

## Cucurbit[8]uril-based host-guest complexation enhancing afterglow of naphthalimide derivative for anti-counterfeiting printing

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Table of Contents	Page
Table of Contents	S1
General experimental section	S2
Synthesis of <b>1</b> and <b>P1</b>	S3-S4
UV/Vis absorption and fluorescence titration spectra of <b>1</b> upon complexation of CB[8]	S5
Normalized fluorescence spectra of <b>1</b> in solvents with different polarities	S6
Fluorescence decay curves of <b>1</b> and CB[8]· <b>1</b> in aqueous solution and on filter paper	S6-S7
<sup>1</sup> H NMR spectrum of <b>P1</b> in D <sub>2</sub> O	S7
Fluorescence and phosphorescence decay curves of <b>P1</b> and complex of <b>P1</b> and CB[8] in solid state	S8
Afterglow images of <b>P1</b> and <b>1</b>	S9
Table S1	S9
<sup>1</sup> H and <sup>13</sup> C NMR and ESI-HRMS data of <b>1b</b> , <b>1</b> and <b>1c</b>	S9-S13
References	S14

## General Experimental Section

NMR measurements:  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Agilent DD2 spectrometers at 600 MHz and 150 MHz.

ESI-MS measurements: ESI-MS was performed using a Aglient 6546 Q-TOF MS.

Isothermal titration calorimetry (ITC) experiment: ITC experiment was carried out on a Nano ITC (TA Instruments) at 298K ([Guest] (syringe) = 800  $\mu\text{M}$ , [CB[8]] (cell) = 100  $\mu\text{M}$ ).

UV/Vis measurements: UV/vis absorption spectra were recorded on a SHIMADZU UV-3600 instrument with 1 cm pathlength cells at 298 K.

Fluorescence measurements: Fluorescence spectra were measured on a PerkinElmer LS-55 machine.

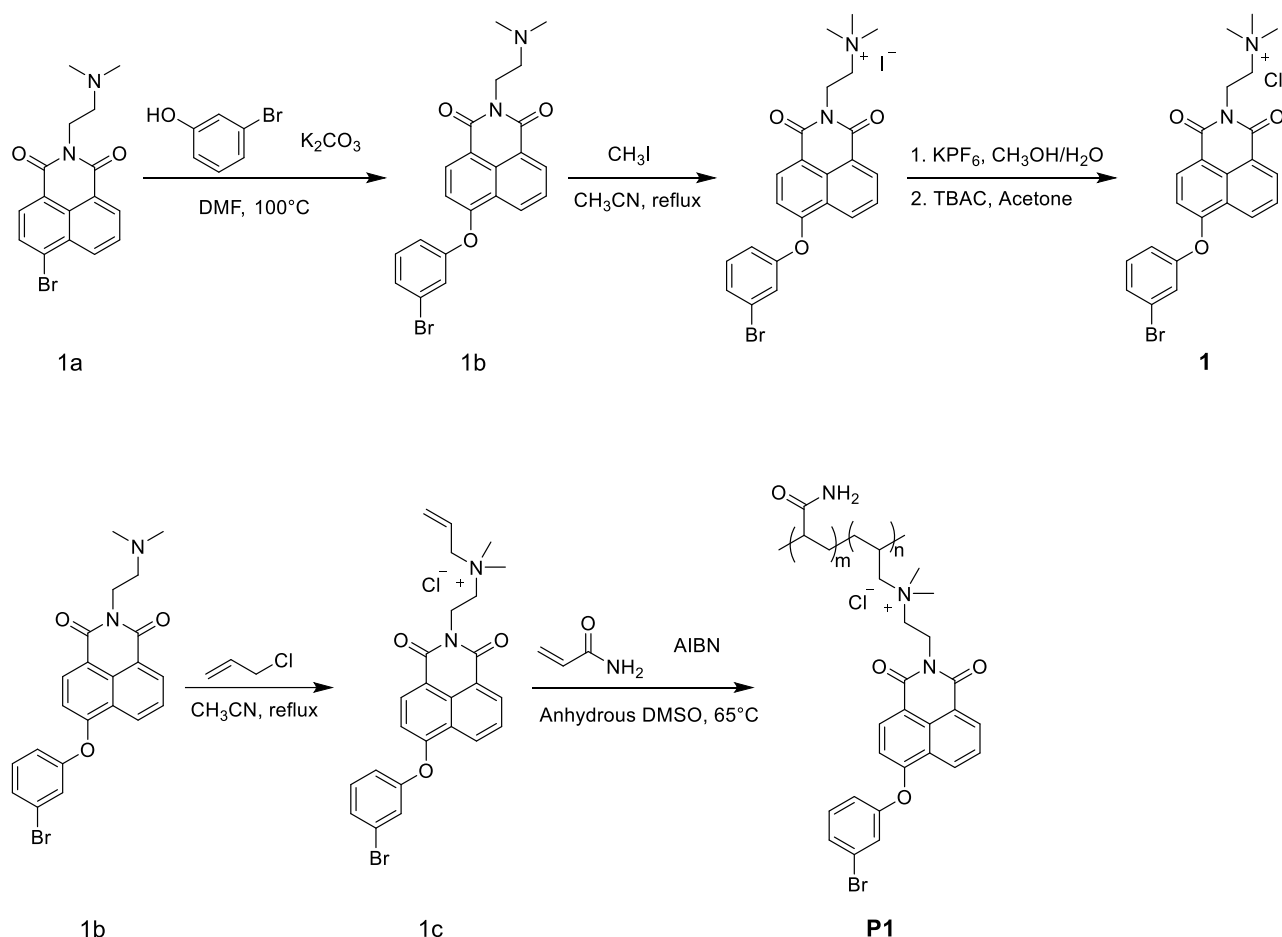
Phosphorescence measurements: Phosphorescence spectra were measured on Edinburgh Instruments FS5 spectrofluorometer. The phosphorescence spectra for each data point were delayed 0.1 ms to ensure that the first 0.1 ms are not collected to eliminate the fluorescence emission.

Lifetime and quantum yield measurements: Lifetime and quantum yield were measured on Edinburgh Instruments FS5 spectrofluorometer. Fluorescence lifetimes were collected by Time-Correlated Single Photon Counting (TCSPC) method using 375 nm laser, phosphorescence lifetimes were collected by Multi-Channel Scaling (MCS) method using microsecond flashlamp. The absolute quantum yield was determined by using a Hamamatsu C9920-02G Instruments Integrating Sphere Module (SC-30).

All the materials were obtained from commercial suppliers and were used without further purification. CB[8] was prepared by the corresponding literature procedures.<sup>1, 2</sup>

Preparation of samples: The filter paper was treated with boiling water two times, the solution (1 mM) of **1** and CB[8]·**1** was dripped onto treated filter paper, the solid samples were obtained after drying. **P1** (20 mg) was dissolved in 20 mL deionized water, CB[8] was added until saturated, and the solid powder was obtained by freeze-drying.

## Synthesis and characterization



**Scheme S1.** Synthesis route of **1** and **P1**

The compound **1a** was synthesized according to literature procedure.<sup>3</sup>

### *Synthesis of 1b:*

3-bromophenol (0.30 g, 1.73 mmol) and potassium carbonate (0.40 g, 2.89 mmol) were added to a solution of **1a** (0.50 g, 1.44 mmol) in DMF (15 mL). The mixture was degassed by nitrogen bubbling for 30 min and then heated to 100°C for 12 h under nitrogen atmosphere. After cooling to room temperature, the solution was diluted with dichloromethane (150 mL) and washed with water ( $5 \times 50$  mL). The organic layer was dried over anhydrous  $Na_2SO_4$ , filtered and concentrated to dryness. The crude was purified by column chromatography (petroleum ether/ethyl acetate 1:5) to yield **1b** as white solid (0.54 g, 85.4%).  $^1H$  NMR (600 MHz,  $DMSO-d_6$ )  $\delta$  8.58 (d,  $J = 8.3$  Hz, 1H), 8.50 (d,  $J = 7.2$  Hz, 1H), 8.37 (d,  $J = 8.2$  Hz, 1H), 7.86 (t,  $J = 7.9$  Hz, 1H), 7.54 (s, 1H), 7.50 (d,  $J = 8.2$  Hz, 1H), 7.45 (t,  $J = 8.1$  Hz, 1H), 7.28 (d,  $J = 8.1$  Hz, 1H), 7.04 (d,  $J = 8.2$  Hz, 1H), 4.09 (t,  $J = 6.9$  Hz, 2H), 2.45 (d,  $J = 6.0$  Hz, 2H), 2.15 (s, 6H).  $^{13}C$  NMR (150 MHz,  $DMSO-d_6$ )  $\delta$  163.45, 162.79, 158.27, 155.73, 132.78, 132.34, 131.65, 128.98, 128.53, 128.25, 127.37, 123.49, 123.39, 122.64, 122.17, 119.67, 116.81, 112.07, 56.55, 45.51, 37.60. HRMS (ESI) ( $m/z$ ):  $[M+H]^+$  calcd for  $C_{22}H_{20}BrN_2O_3$ , 439.0579; found, 439.0655.

### *Synthesis of 1:*

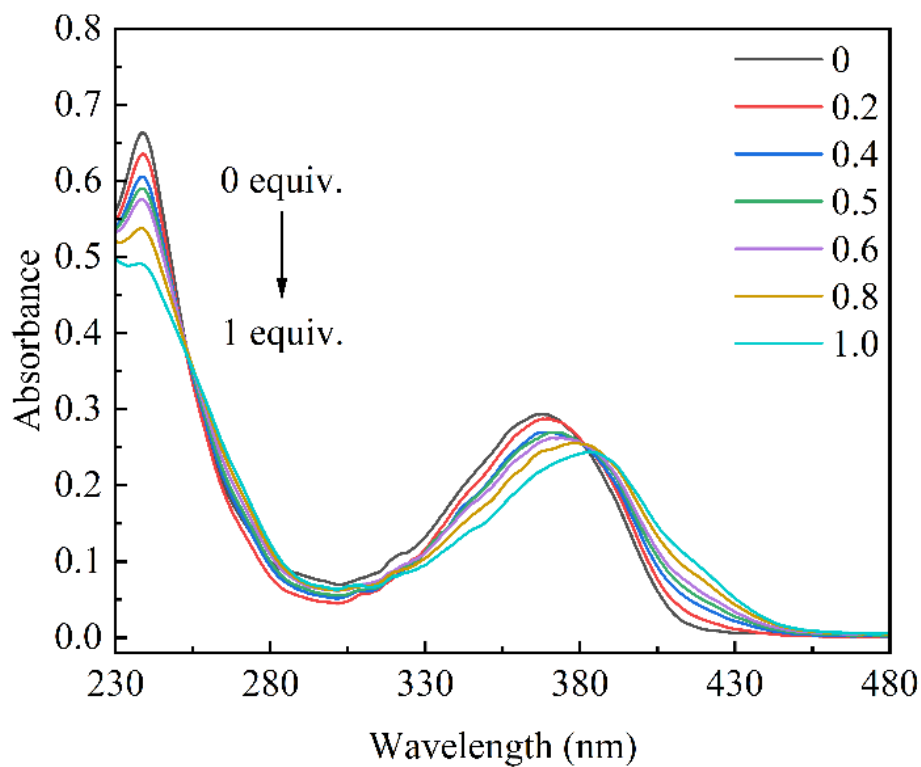
1b (0.22 g, 0.50 mmol) was dissolved in dichloromethane (10 mL) and CH<sub>3</sub>I (0.5 mL) was added. The mixture was stirred at room temperature for 12 h. The precipitate was filtered and washed three times with dichloromethane, and then pure **1** was obtained by anion exchange as white solid powder (0.22 g, 89.8%). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 8.69 (d, J = 8.3 Hz, 1H), 8.55 (d, J = 7.3 Hz, 1H), 8.36 (d, J = 8.4 Hz, 1H), 7.85 (t, J = 7.9 Hz, 1H), 7.57 (d, J = 8.1 Hz, 1H), 7.49 (s, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.28 (d, J = 8.2 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 4.59 (t, J = 7.6 Hz, 2H), 3.67 (t, J = 7.6 Hz, 2H), 3.33 (s, 9H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 163.60, 162.90, 158.61, 155.61, 133.05, 132.42, 131.86, 129.21, 128.69, 128.67, 127.52, 123.52, 123.46, 122.67, 122.15, 119.73, 116.70, 112.08, 61.88, 52.44, 33.65. HRMS (ESI) (m/z): [M-Cl]<sup>+</sup> calcd for C<sub>23</sub>H<sub>22</sub>BrN<sub>2</sub>O<sub>3</sub>, 453.0808; found, 453.0798.

### *Synthesis of 1c:*

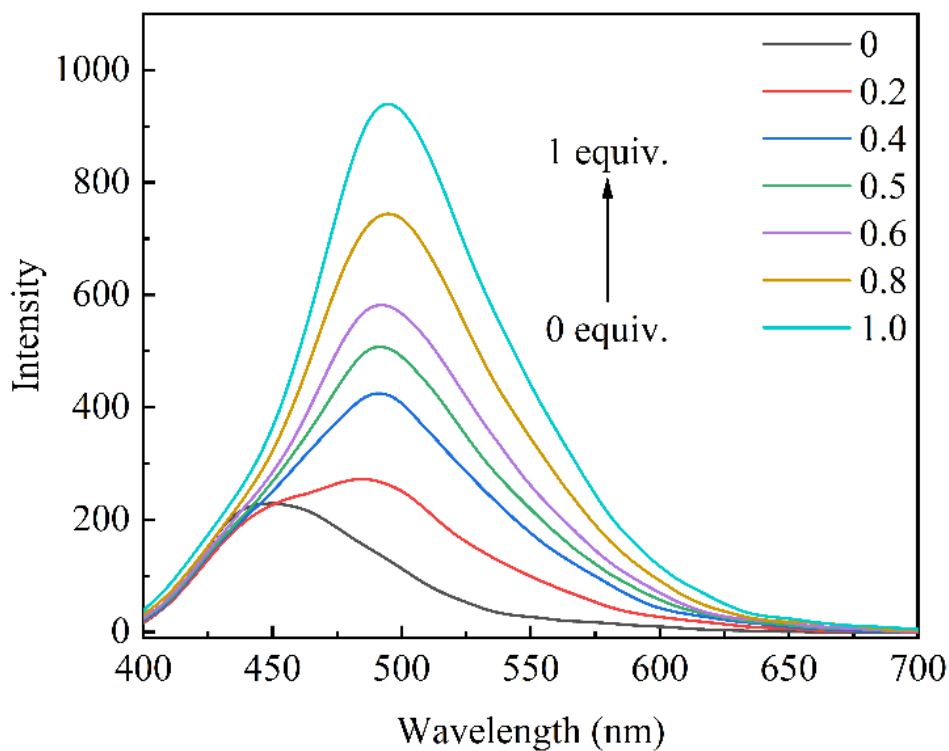
1b (0.50 g, 1.14 mmol) was dissolved in anhydrous acetonitrile (10 mL) and 3-chloropropene (0.2 mL, 2.46 mmol) was injected. The mixture was heated under reflux for 48 h under argon atmosphere. After cooling to room temperature, pouring the solution into anhydrous ether, the resulting precipitation was collected by filtration to afford 1c as grey solid powder (0.32 g, 54.4%). <sup>1</sup>H NMR (600 MHz, D<sub>2</sub>O) δ 8.37 (d, J = 8.4 Hz, 1H), 8.20 (d, J = 7.3 Hz, 1H), 8.01 (d, J = 8.3 Hz, 1H), 7.53 (t, J = 7.9 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 7.21 (s, 1H), 7.18 (d, J = 8.4 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 6.72 (d, J = 8.3 Hz, 1H), 5.85 (dt, J = 17.0, 8.4 Hz, 1H), 5.57 – 5.47 (m, 2H), 4.28 (s, 2H), 3.84 (d, J = 7.4 Hz, 2H), 3.29 (t, J = 7.9 Hz, 2H), 2.99 (s, 6H). <sup>13</sup>C NMR (150 MHz, DMSO-*d*<sub>6</sub>) δ 163.57, 162.87, 158.56, 155.62, 133.02, 132.41, 131.83, 129.19, 128.69, 128.60, 128.25, 127.50, 125.70, 123.47, 123.45, 122.66, 122.15, 119.70, 116.71, 112.10, 65.56, 59.21, 49.97, 33.34. HRMS (ESI) (m/z): [M-Cl]<sup>+</sup> calcd for C<sub>25</sub>H<sub>24</sub>BrN<sub>2</sub>O<sub>3</sub>, 479.0965; found, 479.0971.

### *Synthesis of P1:*

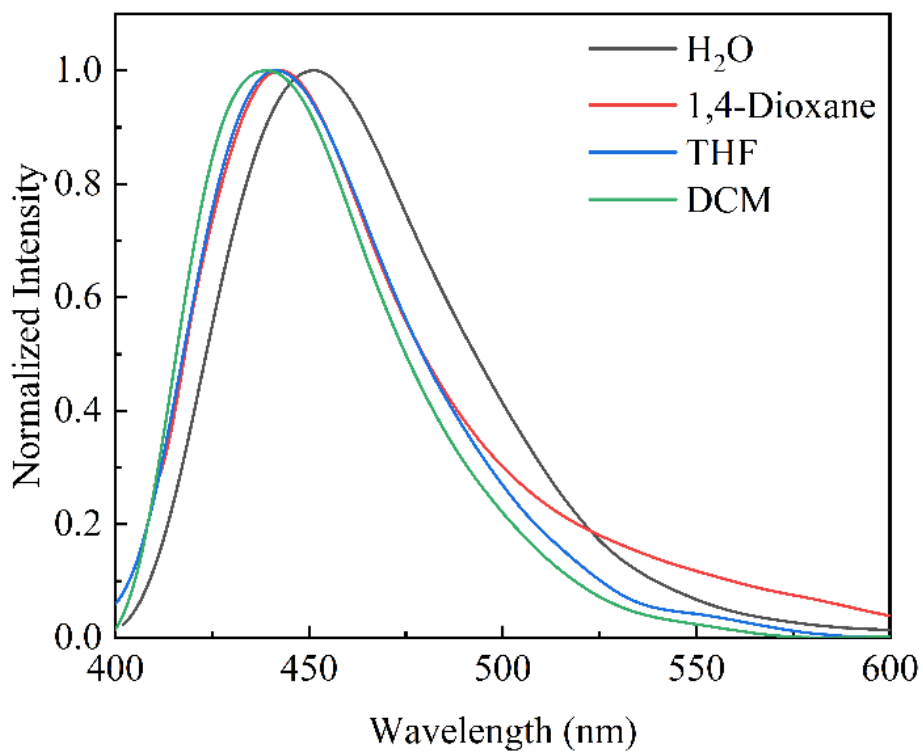
**P1** was prepared by copolymerization of 1c (52 mg, 0.1 mmol) and acrylamide (348.3 mg, 4.9 mmol) with 2,2'-azobis(2-methylpropionitrile) (AIBN) (16.4 mg) as radical initiator in 5 mL anhydrous DMSO at 65°C for 12 h under dark and argon atmosphere. After cooling to room temperature, pouring the solution into acetone, the resulting precipitation was collected by filtration and washed two times with acetone to obtain crude solid. And then the crude solid was dissolved in distilled water and dialyzed (cut off = 3500) against water for 3 days. The resulting solution was lyophilized to obtain solid **P1**.



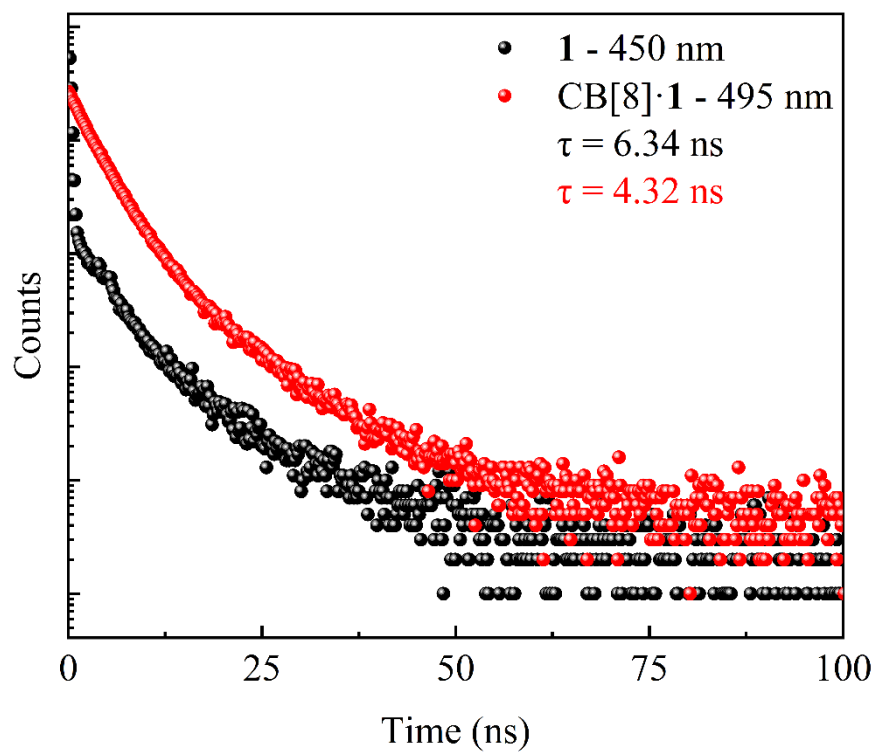
**Fig. S1** UV/Vis absorption titration spectra of **1** (20  $\mu$ M) with addition of different equiv. of CB[8].



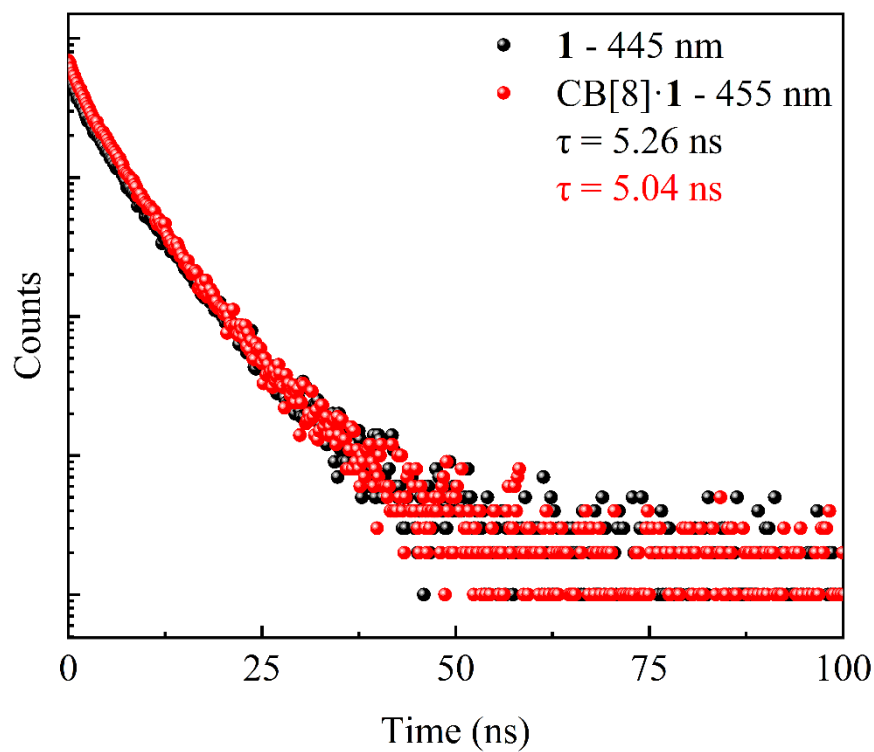
**Fig. S2** Fluorescence titration spectra of **1** (20  $\mu$ M) with addition of different equiv. of CB[8] ( $\lambda_{\text{ex}}$  = 370 nm; Excitation slit = 10 nm; Emission slit = 5 nm).



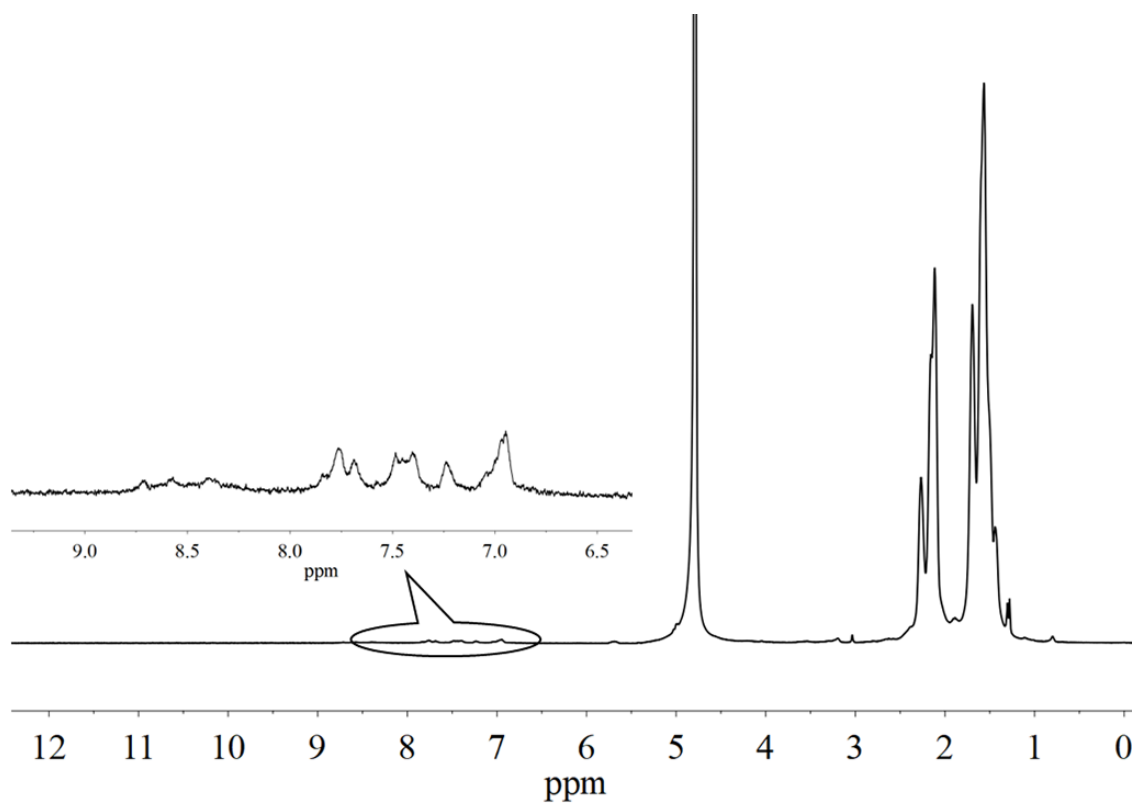
**Fig. S3** Normalized fluorescence spectra of **1** in solvents with different polarities.



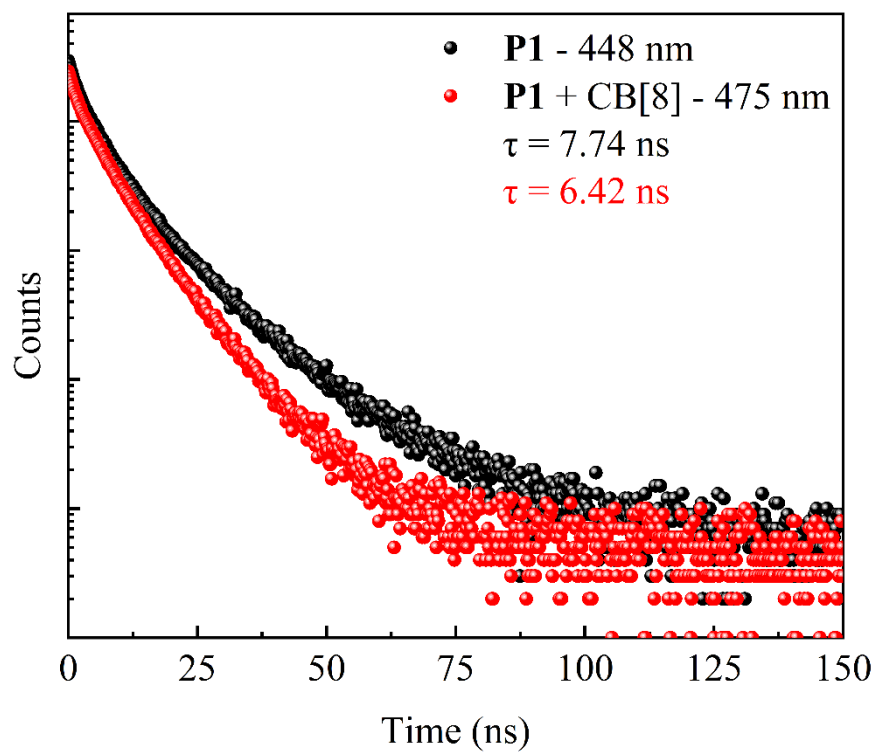
**Fig. S4** Fluorescence decay curves of **1** and CB[8]·**1** in aqueous solution.



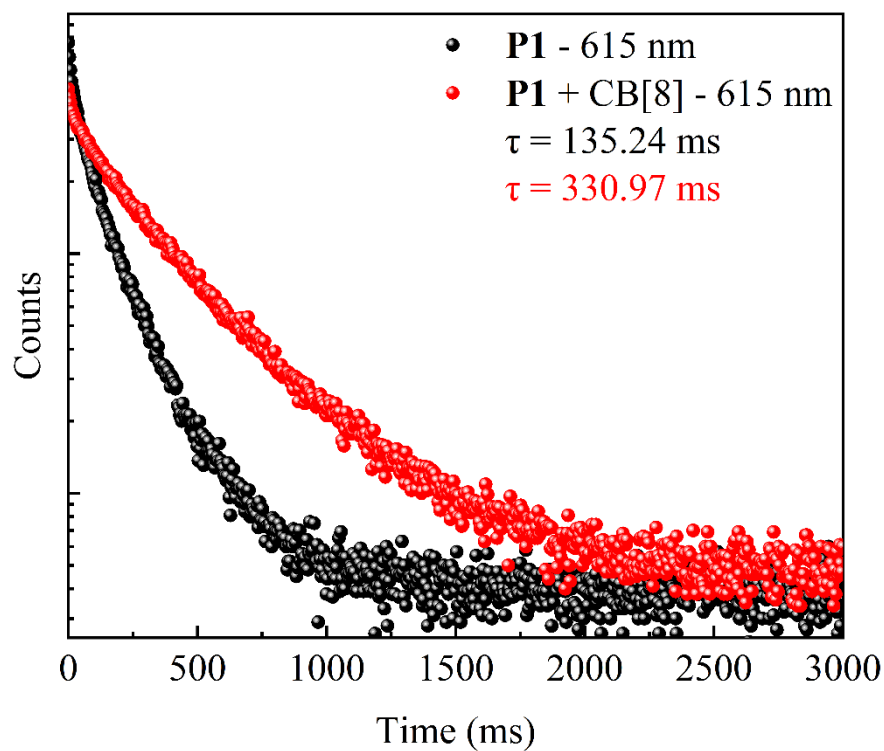
**Fig. S5** Fluorescence decay curves of **1** and **CB[8]·1** on filter paper.



**Fig. S6**  $^1\text{H}$  NMR spectrum of **P1** in  $\text{D}_2\text{O}$  (600 MHz, 298 K).

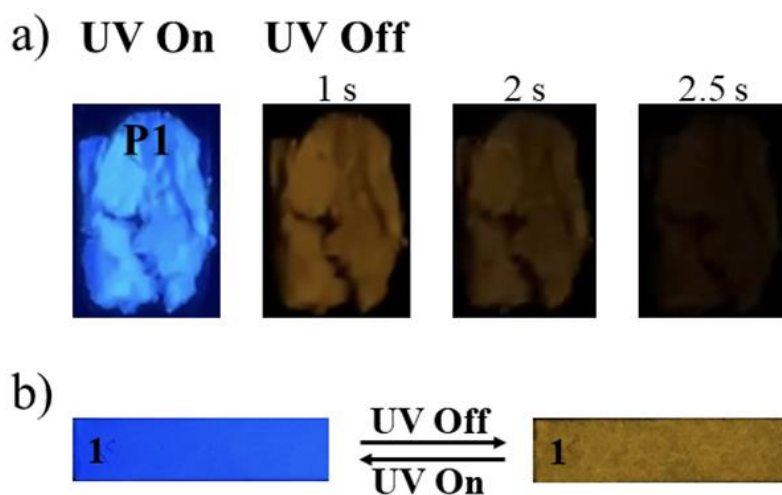


**Fig. S7** Fluorescence decay curves of **P1** and complex of **P1** and CB[8] in solid state.



**Fig. S8** Phosphorescence decay curves of **P1** and complex of **P1** and CB[8] in solid state.

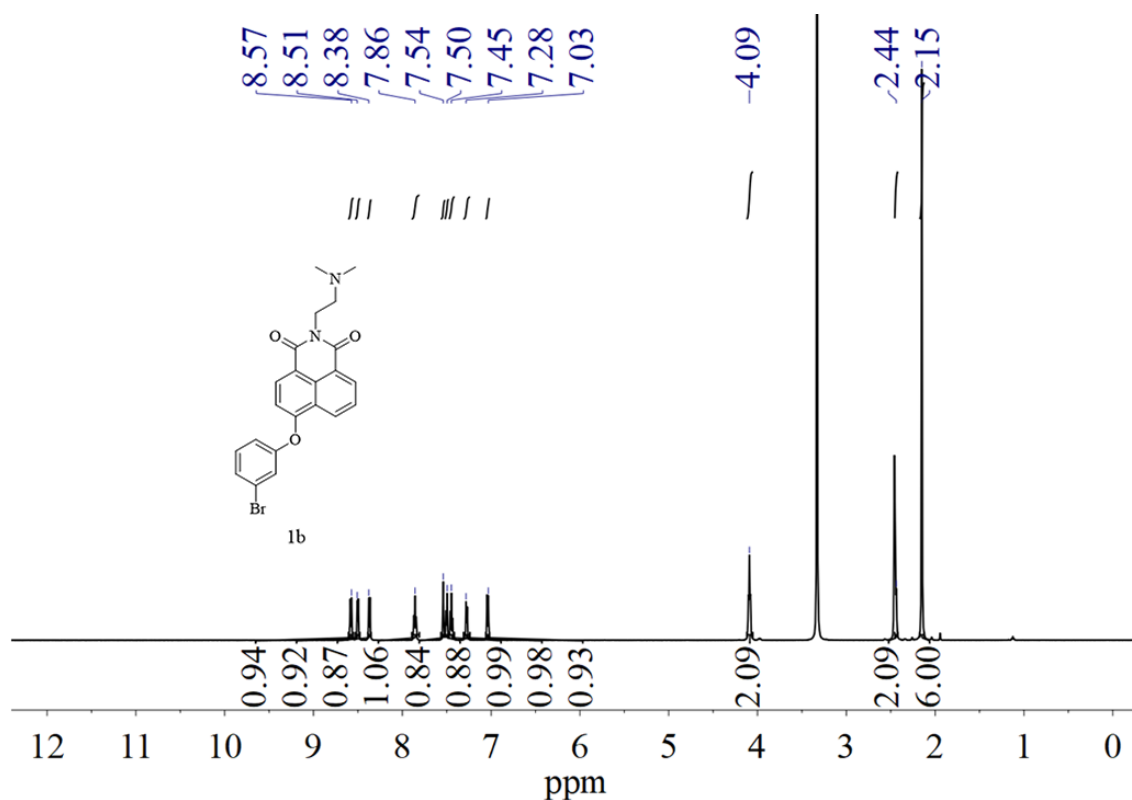




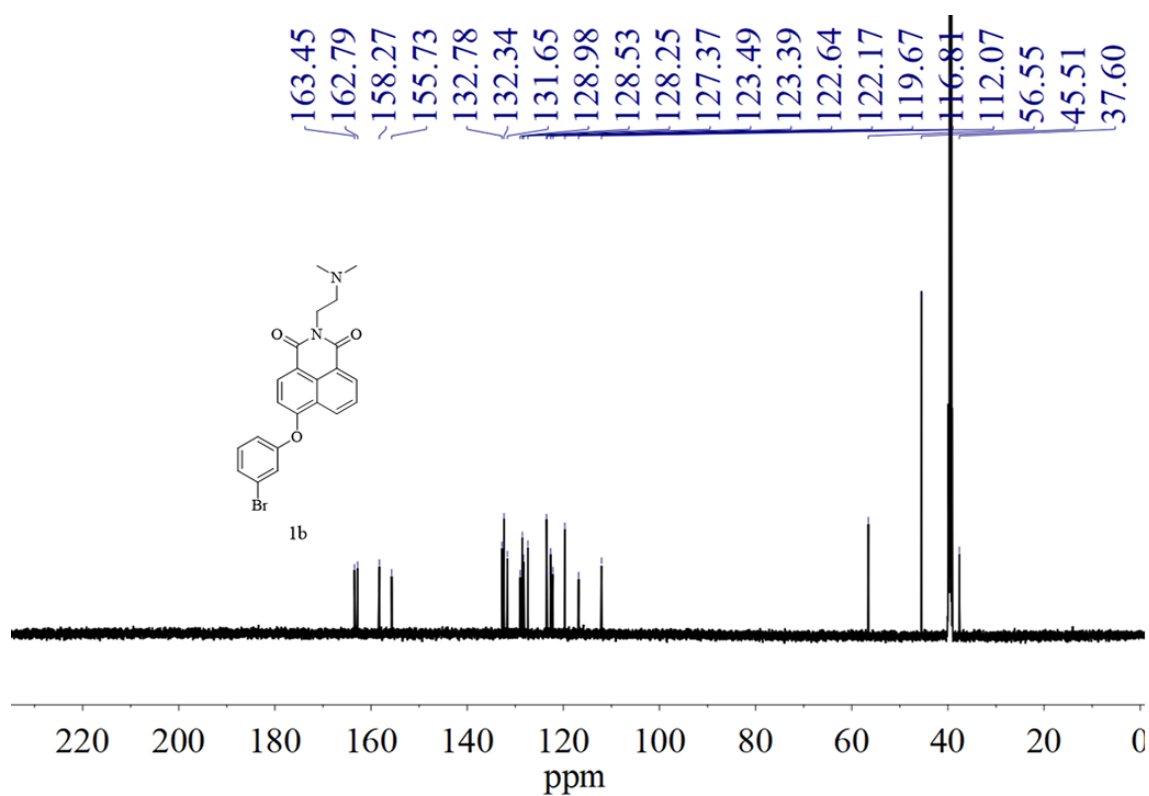
**Fig. S9** Afterglow images of a) **P1** and b) **1** under 365 nm with the excitation source on and off.

**Table S1** Photophysical properties of **1** and **P1** upon complexation with CB[8] in solid state

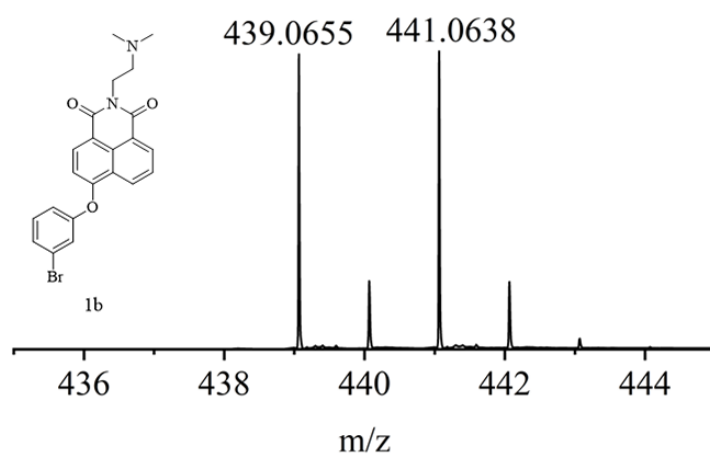
	$\lambda_{\text{Fluo}}$ (nm)	$\lambda_{\text{Phos}}$ (nm)	$\tau_{\text{Fluo}}$ (ns)	$\tau_{\text{Phos}}$ (ms)	$\Phi_{\text{Fluo}}$ (%)	$\Phi_{\text{Phos}}$ (%)
<b>1</b>	445	570	5.26	111.03	13.98	2.74
<b>CB[8]·1</b>	455	570	5.04	163.21	17.72	6.71
<b>P1</b>	448	570	7.74	134.99	33.41	8.77
<b>P1/CB[8]</b>	475	585	6.42	335.30	38.19	13.99



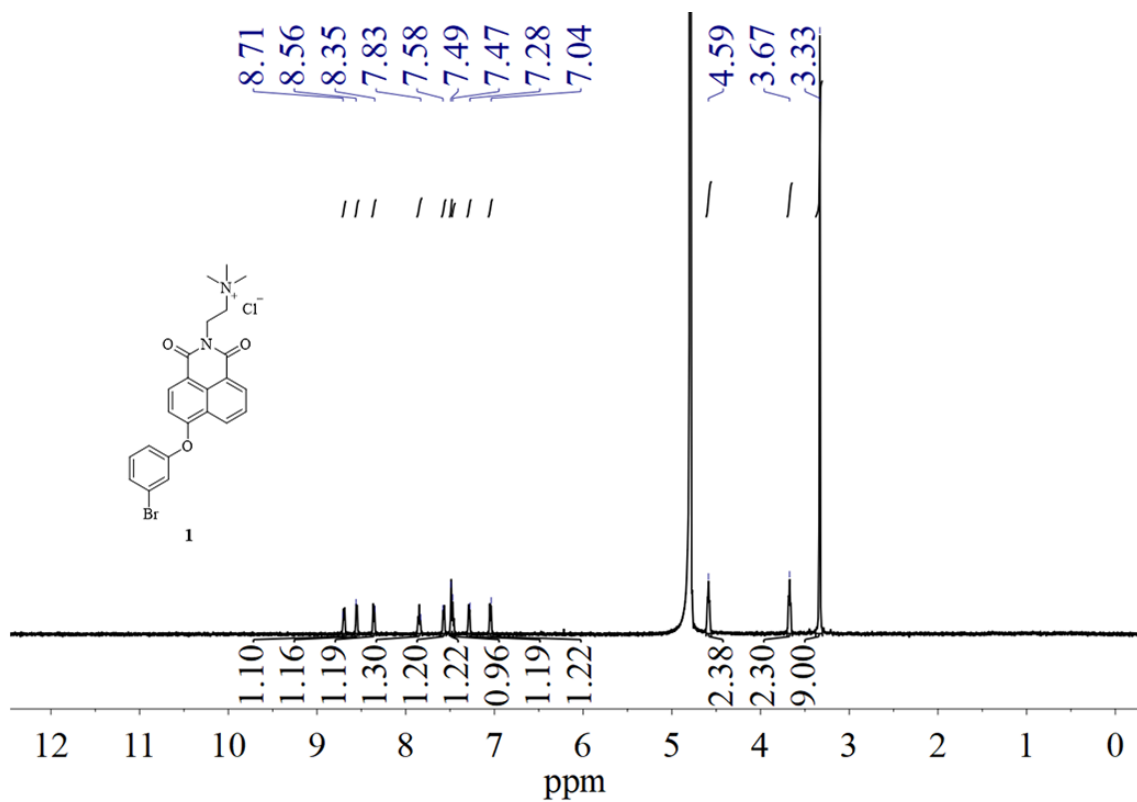
**Fig. S10**  $^1\text{H}$  NMR spectrum of **1b** in  $\text{DMSO-}d_6$  (600 MHz, 298 K).



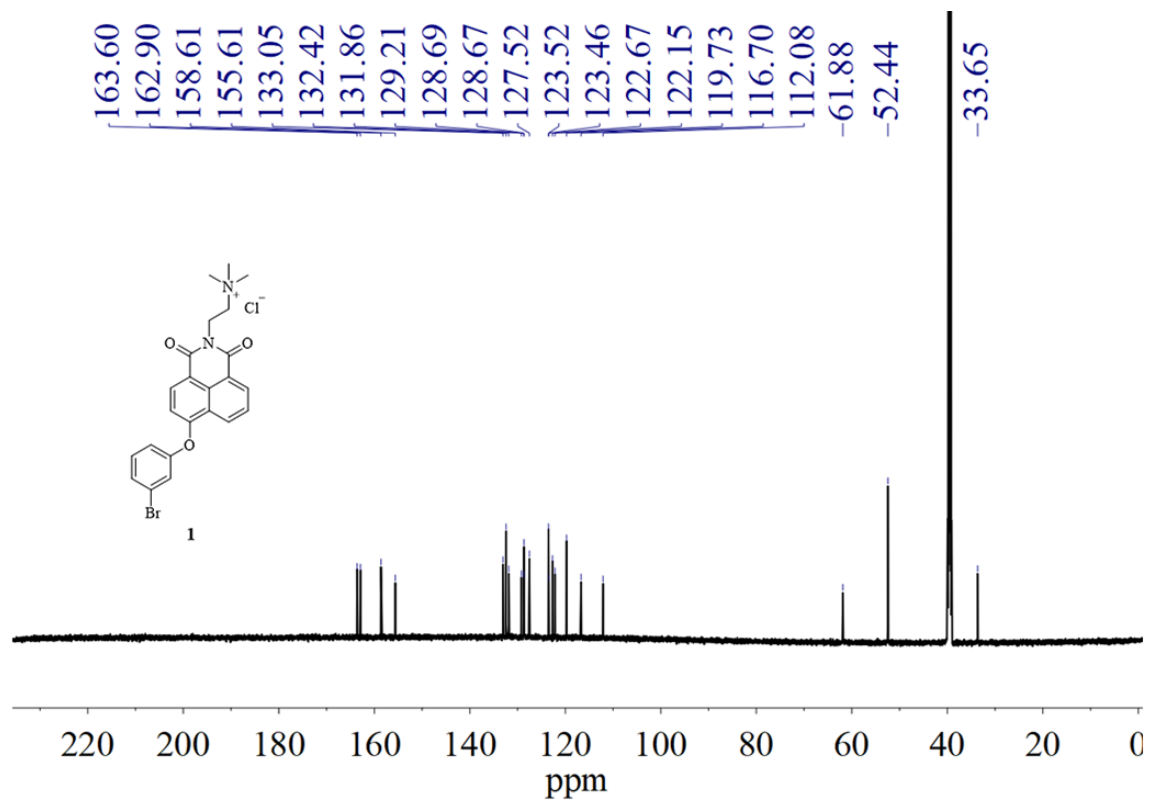
**Fig. S11**  $^{13}\text{C}$  NMR spectrum of 1b in  $\text{DMSO-}d_6$  (150 MHz, 298 K).



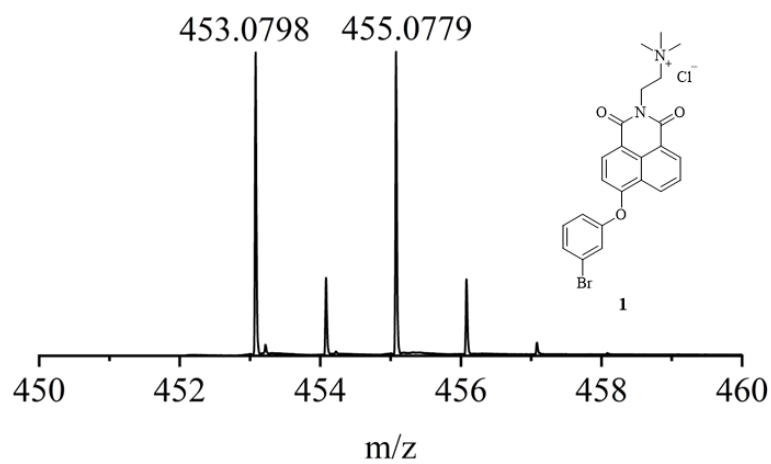
**Fig. S12** HRMS (ESI) of 1b in dichloromethane.



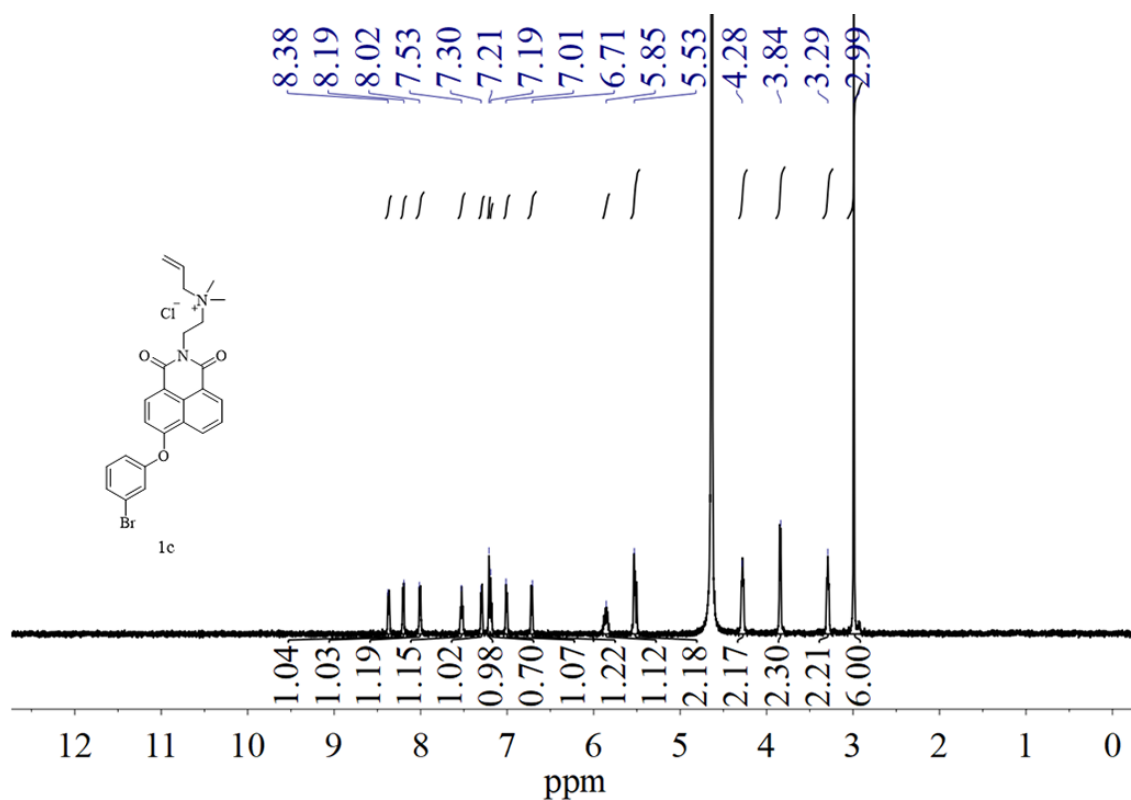
**Fig. S13**  $^1\text{H}$  NMR spectrum of **1** in  $\text{D}_2\text{O}$  (600 MHz, 298 K).



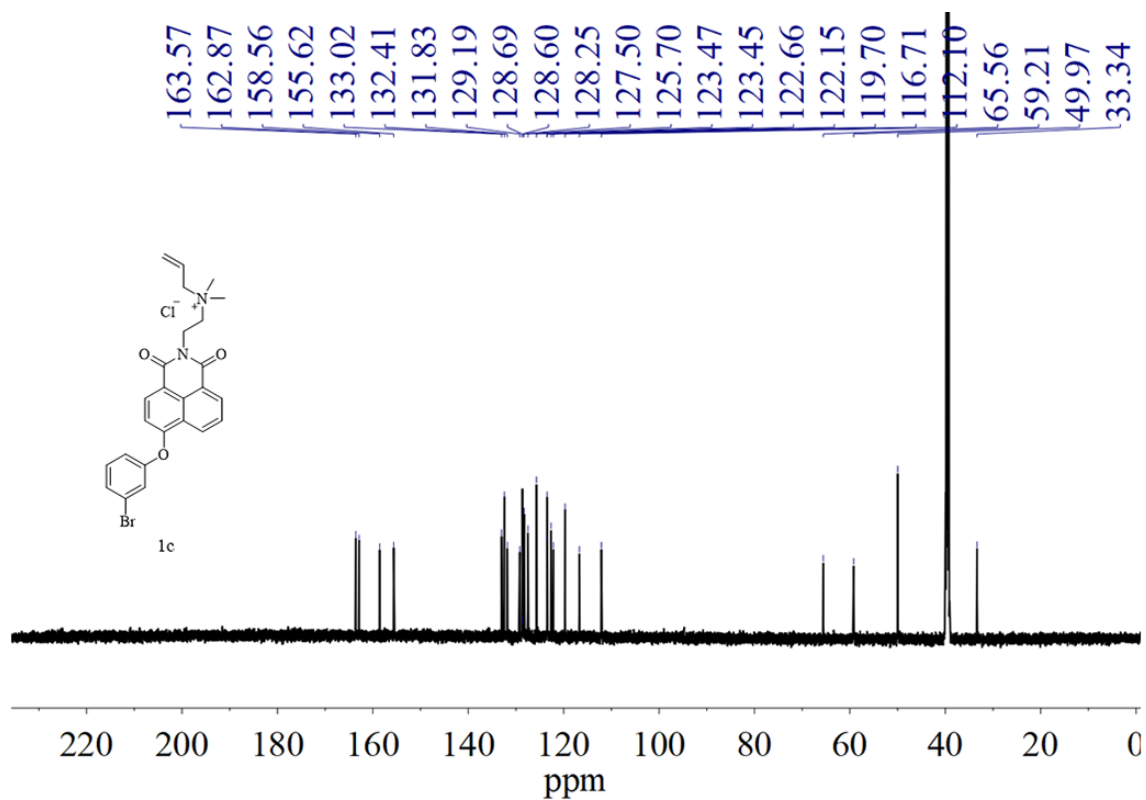
**Fig. S14**  $^{13}\text{C}$  NMR spectrum of **1** in  $\text{DMSO-}d_6$  (150 MHz, 298 K).



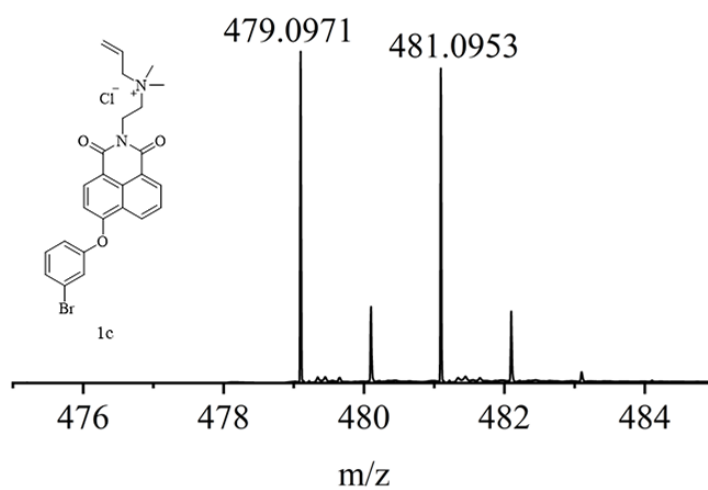
**Fig. S15** HRMS (ESI) of **1** in H<sub>2</sub>O.



**Fig. S16** <sup>1</sup>H NMR spectrum of **1c** in D<sub>2</sub>O (600 MHz, 298 K).



**Fig. S17** <sup>13</sup>C NMR spectrum of 1c in DMSO-*d*<sub>6</sub> (150 MHz, 298 K).



**Fig. S18** HRMS (ESI) of 1c in H<sub>2</sub>O.

References:

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2. X. Yang, Z. Zhao, X. Zhang and S. Liu, *Sci. China Chem.*, 2017, **61**, 787-791.
3. T. Moniz, C. Queirós, R. Ferreira, A. Leite, P. Gameiro, A. M. G. Silva and M. Rangel, *Dyes Pigm.*, 2013, **98**, 201-211.