

## Supporting Information

### Hydrogen Bonding between Hydroxylic Donors and MLCT-Excited Ru(bpy)<sub>2</sub>(bpz)<sup>2+</sup> Complex: Implications for Photoinduced Electron-Proton Transfer

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**Materials and methods.** Dichloromethane (Aldrich, HPLC Plus, ≥99.9%) was passed through activated neutral alumina following by drying over activated 3Å molecular sieves. 2,2,2-trichloroethanol (CCl<sub>3</sub>CH<sub>2</sub>OH, Aldrich, ≥99 %), 2,2,2-trifluoroethanol (CF<sub>3</sub>CH<sub>2</sub>OH, Aldrich, ≥99 %), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (CH<sub>3</sub>C(CF<sub>3</sub>)<sub>2</sub>OH, Aldrich, ≥97 %), nonafluoro-tert-butyl alcohol ((CF<sub>3</sub>)<sub>3</sub>COH, Aldrich, ≥ 99 %) were used as received. Complex **1** ([Ru(bpy)<sub>2</sub>(bpz)]<sup>2+</sup>) has been prepared according to literature procedures.<sup>1</sup>

Samples were prepared in the inert atmosphere of a glove box and transferred into air-tight 1 cm pathlength optical cuvettes. Transient emission and absorption were measured using a home-built flash photolysis system<sup>2</sup> with excitation (475 nm) provided by ~2 ns pulses from a tunable OPO (VersaScan/240/ULD) pumped by the 354.7 nm output of a Nd/YAG laser (SpectraPhysics Lab 170). The excitation energy was maintained in the 7-8 mJ/pulse range. For transient absorption measurements, a pulsed 75 W Xe lamp was used as a probe light source. Kinetics traces were recorded using a Hamamatsu R928 PMT coupled to a double monochromator. Transient emission kinetics was recorded at 680 nm. Transient absorption spectra were emission corrected. Sample integrity during a transient experiment was routinely tested by comparing before-and-after UV/vis spectra measured with an Agilent 8453 spectrophotometer. The temperature of samples was controlled by home-built variable temperature cell holder in the range between -20 °C and 43 °C with a ± 0.5 °C accuracy.

Measured emission decays of **1**(T) were fit to a single exponential function (using Origin 9.5 software) yielding the emission lifetimes:  $\tau_0$  in the absence and  $\tau_{\text{obs}}$  in the presence of a quencher. Stern-Volmer lifetime plots,  $\tau_0/\tau_{\text{obs}} - 1$  were vs. an added quencher concentration, were fit to the function,

$$y = \frac{ax}{1 + bx}$$

from which parameters  $a$  and  $b$  and their standard errors were obtained. This function is a general form of the eq. 1 (main text); that is,

$$\frac{\tau_0}{\tau_{\text{obs}}} = 1 + \frac{\tau_0(k_q - k_0)K_{\text{HB}}[\text{ROH}]}{1 + K_{\text{HB}}[\text{ROH}]}$$

Thus,  $\tau_0/\tau_{\text{obs}} - 1$ ,  $x = [\text{ROH}]$ ,  $a = \tau_0(k_q - k_0)K_{\text{HB}}$ , and  $b = K_{\text{HB}}$ .

Standard error for  $k_q$  and other values derived from  $k_q$  and  $K_{\text{HB}}$ . were a general formalism for propagation of errors; that is,

$$\sigma_f^2 = \left(\frac{\partial f}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial f}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial f}{\partial z}\right)^2 \sigma_z^2 + \dots$$

where  $\sigma_f$  is a standard error of  $f(x, y, z)$  and  $\sigma_x, \sigma_y, \sigma_z$  are errors for independent variables  $x, y, z$ , etc. For example, the values of  $k_q$  for alcohols and their standard errors are obtained as follows:

$$k_q = \frac{a/b + 1}{\tau_0}$$

$$\sigma_{k_q}^2 = \sigma_a^2 \left(\frac{1}{\tau_0 b}\right)^2 + \sigma_b^2 \left(\frac{a}{\tau_0 b^2}\right)^2$$

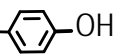
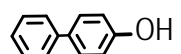
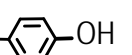
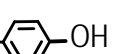
#### References:

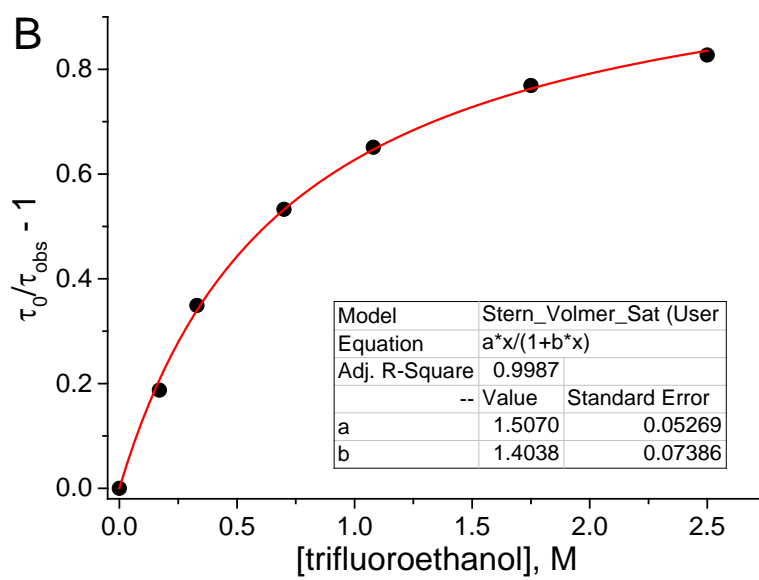
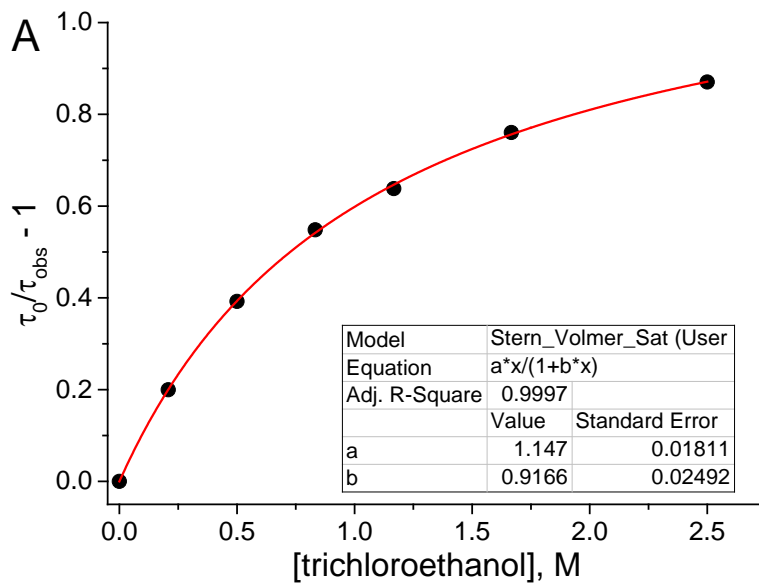
1. D. P. Rillema, G. Allen, T. J. Meyer, and D. Conrad, *Inorg. Chem.*, 1983, **22**, 1617-1622.
2. S. V. Lyamar, M. Z. Ertem, A. Lewandowska-Andralojc, and D. E. Polyansky, *J. Phys. Chem. Lett.*, 2017, **8**, 4043-4048.

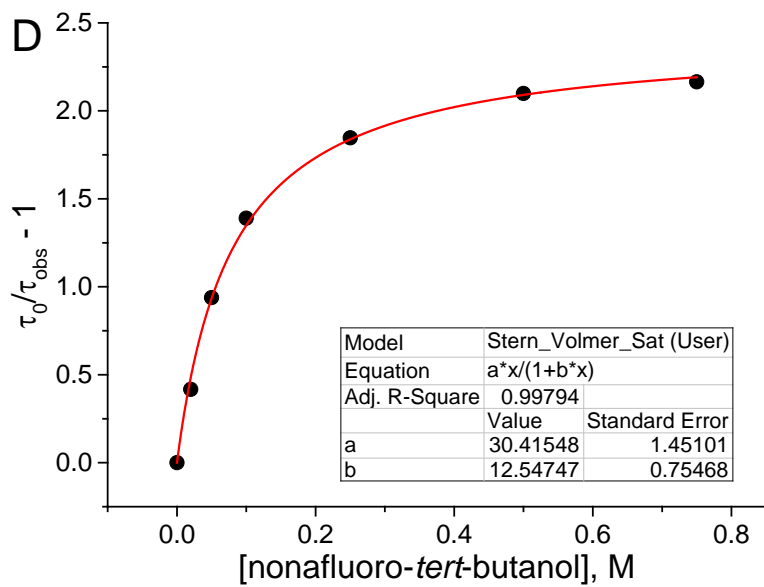
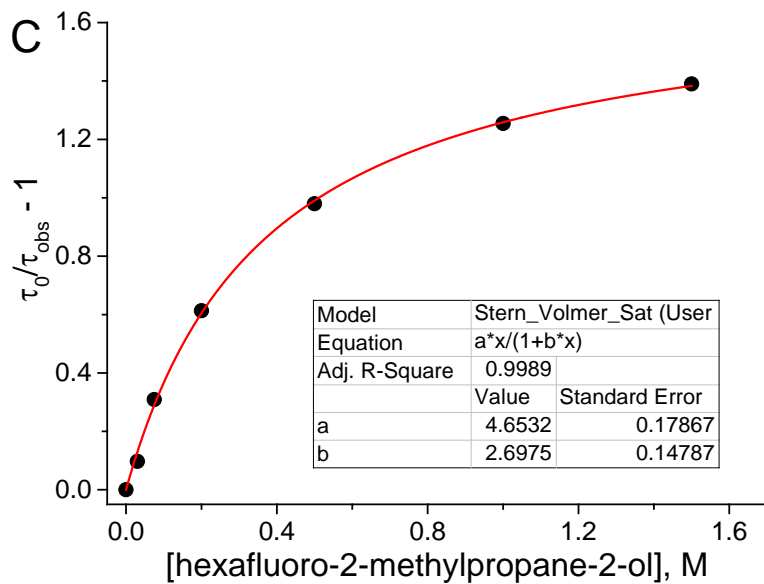
**Table S1.** Equilibrium constants, enthalpies, and entropies ( $K_{\text{HB}}$ ,  $\Delta H_{\text{HB}}$ , and  $\Delta S_{\text{HB}}$ ) for H-bonding of hydroxylic HB acids to **1(T)** and unimolecular rate constants ( $k_q$ ) of emission quenching within the ROH-**1(T)** exciplexes in  $\text{CH}_2\text{Cl}_2$  at 25 °C. Uncertainties are shown as standard errors of data fitting in Figs. S1 and S4.

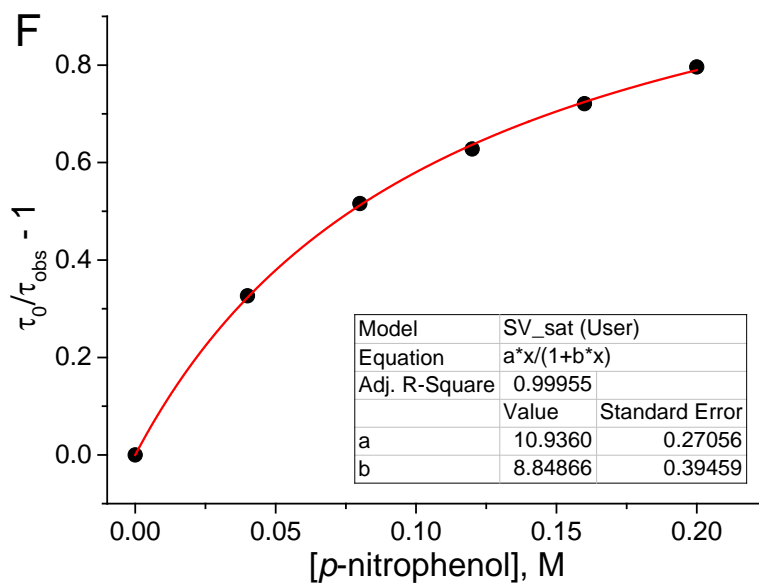
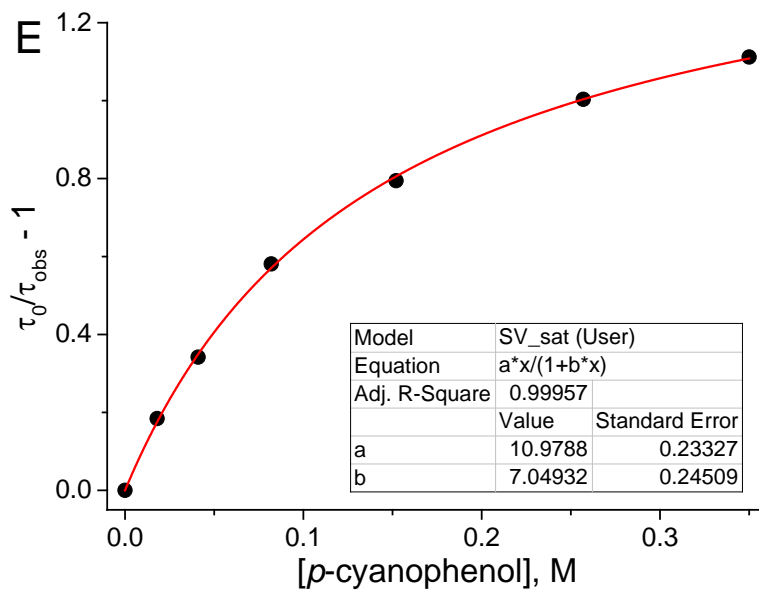
| Entry | R-OH  | $k_q$ ,<br>$10^6 \text{ s}^{-1}$ | $K_{\text{HB}}$ ,<br>$\text{M}^{-1}$ | $-\Delta H_{\text{HB}}$ ,<br>kcal/mol | $-\Delta S_{\text{HB}}$ ,<br>cal/(mol K) |
|-------|---|----------------------------------|--------------------------------------|---------------------------------------|--|
| 1     | $\text{Cl}_3\text{C-CH}_2\text{-OH}$            | $3.85 \pm 0.08$                  | $0.92 \pm 0.03$                      | $4.07 \pm 0.02$                       | $13.83 \pm 0.04$                         |
| 2     | $\text{F}_3\text{C-CH}_2\text{-OH}$             | $3.55 \pm 0.11$                  | $1.40 \pm 0.07$                      | $4.15 \pm 0.03$                       | $13.27 \pm 0.14$                         |
| 3     | $\text{Me-C}(\text{CF}_3)_2\text{-OH}$          | $4.65 \pm 0.20$                  | $2.7 \pm 0.2$                        | $4.30 \pm 0.04$                       | $12.50 \pm 0.16$                         |
| 4     | $\text{NC-C}_6\text{H}_4\text{-OH}$             | $4.37 \pm 0.11$                  | $7.1 \pm 0.3$                        | n/d                                   | n/d                                      |
| 5     | $\text{O}_2\text{N-C}_6\text{H}_4\text{-OH}$    | $3.82 \pm 0.11$                  | $8.9 \pm 0.4$                        | n/d                                   | n/d                                      |
| 6     | $\text{F}_3\text{C-C}(\text{CF}_3)_2\text{-OH}$ | $5.84 \pm 0.32$                  | $12.6 \pm 0.8$                       | $4.8 \pm 0.1$                         | $10.35 \pm 0.34$                         |

**Table S2.** Observed bimolecular rate constants ( $k_q^{\text{obs}}$ ), H-bonding equilibrium constants ( $K_{\text{HB}}$ ), and unimolecular rate constants ( $k_q$  and  $k_0^{\text{HB}}$ ) for reaction of *p*-substituted phenols with **1(T)** in  $\text{CH}_2\text{Cl}_2$  at 25 °C.

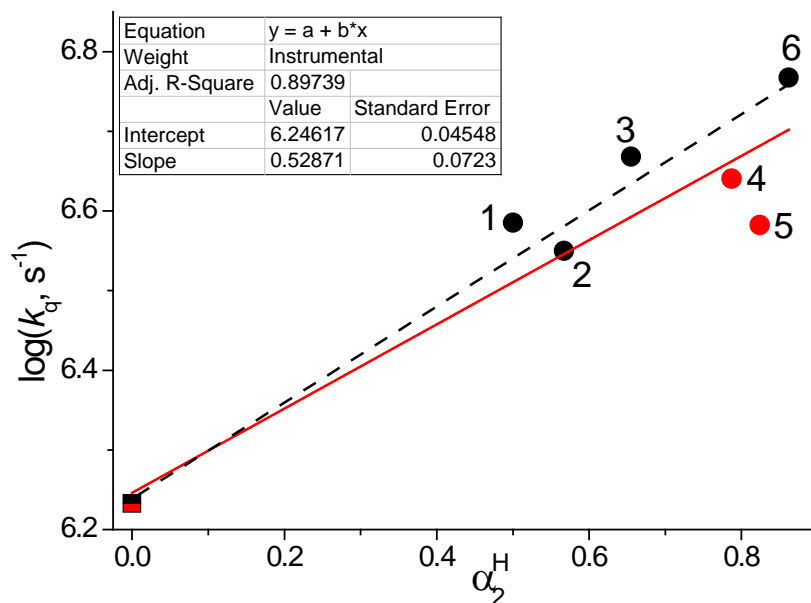
| Phenol   | $K_{\text{HB}}$ ,<br>$\text{M}^{-1}$ | $k_q^{\text{obs}}$ ,<br>$10^7 \text{M}^{-1} \text{s}^{-1}$ | $k_q$ ,<br>$10^6 \text{s}^{-1}$ | $k_0^{\text{HB}}$ ,<br>$10^6 \text{s}^{-1}$ |
|--|--------------------------------------|--|---------------------------------|---|
| MeO-  -OH     | $1.5 \pm 0.14$                       | $150 \pm 51$   | $1000 \pm 100$                  | $3.5 \pm 0.5$                               |
|  -OH          | $1.7 \pm 0.17$                       | $42 \pm 51$  | $240 \pm 24$                    | $3.6 \pm 0.5$                               |
| Cl-  -OH      | $3.0 \pm 0.3$                        | $6.0 \pm 5.1$  | $22 \pm 2.1$                    | $4.0 \pm 0.6$                               |
| MeOC(O)-  -OH | $4.6 \pm 0.5$                        | $2.0 \pm 0.7$  | $6.1 \pm 0.5$                   | $4.3 \pm 0.7$                               |







**Fig. S1** Stern-Volmer lifetime plots for quenching of **1**(T) in CH<sub>2</sub>Cl<sub>2</sub> ( $\tau_0 = 585$  ns) by: 1,1,1-trichloroethanol (A); 1,1,1-trifluoroethanol (B); 1,1,1,3,3,3-Hexafluoro-2-methylpropane-2-ol (C); nonafluoro-*tert*-butanol (D); *p*-cyanophenol (E); and *p*-nitrophenol (F).

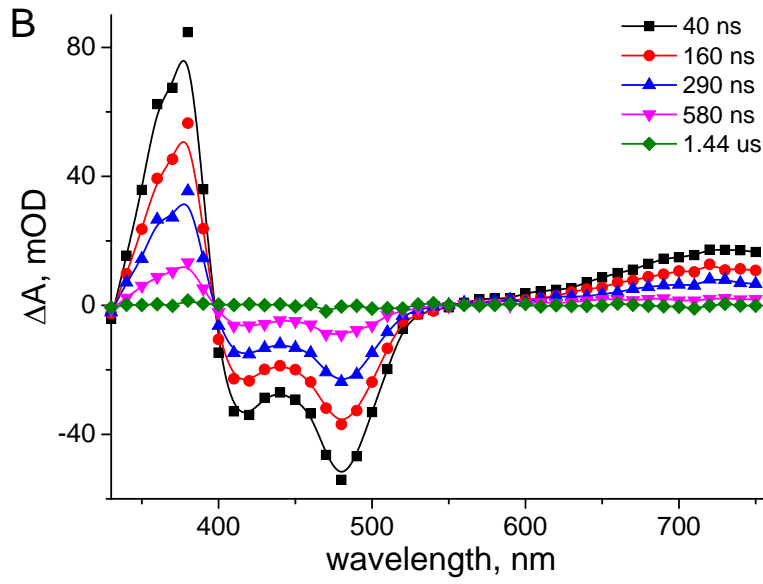
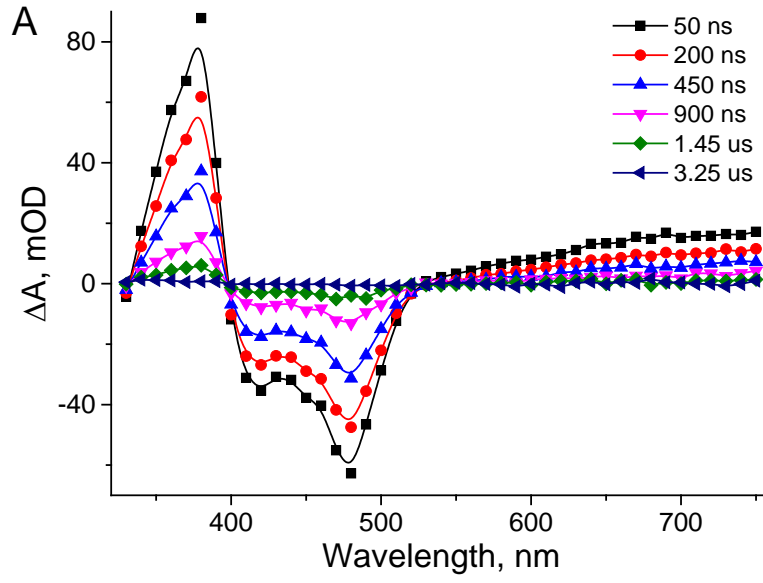


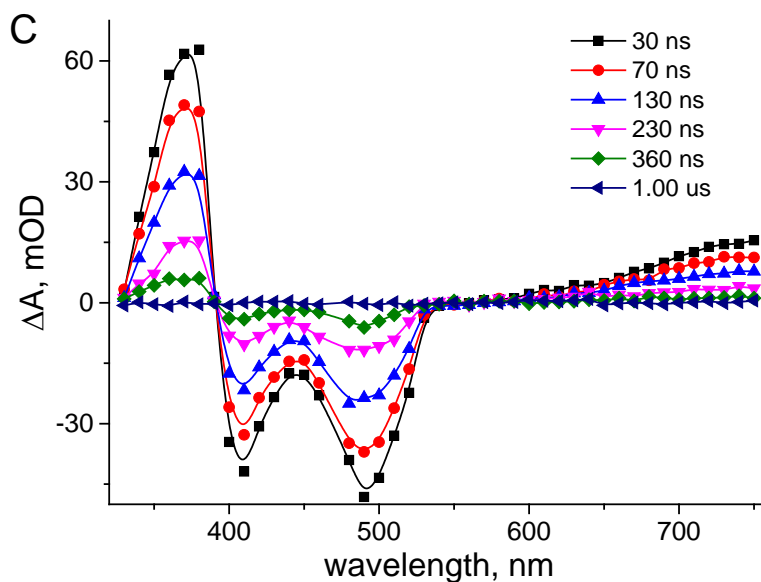
**Fig. S2.** Dependence of  $\log k_q$  obtained from Stern-Volmer lifetime plots for quenching of **1(T)** by ROH in  $\text{CH}_2\text{Cl}_2$  on quencher's hydrogen bonding acidity ( $\alpha_2^{\text{H}}$ ). 2,2,2-trichloroethanol (1), 2,2,2-trifluoroethanol (2), 1,1,1,3,3,3-hexafluoro-2-methyl-2-propanol (3), *p*-cyanophenol (4), *p*-nitrophenol (5), nonafluoro-tert-butyl alcohol (6). The square bi-colored point at  $\alpha_2^{\text{H}} = 0$  corresponds to the rate of **1(T)** decay in the absence of any quenchers. The black dashed line is drawn through the black points only (alcohols and no quencher), and the red gives a linear fit for the entire data set. Assuming that  $k_q = k_0^{\text{HB}}$  for all quenchers in this set, we have,

$$\log k_0^{\text{HB}} = (0.53 \pm 0.07)\alpha_2^{\text{H}} + (6.25 \pm 0.05)$$

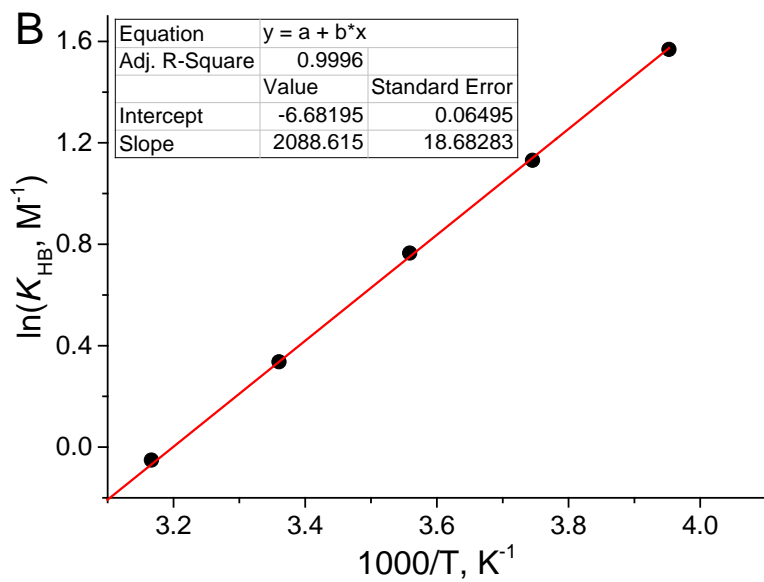
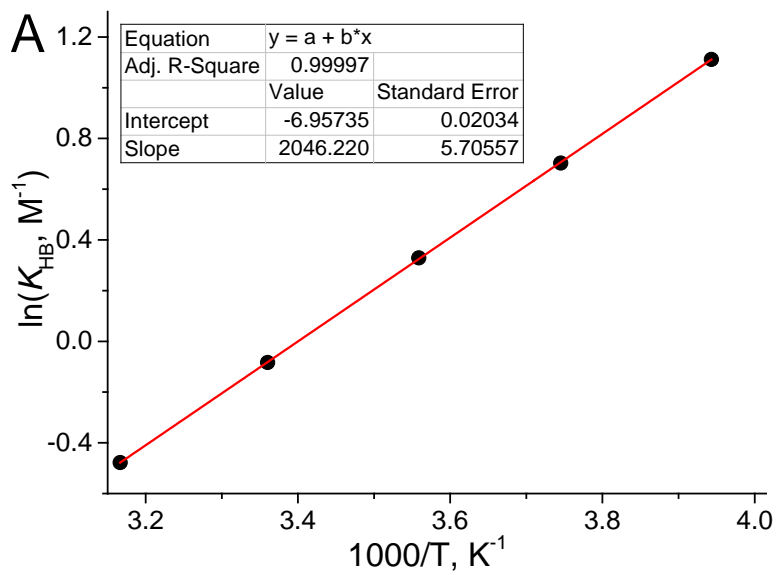
In this equation,  $\alpha_2^{\text{H}}$  serves as a descriptor for the rate of physical quenching through H-bonding, which have been used for evaluating the  $k_0^{\text{HB}}$  values in Table 2, main text.

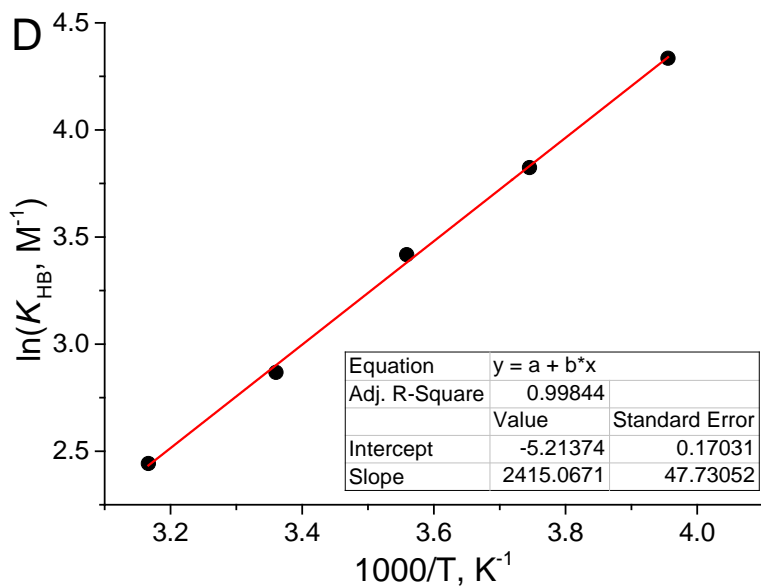
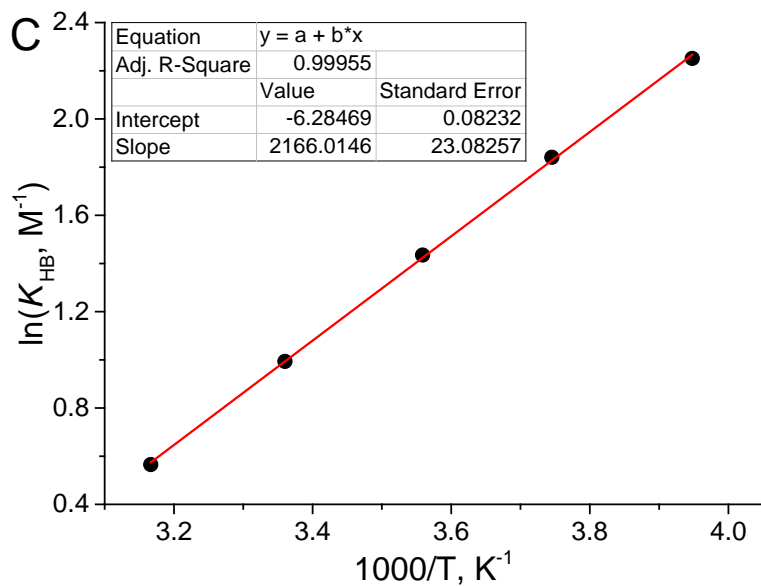




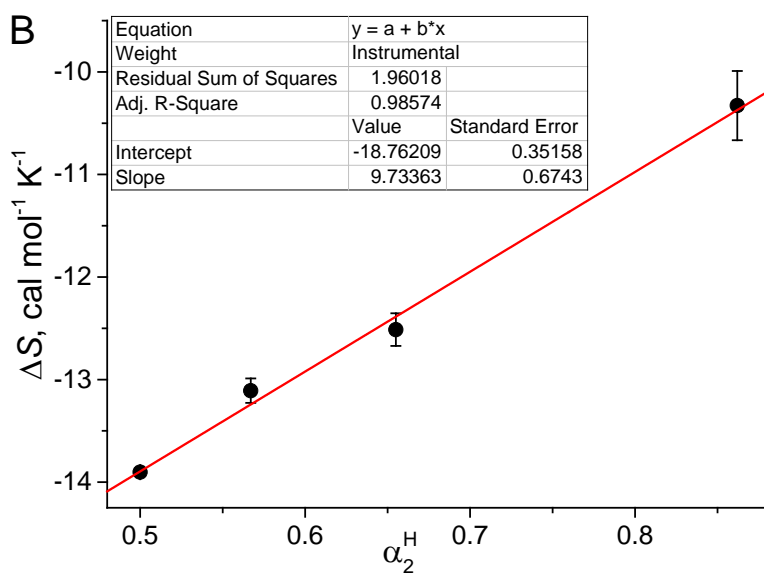
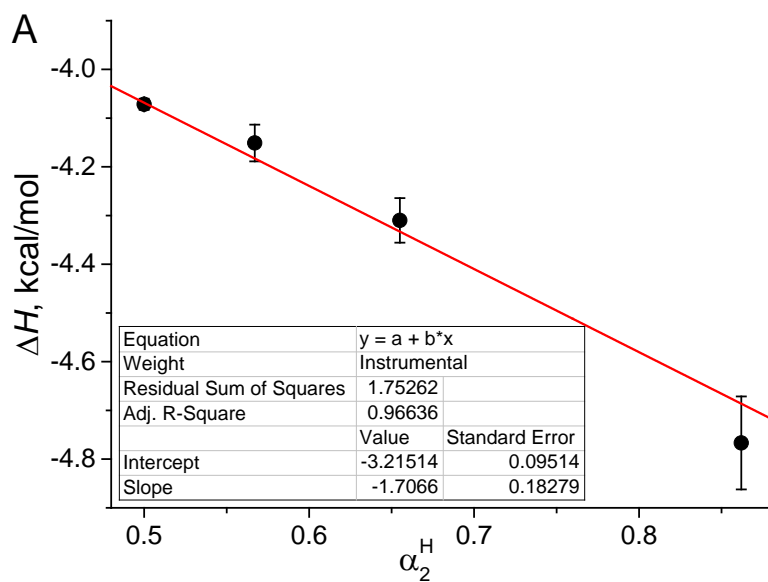


**Fig. S3.** Transient absorption spectra measured following a 480 nm laser excitation of **1** in  $\text{CH}_2\text{Cl}_2$  in the absence of a quencher (A); with 2.5 M of  $\text{CCl}_3\text{CH}_2\text{OH}$  (B); with 0.75 M of  $(\text{CF}_3)_3\text{COH}$  (C). Alcohols with lowest ( $\text{CCl}_3\text{CH}_2\text{OH}$ ,  $\alpha_2^{\text{H}} = 0.5$ ) and highest ( $(\text{CF}_3)_3\text{COH}$ ,  $\alpha_2^{\text{H}} = 0.862$ ) HB acidities in the series used in the current study have been selected for these flash photolysis experiments. The spectra-kinetic data in all 3 panels are similar showing a prompt appearance of the **1(T)** and the bleach of **1** followed by complete recovery of **1** without formation of end products. These observations are consistent with the occurrence of only physical quenching pathway ( $k_0^{\text{HB}}$  in Scheme 1, main text) for both  $\text{CCl}_3\text{CH}_2\text{OH}$  and  $(\text{CF}_3)_3\text{COH}$ .





**Fig. S4.** van't Hoff plot for the H-bonding in  $\text{CH}_2\text{Cl}_2$  between **1**(T) and 1,1,1-trichloroethanol (A); 1,1,1-trifluoroethanol (B); 1,1,1,3,3,3-Hexafluoro-2-methylpropane-2-ol (C); and nonafluoro-*tert*-butanol (D).



**Fig. S5.** Dependencies of the enthalpy (A) and entropy (B) for the H-bonding between **1**(T) and halogenated alcohols from Table 1(main text) in CH<sub>2</sub>Cl<sub>2</sub> on the alcohol's hydrogen bonding acidity.