

**Electronic Supplementary Information for**

**A new visible light triggered Arrhenius photobase and its photo-  
induced reactions**

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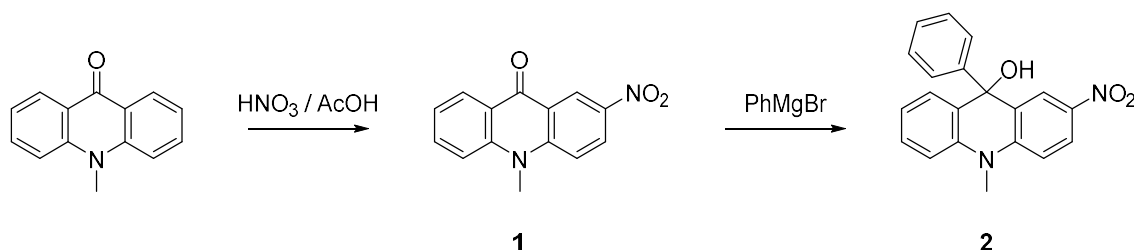
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## 1. Methods

### Synthesis



#### 10-methyl-2-nitroacridin-9(10H)-one (1)

10-Methylacridin-9(10H)-one (0.30 g, 1.4 mmol) in acetic acid (3 mL) was stirred vigorously and then nitric acid (60%, 1.5 mL) was added. After stirring for two hours at 50 °C, the solution was cooled in an ice bath and water was slowly added. The mixture was extracted with dichloromethane twice and the combined organic layers were washed with saturated aqueous NaHCO<sub>3</sub> and brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by SiO<sub>2</sub> chromatography to give compound **1** as a yellow solid (0.33 g, 91%). <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>, TMS): δ=9.05 (d, <sup>4</sup>*J* = 2.9 Hz, 1H), 8.54 (dd, <sup>3</sup>*J* = 9.6 Hz, <sup>4</sup>*J* = 2.9 Hz, 1H), 8.36 (dd, <sup>3</sup>*J* = 7.9 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H), 8.07 (d, <sup>3</sup>*J* = 9.6 Hz, 1H), 7.91–7.98 (m, 2H), 7.47 (m, 1H), 4.02 ppm (s, 3H).

#### 10-methyl-2-nitro-9-phenyl-9,10-dihydroacridin-9-ol (2, NO<sub>2</sub>-Acr-OH)

To the solution of compound **1** (0.10 g, 0.39 mmol) in dry THF (3 mL), phenylmagnesium bromide (3.0 M in diethyl ether, 0.20 mL) was added slowly. After stirring for three hours at room temperature, the reaction was quenched by adding saturated aqueous NH<sub>4</sub>Cl solution (10 mL). The mixture was extracted with dichloromethane twice and the combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by SiO<sub>2</sub> chromatography (EtOAc : hexane = 1 : 4) to give compound **2** as a light brown solid (25 mg, 19%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, TMS): δ=8.46 (d, <sup>4</sup>*J* = 2.8 Hz, 1H), 8.16 (dd, <sup>3</sup>*J* = 9.2 Hz, <sup>4</sup>*J* = 2.8 Hz, 1H), 7.56 (dd, <sup>3</sup>*J* = 7.7 Hz, <sup>4</sup>*J* = 1.5 Hz, 1H), 7.38 (m, 1H), 7.18–7.27 (m, 5H), 7.10–7.14 (m, 2H), 7.03 (d, <sup>3</sup>*J* = 9.1 Hz, 1H), 3.58 (s, 3H), 2.75 ppm

(s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , TMS):  $\delta$ =146.1, 144.5, 141.0, 138.6, 129.2, 129.0, 128.8, 128.3, 127.5, 127.4, 125.9, 124.5, 124.0, 122.7, 113.1, 112.3, 72.8, 34.1 ppm.

### **Sample preparation**

All chemicals were purchased and used as received from Sigma-Aldrich or Tokyo Chemical Industry. For absorption, steady-state emission, and time-resolved fluorescence (TRF) experiments, a stock solution of  $\text{NO}_2\text{-Acr-OH}$  was prepared in methylene chloride and ethanol and diluted to prepare the final solutions. Sample solutions were degassed with argon prior to TRF experiments.

### **Experimental methods**

All UV–visible absorption spectra of the sample solutions in a  $10 \times 10$  mm quartz cuvette were taken by using a UV–visible spectrometer (Cary 100, Varian) in the wavelength range of 200–800 nm. The baselines were corrected by the absorption spectrum of the reference solution. Time-resolved fluorescence (TRF) signals of the sample solutions were collected at a series of wavelengths by using a time-correlated single-photon counting (TCSPC) technique. The excitation pulse duration is about  $\sim 80$  ps and the TRF signals are measured by a photomultiplier tube. The instrumental response time of our TRF experimental setup is measured to be  $\sim 120$  ps. Our TRF experimental method has been described in detail elsewhere.<sup>1</sup> After the TRF experiments were finished, the UV–visible absorption spectrum of the sample solution was measured again and compared with the spectrum measured before the TRF experiment to check any undesired photodegradation during the experiments. We found that there was no significant degradation of the sample.

### **Quantum chemical calculations (QCC)**

For the prediction of  $\text{p}K_{\text{b}}$  values, the geometry optimization and calculation of vibrational frequency and solvation energies of all species are performed using the density functional theory (DFT) and time-dependent DFT with the LC- $\omega$ PBE functional and 6-31+G(d) basis set

as implemented in the Gaussian 16 software package.<sup>2</sup> The solvation energy is computed by using the SMD solvation model.<sup>3</sup> The  $pK_b$  values calculated with the LC- $\omega$ PBE functional agree most with experimental  $pK_b$  values.

## 2. Theoretical estimation of $pK_b$ value of $\text{NO}_2\text{-Acr-OH}$ in water

The  $pK_b$  values of Arrhenius photobases can be readily estimated by using the scheme in Figure S1(a) and quantum chemical calculations. For a dissociation reaction of Arrhenius photobases ( $\text{ROH} \rightarrow \text{R}^+ + \text{OH}^-$ ) in aqueous solutions, the  $pK_b$  value is directly related to the Gibbs energy of a reaction ( $\Delta_{\text{solu}}G$ ) in solution,

$$pK_b = \frac{\Delta_{\text{solu}}G}{RT \ln 10} \quad (1)$$

where  $R$  and  $T$  are the gas constant and 298.15 K, respectively, and

$$\begin{aligned} \Delta_{\text{solu}}G = & \Delta G(\text{R}^+) + \Delta_{\text{solv}}G(\text{R}^+) + \Delta G(\text{OH}^-) \\ & + \Delta_{\text{solv}}G(\text{OH}^-) - \Delta G(\text{ROH}) - \Delta_{\text{solv}}G(\text{ROH}) \end{aligned} \quad (2)$$

where  $\Delta G(\text{R}^+)$  and  $\Delta G(\text{ROH})$  are the Gibbs energies, and  $\Delta_{\text{solv}}G(\text{R}^+)$  and  $\Delta_{\text{solv}}G(\text{ROH})$  are the Gibbs energies of solvation.<sup>3</sup> The Gibbs energies are readily obtained by DFT calculations (LC- $\omega$ PBE/6-31+G(d)) as described in the methods.  $\Delta G(\text{OH}^-)$  and  $\Delta_{\text{solv}}G(\text{OH}^-)$  in Eq.(2) are obtained by the method which was proposed by Matsui and coworkers.<sup>4-6</sup> By introducing a scaling factor,  $s$ , the  $pK_b$  is re-written and rearranged as

$$\begin{aligned} pK_b &= \frac{s\Delta_{\text{solu}}G}{RT \ln 10} \\ &= \frac{s}{RT \ln 10} \{ \Delta G(\text{R}^+) + \Delta_{\text{solv}}G(\text{R}^+) - \Delta G(\text{ROH}) - \Delta_{\text{solv}}G(\text{ROH}) \} \\ &\quad + \frac{s}{RT \ln 10} \{ \Delta G(\text{OH}^-) + \Delta_{\text{solv}}G(\text{OH}^-) \} \\ &= k\Delta G + C \end{aligned} \quad (3)$$

where  $\Delta G = \Delta G(\text{R}^+) + \Delta_{\text{solv}}G(\text{R}^+) - \Delta G(\text{ROH}) - \Delta_{\text{solv}}G(\text{ROH})$ ,  $k = s/RT \ln 10$ , and  $C = s\{\Delta G(\text{OH}^-) + \Delta_{\text{solv}}G(\text{OH}^-)\}/RT \ln 10$ . Note that the scaling factor  $s$  in Eq. (3) is used to include

the activity coefficients in aqueous solution and correct some errors that might result from the exchange-correlation functional in the density functional theory (DFT), the basis set, and the cavity model used in the polarizable continuum model (PCM) method. The  $pK_b$  values of Arrhenius photobases are shown to be linearly proportional to  $\Delta G$  in Eq. (3). As shown in Figure S1, we calculated the  $pK_b$  values for previously studied Arrhenius photobases in Figure 1(a) by using Eq. (3)<sup>7-9</sup> and the calculation results are summarized in Table S1. As shown in Figure S2(b), the  $pK_b$  values of Arrhenius photobases in Figure 1(a) are linearly proportional to  $\Delta G$  with  $k = 0.18536$  mol/kJ,  $C = -36954.1$ , and  $s = 4.427$ . The value of  $\Delta G(\text{OH}^-) + \Delta_{\text{solv}}G(\text{OH}^-)$  is determined to be  $-199360.5$  kJ/mol. Our calculated  $pK_b$  values are in excellent agreement with experimentally determined ones as shown in Figure S2, which indicates that our method is quite reliable to predict the  $pK_b$  values of Arrhenius photobases.

### 3. Temperature-dependent $pK_b$ of $\text{NO}_2\text{-Acr-OH}$ in aqueous solutions

In Figure S3, the absorption spectra of  $\text{NO}_2\text{-Acr-OH}$  and  $\text{NO}_2\text{-Acr}^+$  at temperature from 10 to 80 °C are collected using aqueous solutions containing 10 mM NaOH or 10 mM  $\text{H}_2\text{SO}_4$ , respectively. In phosphate buffer solutions at temperature from 10 to 80 °C,  $\text{NO}_2\text{-Acr-OH}$  exists in acidic and basic forms as shown in Figure S4. The acid and base concentrations can be calculated by decomposing the spectra into the individual spectra of  $\text{NO}_2\text{-Acr-OH}$  and  $\text{NO}_2\text{-Acr}^+$ . The base dissociation constant of  $\text{NO}_2\text{-Acr-OH}$  is

$$K_b = \frac{a(\text{R}^+)a(\text{OH}^-)}{a(\text{ROH})} \quad (4)$$

where  $a(j)$  is the activity of involved species  $j$ . Eq. (4) can be rearranged to

$$pK_b = p\text{OH} - \log \frac{[\text{R}^+] \cdot \gamma_{\text{R}^+}}{[\text{ROH}]} \quad (5)$$

where,  $[j]$  and  $\gamma_j$  are the molar concentration and the activity coefficient of  $j$ , respectively. The activity coefficient of neutral species is assumed to be unity. In phosphate buffer,  $\text{H}_2\text{PO}_4^-$  dissociates as



In phosphate buffer solution, pH of the solution is given by

$$\text{pH} = pK_a + \log \frac{[\text{HPO}_4^{2-}] \cdot \gamma_{\text{HPO}_4^{2-}}}{[\text{H}_2\text{PO}_4^-] \cdot \gamma_{\text{H}_2\text{PO}_4^-}} \quad (7)$$

In this study, temperature-dependent  $pK_a$  of  $\text{H}_2\text{PO}_4^-$  was taken from the literature.<sup>10</sup> In order to calculate the activity coefficient for the ionic species, it is desirable to use the extended Debye-Hückel law in the form

$$\log \gamma_j = \frac{-z_j^2 A \sqrt{I}}{1 + d_j B \sqrt{I}} \quad (8)$$

$$I = \frac{1}{2} \sum_j z_j^2 c_j \gamma_j^2 \quad (9)$$



where  $z_j$  and  $c_j$  are the ionic charge and concentration of the species, respectively, and  $A = 0.509 \text{ mol}^{-1/2} \text{ kg}^{1/2}$ ,  $B = 0.328 \text{ mol}^{-1/2} \text{ kg}^{1/2}$  at 25 °C, and  $d_j$  is the effective diameter of the ionic species. The effective diameters of ions were taken from the literature.<sup>11</sup> The effective diameter of  $\text{NO}_2\text{-Acr}^+$  was assumed to be 8 Å.<sup>1, 11</sup> Calculation of the ionic strength,  $I$ , must include all the ionic species in the phosphate buffer. To get the concentrations of all ionic species, the charge-balance and mass-balance equation and the dissociation constant of water are necessary.

$$[\text{H}^+] + [\text{R}^+] + [\text{Na}^+] = [\text{H}_2\text{PO}_4^-] + 2[\text{HPO}_4^{2-}] + [\text{OH}^-] \quad (10)$$

$$[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = c_0 \quad (11)$$

$$K_w = [\text{H}^+] \gamma_{\text{H}^+} [\text{OH}^-] \gamma_{\text{OH}^-} \quad (12)$$

where  $c_0$  is the total concentration of the phosphate and the concentration of  $\text{Na}^+$  was assumed to be independent of the temperature. The temperature-dependent  $\text{p}K_w$  was taken from the literature.<sup>10</sup> By iterative calculation, the activity coefficient of ionic species, the pH of solutions, the concentration of the species involved in equilibrium, and the  $\text{p}K_b$  of  $\text{NO}_2\text{-Acr-OH}$  were obtained. In Figure S5, temperature-dependent  $\text{p}K_b$  of  $\text{NO}_2\text{-Acr-OH}$  is plotted. The measured  $\text{p}K_b$  values were fitted to the functional form<sup>12</sup> of

$$\text{p}K_b = A + \frac{B}{T} + C \ln(T) + D \cdot T + \frac{E}{T^2} \quad (13)$$

which is the form of  $\text{p}K_b$  when  $\Delta C_p$  is expressed as

$$\Delta C_p(T) = -\ln(10)R(C + 2DT + 2E/T^2) \quad (14)$$

where  $T$  is in Kelvin. The fitting parameters  $A$ - $E$  were obtained by non-linear regression to give

$$\text{p}K_b = 14350 + \frac{-771867}{T} - 2286.99 \cdot \ln(T) + 2.5 \cdot T + \frac{47241800}{T^2} \quad (15)$$

The  $\text{p}K_b$  of  $\text{NO}_2\text{-Acr-OH}$  is calculated to be 7.63 at 25 °C, which is in good agreement with the estimated value of 7.69, within experimental error.

To calculate the thermodynamic functions, Eq. (13) can be differentiated to give

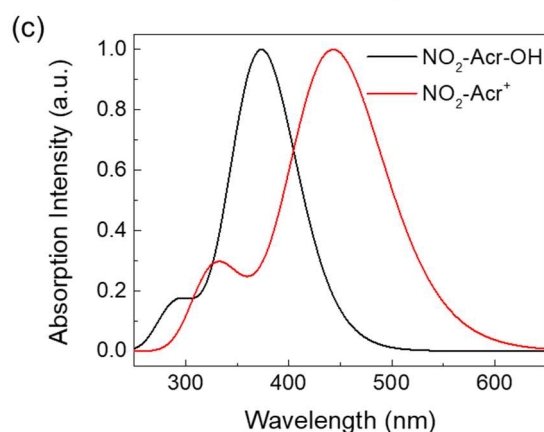
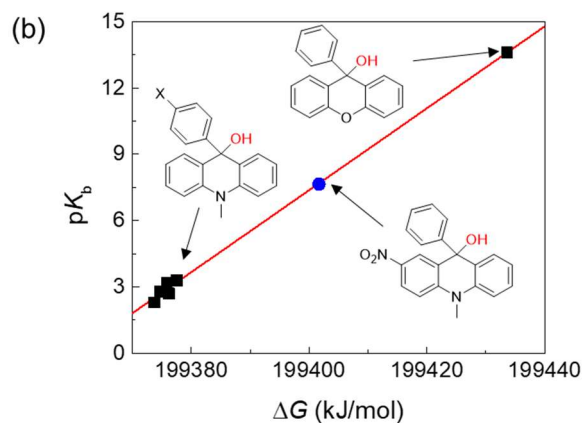
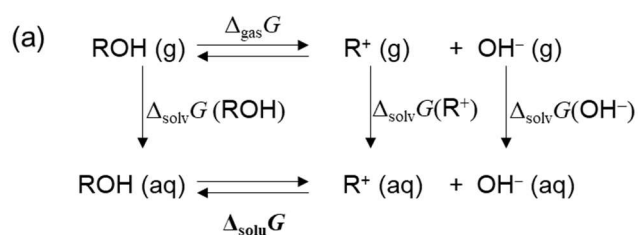
$$\Delta H(T) = \ln(10)R(B - CT - DT^2 + 2E/T) \quad (16)$$

$$\Delta S(T) = -\ln(10)R(A + C + C \ln T + 2DT - E/T^2) \quad (17)$$

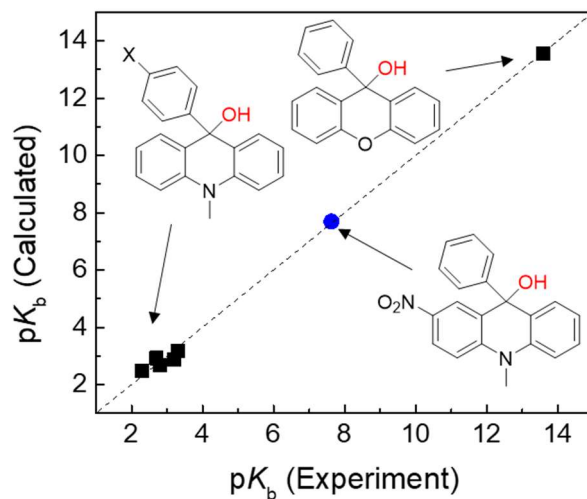
At 25 °C,  $\Delta H$ ,  $\Delta S$ , and  $\Delta C_p$  is calculated to be 89.2 kJ mol<sup>-1</sup>, 153 J mol<sup>-1</sup> K<sup>-1</sup>, and 5105 J mol<sup>-1</sup> K<sup>-1</sup>, respectively.

**Table S1.** Calculated  $pK_b$  value, Gibbs energy, and solvation energy of various Arrhenius photobases.

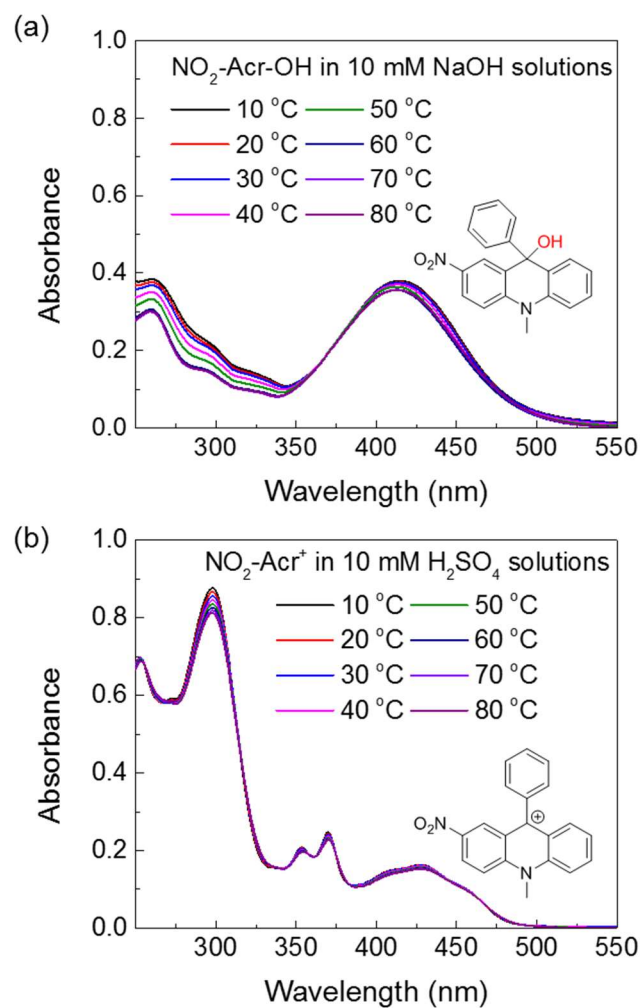
Photobase	Gibbs energy (Hartree)		Solvation energy (kJ/mol)		$\Delta G$ (kJ/mol)	Exp. $pK_b$	Calc. $pK_b$	Error
	ROH	R <sup>+</sup>	ROH	R <sup>+</sup>				
Xanthenol	-882.04832	-806.03412	-34.3088	-175.9372	199433.6079	13.6	13.6	0.0
Acr-OH	-901.43896	-825.44748	-39.9572	-180.7906	199374.7673	2.8	2.7	-0.1
CF <sub>3</sub> -Acr-OH	-1238.32436	-1162.32653	-35.06192	-191.4598	199375.859	3.2	2.9	-0.3
CN-Acr-OH	-993.61607	-917.61469	-47.94864	-212.0033	199377.5516	3.3	3.2	-0.1
(CH <sub>3</sub> ) <sub>2</sub> N-Acr-OH	-1035.25919	-959.27538	-47.36288	-169.0754	199373.7584	2.3	2.5	0.2
CH <sub>3</sub> O-Acr-OH	-1015.86819	-939.87862	-45.43824	-179.8283	199376.1802	2.7	3.0	0.3
<b>NO<sub>2</sub>-Acr-OH</b>	-1105.82982	-1029.82128	-49.53856	-208.2377	199401.6926	7.63	7.69	0.06



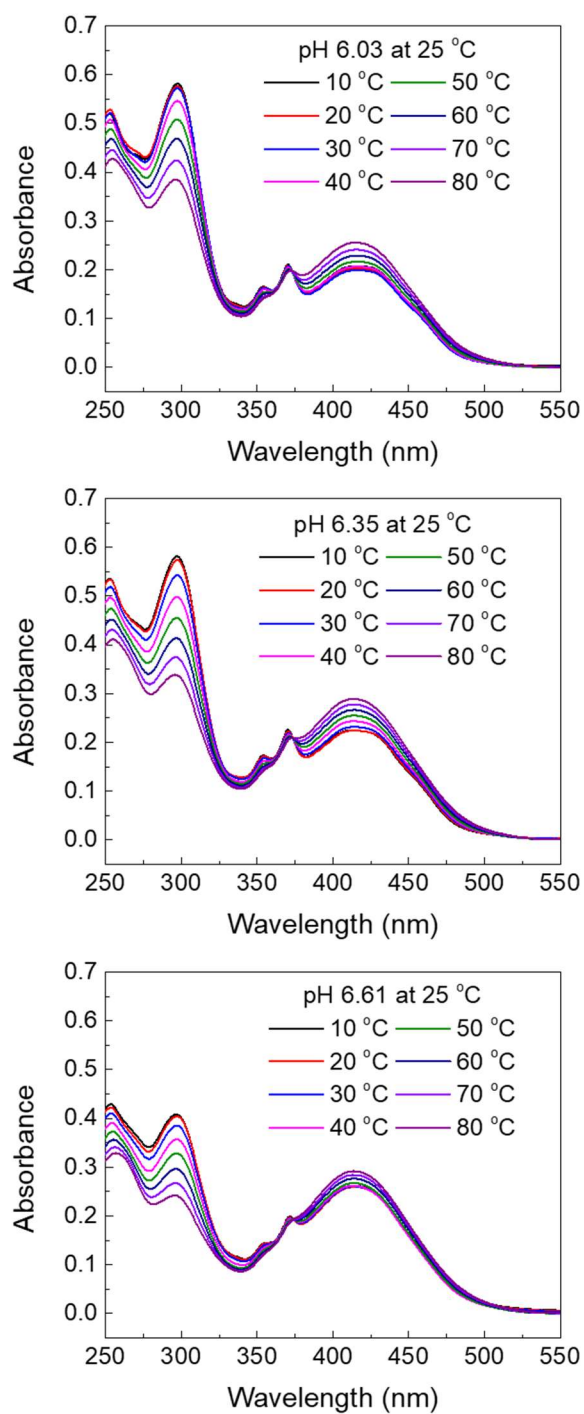
**Figure S1.** (a) The Born-Haber cycle of Arrhenius photobase. (b) Calculated  $\Delta_{\text{solu}}G$  of hydroxide ion dissociation reaction and experimentally determined  $pK_b$  values. The red line is a linear fit to the data points. The fitting parameters are obtained to be  $k=0.18536$  mol/kJ and  $C=-36954.1$  in Eq. (3). (c) Calculated absorption spectra of  $\text{NO}_2\text{-Acr-OH}$  and  $\text{NO}_2\text{-Acr}^+$ .



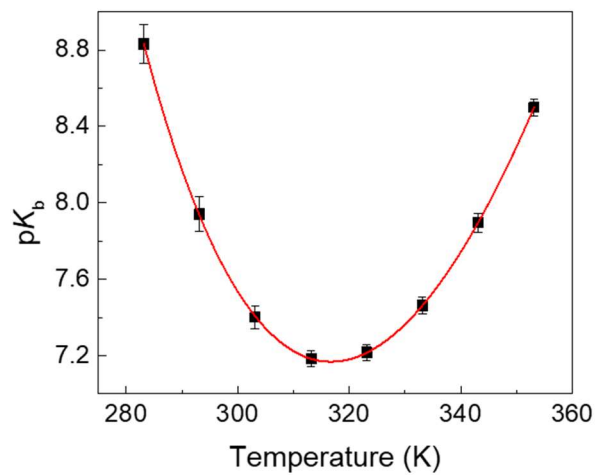
**Figure S2.** The plot of experimental  $pK_b$  values against calculated  $pK_b$  values. The dashed line is obtained by connecting the points where the calculated  $pK_b$  values are equal to the experimental  $pK_b$  values.



**Figure S3.** Temperature-dependent absorption spectra of NO<sub>2</sub>-Acr-OH in (a) aqueous 10 mM NaOH solution, (b) aqueous 10 mM H<sub>2</sub>SO<sub>4</sub> solution

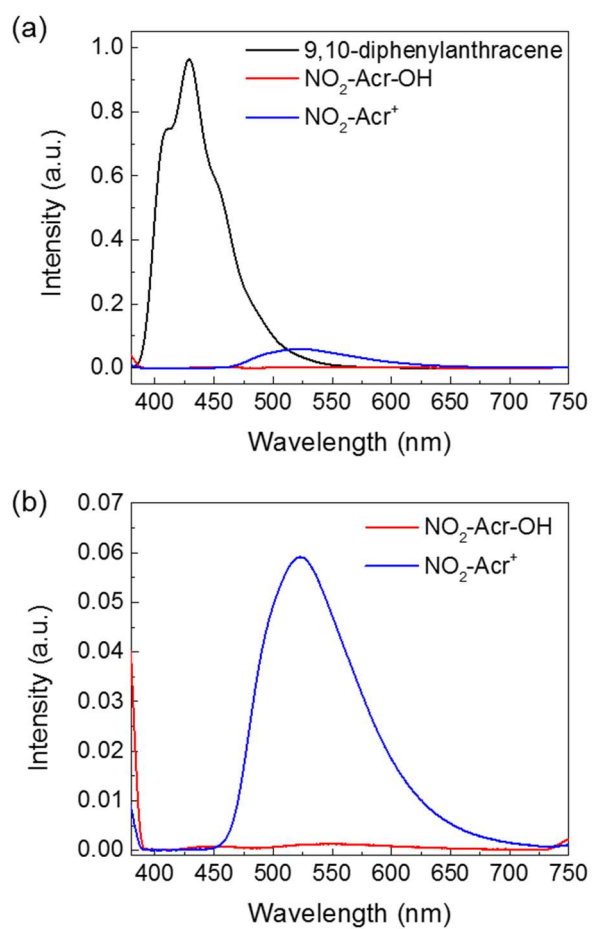


**Figure S4.** Temperature-dependent absorption spectra of  $\text{NO}_2\text{-Acr-OH}$  in phosphate buffer solutions.

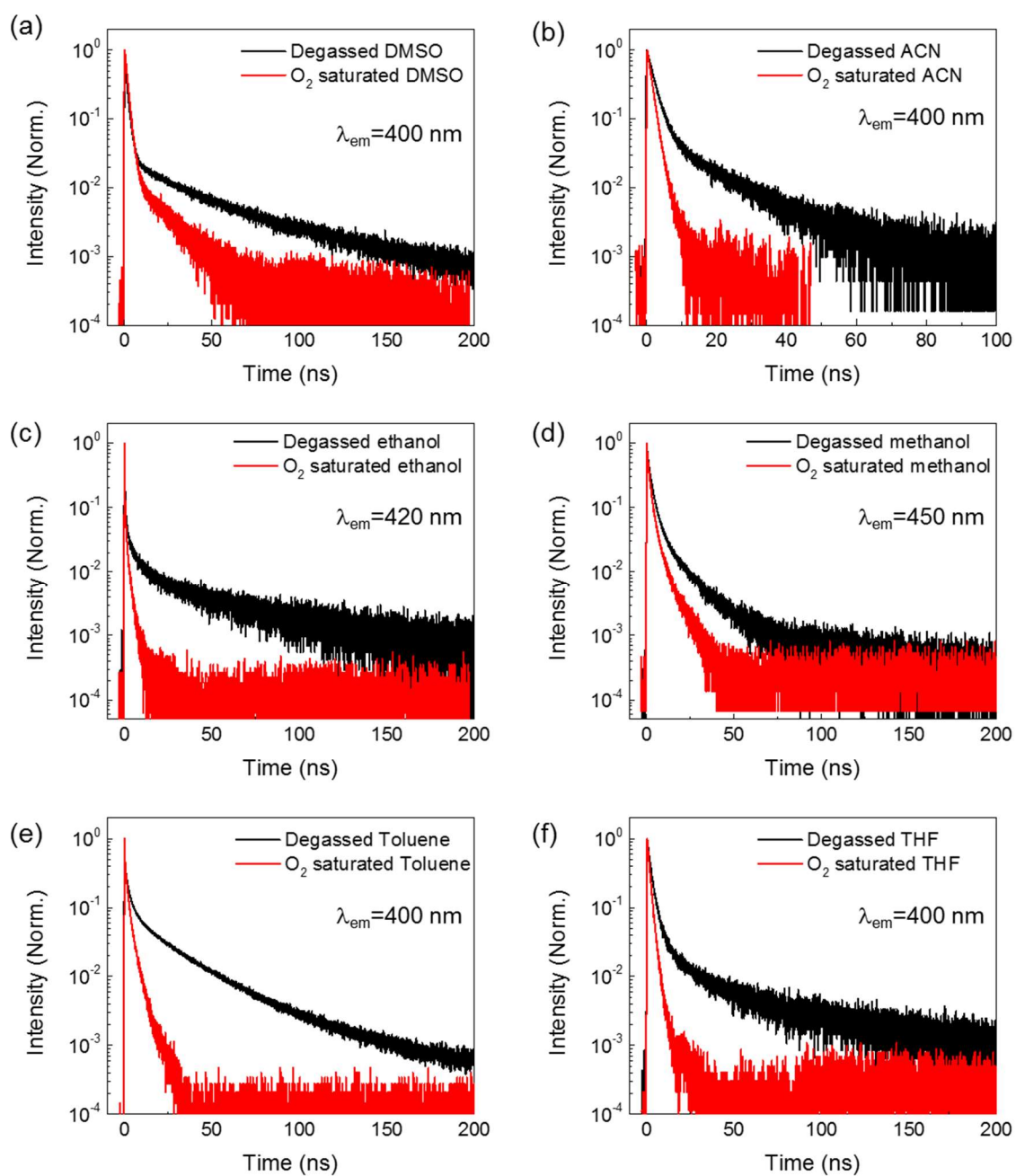


**Figure S5.** Temperature-dependent  $pK_b$  values of  $\text{NO}_2\text{-Acr-OH}$  in aqueous solution.

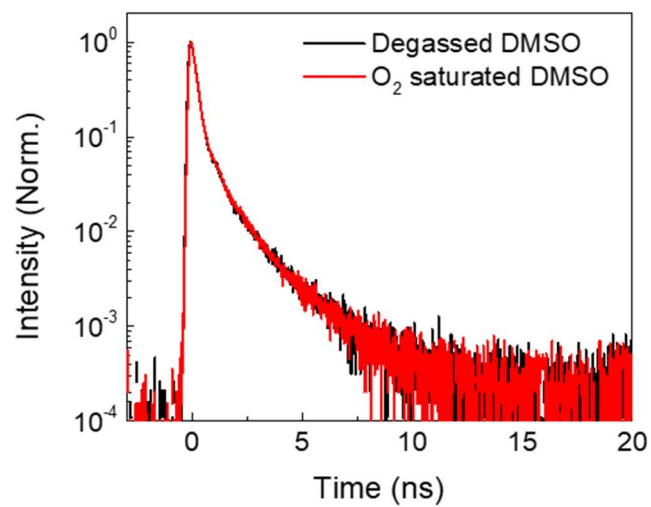




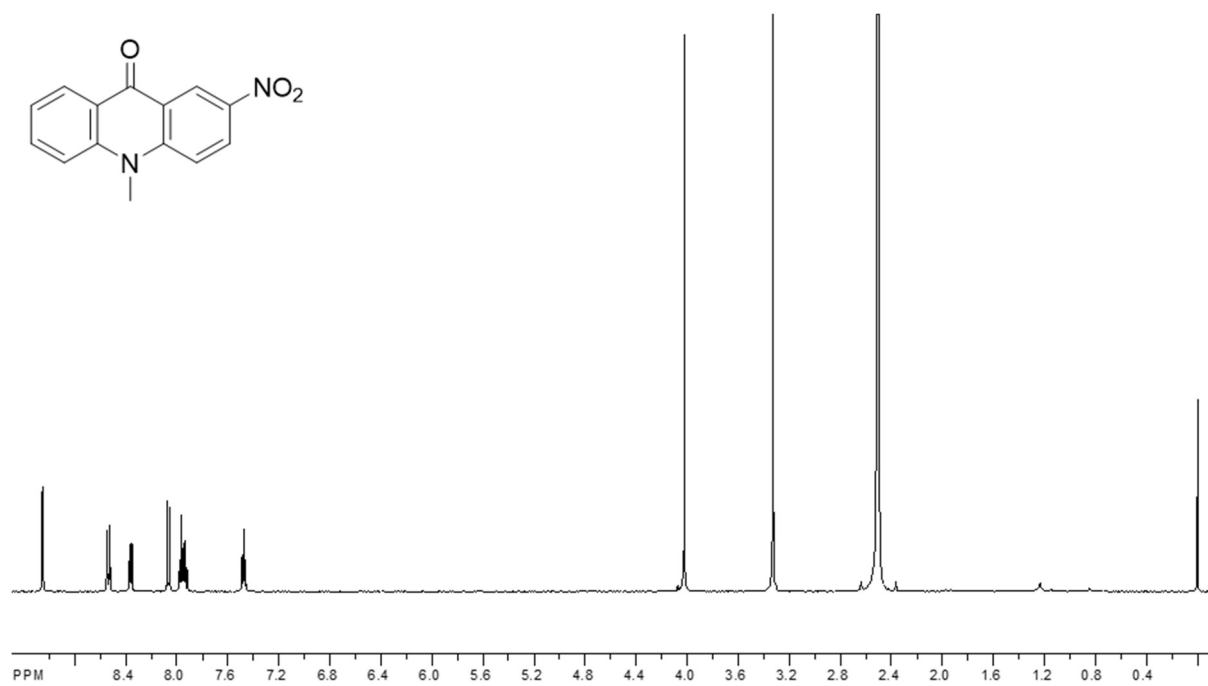
**Figure S6.** Absorption-corrected emission spectra of (a) 9,10-diphenylanthracene in ethanol ( $\Phi_{\text{PLQY}}=0.95$ ) and (b) NO<sub>2</sub>-Acr-OH and NO<sub>2</sub>-Acr<sup>+</sup> in aqueous solution ( $\lambda_{\text{ex}}=375$  nm).



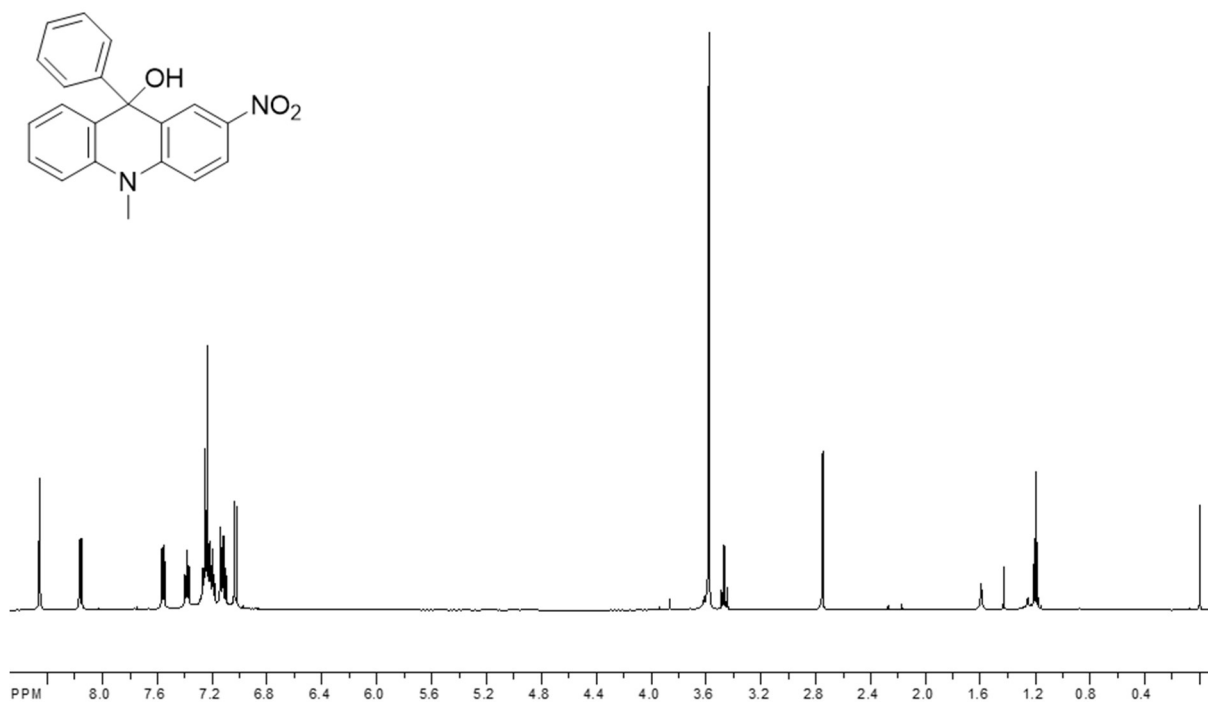
**Figure S7.** TRF signals of NO<sub>2</sub>-Acr-OH in degassed and O<sub>2</sub> saturated (a) DMSO, (b) ACN, (c) ethanol, (d) methanol, (e) toluene, and (f) THF. ( $\lambda_{ex}$ =375 nm)



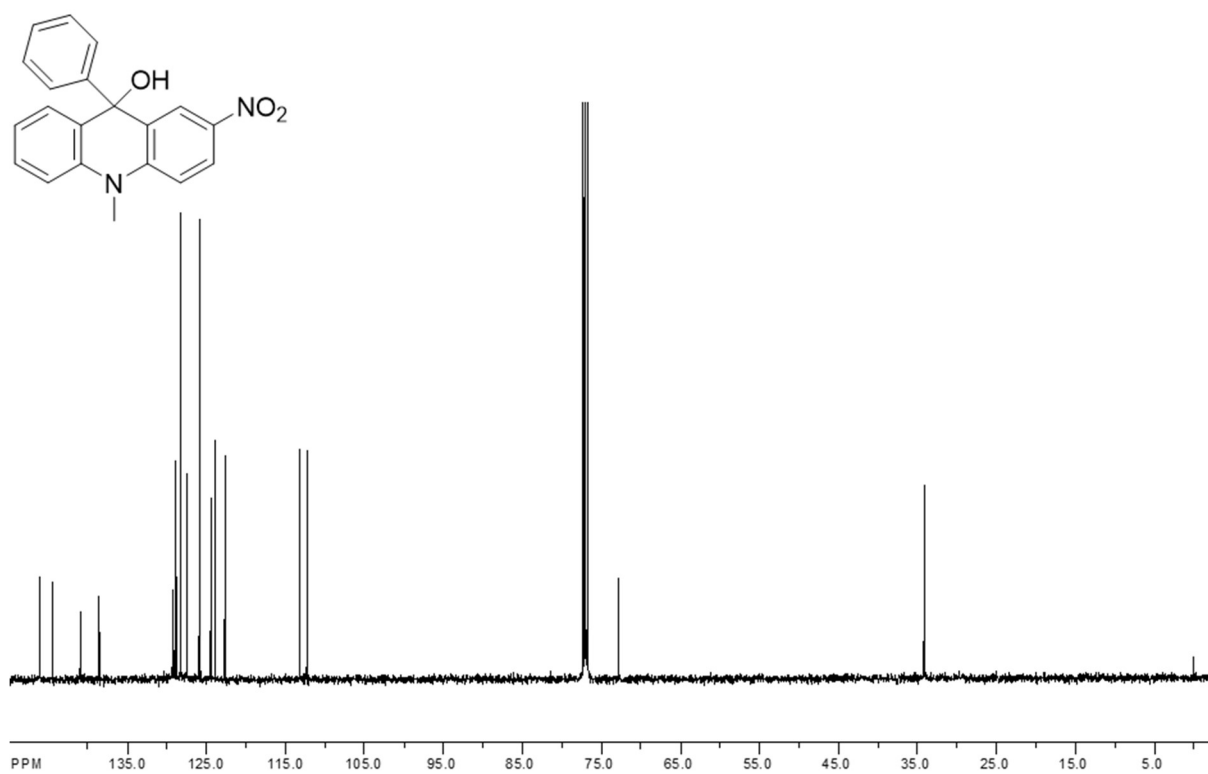
**Figure S8.** TRF signals of NO<sub>2</sub>-Acr-OH in degassed and O<sub>2</sub> saturated DMSO measured at  $\lambda_{em}=600$  nm. ( $\lambda_{ex}=375$  nm)



**Figure S9.** <sup>1</sup>H NMR spectrum of **1**



**Figure S10.** <sup>1</sup>H NMR spectrum of **2**



**Figure S11.** <sup>13</sup>C NMR spectrum of **2**

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