Supplemental Information to:

Correlating Photoacidity to Hydrogen-Bond Structure by Using the Local O-H Stretching Probe in Hydrogen-Bonded Complexes of Aromatic Alcohols

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■ SUPPLEMENTAL INFORMATION CONTENTS

1. Full Listing of References with more that 10 authors

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2. Synthesis of 2,3,5,6-tetrafluoro-4-nitrophenol (tFNP)

1.0 g 2,3,5,6-tetrafluorophenol (6.0 mmol) were dissolved in 5 mL of dichloromethane. After addition of 1.8 g 65 % nitric acid, an exothermic reaction was observed during which the mixture turned orange colored. TLC (silica gel, dichloromethane:methanol: acetic acid 20:1:0.1) indicated that the starting material (R_f = 0.6) had been consumed completely. Water was added to the mixture and after extraction with dichloromethane, drying of the organic phase with $MgSO_4$ and removal of the solvent under reduced pressure 0.68 g raw product were obtained. Column chromatography over silica gel using the above solvent mixture afforded 0.57 g 2,3,5,6-tetrafluoro-4-nitrophenol (45 %) as yellow crystals (R_f = 0.2).
^{1}H NMR (300 MHz, DMSO-d_6): 7.32 (s, broad).
^{19}F NMR (282 MHz, DMSO-d_6): -148.81 ppm (m, J= 18 Hz), -161.02 ppm (m, J= 18 Hz).

The dissociation constant of tFNP was determined by titration of an aqueous solution (50 μM) with HCl under monitoring of p*H* and UV-vis absorption spectra. The value pK_a = 2.81 was obtained as the inflection point of a sigmoid fit on experimental data of extinction (at a suitable wavelength) as a function of p*H*. This value is in agreement with the prediction of 2.84 ± 0.49 reported in ACS SciFinder (Advanced Chemistry Development Software V11.02).

Figure S1. Steady-state FT-IR spectra of selected substituted phenols and 1-naphthol hydrogen-bonded complexes in different solutions.

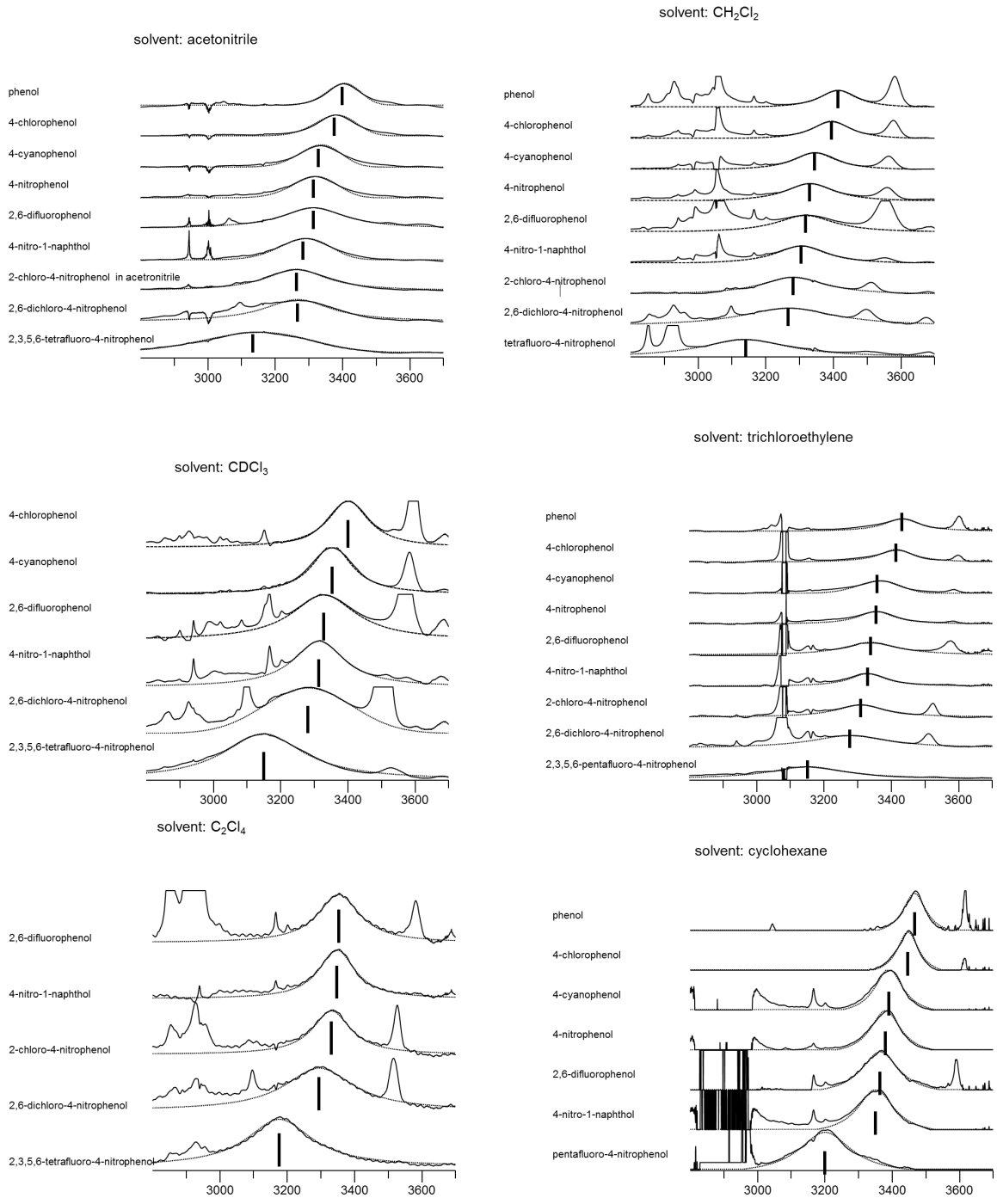

Figure S2. Correlation plot between calculated and measured[1-3] gas phase O-H stretching frequencies for 2-naphthol complexes in (a) the ground and (b) the first electronic excited state. Labels for each complex correspond to the substituent in complex with 2-naphthol (2N).

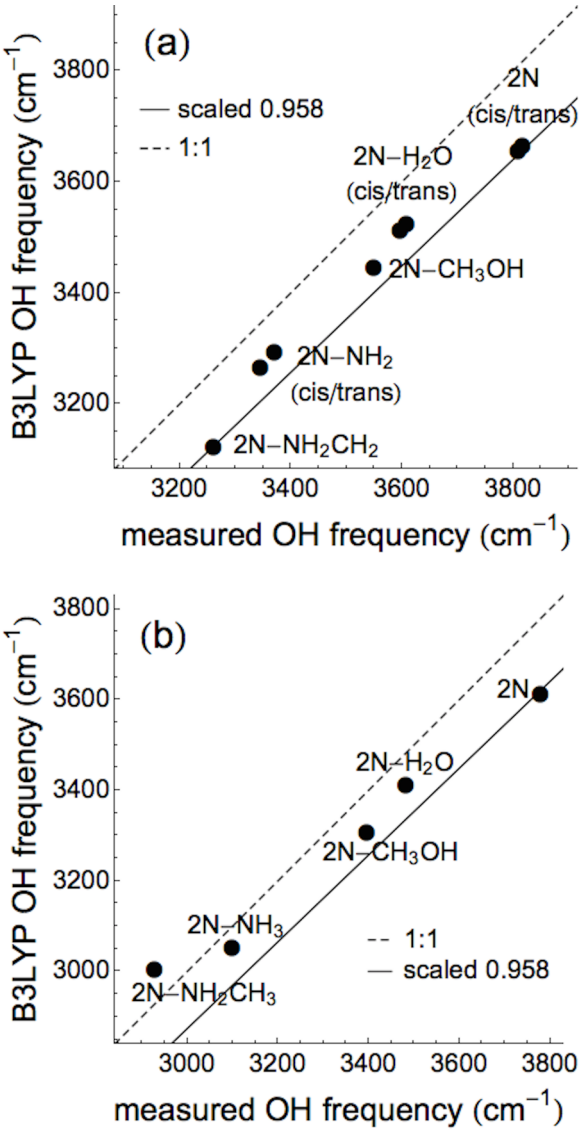

Figure S3 Calculated O-H stretching frequency versus O-H distance for the hydrogen-bonded complex. The upper panel shows the calculated intercept value representing the O-H stretching frequency for the gas phase case, the lower panel shows the frequency spread for eight different solvent dielectric models, representing the different solvents studied. (Each complex is indicated with a specific color.)

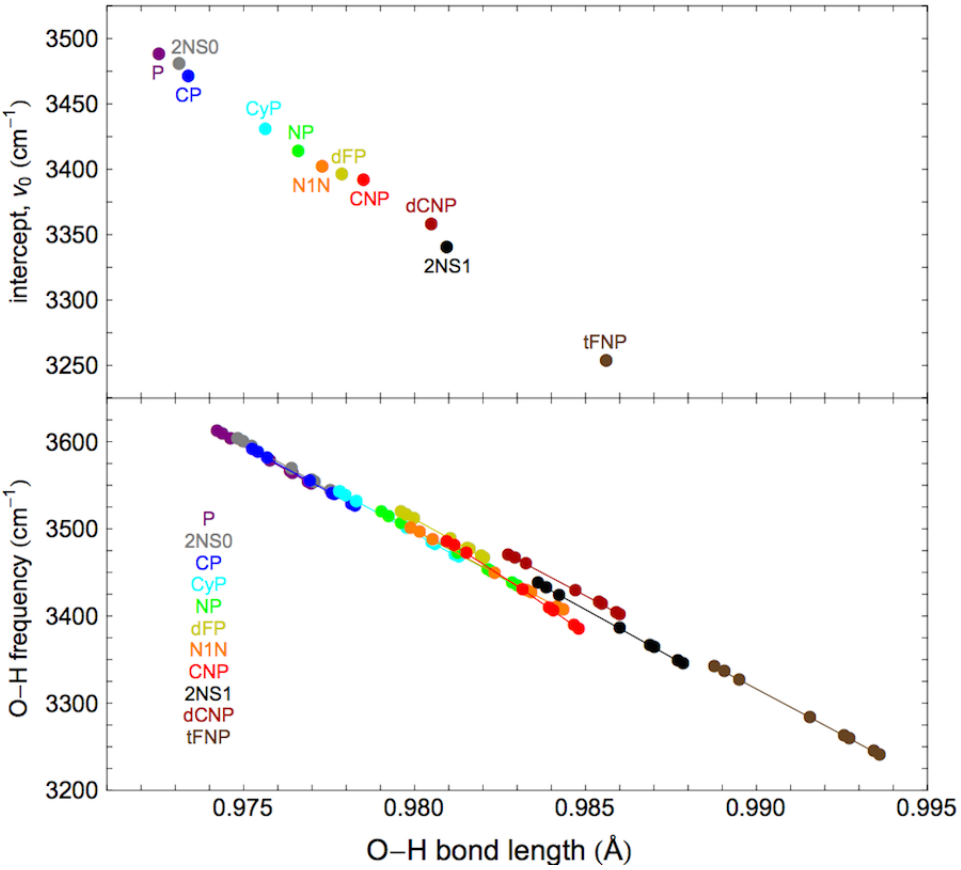

Figure S4. Calculated (a) O···N and (b) O–H distances for each complex for eight different dielectric constants representing different solvents used in this study. The calculated gas phase value at $F_0 = 0$ is shown as well. (Points corresponding to particular complexes are distinguished by color.)

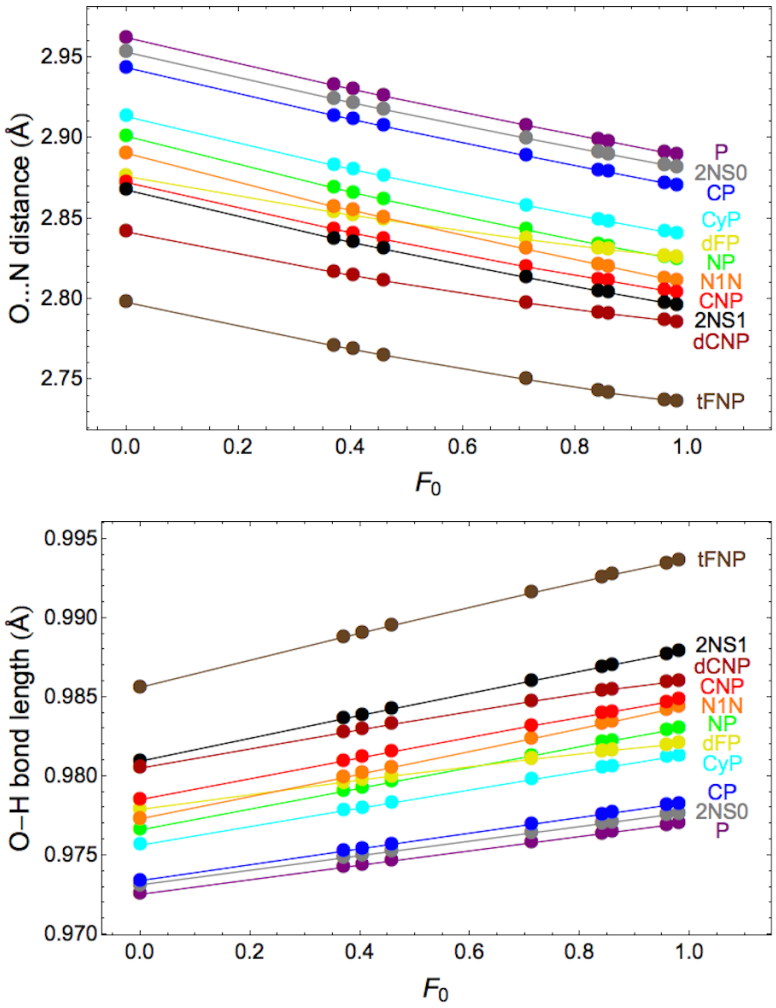

Table S1. Change in calculated Mulliken atomic charge versus solvent dielectric function (F_0) for atoms and functional groups of aromatic alcohol complexes at the B3LYP level of theory.

Complex	O	H	ACN	α-C
P	–0.0218	+0.0081	+0.0111	+0.0005
2NS0	–0.0205	+0.0071	+0.0110	+0.0017
CP	–0.0194	+0.0083	+0.0115	+0.0062
CyP	–0.0137	+0.0087	+0.0126	+0.0121
NP	–0.0102	+0.0088	+0.0139	+0.0115
dFP	–0.0298	+0.0059	+0.0090	+0.0075
N1N	–0.0023	+0.0069	+0.0153	+0.0107
CNP	–0.0142	+0.0091	+0.0158	+0.0100
2NS1	–0.0185	+0.0054	+0.0155	+0.0022
dCNP	–0.0165	+0.0070	+0.0102	+0.0167
tFNP	–0.0178	+0.0054	+0.0156	+0.0295

Complex	*o*-C	*m*-C	*p*-C	Other
P	–0.0434	–0.0497	–0.0182	+0.1134
2NS0	–0.0368	–0.0472	–0.0068	+0.0916
CP	–0.0479	–0.0420	–0.0016	+0.0849
CyP	–0.0392	–0.0281	–0.0126	+0.0602
NP	–0.0364	–0.0328	+0.0434	+0.0015
dFP	–0.0112	–0.0184	–0.0224	+0.0616
N1N	–0.0139	–0.0134	+0.0315	–0.0348
CNP	–0.0216	–0.0138	+0.0364	–0.0218
2NS1	–0.0445	–0.0432	–0.0086	+0.0917
dCNP	–0.0225	+0.0066	+0.0309	–0.0324
tFNP	+0.0202	–0.0150	+0.0474	–0.0852

Table S2. Calculated Mulliken gas phase atomic charges for atoms and functional group of uncomplexed aromatic alcohols.

Complex	O	H	α-C	*o*-C	*m*-C	*p*-C	Other
P	–0.292	+0.276	+0.115	–0.338	–0.196	–0.135	+0.570
2NS0	–0.284	+0.277	+0.129	–0.368	–0.039	+0.040	+0.244
CP	–0.287	+0.279	+0.114	–0.322	–0.070	–0.132	+0.418
CyP	–0.273	+0.284	+0.124	–0.312	–0.170	–0.048	+0.396
NP	–0.264	+0.287	+0.125	–0.290	–0.244	–0.032	+0.418
dFP	–0.266	+0.298	–0.131	+0.506	–0.345	–0.068	+0.005
N1N	–0.271	+0.293	+0.092	–0.214	–0.149	+0.019	+0.229
CNP	–0.245	+0.292	+0.196	–0.301	–0.187	–0.016	+0.262
2NS1	–0.284	+0.277	+0.129	–0.368	–0.039	+0.040	+0.244
dCNP	–0.242	+0.299	+0.284	–0.375	–0.087	–0.009	+0.130
tFNP	–0.243	+0.313	–0.048	+0.351	+0.521	–0.202	–0.691

Table S3. Differences between alcohol-acetonitrile complexes and uncomplexed alcohols (comp – uncomp).

Complex	Oxy	Hyd	a-C	o-C	m-C	p-C	Other
P	–0.007	+0.024	–0.020	+0.254	+0.003	+0.001	–0.021
2NS0	–0.008	+0.026	–0.016	+0.008	+0.010	+0.001	–0.035
CP	–0.007	+0.024	–0.020	+0.266	–0.001	+0.008	–0.026
CyP	–0.006	+0.025	–0.019	+0.268	–0.004	+0.006	–0.028
NP	–0.005	+0.024	–0.020	+0.270	–0.007	+0.010	–0.032
dFP	+0.001	+0.023	+0.025	–0.172	–0.007	–0.005	–0.025
N1N	–0.001	+0.025	–0.009	+0.224	–0.003	+0.010	–0.046
CNP	–0.004	+0.021	–0.012	+0.248	–0.015	+0.011	–0.037
2NS1	–0.004	+0.031	–0.012	+0.039	–0.032	+0.003	–0.025
dCNP	+0.004	+0.030	+0.046	+0.297	–0.011	+0.008	–0.041
tFNP	+0.005	+0.015	+0.021	–0.365	–0.030	+0.005	–0.031

Table S4. Calculated parameters for Pullin model slopes.

Species	$\mu^{(2)} \cdot \mu^{0}$ [a]	$\mu^{(1)} \cdot \mu^{0}$ [b]	$V^{(3)} / V^{(2)}$ [c]	E_{sol} [d]
P	60.1	30.1	–7.57	–4.9
2NS0	65.6	32.9	–7.60	–5.2
CP	79.6	40.3	–7.63	–4.8
CyP	114.1	59.2	–7.72	–6.6
NP	122.0	63.2	–7.76	–6.4
dFP	59.2	29.4	–7.74	–4.9
N1N	125.5	65.2	–7.79	–6.6
CNP	111.1	61.7	–7.78	–6.2
2NS1	64.6	49.7	–7.89	–6.4
dCNP	84.9	56.0	–7.77	–5.7
tFNP	142.8	75.3	–8.11	–6.2

[a] Dot product of dipole second derivative and dipole moment has units of (D^2 $Å^{-2}$ amu^{-1}). [b] Dot product of dipole first derivative and dipole moment has units of (D^2 $Å^{-1}$ $amu^{-1/2}$). [c] Cubic force constant divided by quadratic force constant has units of ($Å^{-1}$ $amu^{-1/2}$). [d] Solvation energy has units of (kcal/mol).

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