Supplementary Material (ESI) for PCCP

Electronic Supplementary Information

Ground-state proton-transfer dynamics governed by configurational optimization

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1. Steady-state absorption spectra

Absorption spectra of 7HQ in *n*-heptane having various alcohols display only the normal absorption band with the maximum around 330 nm (Fig. S1). The tautomeric absorption band, presumably around 410 nm,[1] has not been observed in any explored alcohols, indicating that proton-translocated T does not exist in the ground state. On the other hand, all the absorption spectra shown in Fig. S1 shift to the red and lose vibronic structures with the concentration increment of alcohols, implying that 7HQ molecules associate with alcohol molecules via H-bonding to produce 7HQ-alcohol complexes in *n*-heptane.[2,3] The complex formation of 7HQ with *n* molecules of an alcohol (ROH) in the ground state can be described by eqn S1.

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

The association constant of K_n can be estimated by eqn S2,[2]

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

where A denotes absorbance measured at the molar alcohol concentration of C, a is the concentration of 7HQ, and $\varepsilon_{\mathrm{AB}}$ and ε_{A} are the molar extinction coefficients of complexed 7HQ and uncomplexed 7HQ, respectively. If the reciprocal of an alcohol concentration powered by n ($1/C^n$) is linearly correlated with the reciprocal of absorbance at 345 nm ($1/A$), the 1:n stoichiometry of 7HQ-alcohol association is apparent and K_n can be determined from the intercept of the straight line. The insets of Fig. S1 show linear relationships between $1/C^2$ and $1/A$, signifying that a 7HQ molecule and two alcohol molecules associate to form a complex of 7HQ·(alcohol)$_2$ with an association constant of K. Table 1 shows that the K value of the 7HQ·(alcohol)$_2$ complex decreases with the structural complexity of the alcohol but increases with the Kamlet-Taft acidity (α) of the alcohol. Accordingly, we infer that the acidity, as well as the structural complexity, of the alcohol plays an important role in the formation of 7HQ·(alcohol)$_2$ complexes. The strengths of α and the Kamlet-Taft basicity (β) indicate explicitly the proton-donating ability and the proton-accepting ability of H-bonding molecules, respectively.[4–6] The most stable ground-state structure of the 7HQ·(alcohol)$_2$ complex is reported to have the cyclic geometry shown in Scheme S1.[7]

2. Steady-state emission spectra

Fig. S2 shows the N* fluorescence-normalized emission spectra of 7HQ·(alcohol)$_2$ complexes in n-heptane with variation of alcohols. The excitation of cyclic 7HQ·(alcohol)$_2$ complexes at 345 nm gives rise to prominent T* fluorescence at 530 nm as well as N* fluorescence at 370 nm, implying that the

ESPT of 7HQ is operative along H-bonded alcohol molecules in the nonpolar aprotic medium of *n*-heptane (Scheme S1).[8] The intensity of T* fluorescence increases with the α value of the alcohol (Fig. S2), implying that the strength of α determines the facileness of the ESPT of the cyclic complex.

3. References

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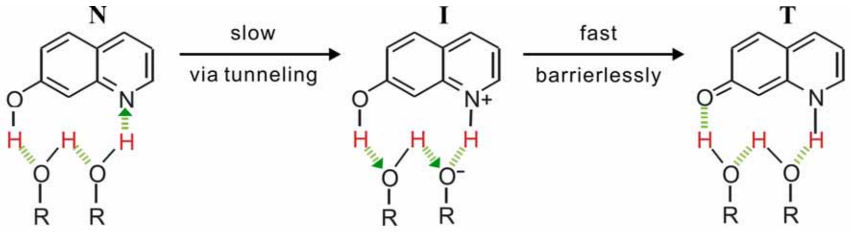

Scheme S1 Excited-state triple proton transfer of 7HQ along a H-bonded alcohol chain

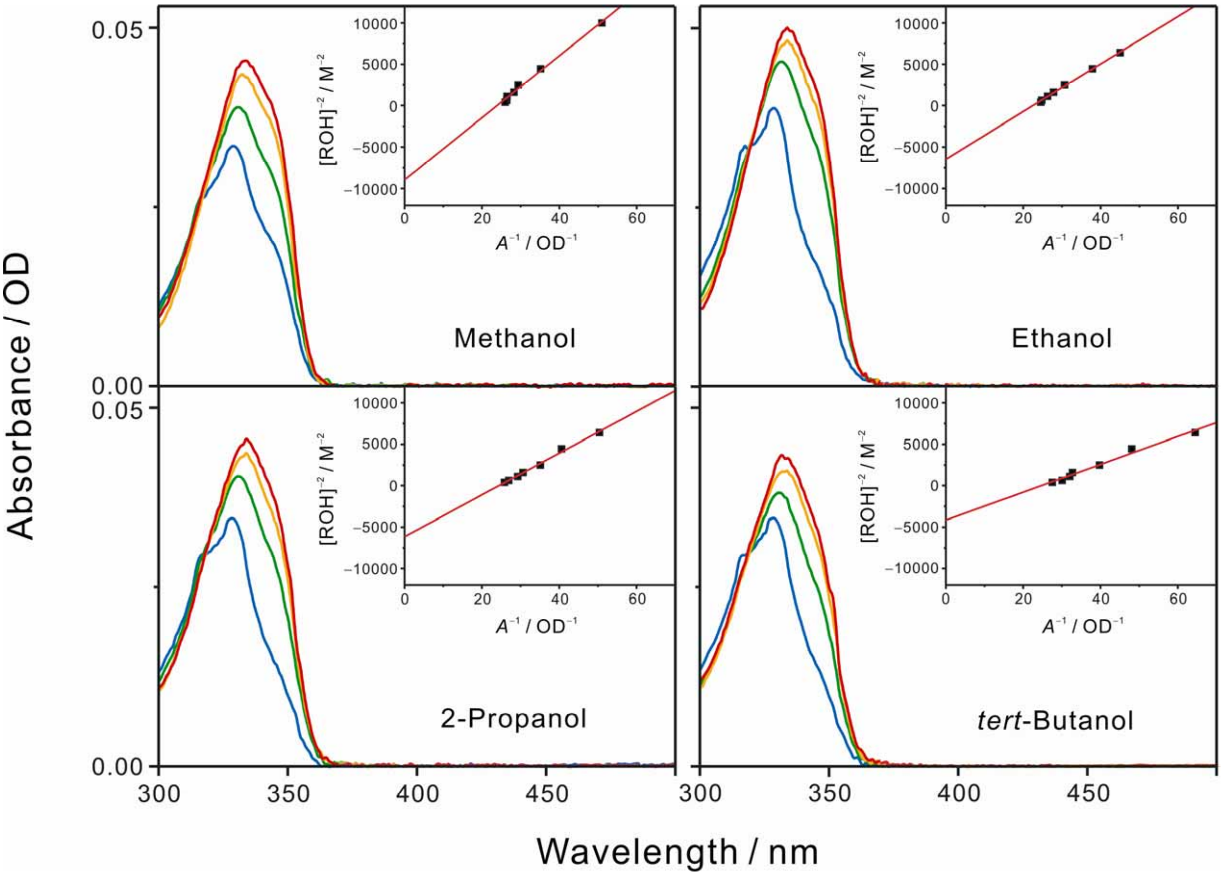

Fig. S1 Absorption spectra of 10 μM 7HQ in *n*-heptane having indicated alcohols of 10 mM (blue), 20 mM (green), 30 mM (yellow), and 40 mM (red). Insets: Plots of $[\mathrm{ROH}]^{-2}$ versus A^{-1} at 345 nm. The best-fitted lines yield the association constants, given in Table 1, of a 7HQ molecule with two alcohol molecules.

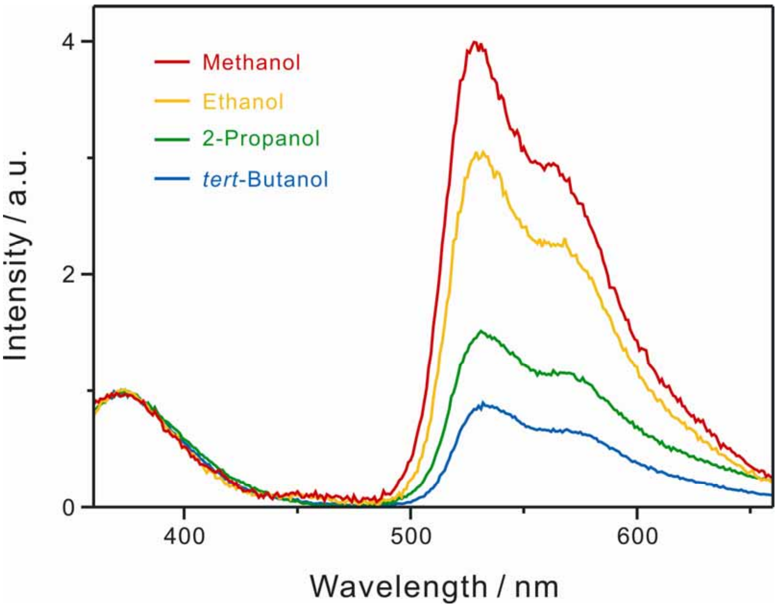

Fig. S2 N* fluorescence-normalized emission spectra of 10 μM 7HQ in *n*-heptane having indicated alcohols. Samples were excited at 345 nm, and the concentration of each alcohol was kept to be 30 mM.