Electronic Supplementary Information (ESI) for

Critical size of hydrogen-bonded alcohol clusters as effective Brønsted base in solutions

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1. Fluorescence lifetimes

Table S1. Fluorescence time constants observed from TCSPC measurements according to the concentration of bases in MeCN

Base	[Base] (M)	λ_{mon}[a] (nm)	rise time (ns)	decay time (ns)	χ^2
	0.00 (0.0%)[b]	445	-[c]	3.2 (7%)[d] + 9.1 (93%)	1.067
MeOH	0.60 (2.4%)	445	-	0.5 (11%) + 8.9 (89%)	1.173
	1.18 (4.8%)	445	-	0.3 (16%) + 7.3 (84%)	1.235
	1.72 (7.0%)	445	-	0.3 (17%) + 6.0 (83%)	1.245
	2.25 (9.1%)	445	-	0.3 (16%) + 4.8 (84%)	1.211
		580	1.6 (1%) + 4.7 (88%)	6.4 (100%)	1.581
	2.75 (11.1%)	445	-	0.4 (13%) + 3.8 (87%)	1.228
EtOH	0.62 (3.6 %)	445	-	0.7 (8%) + 8.1 (92%)	1.106
	0.82 (4.8%)	445	-	0.8 (4%) + 7.5 (96%)	1.222
	1.19 (7.0%)	445	-	0.7 (6%) + 6.0 (94%)	1.094
	1.56 (9.1%)	445	-	0.7 (8%) + 4.7 (92%)	1.084
		580	0.5 (1%) + 4.5 (88%)	6.5 (100%)	1.441
	1.90 (11.1%)	445	-	0.8 (8%) + 4.0 (92%)	1.143
n-PrOH	0.64 (4.8%)	445	-	0.3 (20%) + 8.0 (80%)	1.152
	0.93 (7.0%)	445	-	0.4 (18%) + 6.9 (82%)	1.269
	1.22 (9.1%)	445	-	0.3 (19%) + 5.9 (81%)	1.323
	1.49 (11.1%)	445	-	0.3 (16%) + 5.1 (84%)	1.326
		580	0.9 (1%) + 4.8 (88%)	6.4 (100%)	1.543
	1.74 (13.0%)	445	-	0.3 (17%) + 4.3 (83%)	1.392

i-PrOH	0.62 (4.8%)	445	-	0.7 (12%) + 8.0 (88%)	1.070
	0.91 (7.0%)	445	-	0.7 (22%) + 6.9 (78%)	1.339
	1.19 (9.1%)	445	-	0.7 (9%) + 5.9 (91%)	1.162
	1.45 (11.1%)	445	-	0.6 (10%) + 5.1 (90%)	0.943
		580	0.6 (1%) + 4.9 (90%)	6.4 (100%)	1.482
	1.70 (13.0%)	445	-	0.7 (10%) + 4.4 (90%)	1.118
n-BuOH	0.52 (4.8%)	445	-	0.9 (7%) + 8.5 (93%)	1.147
	0.76 (7.0%)	445	-	0.6 (9%) + 7.7 (91%)	1.153
	0.99 (9.1%)	445	-	0.6 (12%) + 6.9 (88%)	1.076
	1.21 (11.1%)	445	-	0.9 (8%) + 6.2 (92%)	1.155
	1.43 (13.0%)	445		0.7 (9%) + 5.5 (91%)	1.039
		580	0.9 (1%) + 5.6 (94%)	6.3 (100%)	1.597
t-BuOH	0.50 (4.8%)	445	-	1.2 (9%) + 8.8 (91%)	1.079
	0.73 (7.0%)	445	-	0.7 (10%) + 8.3 (90%)	1.123
	0.95 (9.1%)	445	-	0.8 (13%) + 7.7 (87%)	1.091
	1.16 (11.1%)	445	-	0.7 (10%) + 7.2 (90%)	1.129
	1.36 (13.0%)	445	-	0.6 (19%) + 6.6 (81%)	1.093
		580	0.8 (1%) + 6.0 (93%)	6.7 (100%)	1.470
DMSO	0.34 (2.4%)	445	-	0.4 (20%) + 3.2 (80%)	1.006
	0.67 (4.8%)	445	-	0.4 (14%) + 2.0 (86%)	0.964
	0.98 (7.0%)	445	-	0.4 (10%) + 1.4 (90%)	1.050
	1.29 (9.1%)	445	-	0.4 (14%) + 1.1 (86%)	1.007
		580	1.1 (8%)	6.0 (100%)	1.043
	1.60 (11.1%)	445	-	0.5 (24%) + 0.9 (76%)	1.130

[a]Monitored wavelength of fluorescence. [b]Volume fraction of each base in MeCN. [c]Instant. [d]Negative and positive values of initial fractional amplitudes indicate those for rise and decay components, respectively.

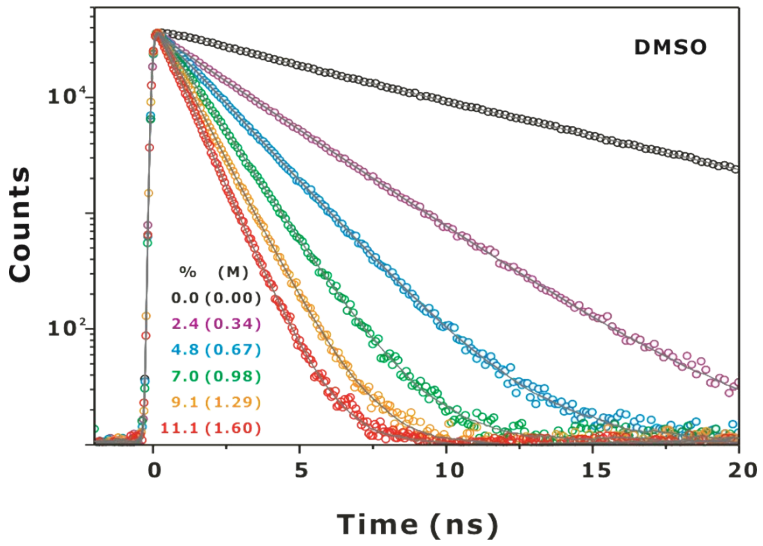


Figure S1. Fluorescence kinetic profiles measured at the various concentrations of DMSO in MeCN. The contents of DMSO are given in molar concentration (M) as well as in volume fraction (% v/v) in the panel. Samples were excited at 375 nm and their fluorescence kinetic profiles were monitored at 445 nm. Solid lines are the best-fitted curves to extract kinetic constants, shown in Table S1.

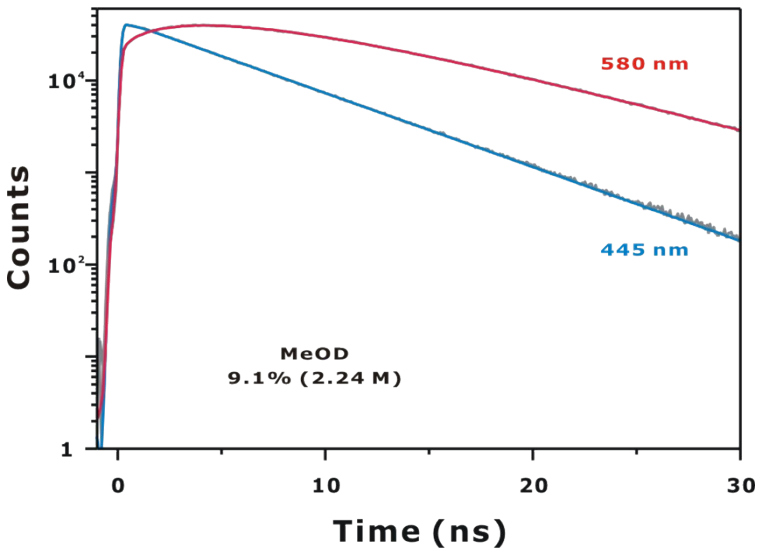
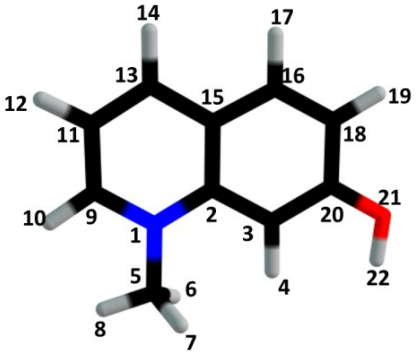


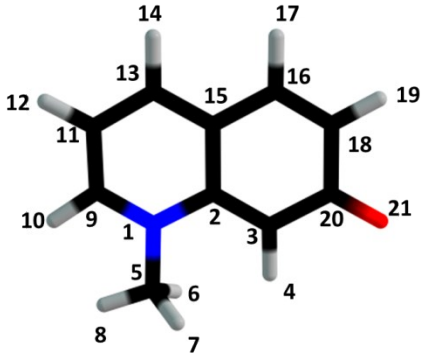
Figure S2. Fluorescence dynamic with MeOD in the MeCN solvent. The sample was excited at 375 nm and its fluorescence kinetic profiles were monitored at 445 and 580 nm. Blue and red lines are the best-fitted curves to extract kinetic constants; at [MeOD] = 2.24 M, $I(t) = 0.157\ e^{-t/(0.3\ \mathrm{ns})} + 0.843\ e^{-t/(5.4\ \mathrm{ns})}$ at 445 nm while $I(t) = -0.002\ e^{-t/(1.0\ \mathrm{ns})} - 0.890\ e^{-t/(4.9\ \mathrm{ns})} + e^{-t/(7.1\ \mathrm{ns})}$ at 580 nm.

2. CHELPG charges of AH^+ (S_0/S_1) and A (S_0/S_1)



AH^+ geometry

S0		S1	
1 N	0.202015	1 N	0.215837
2 C	0.195774	2 C	0.062175
3 C	-0.523410	3 C	0.065017
4 H	0.215992	4 H	0.147541
5 C	-0.290101	5 C	-0.322466
6 H	0.146542	6 H	0.144117
7 H	0.146575	7 H	0.144065
8 H	0.149241	8 H	0.159447
9 C	-0.119094	9 C	-0.542056
10 H	0.203917	10 H	0.240794
11 C	-0.143709	11 C	0.040894
12 H	0.186244	12 H	0.174406
13 C	-0.092982	13 C	-0.526926
14 H	0.178479	14 H	0.215590
15 C	0.117367	15 C	0.234096
16 C	-0.213643	16 C	-0.091332
17 H	0.190208	17 H	0.185590
18 C	-0.188133	18 C	-0.284275
19 H	0.208140	19 H	0.216921
20 C	0.541785	20 C	0.551002
21 O	-0.573755	21 O	-0.483933
22 H	0.462547	22 H	0.453494



A geometry

S0		S1	
1 N	0.235222	1 N	0.265857
2 C	0.151354	2 C	0.107640
3 C	-0.594029	3 C	0.010925
4 H	0.215943	4 H	0.139971
5 C	-0.281026	5 C	-0.320674
6 H	0.115335	6 H	0.129114
7 H	0.115671	7 H	0.128883
8 H	0.118285	8 H	0.122967
9 C	-0.229744	9 C	-0.607020
10 H	0.188072	10 H	0.217501
11 C	-0.186234	11 C	-0.043516
12 H	0.155864	12 H	0.152103
13 C	-0.161557	13 C	-0.478681
14 H	0.150434	14 H	0.174601
15 C	0.123979	15 C	0.157334
16 C	-0.230906	16 C	-0.283656
17 H	0.153780	17 H	0.180589
18 C	-0.274028	18 C	-0.453655
19 H	0.155910	19 H	0.177712
20 C	0.733544	20 C	0.710482
21 O	-0.655871	21 O	-0.488477

Geometries of ground and excited states are optimized at B3LYP/6-31+G* and TD-B3LYP/6-31+G* respectively to calculate the CHELPG values.

3. MD simulation data

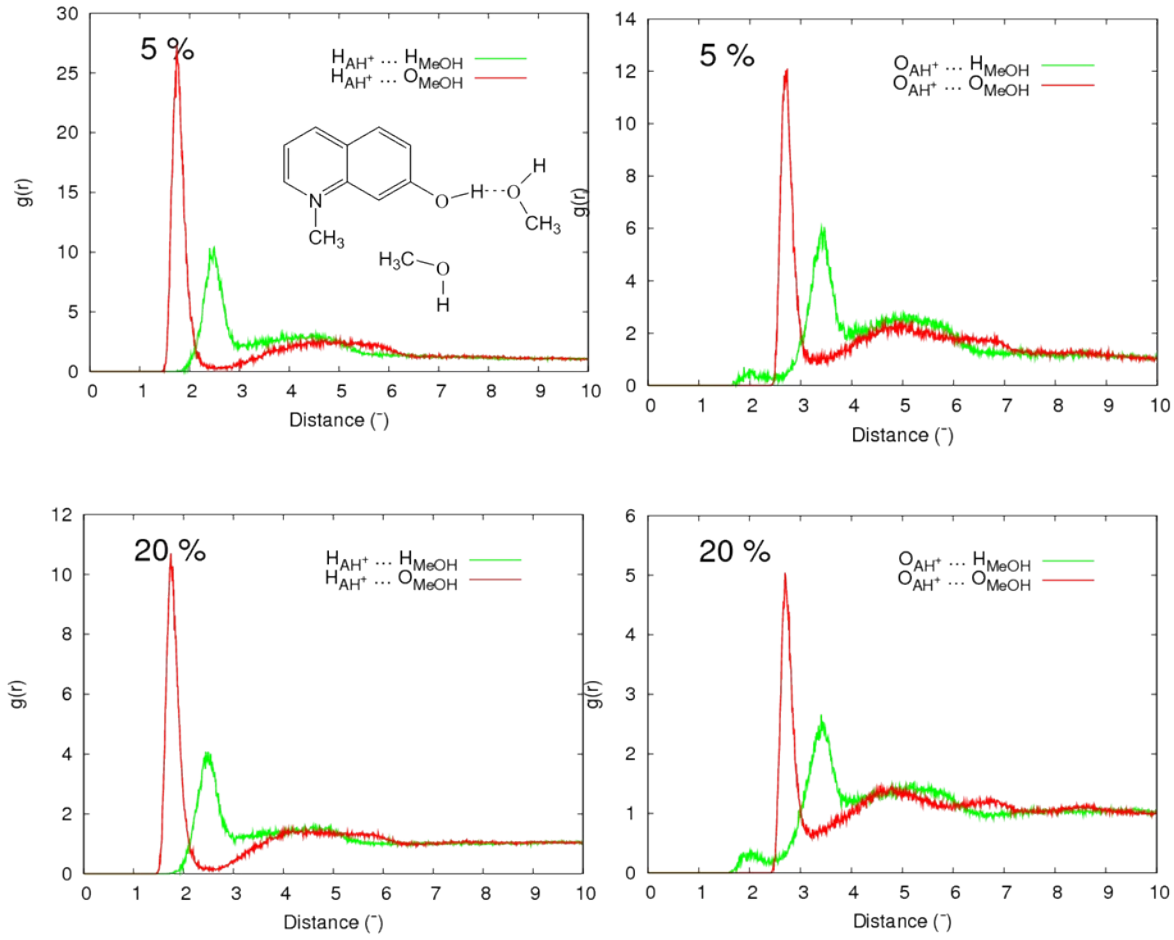


Figure S3. (Left column) Radial distribution functions of O and H atoms of methanol molecules with respect to the hydroxyl H atom of AH^+. (Right column) Radial distribution functions of H and O atoms of methanol molecules with respect to the hydroxyl O atom of AH^+.

4. PES of scanned $A(S_0/S_1)\cdots H^+$ bond alteration

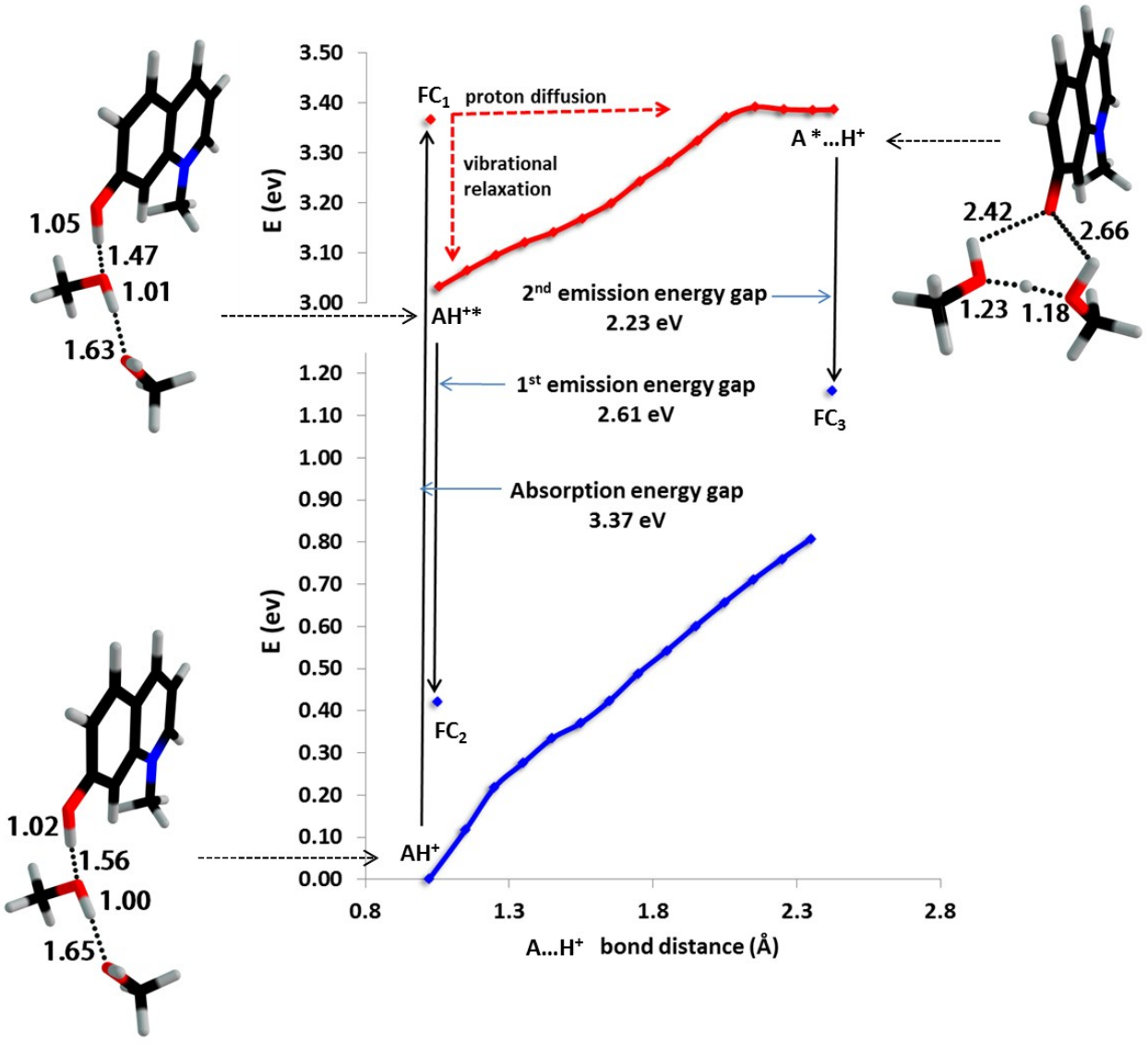


Figure S4. Potential energy surfaces (PES) of scanned A···H^+ bond alteration in the ground and excited state with the assistance of a methanol dimer (blue dots correspond to the ground states and red dots correspond to the excited states). Bond lengths are given in Å.

5. Nature of a solvated proton in MeOH dimers

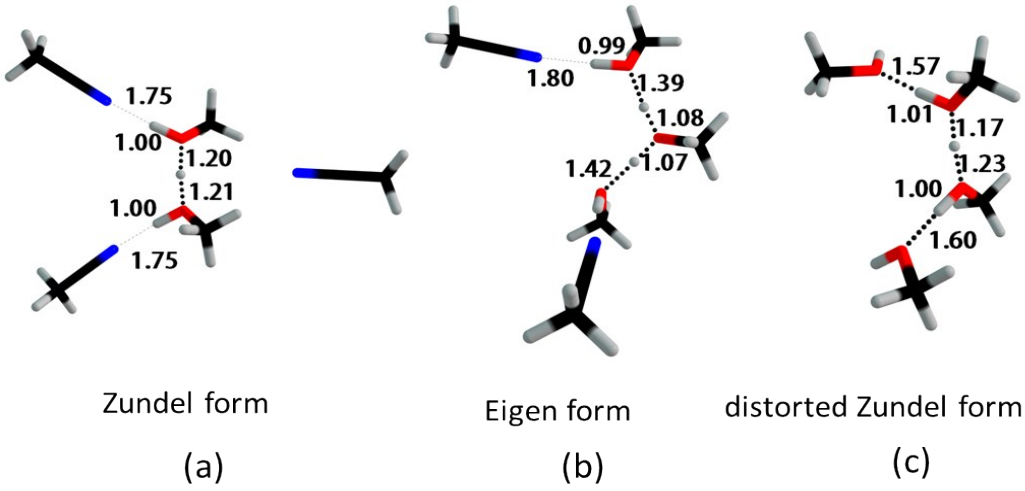


Figure S5. Nature of solvated proton in MeOH dimers surrounded by (a) three MeCN molecules (b) one MeOH and two MeCN molecules (c) two MeOH molecules.