Supporting Information

Ab initio trajectory surface-hopping dynamics studies of excited-state proton-coupled electron transfer reactions in trianisoleheptazine-phenol complexes

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Table S1. Vertical excitation energies (in eV) and oscillator strengths (in parentheses) of the lowest eight singlet excited states of the TAHz···HOPh-R (R=H, Cl, Me, MeO) complexes computed at MP2/cc-pVDZ ground-state equilibrium geometries in C_s symmetry with three different functionals at the TDDFT/def2-SV(P) level. The CT state is marked bold.

	CAM-B3LYP	ωB97X	ωB97X-D	CAM-B3LYP	ωB97X	ωB97X-D
state		TAHz···HOPh-H			TAHz···HOPh-Cl	
S_1	3.18	3.35	3.23	3.18	3.36	3.23
S_2	**3.72**	4.14	3.95	**3.72**	4.14	3.94
S_3	3.85	4.28	**3.99**	3.85	4.27	**4.02**
S_4	4.00	**4.65**	4.09	4.00	**4.67**	4.08
S_5	4.47	4.75	4.56	4.47	4.74	4.55
S_6	4.15	4.32	4.13	4.15	4.32	4.12
S_7	4.25	4.43	4.23	4.25	4.43	4.23
S_8	4.35	4.51	4.32	4.35	4.53	4.33
state		TAHz···HOPh-Me			TAHz···HOPh-MeO	
S_1	3.18	3.35	3.23	3.17	3.35	3.22
S_2	**3.53**	4.14	**3.81**	**3.26**	4.14	**3.56**
S_3	3.85	4.29	3.95	3.85	**4.18**	3.95
S_4	4.00	**4.47**	4.10	4.00	4.29	4.10
S_5	4.47	4.75	4.56	4.47	4.74	4.56
S_6	4.15	4.32	4.13	4.15	4.32	4.13
S_7	4.25	4.41	4.22	4.25	4.43	4.22
S_8	4.34	4.51	4.32	4.35	4.51	4.32

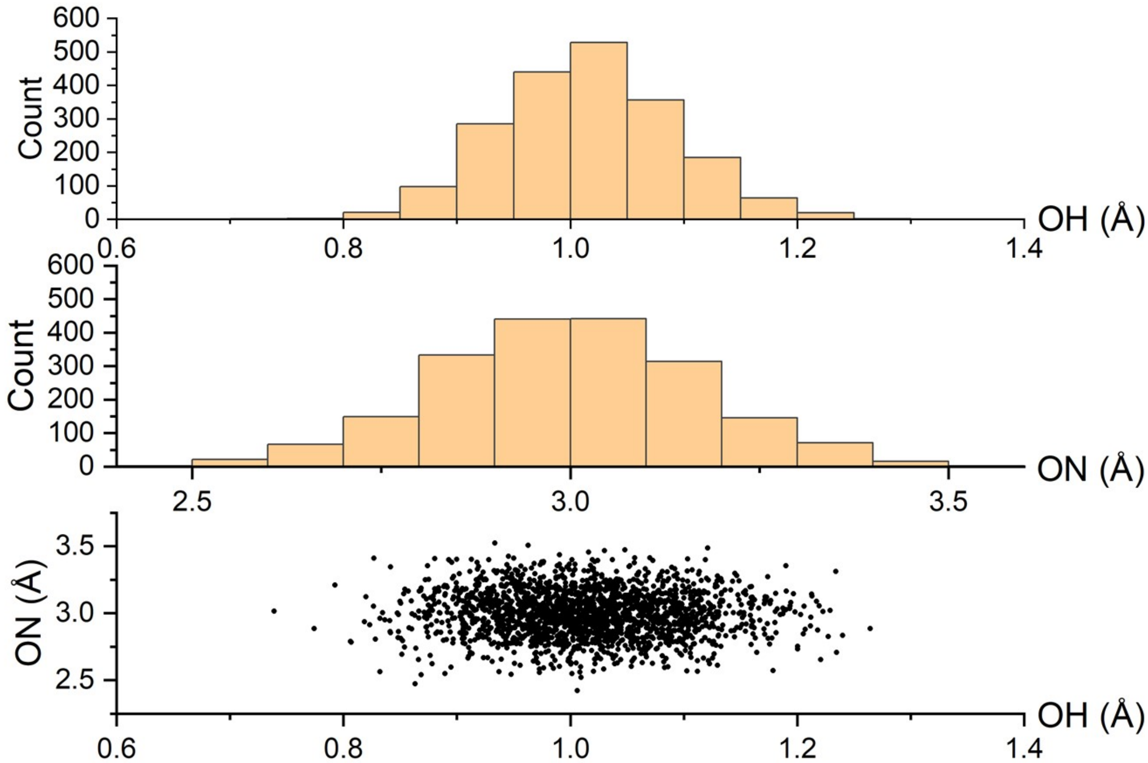
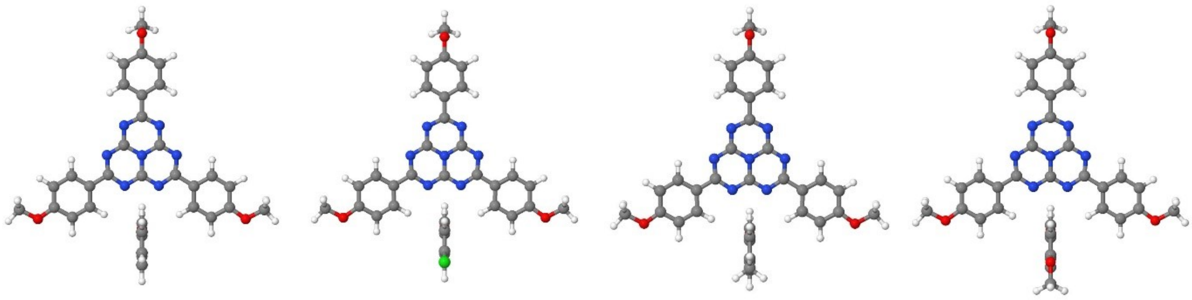


Figure S1. The distribution of the OH bond length (the H-atom transfer coordinate) and the ON bond length (the donor-acceptor distance of the H-atom transfer) in the ground-state thermal Wigner sample comprising 2000 phase space points.



a) b) c) d)

Figure S2. Ground-state equilibrium structures of TAHz···HOPh-H (a), TAHz···HOPh-Cl (b), TAHz···HOPh-Me (c) and TAHz···HOPh-MeO (d) optimized with C_s symmetry constraint. The OH bond lengths are 2.25 Å (a), 2.26 Å (b), 2.26 Å (c) and 2.26 Å (d); the ON bond lengths are 3.14 Å (a), 3.13 Å (b), 3.14 Å (c) and 3.14 Å (d).

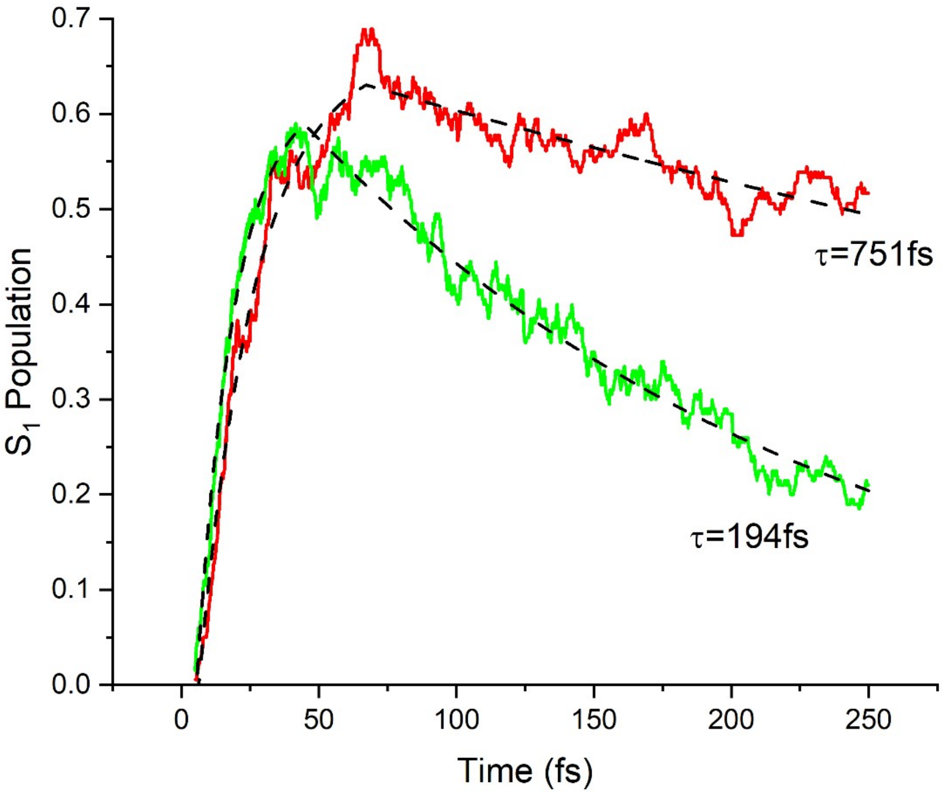


Figure S3. Fit of the populations of the adiabatic S_1 state of TAHz···HOPh-H (red) and TAHz···HOPh-MeO (green) with an exponential growth-decay model. The fitted function is

$$y = f(x) = \begin{cases} A_d + A_g\left(e^{-x_c/t_g} - e^{-x/t_g}\right), & x \le x_c \\ A_d e^{-(x-x_c)/\tau} & , \ x > x_c \end{cases}$$