

## Electronic Supplementary Information

# Controlled Assembly of Photosensitizers through Directional Interactions for Effective Photooxidation

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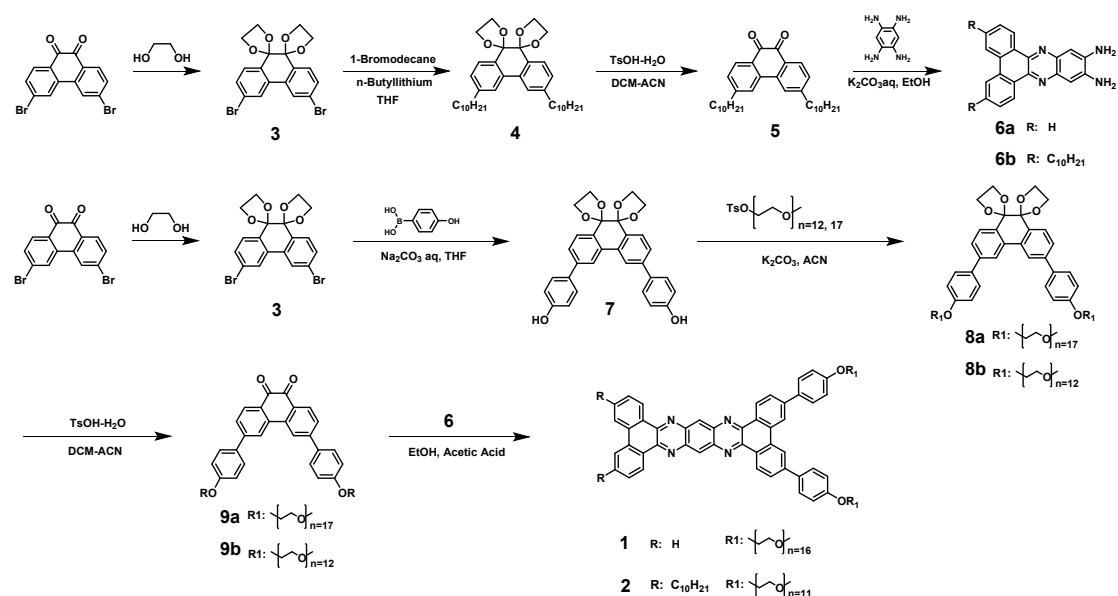
### EXPERIMENTAL SECTION

**Materials.** 3,6-dibromo-9,10-phenanthrenedione, (4-Hydroxyphenyl) boronic acid, Benzene-1,2,4,5-tetraamine tetrahydrochloride, Ethylene glycol, (from aladdin), n-Butyllithium solution (1.6 M in hexane), Poly(ethylene glycol) methyl ether ( $M_w$  550 and 750), 1-Bromodecane, toluene-p-sulfonyl chloride, p-toluenesulfonyl chloride, p-toluenesulfonic acid monohydrate (from macklin), tetrakis (triphenylphosphine) palladium(0) (from J&K), and conventional reagents were used without further purification.

#### General.

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on Bruker Avance III 400 MHz. Fourier transform infrared spectroscopy (FT-IR) experiments were carried out on the Perkin Elmer Frontier IR spectrometer using ATR mode under ambient conditions. Vapor pressure osmometry (VPO) experiment was recorded on OSMOMAT 07 instrument. The UV-vis spectra were obtained from a Metash UV-8000S Spectrophotometer. Fluorescence spectra were obtained from Shimadzu RF-6000 Spectrofluorophotometer. The lifetime decay curves were obtained on a Horiba JY FL-3 spectrophotometer. Transmission electron microscope (TEM) experiments were performed with a JEOL 2010Plus microscope.

## Synthesis



Scheme. S1 Synthesis of **1** and **2**.

## Synthesis of compounds 7-9 and 1 and 2.

**Compounds 3-6** was prepared according to the similar procedures reported previously and they gave the following spectroscopic data.<sup>[1-3]</sup>

**Compound 3:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.96 (s, 2H), 7.62 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 4.0 Hz, 2H), 4.26-4.06 (m, 4H), 3.72-3.52 (m, 4H).

**Compound 4:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 7.71 (s, 2H), 7.63 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 4.28-4.10 (m, 4H), 3.75-3.61 (m, 4H), 2.68 (t, J = 8.0 Hz, 4H), 1.70-1.62 (m, 4H), 1.37-1.23 (m, 28H), 0.88 (t, J = 8.0 Hz, 6H).

**Compound 5:** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.10 (d, J = 8.0 Hz, 2H), 7.79 (s, 2H), 7.27 (d, J = 8.0 Hz, 2H), 2.75 (t, J = 8.0 Hz, 4H), 1.74-1.67 (m, 4H), 1.41-1.26 (m, 28H), 0.88 (t, J = 4.0 Hz, 6H).

**Compound 6a:** <sup>1</sup>H NMR (400 MHz, DMSO, δ, ppm): 9.18 (t, J = 8.0 Hz, 2H), 8.75 (t, J = 4.0 Hz, 2H), 7.77-7.72 (m, 4H), 7.14 (s, 2H) 6.14 (s, 4H).

**Compound 6b:** <sup>1</sup>H NMR (400 MHz, DMSO, δ, ppm): 9.05 (d, J = 8.0 Hz, 2H), 8.53 (s, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.10 (s, 2H) 6.02 (s, 4H), 2.86 (t, J = 8.0 Hz, 4H), 1.78-1.71 (m, 4H), 1.42-1.21 (m, 28H), 0.82 (t, J = 4.0 Hz, 6H).

## Synthesis of compound 7

**Compound 3** (2.20 g, 4.84 mmol) and 4-Hydroxyphenylboronic acid (2.33 g, 16.89 mmol) were dissolved in degassed THF (70 mL). 2 M Na<sub>2</sub>CO<sub>3</sub> aqueous (60 mL) and Pd (0) (0.56 g, 0.48 mmol) was added. The mixture was degassed and then heated at reflux for 20 h with vigorous

stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using ethyl acetate/methanol (10:1 v/v) as eluent to yield cream-yellow solid (1.80 g, 77%).

$^1\text{H}$  NMR (400 MHz, DMSO,  $\delta$ , ppm): 9.60 (s, 2H), 8.29 (s, 2H), 7.69-7.65 (m, 8H), 6.90 (d,  $J$  = 8.0 Hz, 4H), 4.17-4.08 (m, 4H), 3.63-3.51 (m, 4H).  $^{13}\text{C}$ -NMR (100 MHz, DMSO)  $\delta$ ; 157.36, 141.70, 133.10, 130.91, 130.34, 128.17, 126.55, 126.16, 121.46, 115.58, 92.00, 60.60. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{30}\text{H}_{24}\text{O}_6$  [M], 480.16; found: [M] 480.15 [M+H]<sup>+</sup> 481.16.

### Synthesis of compounds 8a and 8b

**Compounds 8a and 8b** were synthesized using the same procedure. A representative example is described for **8b**. **Compound 7** (0.8 g, 1.66 mmol), monotosylated poly(ethylene glycol) ( $M_w$  = 550, 2.98 g, 4.17 mmol), and excess  $\text{K}_2\text{CO}_3$  were dissolved in acetonitrile (60 mL). The mixture was heated to reflux for 24 h. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride/methanol (10:1 v/v) as eluent to yield a maroon sticky liquid (1.90 g, 73%).

**Compound 8a**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.10 (d,  $J$  = 4.0 Hz, 2H), 7.81 (d,  $J$  = 8.0 Hz, 2H), 7.61-7.57 (m, 6H), 7.03 (d,  $J$  = 8.0 Hz, 4H), 4.31-4.22 (m, 4H), 4.19 (t,  $J$  = 4.0 Hz, 4H), 3.89 (t,  $J$  = 4.0 Hz, 4H), 3.78-3.53 (m, 128H), 3.37 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 158.72, 142.53, 133.51, 133.28, 131.36, 128.31, 127.31, 126.70, 122.37, 115.02, 92.74, 71.93, 70.85, 70.63, 70.56, 70.49, 69.73, 67.57, 61.51, 59.00. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{100}\text{H}_{164}\text{O}_{40}$  [M], 2006.08; found: [M+Na]<sup>+</sup> 2029.02.

**Compound 8b**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.10 (d,  $J$  = 4.0 Hz, 2H), 7.80 (d,  $J$  = 8.0 Hz, 2H), 7.61-7.57 (m, 6H), 7.03 (d,  $J$  = 8.0 Hz, 4H), 4.30-4.21 (m, 4H), 4.19 (t,  $J$  = 4.0 Hz, 4H), 3.89 (t,  $J$  = 4.0 Hz, 4H), 3.77-3.53 (m, 88H), 3.38 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 158.70, 142.52, 133.49, 133.27, 131.35, 128.31, 127.30, 126.70, 122.35, 115.02, 92.73, 71.89, 70.82, 70.59, 70.51, 70.45, 69.71, 67.55, 61.47, 58.98. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{80}\text{H}_{124}\text{O}_{30}$  [M], 1564.82; found: [M+Na]<sup>+</sup> 1587.78.

### Synthesis of compounds 9a and 9b

**Compounds 9a and 9b** were synthesized using the same procedure. A representative example is described for **9b**. **Compound 8b** (0.90 g, 0.57 mmol) and  $\text{TsOH}\cdot\text{H}_2\text{O}$  (0.98 g, 5.15 mmol) were dissolved in  $\text{CH}_2\text{Cl}_2$  (12 mL),  $\text{H}_2\text{O}$  (8 mL) and acetonitrile (20 mL). The mixture was degassed and then heated at reflux for 16 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was

evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride/methanol (10:1 v/v) as eluent to yield a maroon liquid (0.75g, 88 %).

**Compound 9a:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.24 (t,  $J = 8.0$  Hz, 4H), 7.68-7.64 (m, 6H), 7.08 (d,  $J = 8.0$  Hz, 4H), 4.22 (t,  $J = 4.0$  Hz, 4H), 3.91 (t,  $J = 4.0$  Hz, 4H), 3.78-3.63 (m, 128H), 3.38 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 180.08, 159.84, 148.36, 136.24, 132.00, 131.22, 129.47, 128.59, 127.76, 121.96, 115.32, 71.94, 70.90, 70.66, 70.58, 70.51, 69.69, 67.67, 59.03. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{96}\text{H}_{156}\text{O}_{38}$  [M], 1918.03; found:  $[\text{M}+\text{K}]^+$  1957.116.

**Compound 9b:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.23 (t,  $J = 8.0$  Hz, 4H), 7.67-7.63 (m, 6H), 7.08 (d,  $J = 8.0$  Hz, 4H), 4.22 (t,  $J = 4.0$  Hz, 4H), 3.91 (t,  $J = 4.0$  Hz, 4H), 3.77-3.53 (m, 88H), 3.37 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 180.09, 159.83, 148.36, 136.25, 132.00, 131.23, 129.47, 128.59, 127.76, 121.96, 115.32, 71.93, 70.89, 70.64, 70.55, 70.49, 69.68, 67.65, 59.01. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{77}\text{H}_{118}\text{O}_{28}$  [M], 1490.78; found:  $[\text{M}+\text{Na}]^+$ .

### Synthesis of compounds 1 and 2

**Compounds 1 and 2** were synthesized using the same procedure. A representative example is described for **2**. **Compound 6b** (0.12 g, 0.20 mmol) and **Compound 9b** (0.23 g, 0.16 mmol) were dissolved in ethanol (10 mL) and acetic acid (20 mL). The mixture was heated at reflux for 12 h with vigorous stirring under nitrogen. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride / methanol (10:1 v/v) as eluent to yield a maroon ropy solid (0.18 g, 56 %).

**1:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 9.10 (t,  $J = 4.0$  Hz, 4H), 8.79 (s, 2H), 8.23-8.13 (m, 4H), 7.71-7.52 (m, 10H), 7.06 (d,  $J = 8.0$  Hz, 4H), 4.24 (t,  $J = 4.0$  Hz, 4H), 3.96 (t,  $J = 4.0$  Hz, 4H), 3.83-3.46 (m, 120H), 3.38 (s, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 158.99, 143.87, 142.76, 142.40, 140.33, 133.08, 132.57, 132.21, 130.71, 129.99, 128.94, 128.43, 127.78, 127.37, 126.81, 126.42, 124.48, 123.98, 122.74, 115.09, 71.94, 70.93, 70.69, 70.56, 69.82, 67.62, 59.02. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{112}\text{H}_{158}\text{N}_4\text{O}_{34}$  [M], 2104.08; found:  $[\text{M}+\text{Na}]^+$ , 2127.067.

**2:**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 9.41 (d,  $J = 8.0$  Hz, 2H), 9.28 (d,  $J = 8.0$  Hz, 2H), 9.20 (s, 2H), 8.58 (s, 2H), 8.17 (s, 2H), 7.90 (d,  $J = 8.0$  Hz, 2H), 7.75 (d,  $J = 8.0$  Hz, 4H), 7.53 (d,  $J = 8.0$  Hz, 2H), 7.11 (d,  $J = 8.0$  Hz, 4H), 4.25 (t,  $J = 4.0$  Hz, 4H), 3.94 (t,  $J = 4.0$  Hz, 4H), 3.80-3.53 (m, 80H), 3.37 (s, 6H), 2.86 (t,  $J = 8.0$  Hz, 4H), 1.82-1.76 (m, 4H), 1.46-1.26 (m, 28H), 0.89 (t,  $J = 4.0$  Hz, 6H).  $^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ ; 159.00, 146.07, 144.13, 143.76, 142.82, 140.35, 140.29, 133.21, 132.55, 132.38, 128.78, 128.48, 128.02, 127.66, 127.44, 126.94, 126.53, 123.98, 122.36, 120.56, 115.13, 71.94, 70.92, 70.68, 70.60, 70.57, 70.51, 69.81, 67.61, 59.02, 36.63, 31.96, 31.51, 29.75, 29.71, 29.67, 29.63, 29.40, 22.72, 14.14. TIMS-TOF mass:  $m/z$  calculated for  $\text{C}_{112}\text{H}_{158}\text{N}_4\text{O}_{24}$  [M], 1944.13; found:  $[\text{M}+\text{Na}]^+$ , 1967.116.

**Singlet oxygen generation in solutions:** ABDA (9,10-Anthracenedipropanoic acid) was used as an indicator for the detection of singlet oxygen in aqueous solution. ABDA (0.123  $\mu\text{mol}$  in 1% THF) was added into of Photosensitizers or RB in 1 mL solution. The mixture was then placed in a cuvette and irradiated with white light (100  $\text{mW}/\text{cm}^2$ ).

**Photo-stability of singlet oxygen generation in solutions:** Photosensitizers were irradiated with white light after different time, ABDA was additional added for the trace of  $^1\text{O}_2$  generation efficiency. The absorption change of sample around 400 nm was recorded by the UV-vis absorption spectrophotometer.

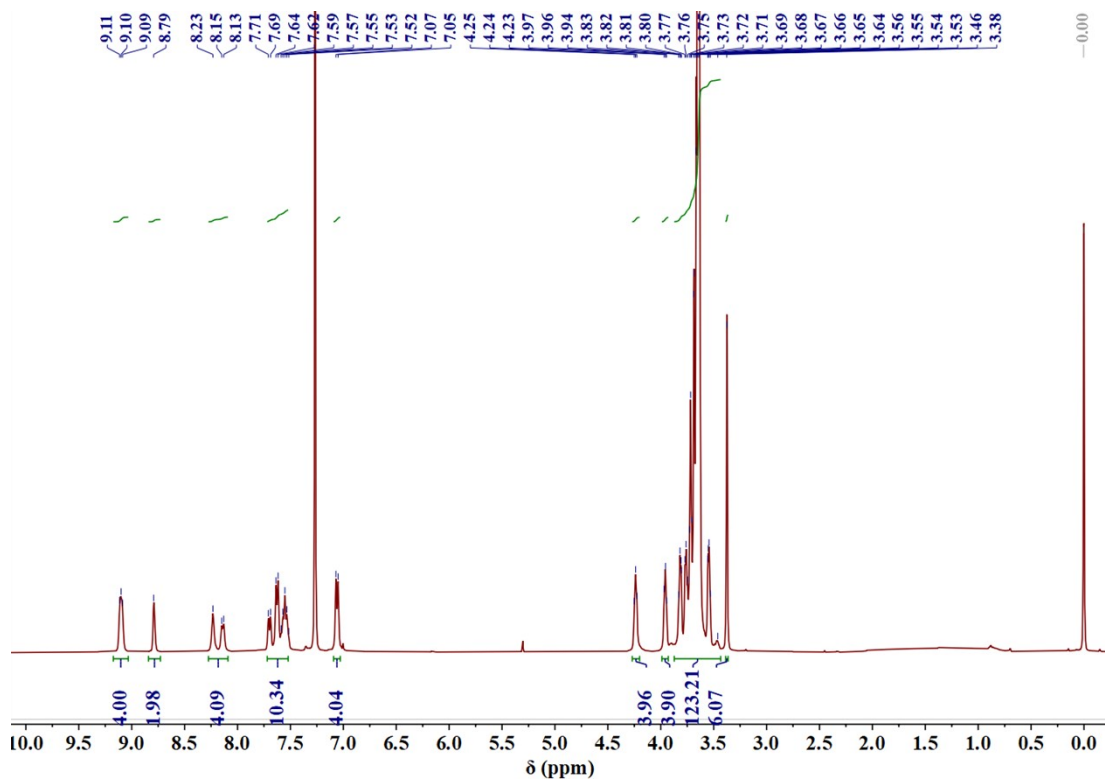


Fig. S1  $^1\text{H-NMR}$  spectrum of **1** in  $\text{CDCl}_3$ .

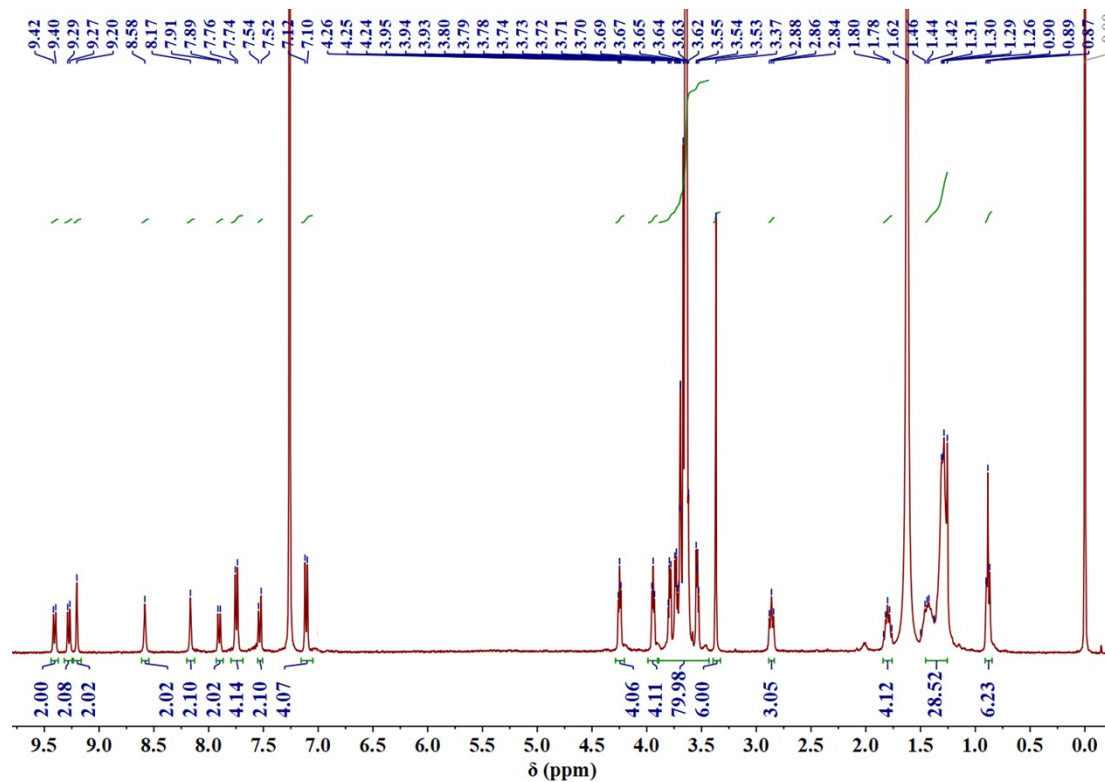


Fig. S2  $^1\text{H-NMR}$  spectrum of **2** in  $\text{CDCl}_3$ .

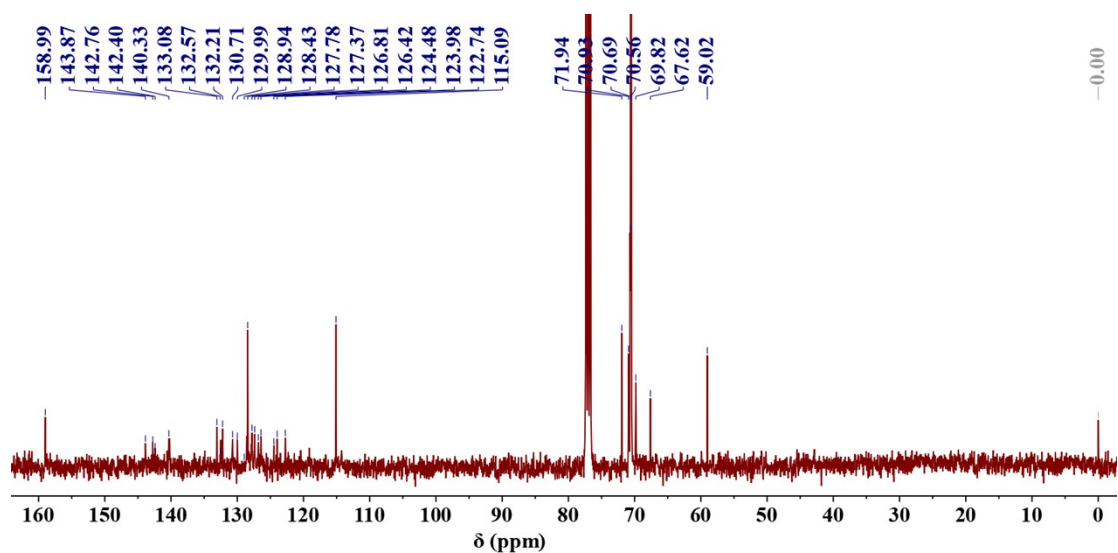


Fig. S3  $^{13}\text{C}$ -NMR spectrum of **1** in  $\text{CDCl}_3$ .

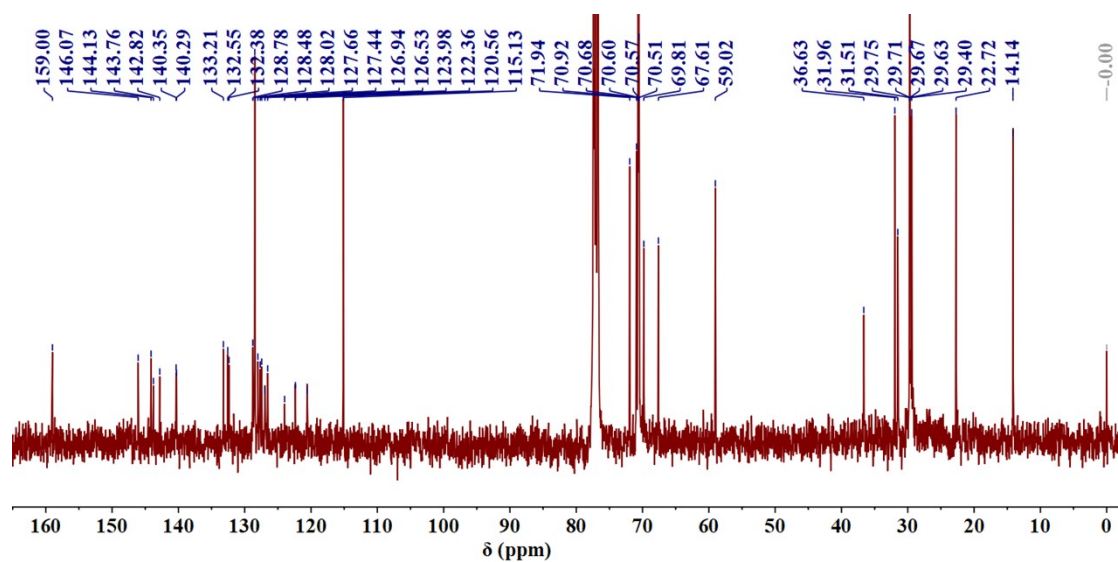


Fig. S4  $^{13}\text{C}$ -NMR spectrum of **2** in  $\text{CDCl}_3$ .

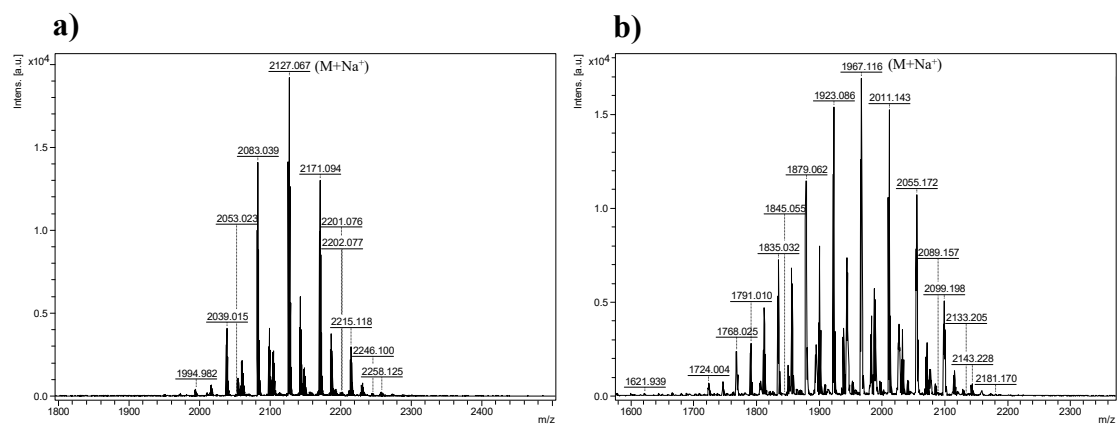
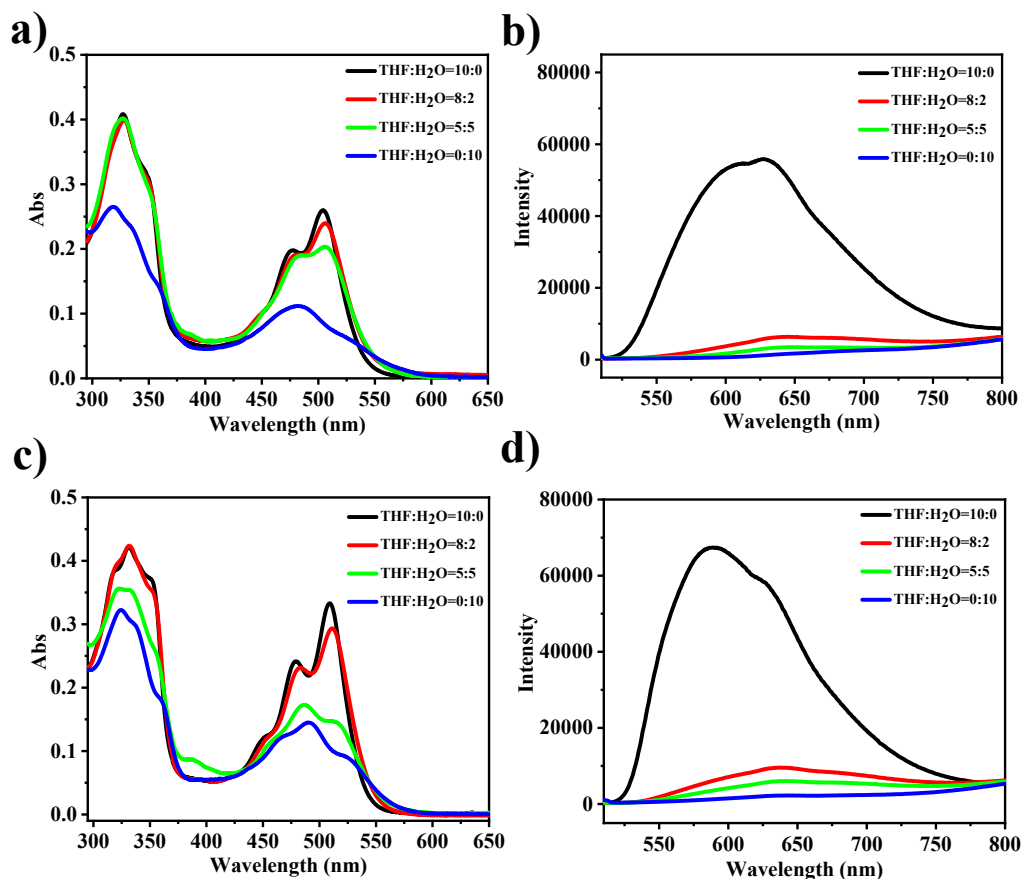
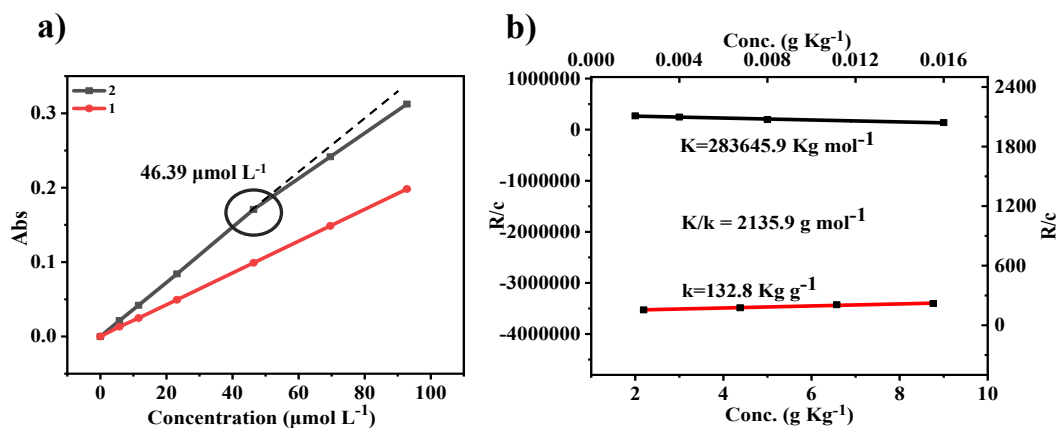


Fig. S5. MALDI-TOF-Mass spectra of **1** (a) and **2** (b).

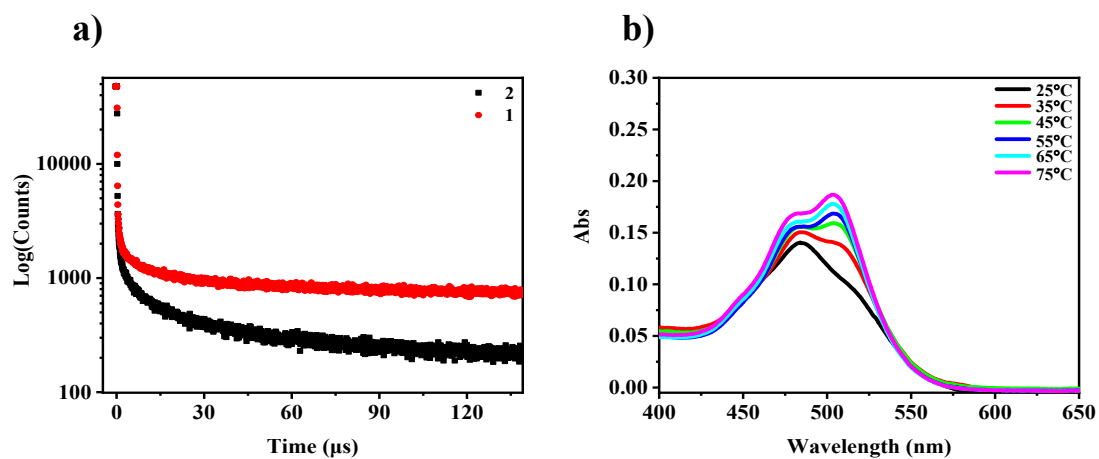


**Fig. S6** Absorption (a) and emission (b) spectra of **1** (51  $\mu\text{M}$ ) in tetrahydrofuran and aqueous solution. Absorption (c) and emission (d) spectra of **2** (51  $\mu\text{M}$ ) in tetrahydrofuran and aqueous solution.

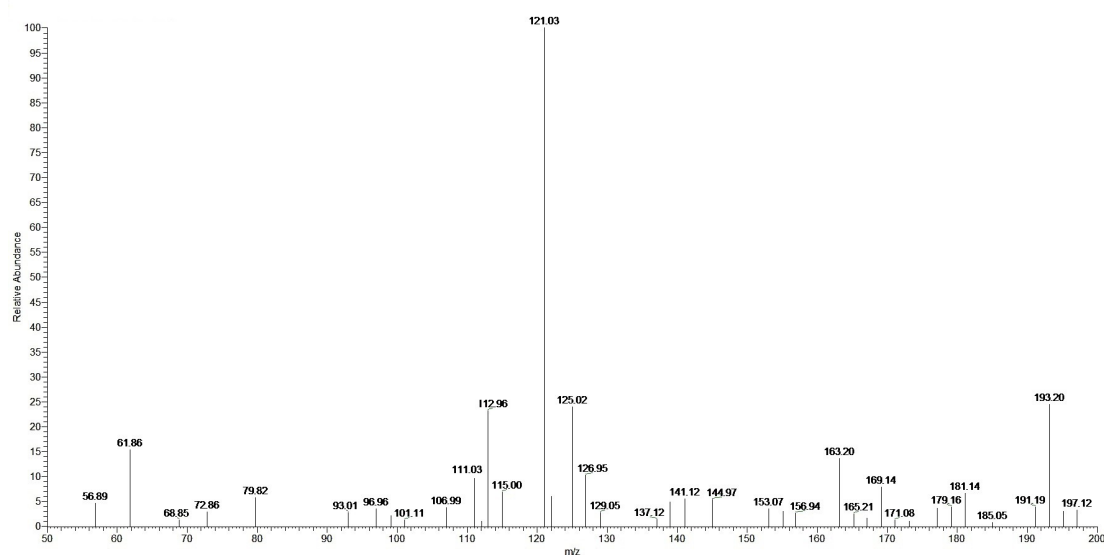


**Fig. S7** (a) Concentration-dependent absorbance around 505 nm and 509 nm of **1** and **2** in tetrahydrofuran. (b) VPO results of **1** in tetrahydrofuran.

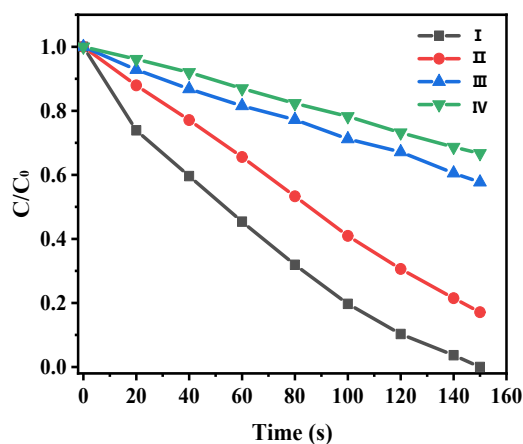




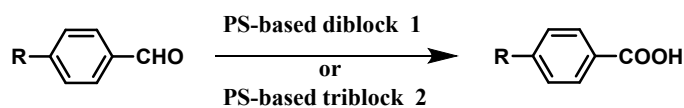
**Fig. S8** (a) Decay lifetime of **1** and **2** in aqueous solution (the excitation wavelength at 333 nm). (b) Temperature-dependent UV-vis spectrum of **1** in THF/H<sub>2</sub>O mixture (40% THF, v/v).



**Fig. S9** ESI-ITMS of benzaldehyde solution after photo-oxidation in the presence of **2**.



**Fig. S10** The detection of <sup>1</sup>O<sub>2</sub> generation by the degrading of ABDA indicator in the presence of **2** (I) and **1** (II) in aqueous solution, **2** (III) and **1** (IV) in tetrahydrofuran after irradiation (100 mW/cm<sup>2</sup>, white light), respectively; [photosensitizers] = 0.051 μmol, [ABDA] = 0.123 μmol.



Ps catalyst	Reactant	Time (min)	Conversion (%)
2		60	98
1		60	66
2		55	97
1		60	73

**Fig. S11** The comparable photo-oxidation of benzaldehyde derivatives with **1** and **2** in aqueous media (containing 1% THF). Conditions: [4-fluoro-benzaldehyde] = 0.0283 mmol; photosensitizers, [photosensitizers] = 0.051  $\mu$ mol. The conversion efficiency was measured by high-performance liquid chromatography.

#### Referecnces

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- [3] C. Lochenie, K. G. Wagner, M. Karg and B. Weber, *J. Mater. Chem. C*, 2015, **3**, 7925-7935.