



Title	Photoinduced Betaine Generation for Efficient Photothermal Energy Conversion
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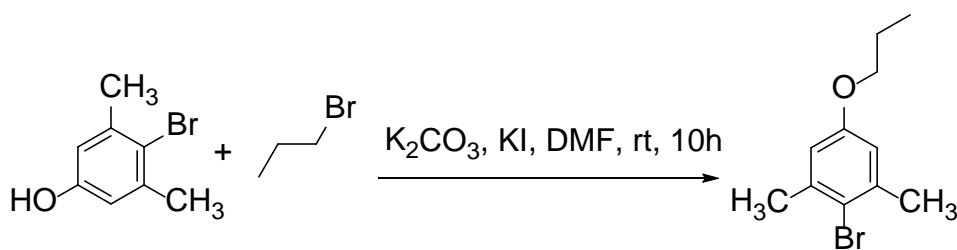
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## Materials;

All chemicals used in the study were analytical grade and used as-received unless otherwise stated. 10-methylacridinium perchlorate, 9-mesityl-10-methylacridinium perchlorate, 10-methyl acridone were obtained from Tokyo Chemical Industry (Japan). Solvents such as anhydrous tetrahydrofuran, anhydrous dichloromethane, methanol, acetonitrile, and deionized water were obtained from FUJIFILM Wako Pure Chemical Corporation (Japan). Phosphate buffer solution at pH 7.4 was used for the studies. For acidic pH, aqueous hydrochloric acid and for the basic pH aqueous NaOH solution was used.

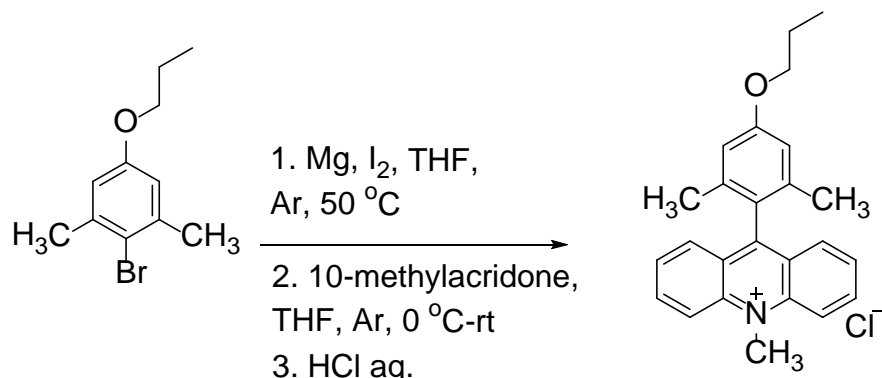
## Synthesis;

### Preparation of 2-bromo-1,3-dimethyl-5-propoxybenzene



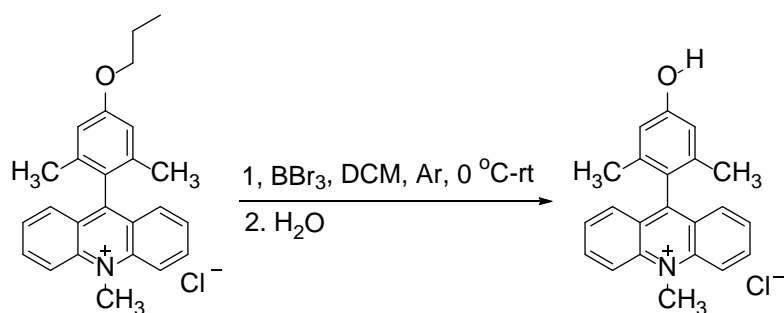
2-bromo-1,3-dimethylphenol (4.00 g, 19.89 mmol) is dissolved in DMF (20 mL) at room temperature. Bromopropane (8.16 g, 47.03 mmol), potassium carbonate (6.50 g) and catalytic amount of potassium iodide is added. The reaction was stirred for 10 hrs at room temperature. The reaction mixture was poured into water (50 mL) and extracted with ethyl acetate (3×50). The organic layer was dried using sodium sulphate. The product was isolated as colourless dense liquid after purification by column chromatography on silica gel (200 mesh) using a mixture (1:20, v/v) of ethyl acetate and hexane as the eluent to provide 4.2 g of colourless liquid as the product (87.5 %).  $^1H$  NMR (500 MHz,  $[D_1]$  chloroform):  $\delta$ = 6.62 (s, 2H; Ar-H), 3.83-3.85 (t, 2H;  $CH_2$ ), 2.35 (s, 3H;  $CH_3$ ), 1.74-1.79 (m, 2H;  $CH_2$ ), 0.99-1.02 (t, 3H;  $CH_3$ ).

Preparation of 9-(2,6-dimethyl-4-propoxyphenyl)-10-methylacridinium chloride.

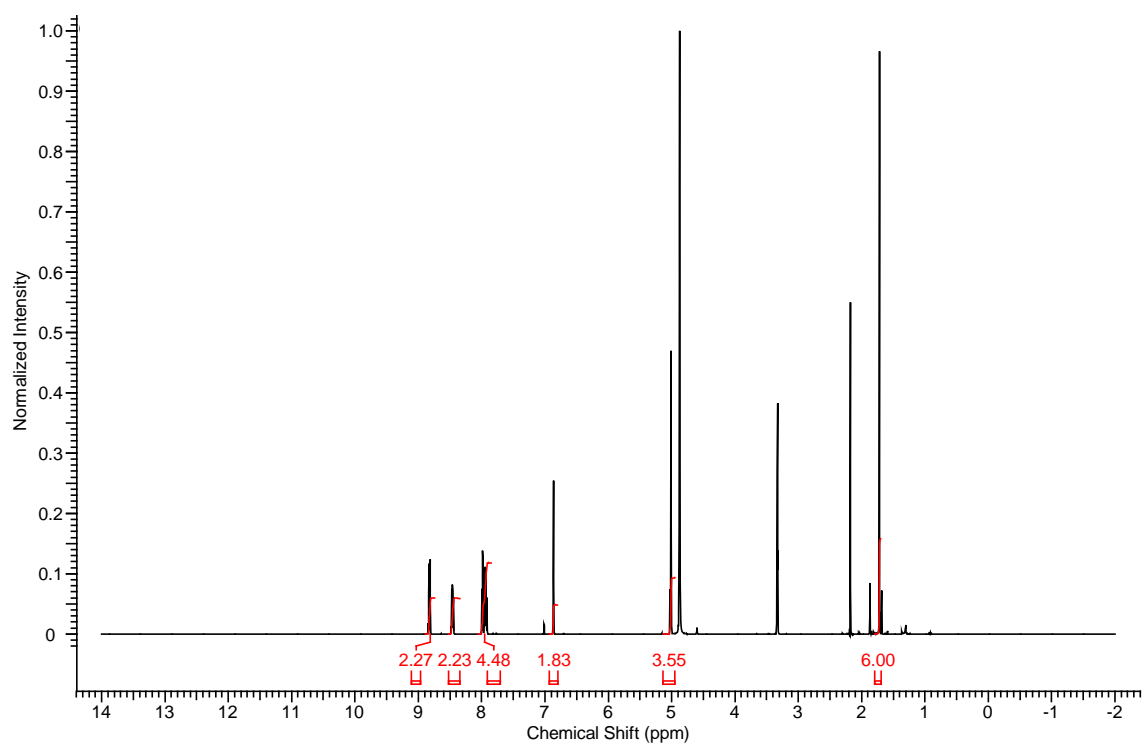


A three neck RB was charged with 2-bromo-1,3-dimethyl-5-propoxybenzene (800 mg, 3.29 mmol), magnesium turnings (95 mg, 3.94 mmol) and catalytic amount of Iodine in dry THF (10 mL). The resulted solution was heated up to 50 °C in presence of argon. The brown colour of the solution was disappeared, and the solution turned to white. The Grignard reagent formed is transferred to a solution of 10-methyl-9(10 H)-acridone (756 mg, 3.61 mmol) in dry THF, kept at 0 °C. The reaction solution is stirred for 24 hours at room temperature in presence of argon. After 24 hours, HCl aq. is added to maintain neutral pH. The reaction mixture was extracted using dichloromethane (4×50). The organic layer dried over MgSO<sub>4</sub> and purified by silica-gel chromatography using a mixture (1:20, v/v) of methanol and dichloromethane (DCM) as the eluent. 9-(2,6-dimethyl-4-propoxyphenyl)-10-methylacridin-10-ium chloride was obtained as dark brown solid (yield: 38 %, 489 mg). <sup>1</sup>H NMR (500 MHz, [D<sub>4</sub>] methanol): δ= 8.81-8.85 (d, 2H; Ar-H), 8.43-8.47 (t, 2H; Ar-H), 7.90-7.96 (m, 4H; Ar-H), 6.99 (s, 2H; Ar-H), 5 (s, 3H; CH<sub>3</sub>), 4.08-4.11 (t, 2H; CH<sub>2</sub>), 1.87-1.91 (m, 2H; CH<sub>2</sub>), 1.75 (s, 6H; CH<sub>3</sub>), 1.11-1.14 (t, 3H; CH<sub>3</sub>).

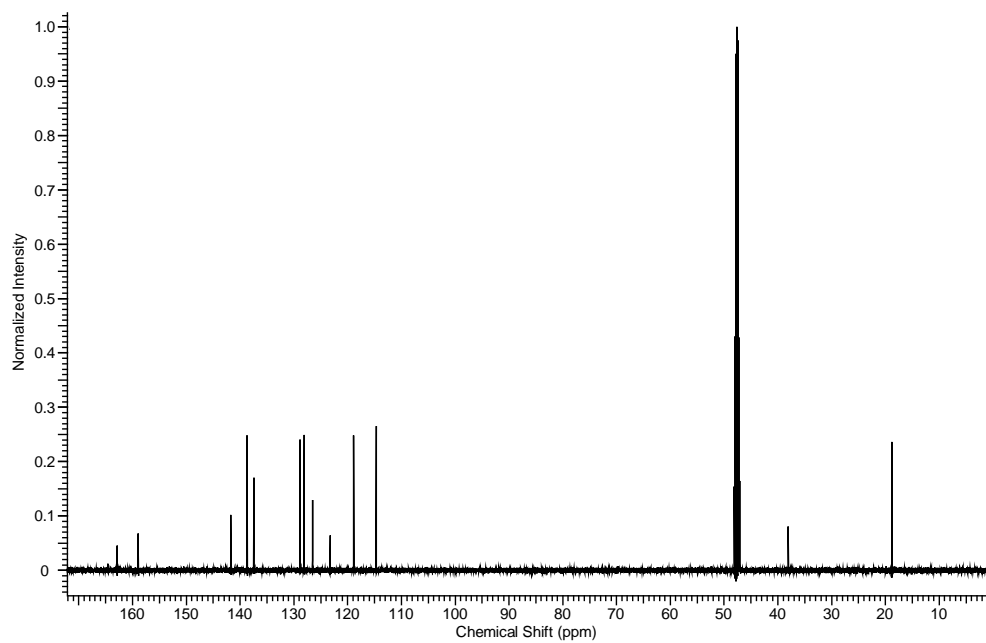
Preparation of 9-(4-hydroxy-2,6-dimethylphenyl)-10-methylacridinium chloride (1)



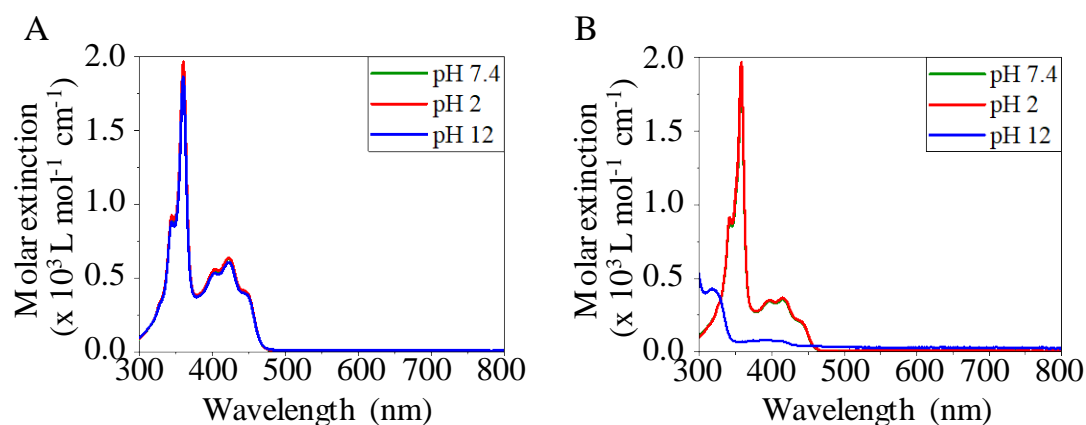
9-(2,6-dimethyl-4-propoxyphenyl)-10-methylacridin-10-ium chloride (122 mg, 0.31 mmol) was dissolved in dry DCM (5 mL) in the presence of argon. The reaction mixture was cooled to 0 °C. Boron tribromide (233.73 mg, 0.93 mmol) was added dropwise. The reaction mixture was stirred for 18 hours at room temperature. Then excess of water was added. The yellow precipitate formed was filtered and washed with DCM (yield: 73 %, 80 mg). <sup>1</sup>H NMR (500 MHz, [D<sub>4</sub>] methanol): δ= 8.79-8.81 (d, 2H; Ar-H), 8.42-8.46(t, 2H; Ar-H), 7.96-7.98 (t, 2H; Ar-H), 7.90-7.93 (d, 2H; Ar-H), 6.85 (s, 2H; Ar-H), 4.99 (s, 3H; CH<sub>3</sub>), 1.70 (s, 6H; CH<sub>3</sub>); <sup>13</sup>C NMR (500 MHz, [D<sub>4</sub>] methanol) δ= 164.40 (C-CH), 160.47 (C-CH), 143.24 (C-CH), 140.24 (C-CH), 138.95(C-C), 130.38 (C-CH), 129.60 (C-CH), 128.07 (C-CH), 124.80 (C-CH), 120.41(C-CH), 116.23(C-CH), 39.62 (s; CH<sub>3</sub>), 20.34 (s; CH<sub>3</sub>); FTIR (KBr): ν= 3055 (vs) cm<sup>-1</sup> (-OH), 2281 cm<sup>-1</sup> (s), 1609 cm<sup>-1</sup> (vs), 1547 cm<sup>-1</sup> (s), 1442 cm<sup>-1</sup> (s), 1387 cm<sup>-1</sup> (s), 1316 (s) cm<sup>-1</sup>, 1196 cm<sup>-1</sup>, 1159 (s) cm<sup>-1</sup>, 875 (s) cm<sup>-1</sup>, 757 (s) cm<sup>-1</sup>; HRMS (ESI): *m/z* -mass calculated for C<sub>22</sub>H<sub>20</sub>NO<sup>+</sup>: 314.1539 [M]<sup>+</sup>; found 314.1538.



**Figure Sa:**  $^1\text{H}$  NMR spectrum of **1** in methanol- $\text{d}_4$ .



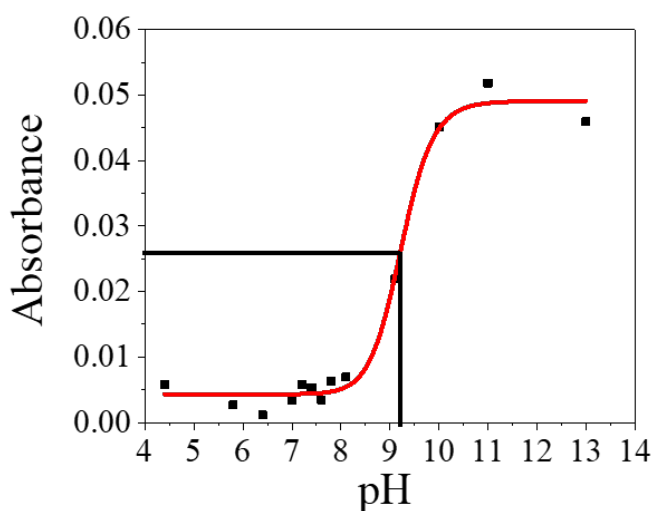
**Figure Sb:**  $^{13}\text{C}$  NMR spectrum of **1** in methanol- $\text{d}_4$ .



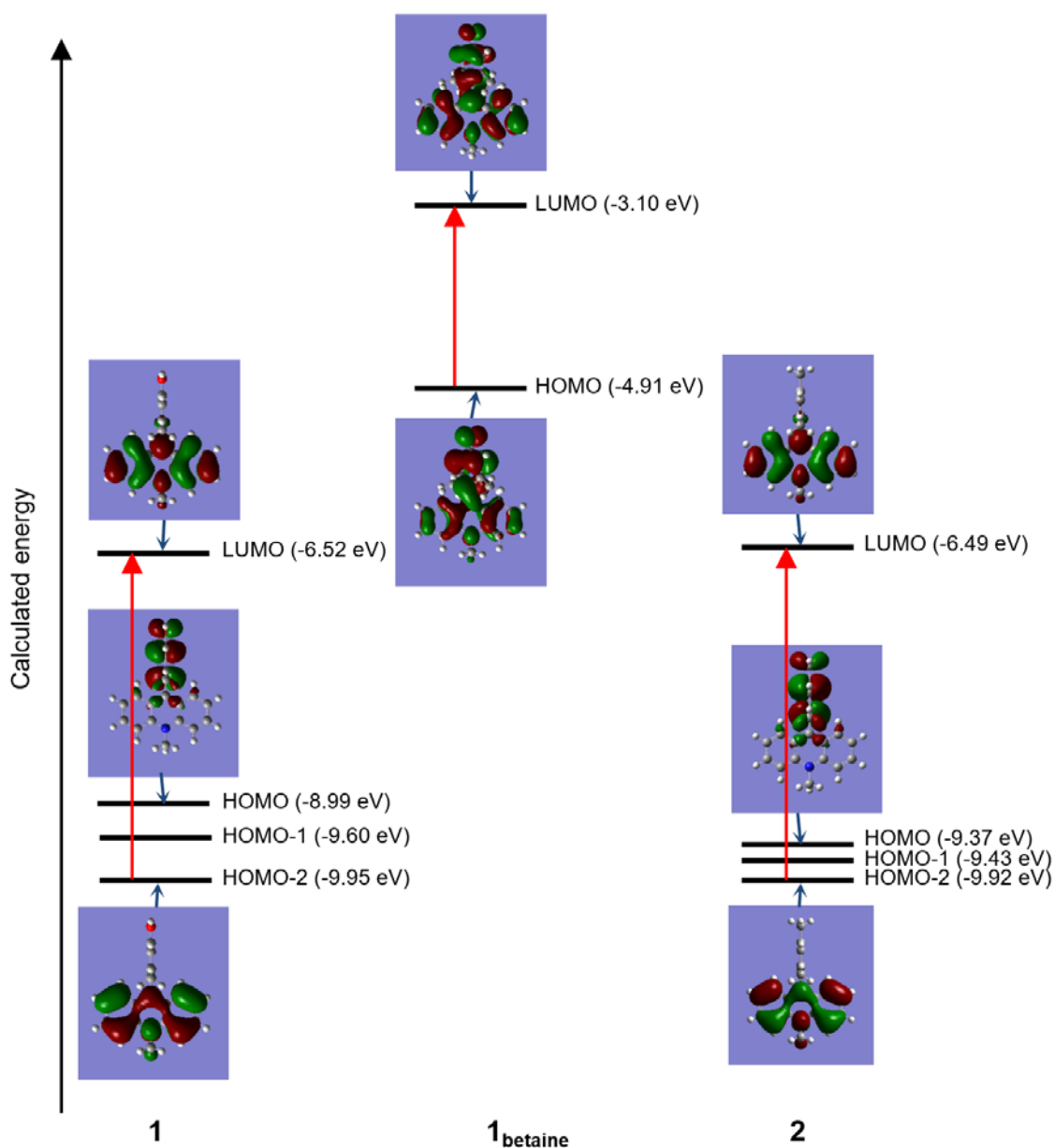
**Figure S1:** Absorbance spectra **2** and **3** at pH 2 (A), pH 7.4 (B) and pH 12 (C).

### Determination of pKa of **1**

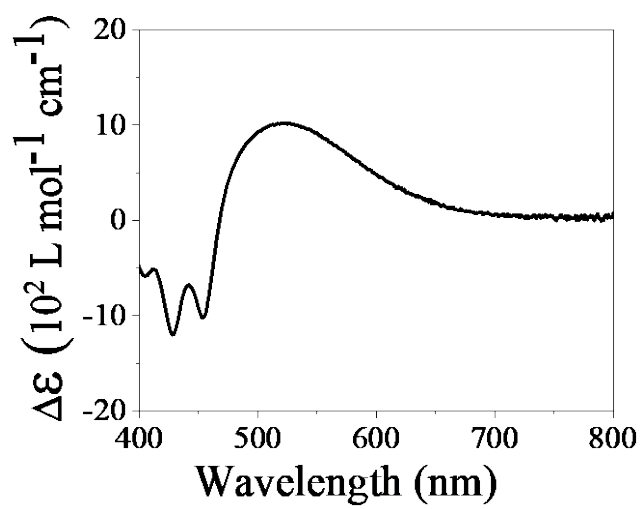
Using UV-VIS spectroscopy it is possible to determine the pKa value of a compound by monitoring absorbance at different pH. pKa value can be determined by plotting the absorbance value against the pH and can be found as the pH value corresponding to half the maximum of absorbance. Thus, we recorded the absorbance spectra of **1** in phosphate buffer solution at different pH and determined the pKa value as 9.2 (Figure S2).



**Figure S2:** Plots of absorbance (510 nm) vs pH of the solutions (**1**, 50  $\mu$ M in phosphate buffer). Red curve is a sigmoidal fitting, which gives pKa = 9.2.

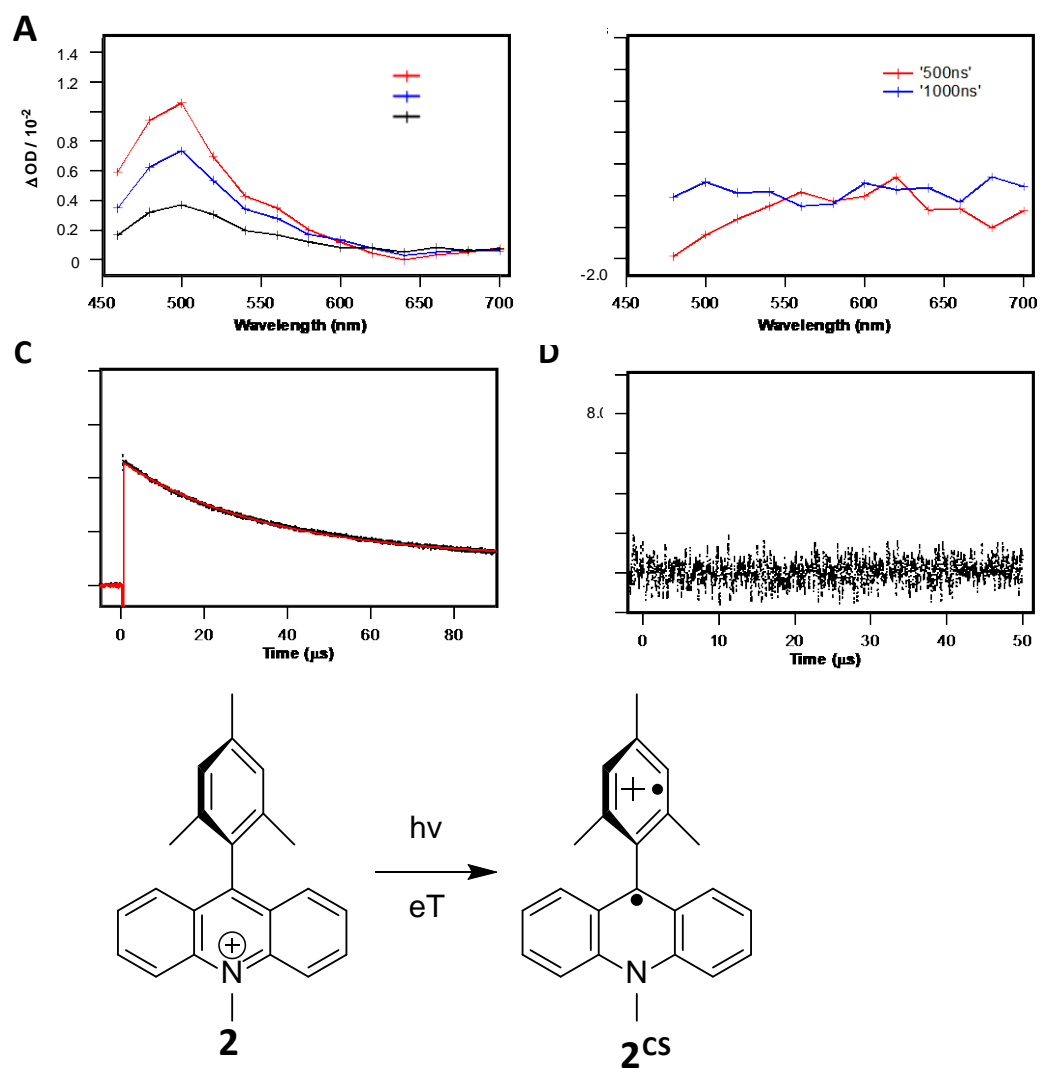


**Figure S3.** HOMOs and LUMOs of **1**, **1<sub>betaine</sub>** and **2**, obtained by the DFT calculation at UB3LYP-D3/6-31G\* level of theory. The chloride anion was omitted for the simplification of the calculations. 3D structures of the representative orbital distributions with molecules are shown with arrows. Red arrows indicate the first singlet-singlet transition predicted by the DFT calculations. It is confirmed by this figure that (i) **1<sub>betaine</sub>** has narrower energy gap of the singlet-singlet transition than those of **1** and **2**, which results in the longer wavelength of the absorption band around 530 nm of **1<sub>betaine</sub>** as shown in Figure 2C, and (ii) photoinduced electron transfer between the donor unit and acceptor (acridinium) unit is feasible in both **1** and **2**.



**Figure S4:** Differential absorption spectra where the spectrum of **1(betaine)** is subtracted with that of **1**.





**Figure S5:** ns-transient absorption spectra of **2** in aqueous solution at pH 7 (A), and **1** at pH 5 (B). Decay profiles at 500 nm arising from the cation radical of the acridinium moiety of **2** at pH 7 (C) and the profiles at 540 nm arising from the **1**(betaine) in aqueous solution at pH 5 (D). Observed signals (Black dot) and mono-exponential fitting curve (red line).  $\Delta OD$  is a change in optical density. E) Scheme of photoinduced electron transfer (eT) in **2** and subsequent formation of **2<sup>CS</sup>**.

### Calculation of photothermal efficiency of **1** at pH 7.4

The photothermal conversion efficiency of **1** was determined according to the previous reports. [1]

$$\eta = \frac{hS(T_{\text{Max}} - T_{\text{Surr}}) - Q_{\text{dis}}}{I(1 - 10^{-A_{446}})} \quad \text{eq (1)}$$

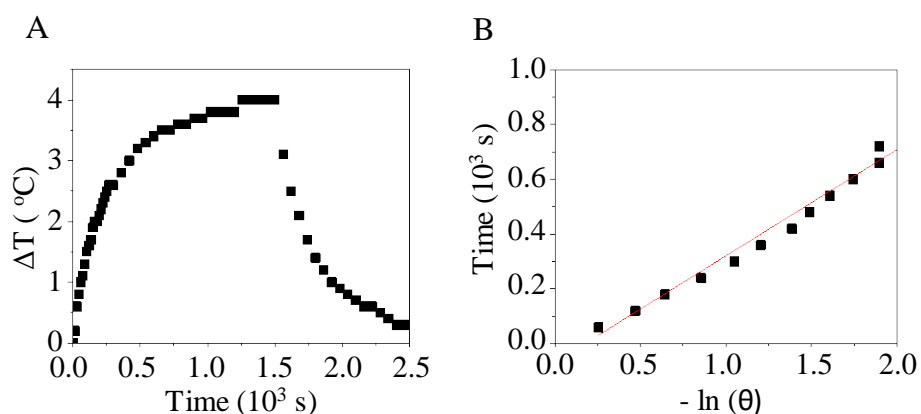
Where,  $h$  is the heat transfer coefficient,  $S$  is the surface area of the container,  $T_{\text{max}}$  is the maximum temperature achieved by illumination, and  $T_{\text{surr}}$  is the temperature of the surroundings.  $I$  correspond to the intensity of the power source (446 nm laser at  $0.075 \text{ W cm}^{-2}$ ), and  $A_{446}$  represents the absorbance of the sample solution at 446 nm.  $hS$  is calculated according to eq 2.

$$hS = \frac{m_D C_D}{\tau_s} \quad \text{eq (2)}$$

Where,  $m_D$  and  $C_D$  are the mass and heat capacity of deionized water and  $\tau_s$  is the sample system time constant and determined according to the equation (3)

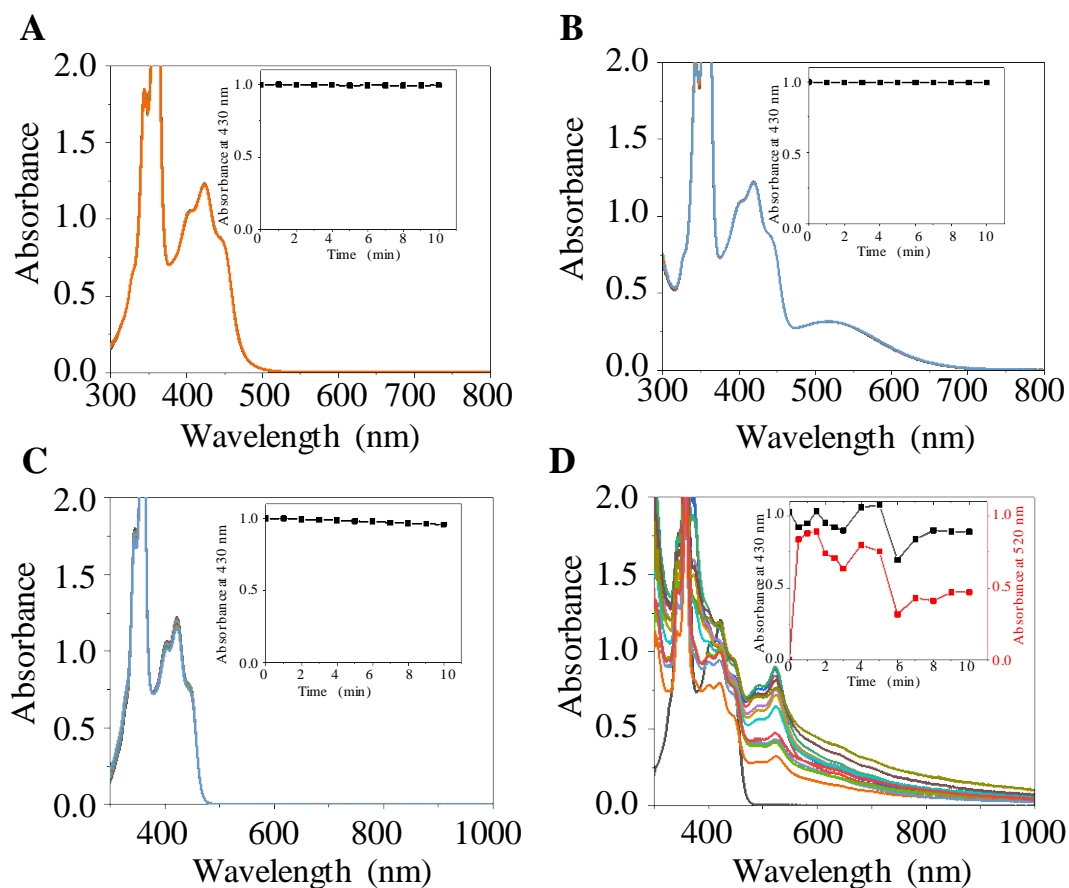
$$t = -\tau_s \ln \theta \quad \text{eq (3)}$$

$$\theta = \frac{(T - T_{\text{Surr}})}{(T_{\text{Max}} - T_{\text{Surr}})} \quad \text{eq (4)}$$



**Figure S6:** (A) Photothermal effect showed by aqueous solution of **1** at pH 7.4 (0.72 mM in a glass cuvette with 0.2 cm thickness) by a 446 nm laser (at  $0.075 \text{ W cm}^{-2}$ ) in which the irradiation was continued for 1500 s, and then the laser was turned off, and cooling

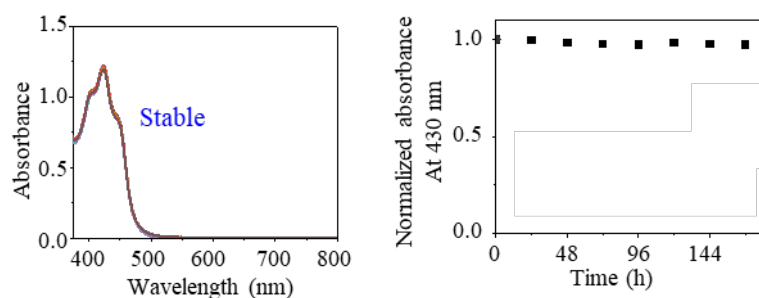
pattern was monitored. (B) The plot of the cooling period versus the negative logarithm of the driving force( $\theta$ ). The linear fitting affords  $\tau_s = 390 \text{ s}^{-1}$ .



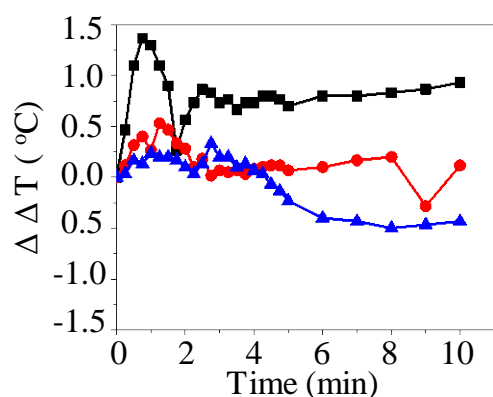
**Figure S7:** Absorbance spectra recorded as a function of time under photoirradiation with both the light source (blue light 420-440 nm at  $140 \text{ mW cm}^{-2}$  and the yellow light, 480-650 nm at  $440 \text{ mW cm}^{-2}$ ) of **1** at pH 2 (A), pH 12 (B) and **2** at pH 2 (C), pH 12 (D). The insets provide the absorbance at 430 nm and at 520 nm plotted as a function of time under photoirradiation.

### Long-term photostability studies of **1** at pH 7.4.

The aqueous solution of **1** was prepared in phosphate buffer at pH 7.4. The absorbencies of the sample solutions were set at 1.0 at 430 nm. The sample solutions were irradiated with white light from a Xenon lamp (500 W). The photo illumination continued for 7 days, and the absorption spectra of the samples were recorded every 24 h. The normalized absorbance is plotted as a function of the time under photo illumination. The compound **1** showed outstanding photostability throughout the days of illumination.



**Figure S8.** Change in the absorption spectra of (left) **1** with illumination (500W-Xe lamp, 390-780 nm). (Right) Time profiles of the normalized absorption at 430 nm with the illumination on **1**.



**Figure S9:** The power dependent photothermal response of **1** at pH 7.4 by the dual photoexcitation. The powers of the LED were  $140\text{mW cm}^{-2}$  (black),  $100\text{mW cm}^{-2}$  (red), and  $53\text{ mW cm}^{-2}$  (blue).

## References

- [1] a) X. Liu, B. Li, F. Fu, K. Xu, R. Zou, Q. Wang, B. Zhang, Z. Chen and J. Hu, *Dalt. Trans.* **2014**, 43, 11709–11715; b) M. Lan, L. Guo, S. Zhao, Z. Zhang, Q. Jia, L. Yan, J. Xia, H. Zhang, P. Wang and W. Zhang, *Adv. Ther.* **2018**, **1**, 1800077.