Electronic Supplementary Information

Proton Transport of a Water Bridge in an Acid−Base Reaction

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Experimental

7HQ (99%) from Acros, diethyl ether (anhydrous) from Sigma-Aldrich, and triply distilled water (≥18 MΩ/cm) were used. The protic hydrogen atoms of both 7HQ and water were exchanged with ^{2}H atoms by dissolving 7HQ in diethyl ether containing ^2H_2O (isotropic purity ≥ 99.9%) for the measurements of kinetic isotope effects. Absorption spectra were obtained using a UV/vis spectrometer (Scinco, S-3100). Fluorescence spectra were obtained by using a home-built fluorimeter consisting of a 75 W Xe lamp (ARC, XS 432), 0.15 and 0.30 m monochromators (ARC, Spectrapro 150 and 300, respectively), and a photomultiplier tube (ARC, PD 438). Fluorescence spectra were not corrected for the wavelength-dependent sensitivity variation of the detector. An actively/passively mode-locked 25 ps Nd:YAG laser (Quantel, YG 701) and a 10 ps streak camera (Hamamatsu, C2830) attached to a CCD detector (Princeton Instruments, RTE128H) were employed for the excitation and the detection of time-resolved fluorescence measurements, respectively. Samples were excited with the third harmonic pulses (355 nm) of the laser. Emission wavelengths were selected by combining band-pass and cutoff filters. Fluorescence kinetic constants were extracted by fitting kinetic profiles to computer-simulated exponential curves convoluted with instrumental response functions. Sample temperature was controlled using a closed-cycle He cryostat (Janis, CCS-100) or a refrigerated bath circulator (Jeio Tech, RC-10V). Unless specified otherwise, static and kinetic measurements were carried out at room temperature.

Absorption Spectra

Fig. S1 shows that the lowest absorption band of N in diethyl ether shifts to the red and loses its vibronic structure with the concentration increase of water. The tautomeric absorption band of 7HQ, presumably around 420 nm,[1] was not observed at any explored water concentrations. The spectral changes of the N band imply that 7HQ molecules associate with water molecules via H bonding to produce complexes in the polar aprotic solvent.[2,3] The complex formation of 7HQ with n molecules of water at the ground state can be described by eqn (S1).

$$\mathrm{7HQ} + n\mathrm{H_2O} \rightleftharpoons \mathrm{7HQ{\cdot}(H_2O)}_n \qquad \text{(S1)}$$

The K_n value can be estimated by eqn (S2),[2]

$$\frac{1}{C^n} = K_n a\,(\varepsilon_{\mathrm{AB}} - \varepsilon_{\mathrm{A}})\frac{10}{A - A_0} - K_n \qquad \text{(S2)}$$

where A and A_0 denote the absorbance measured at the molar water concentrations of C and 0, respectively, a is the concentration of 7HQ, and ε_{A} and $\varepsilon_{\mathrm{AB}}$ are the molar extinction coefficients of the uncomplexed and the complexed 7HQ, respectively. If reciprocals of water concentrations powered by n, $1/C^n$, are linearly correlated with reciprocals of the absorbance changes at 345 nm, $1/(A - A_0)$, the 1:n stoichiometry of 7HQ-water association is apparent and the K_n value can be determined from the intercept of the straight line. The inset of Fig. S1 shows a linear relationship between $1/C^2$ and $1/(A - A_0)$ at >100 mM of water, indicating that a 7HQ molecule forms a complex of 7HQ·$(H_2O)_2$ with the K_2 value of 9.8 M^{-2}. However, at low water concentrations of <100 mM, a linear relationship has been observed between $1/C$ and $1/(A - A_0)$, suggesting that 7HQ and water form 7HQ·H_2O with the K_1 value of 49 M^{-1}. The observed values of K_1 and K_2 imply that 7HQ monomers, 1:1 complexes, and 1:2 complexes are present together at the water concentration of 220 mM adopted for fluorescence kinetics measurements. While the most stable structure of the 1:1 complexes is reported to be H-bonded between the enol group of 7HQ and water,[4] the most stable structure of the 1:2 complexes to be cyclically H-bonded between the enol and the imino groups of 7HQ via two water molecules.[4]

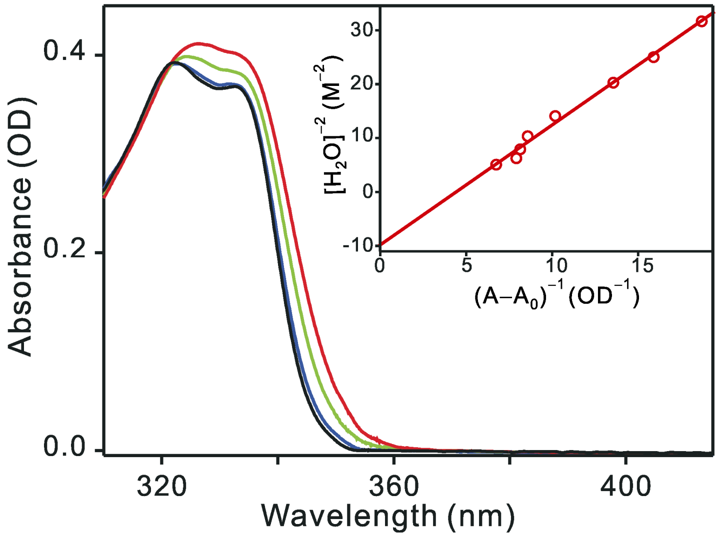

Fig. S1 Absorption spectra of 0.1 mM 7HQ in diethyl ether having water concentrations of 0 (black), 44 (blue), 180 (green), and 330 mM (red). Inset: Plot of $[H_2O]^{-2}$ versus $(A - A_0)^{-1}$, where A and A_0 are absorbances at 345 nm with and without adding water, respectively. The best-fitted line yields 9.8 M^{-2} for the association constant of a 7HQ molecule with two water molecules.

Emission Spectra

Because we inferred that the absorption of cyclic $7HQ\cdot(H_2O)_2$ interferes with that of $7HQ\cdot H_2O$ and noncyclic $7HQ\cdot(H_2O)_2$ (Fig. S1), we have decided to estimate the formation constant of cyclic $7HQ\cdot(H_2O)_2$ (K_{Nc}) with tautomeric fluorescence. K_{Nc} can be estimated by eqn (S3),[5]

$$\frac{1}{C^2} = \frac{c}{F} - K_{Nc} \tag{S3}$$

where C and F denote $[H_2O]$ and fluorescence intensity at 575 nm, respectively, and c is a proportionality constant. The linear plots of Fig. S3 confirm that T* fluorescence originates from cyclically H-bonded 7HQ·$(H_2O)_2$. K_{Nc} values are found to be 140 M^{-2} at 281 K and 11 M^{-2} at 296 K with H and 3.3 M^{-2} at 296 K with D. The temperature dependence of K_{Nc} allows us to calculate the standard formation enthalpy ($\Delta H°$) of cyclically H-bonded 7HQ·$(H_2O)_2$ using the van't Hoff equation of $\ln(K_2/K_1) = -(\Delta H°/R)(1/T_2 - 1/T_1)$, where K_1 and K_2 are equilibrium constants at temperatures T_1 and T_2, respectively, and R is the universal gas constant. Our calculated $\Delta H°$ is –28 kcal/mol, suggesting that strong H-bonds are involved in the formation of cyclic 7HQ·$(H_2O)_2$. We consider that –28 kcal/mol is a reasonable value for the formation of one O–H···N and four O–H···O.[6] Two out of the four O–H···O have been attributed to H-bonds between diethyl ether molecules and water molecules in a complex molecule.

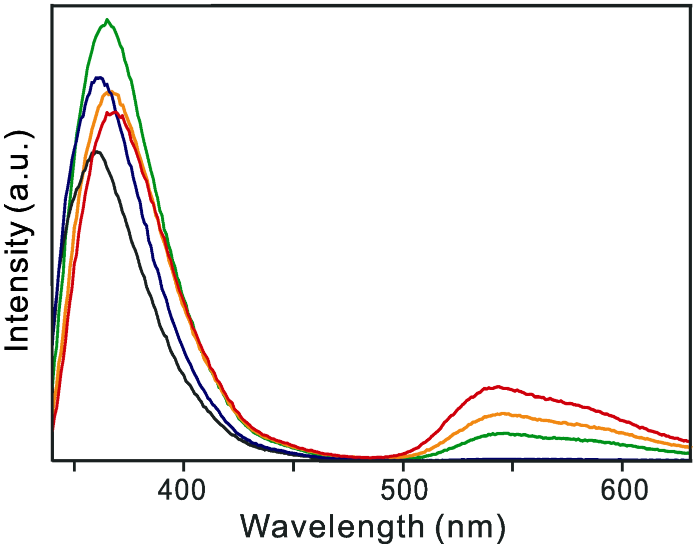

Fig. S2 Emission spectra of 0.1 mM 7HQ in diethyl ether having water concentrations of 0 (black), 44 (blue), 220 (green), 330 (orange), and 440 mM (red) with excitation at 330 nm.

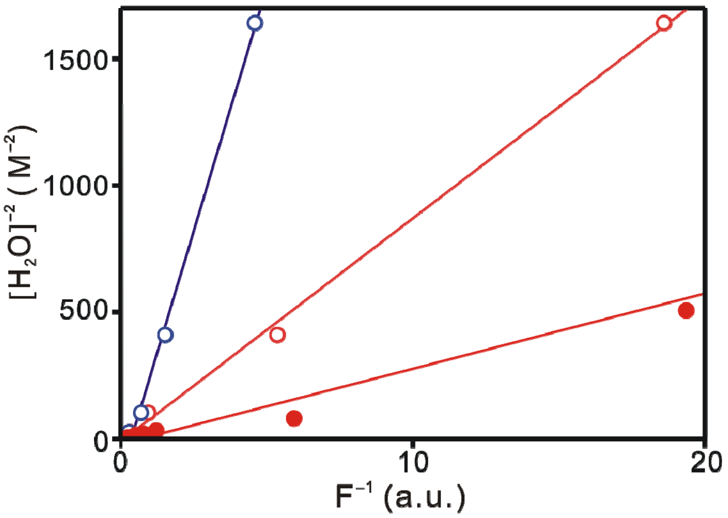

Fig. S3 $[H_2O]^{-2}$ with isotopes of H (open) and D (closed) versus reciprocal fluorescence intensity at 575 nm (F^{-1}) at 281 (blue) and 296 K (red). The best-fitted solid lines for the formation constants of cyclic $7HQ\cdot(H_2O)_2$ complexes yield 140 M^{-2} at 281 K and 11 M^{-2} at 296 K with H and 3.3 M^{-2} at 296 K with D.

Excitation Spectra

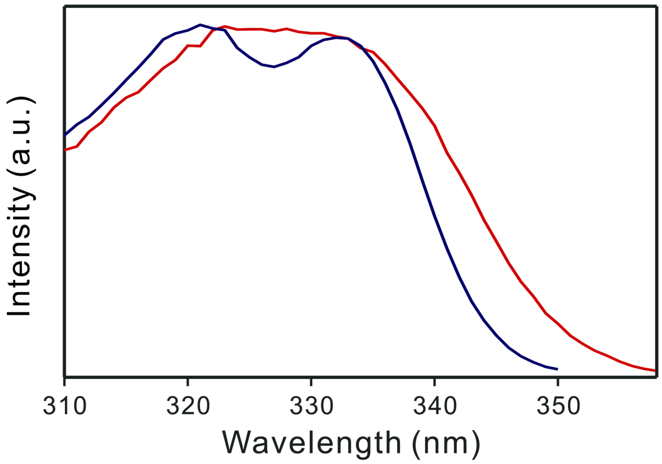

Fig. S4 Excitation spectra of 0.1 mM 7HQ in diethyl ether monitored at 355 nm without water (blue) and at 550 nm with water of 220 mM (red).

Fluorescence Kinetic Constants

Table S1 Fluorescence kinetic constants of 0.1 mM 7HQ in water-added diethyl ether with excitation at 355 nm

$[H_2O]$ / mM	Isotope	Wavelength[a] / nm	Rise time / ps	Decay time / ps
0	H	380	Instant	460
44	H	420	Instant	38 (33%)[b] + 860
44	H	570	40	1500
220	H	420	Instant	38 (66%) + 900
220	H	570	40	1500
220	D	420	Instant	120 (65%) + 900
220	D	570	115	3300

[a] Wavelength of monitored fluorescence. [b] Initial intensity percentage of each decay component.

Proton-Inventory Experiments

Nc can have eight different types of isotopic exchange: HHH, HDH, HHD, HDD, DHH, DDH, DHD, and DDD, where the successive three isotopes denote protic hydrogen atoms in turn attached to the O of the enol group and two water molecules of Nc. The k_{pt} values of the above Nc* complexes are k^{HHH}, k^{HDH}, k^{HHD}, k^{HDD}, k^{DHH}, k^{DDH}, k^{DHD}, and k^{DDD}, respectively. If $X_{\mathrm{D}} = [\mathrm{D}]/([\mathrm{H}] + [\mathrm{D}])$ and $X_{\mathrm{H}} = 1 - X_{\mathrm{D}}$, then we can deduce eqn (S4) and (S5) according to the protic isotopes of the enol group of Nc.

$$\mathrm{d}[\mathrm{H}^{**}]/\mathrm{d}t = -\{X_{\mathrm{H}}^2\, k^{\mathrm{HHH}} + X_{\mathrm{H}}X_{\mathrm{D}}(k^{\mathrm{HDH}} + k^{\mathrm{HHD}}) + X_{\mathrm{D}}^2\, k^{\mathrm{HDD}}\}[\mathrm{H}^{**}] \qquad (\mathrm{S4})$$

$$\mathrm{d}[\mathrm{D}^{**}]/\mathrm{d}t = -\{X_\mathrm{H}^2\, k^\mathrm{DHH} + X_\mathrm{H}X_\mathrm{D}(k^\mathrm{DDH} + k^\mathrm{DHD}) + X_\mathrm{D}^2\, k^\mathrm{DDD}\}[\mathrm{D}^{**}] \qquad \text{(S5)}$$

where * denotes H or D. Because the formation constants of Nc vary considerably with isotope exchange (Fig. S3), actual isotope fraction constants of H and D are different from X_H and X_D, respectively.[7–10] Thus, we have calibrated X_H and X_D considering different K_Nc values with H and D. When both X_H and X_D are 0.5, their calibrated values become 0.646 and 0.354, respectively.

The fluorescence decay component of Nc giving k_pt can be decomposed as eqn (S6)

$$\exp(-k_\mathrm{pt}\, t) = X_\mathrm{H} \exp(-k^\mathrm{H}\, t) + X_\mathrm{D} \exp(-k^\mathrm{D}\, t) \qquad \text{(S6)}$$

where k^H and k^D consist of the eight different k_pt values according to eqn (S7) and (S8), respectively.

$$k^\mathrm{H} = k^\mathrm{HHH} + (k^\mathrm{HHD} + k^\mathrm{HDH} - 2\, k^\mathrm{HHH})X_\mathrm{D} + (k^\mathrm{HHH} + k^\mathrm{HDD} - k^\mathrm{HHD} - k^\mathrm{HDH})X_\mathrm{D}^2 \qquad \text{(S7)}$$

$$k^\mathrm{D} = k^\mathrm{DHH} + (k^\mathrm{DDH} + k^\mathrm{DHD} - 2\, k^\mathrm{DHH})X_\mathrm{D} + (k^\mathrm{DHH} + k^\mathrm{DDD} - k^\mathrm{DDH} - k^\mathrm{DHD})X_\mathrm{D}^2 \qquad \text{(S8)}$$

Dependence of k_{pt} on the Acidity of the Complexed Solvent

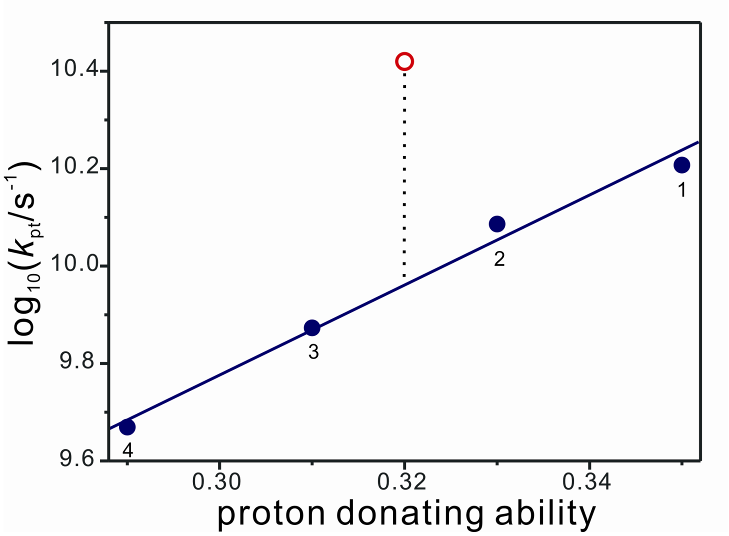

Fig. S5 Plot of $\log_{10}(k_{pt})$ of 7HQ·(alcohol)$_2$ in *n*-heptane (closed) and 7HQ·(H$_2$O)$_2$ in diethyl ether (open) versus the proton donating ability of the complexed hydroxyl solvent.[11] The solid line is the best linear fit for (7HQ)·(alcohol)$_2$ only. The circles of 1, 2, 3, and 4 are cited from ref. 12 to show k_{pt} with methanol, ethanol, 2-propanol, and *t*-butanol, respectively.

Temperature-Dependent Fluorescence Kinetics

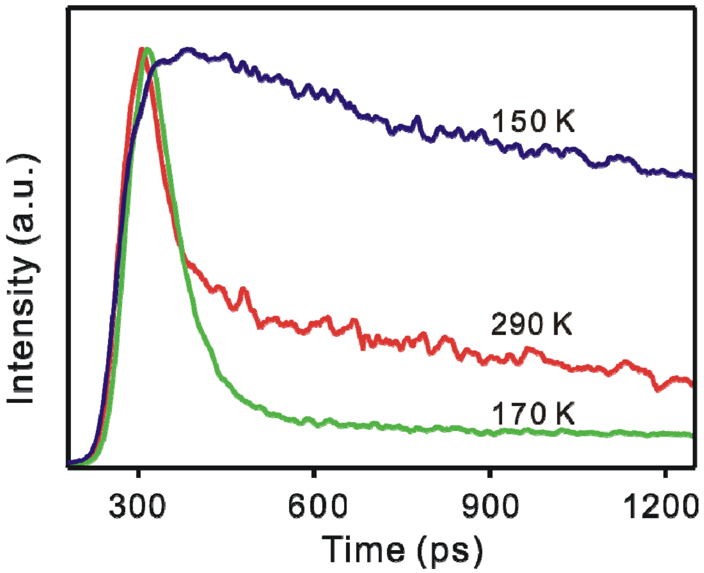

Fig. S6 Temperature-dependent fluorescence kinetic profiles of 0.1 mM 7HQ in diethyl ether having water of 220 mM, excited at 315 nm, monitored at 420 nm, and measured at indicated temperatures. The decrease of the fast component contribution with temperature increase from 170 K to 290 K is due to decrease in the association constant of Nc with temperature increase.

References

1. S.-I. Lee, D.-J. Jang, *J. Phys. Chem.* **1995**, *99*, 7537–7541.
2. S. Kohtani, A. Tagami, R. Nakagaki, *Chem. Phys. Lett.* **2000**, *316*, 88–93.
3. P.-T. Chou, C.-Y. Wei, C.-R. Wang, C. F.-T.Hung, C.-P. Chang, *J. Phys. Chem. A* **1999**, *103*, 1939–1949.
4. W.-H. Fang, *J. Phys. Chem. A* **1999**, *103*, 5567–5573.
5. Y. Tanimoto, M. Itoh, *Chem. Phys. Lett.* **1978**, *57*, 179–182.
6. G. A. Jeffrey, *An Introduction to Hydrogen Bonding*; Oxford Univ. Press: Oxford, 1997; pp 11–32.

7. D. Gerritzen, H.-H. Limbach, *J. Am. Chem. Soc.* **1984**, *106*, 869–879.
8. P. M. Tolstoy, P. Schah-Mohammedi, S. N. Smirnov, N. S. Golubev, G. S. Denisov, H.-H. Limbach, *J. Am. Chem. Soc.* **2004**, *126*, 5621–5634.
9. O.-H. Kwon, A. H. Zewail, *Proc. Natl. Acad. Sci. USA*. **2007**, *104*, 8703–8708.
10. J. M. Lopez, F. Männle, I. Wawer, G. Buntkowsky, H.-H. Limbach, *Phys. Chem. Chem. Phys.* **2007**, *9*, 4498–4513.
11. Y. Marcus, *J. Phys. Chem.* **1991**, *95*, 8886–8891.
12. O.-H. Kwon, Y.-S. Lee, B. K. Yoo, Jang, D.-J. *Angew. Chem. Int. Ed.* **2006**, *45*, 415–419.