Supporting Information

Molecular Electrostatic Potential on the Proton-Donating Nuclei as a Theoretical Descriptor of Excited State Acidity

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In this Supporting Information we include additional tables and figures to supplement our paper.

TABLE S1: Experimental ground-state pKa and calculated MEP on the hydroxyl oxygen

Compound	pK_a	ϕ_O[a]	references
a	10	-22.279699	[1]
b	10.26	-22.282544	[1,2]
c	9.36	-22.267743	[1,2]
d	9.65	-22.281937	[1,2]
e	7.74	-22.252469	[3]
f	8.34	-22.256886	[3]
g	6.97	-22.254377	[3]
h	9.5	-22.276209	[2,4]
i	8.5	-22.261989	[5]
j	7.8	-22.249009	[6]
k	5.6	-22.242754	[7]
l	4.4	-22.223578	[7]
m	8.35	-22.148742	[1,2]
n	7.0	-22.133574	[8]

[a] MEP calculated at the ωB97X-D/6-31G(d) level in vacuum (unit: E_h/e)

TABLE S2: Partial charge on the hydroxyl oxygen[a]

Compound	Mulliken (S_0)	Mulliken (S_1)	Hirshfeld (S_0)	Hirshfeld (S_1)
a	-0.658858	-0.591177	-0.217431	-0.160016
b	-0.661529	-0.595271	-0.215731	-0.162852
c	-0.654950	-0.593737	-0.212095	-0.159908
d	-0.659875	-0.623215	-0.215731	-0.188307
e	-0.646226	-0.595636	-0.202395	-0.160366
f	-0.651876	-0.573898	-0.206603	-0.137904
g	-0.648316	-0.603857	-0.197269	-0.145611
h	-0.660295	-0.613058	-0.214645	-0.172485
i	-0.652729	-0.590324	-0.209415	-0.151416
j	-0.649297	-0.600286	-0.198962	-0.152685
k	-0.650061	-0.614025	-0.191065	-0.159633
l	-0.642976	-0.604042	-0.182144	-0.148160
m	-0.625182	-0.544841	-0.178751	-0.107561
n	-0.621686	-0.549598	-0.171868	-0.104268

[a] Calculated at the ωB97X-D/6-31G(d) level in vacuum

TABLE S3: Experimental excited-state pKa* and theoretical excited-state MEP on the hydroxyl oxygen

Compound	pK_a^*	ϕ_O^* [a]	references
a	4.0	-22.242943	[1]
b	4.3	-22.247192	[1,2]
c	3.1	-22.239394	[1,2]
d	4.6	-22.267015	[1,2]
e	3.33	-22.228112	[3]
f	1.89	-22.209435	[3]
g	0.66	-22.216831	[3]
h	3.1	-22.245400	[1,4]
i	-2.8	-22.209846	[5,9]
j	-4.5	-22.199538	[6,9]
k	-1.0	-22.216337	[7]
l	-3.9	-22.194324	[7]
m	1.7	-22.104657	[1,2]
n	-7	-22.066625	[9,10]

[a] MEP calculated at the ωB97X-D/6-31G(d) level in vacuum (unit: E_h/e)

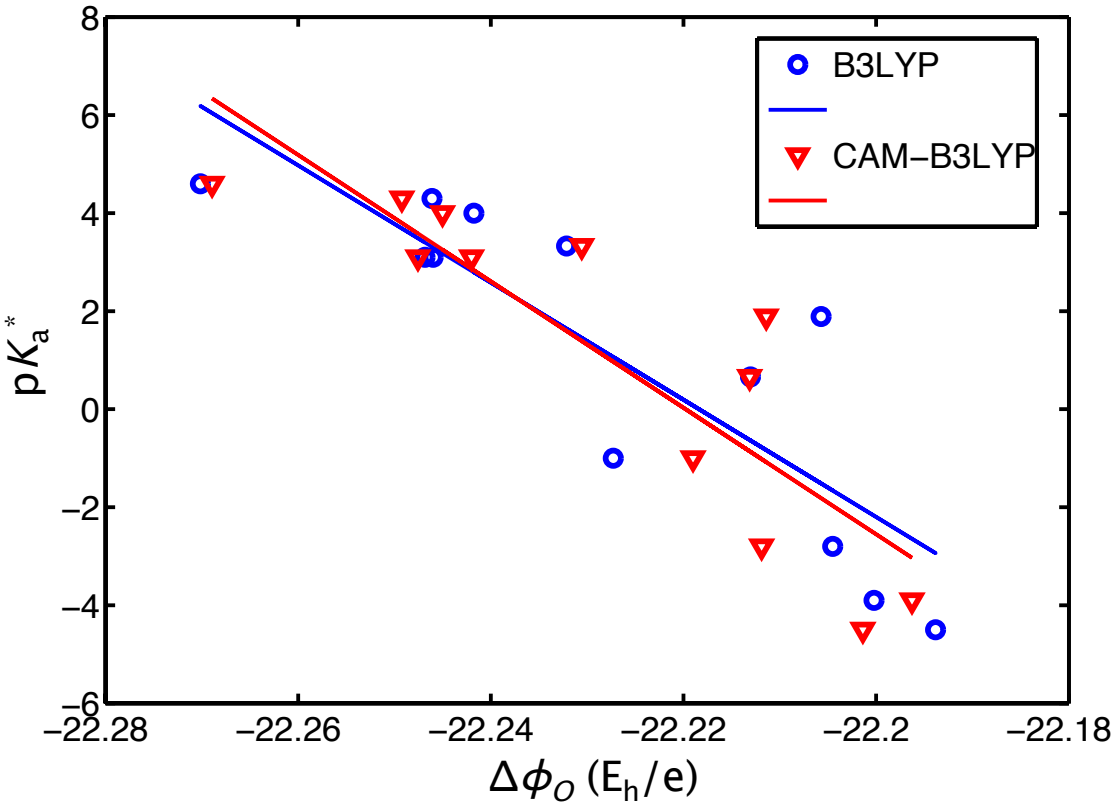

FIG. S1: DFT functional dependence of the correlation between the excited-state acidity and the calculated S_1 excited-state MEP on the oxygen atom of the hydroxyl group. Data of the 12 neutral molecules shown in FIG. 1 (compound (a) to compound (l)) are shown here. The blue circle and the red triangle markers correspond to the results calculated by utilizing B3LYP and CAM-B3LYP functionals, respectively. The blue line represents the best linear regression fit to the B3LYP calculated dataset: $y = -119.5 \cdot x - 2.6555 \times 10^3$ with $R^2 = 0.7332$. The red line represents the best linear regression fit to the CAM-B3LYP calculated dataset: $y = -129.0 \cdot x - 2.8658 \times 10^3$ with $R^2 = 0.7656$.

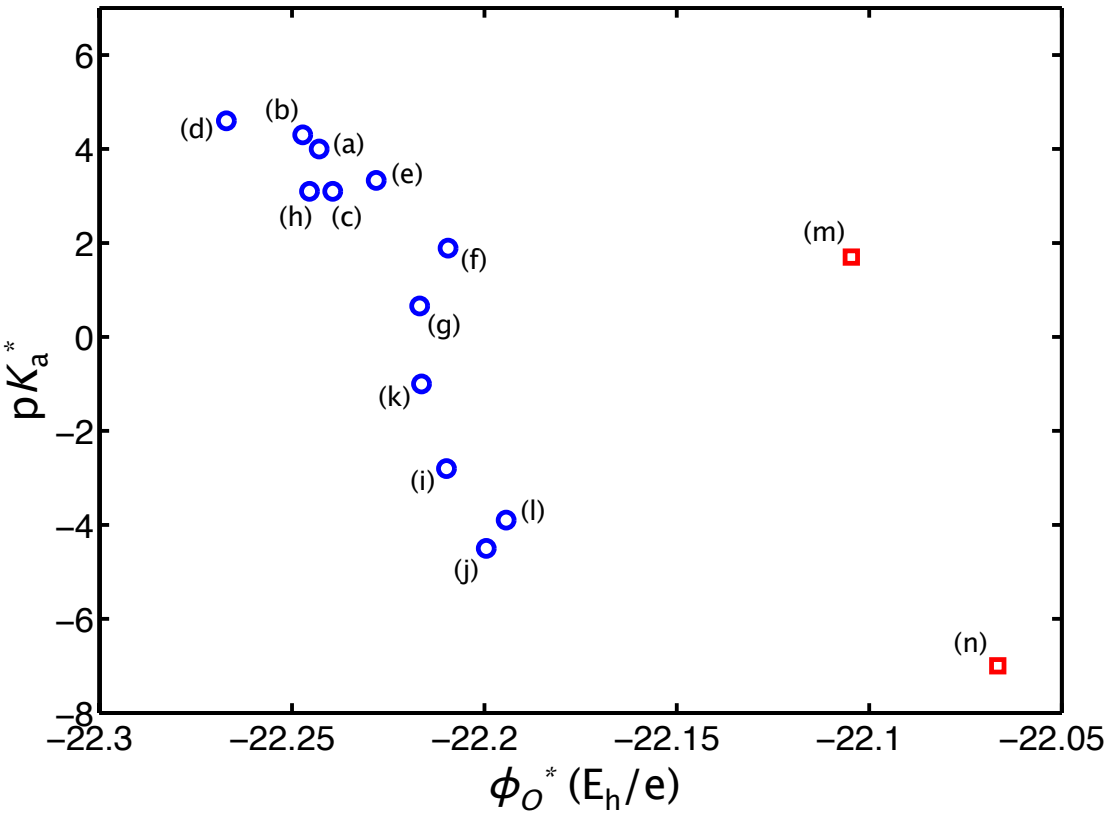

FIG. S2: Correlations between the excited-state acidity and the excited-state MEP on the oxygen atom of hydroxyl group in vacuum condition, including neutrally and positively charged molecules. The blue circle marks correspond to neutral photoacids (compound (a) to compound (l)) while the red square marks correspond to cations (compound (m) and compound (n)).

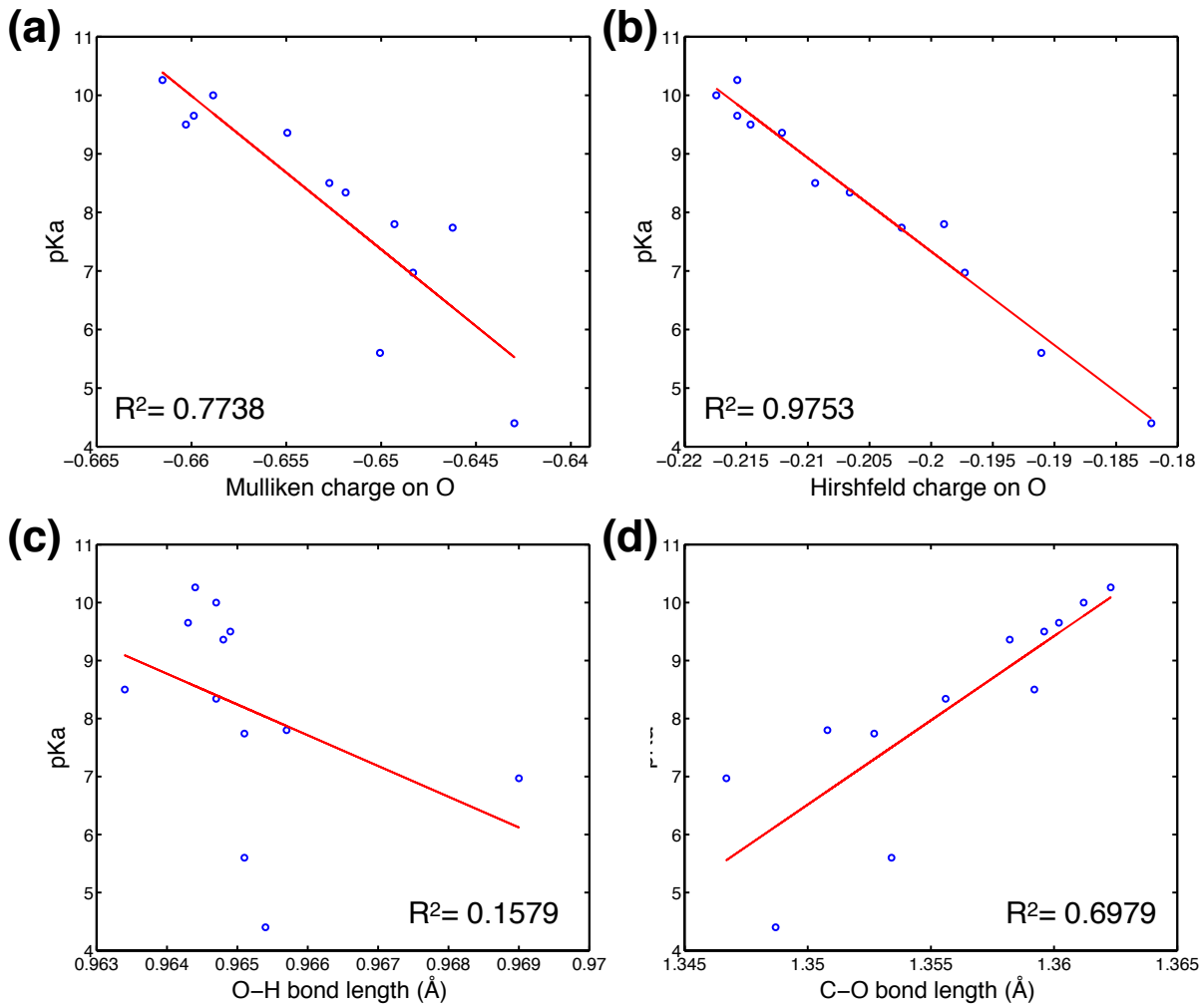

FIG. S3: Correlations between the ground-state acidity and various theoretical acidity descriptors proposed previously: (a) Mulliken charge on the oxygen atom of hydroxyl group, (b) Hirshfeld charge on the oxygen atom of hydroxyl group, (c) the O-H bond length, (d) the C-O bond length.

TABLE S4: Excited-state MEP[a] on O in different solvent conditions

Compound	vacuum	cyclohexane	THF	DCM	ethanol	methanol	water
a	-22.242943	-22.240465	-22.237021	-22.236716	-22.235671	-22.235519	-22.235225
b	-22.247192	-22.245755	-22.243553	-22.243357	-22.242671	-22.242570	-22.242378
c	-22.239394	-22.235844	-22.231262	-22.230873	-22.229524	-22.229329	-22.228957
d	-22.267015	-22.268567	-22.270191	-22.270306	-22.270710	-22.270764	-22.270857
e	-22.228112	-22.223500	-22.218183	-22.217750	-22.216264	-22.216049	-22.215638
f	-22.209435	-22.201556	-22.192826	-22.192149	-22.189868	-22.189548	-22.188938
g	-22.216831	-22.207549	-22.203691	-22.203366	-22.202272	-22.202113	-22.201814
h	-22.245400	-22.244317	-22.243375	-22.243305	-22.243047	-22.243009	-22.242938
i	-22.209846	-22.204158	-22.198175	-22.197701	-22.196077	-22.195846	-22.195405
j	-22.199538	-22.191677	-22.183648	-22.183044	-22.181057	-22.180780	-22.180259
k	-22.216337	-22.206275	-22.192820	-22.191630	-22.187450	-22.186842	-22.185669
l	-22.194324	-22.181625	-22.166864	-22.165656	-22.161545	-22.160960	-22.159830
m	-22.104657	-22.110905	-22.116789	-22.117214	-22.118594	-22.118783	-22.119142
n	-22.066625	-22.067154	-22.068405	-22.068528	-22.068968	-22.069039	-22.069172

[a] MEP calculated at the ωB97X-D/6-31G(d) level (unit: E_h/e)

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