxed/relaxed neutrals.

		Anionic / unrelaxed / relaxed neutral complexes		
		C_6F_5O	H	A
	$C_6F_5O•H$	-0.487	0.487	
Type I	$[C_6F_5O•H•Br]^-$	-0.650/-0.307/-0.361	0.487/0.468/0.499	-0.837/-0.161/-0.138
	$[C_6F_5O•H•I]^-$	-0.651/-0.490/-0.456	0.483/0.461/0.494	-0.832/0.029/-0.038
	$[C_6F_5O•H•SCN]^-$	-0.627/-0.439/-0.491	0.481/0.465/0.489	-0.854/-0.026/0.002
Type II	$[C_6F_5O•H•OCH_3$	-0.958/0.012/0.006	0.511/0.481/0.478	-0.553/-0.493/-0.484
	$[C_6F_5O•H•NO_2]^-$	-0.881/0.044/0.019(-0.508)[a]	0.500/0.482/0.490(0.499)[a]	-0.619/-0.526/-0.509(0.009)[a]
	$[C_6F_5O•H•OH]^-$	-0.967/0.011/0.008	0.507/0.478/0.478	-0.540/-0.489/-0.486
	$[C_6F_5O•H•F]^-$	-0.909/0.068/0.027	0.559/0.542/0.560	-0.650/-0.610/-0.587
Type III	$[C_6F_5O•H•NO_3]^-$	-0.653/-0.090/0.033	0.504/0.499/0.504	-0.851/-0.409/-0.537
	$[C_6F_5O•H•ClO_4]$	-0.599/0.037/0.039	0.523/0.526/0.511	-0.924/-0.563/-0.550
	$[C_6F_5O•H•HSO_4]$	-0.617/-0.06/0.034	0.528/0.527/0.522	-0.911/-0.467/-0.556
Type IV	$[C_6F_5O•H•Cl]^-$	-0.672/-0.172/-0.176(0.022)[a]	0.472/0.456/0.478(0.279)[a]	-0.800/-0.284/-0.302(-0.301)[a]

[a] NPA charges for the 2nd more stable proton transferred structures of the neutrals.

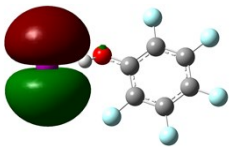
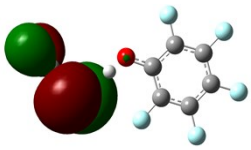
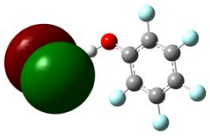
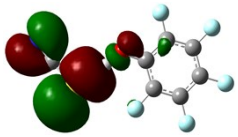
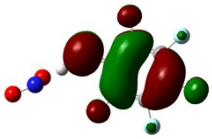
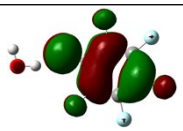
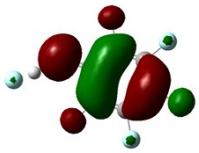
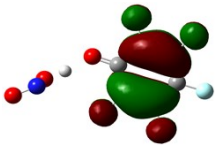
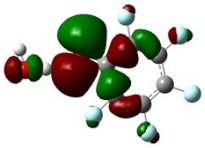
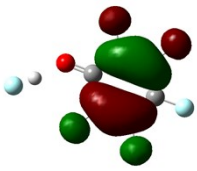
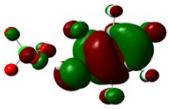
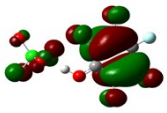
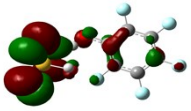
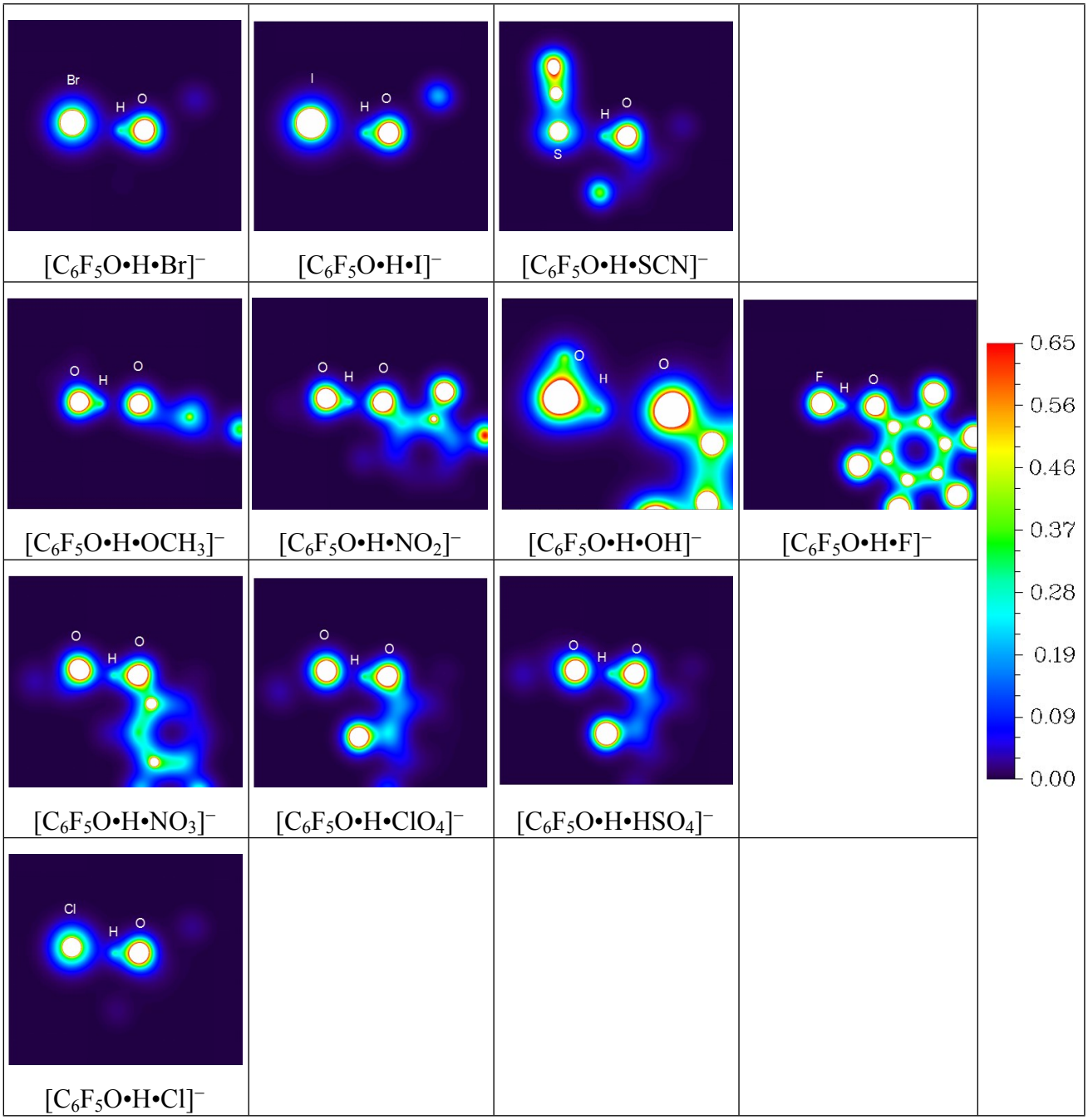
	$[C_6F_5O•H•I]^-$	$[C_6F_5O•H•SCN]^-$	
HOMO			
HOMO-1			
	$[C_6F_5O•H•NO_2]^-$	$[C_6F_5O•H•OH]^-$	$[C_6F_5O•H•F]^-$
HOMO			
HOMO-1			
	$[C_6F_5O•H•ClO_4]^-$	$[C_6F_5O•H•HSO_4]^-$	
HOMO			
HOMO-1			

Figure S3. The HOMO and HOMO-1 for the anion complexes $[C_6F_5O•H•A]^-$, A = I, SCN, NO_2, OH, F, ClO_4, and HSO_4.

Table S2. Electron density of the anion complexes. The density is plotted in the plane of the three atoms consisting of the hydrogen and the two bonded atoms from C_6F_5O and A (A = F, Cl, Br, I, SCN, CH_3O, OH, NO_2, NO_3, ClO_4, and HSO_4).

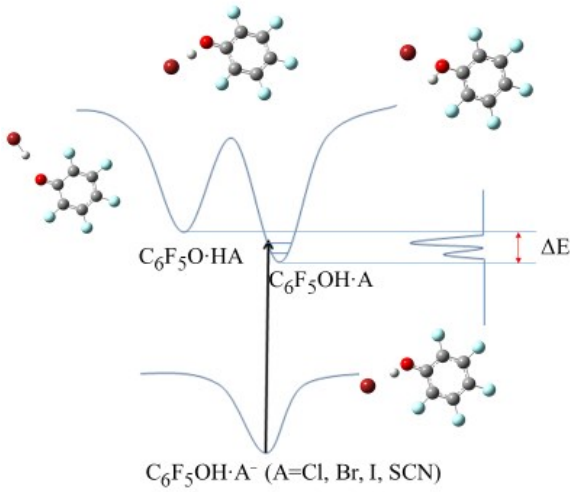


$[C_6F_5O•H•Br]^-$ $[C_6F_5O•H•I]^-$ $[C_6F_5O•H•SCN]^-$

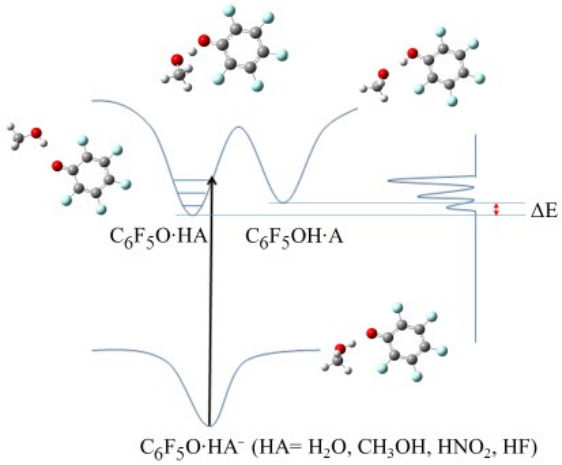
$[C_6F_5O•H•OCH_3]^-$ $[C_6F_5O•H•NO_2]^-$ $[C_6F_5O•H•OH]^-$ $[C_6F_5O•H•F]^-$

$[C_6F_5O•H•NO_3]^-$ $[C_6F_5O•H•ClO_4]^-$ $[C_6F_5O•H•HSO_4]^-$

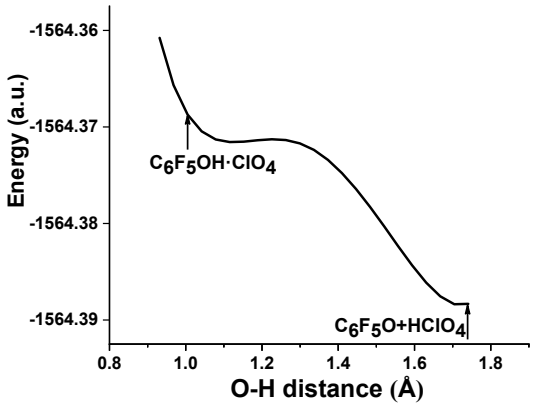
$[C_6F_5O•H•Cl]^-$


ΔE
$C_6F_5O{\cdot}HA$
$C_6F_5OH{\cdot}A$
$C_6F_5OH{\cdot}A^-$ (A=Cl, Br, I, SCN)

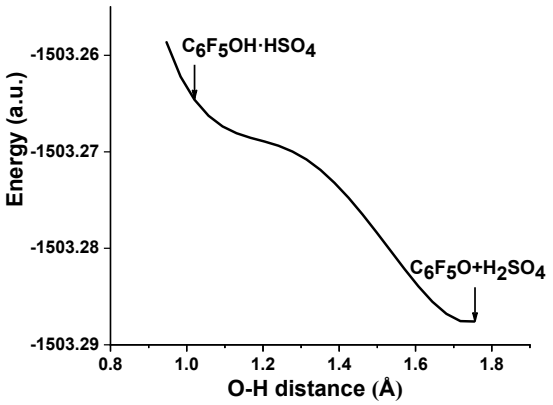
(a)


ΔE
$C_6F_5O{\cdot}HA$
$C_6F_5OH{\cdot}A$
$C_6F_5O{\cdot}HA^-$ (HA= H_2O, CH_3OH, HNO_2, HF)

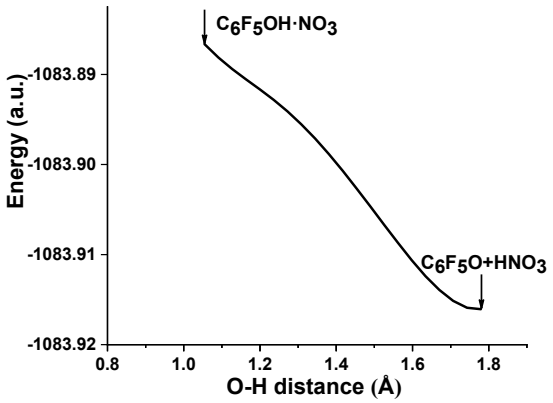
(b)


-1564.36
-1564.37
-1564.38
-1564.39
Energy (a.u.)
$C_6F_5OH{\cdot}ClO_4$
C_6F_5O+$HClO_4$
0.8
1.0
1.2
1.4
1.6
1.8
O-H distance (Å)

(c)



(d)



(e)

Figure S4. Schematic potential curves for $[C_6F_5O•H•A]^-$ and $[C_6F_5O•H•A]$ A = Cl, Br, I, SCN (a), A= CH_3O, NO_2, OH and F (b), and the calculated one-dimension energy curves for the neutral complexes with A = ClO_4 (c), A = HSO_4 (d), and A = NO_3 (e). The potential curves in (c), (d) and (e) are calculated by moving H atom between C_6F_5O and the respective anion A. The first arrow denotes the vertical position on the neutral surface with the anionic geometry of $[C_6F_5O\text{-}H\cdots A]$ and the second arrow indicates the PT product on the neutral surface with the optimized $[C_6F_5O\cdots H\text{-}A]$ configuration. We divided the H atom moving process into 20 steps by adjusting the bond length of O--H and H--A at the same time (note the total O ····· A distance also varied from the initial to the final values) and fixing all other atoms without further optimization. The potential curves are obtained by calculating the M06-2X/aug-cc-pvtz single point energy of each geometry in each step.