

Supporting Information

**A cyanine dye based supramolecular photosensitizer enabling visible-light-driven organic reaction in water**

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## 1. Materials, Instruments, and Methods

### Materials and Instruments

**DiI-C18** and **DiI-C2** were purchased respectively from FUJIFILM Wako Pure Chemical Corporation (**DiI-C18**: 1,1'-Dioctadecyl-3,3,3',3'-tetramethylindocarbocyanine perchlorate; counter anion: perchlorate ion, product number: 041-33423) and Tokyo Chemical Industry (TCI) (**DiI-C2**: 1,1'-Diethyl-3,3,3',3'-tetramethylindocarbocyanine iodide; counter anion: iodide ion, product number: A2684). The chloroform solution of **DiI-C18** was subjected to short-pad column chromatography (silica gel) for purification. The solvent of the filtrate was removed under reduced pressure and the obtained **DiI-C18** solid was used for the experiments. All other commercial reagents were used as received. A 1.0 mM phosphate buffer solution was prepared by diluting a 0.1 M phosphate buffer solution (pH 7.4) purchased from Nacalai Tesque (product number: 37244-35) with water. Water was purified using a Milli-Q water system (Direct-Q 3UV, Millipore). UV-vis absorption and photoluminescence spectra were recorded on JASCO V-750 and JASCO FP-8500, respectively. DLS measurements were conducted using Malvern Panalytical Zetasizer Nano ZS. For TEM analysis, samples were deposited onto formvar support film-coated Cu grids that were subjected to hydrophilic treatment for 60 s using the JEOL HDT-400 device. To examine the photocatalytic activities of the samples toward **HITCI** (Sigma-Aldrich, product number: 252034-100MG), the samples were irradiated with an ASAHI SPECTRA MAX-301 Xe light source (300 W) with a light band-pass filter (520 nm, FWHM: 10 nm). Electron spin resonance (ESR) spectroscopy experiments were performed using 4-hydroxy-2,2,6,6-tetramethylpiperidine (TCI, product number: T0910) and CPH. HCl (Enzo, product number: ALX-430-078-M010) as a spin-trapping reagent for the detection of singlet oxygen and superoxide on a Bruker EMXmicro spectrometer, respectively. Cyclic voltammetry (CV) and second harmonic alternating current voltammograms (SHACVs) were performed on an electrochemical workstation (ALS630B, BAS) using a conventional three-electrode configuration. The device included a carbon working electrode, a Pt wire counter electrode, and an Ag/AgCl reference electrode. The electrolyte was an argon-purged water solution containing 0.1 M KCl.

### UV-vis and PL spectroscopies

The solution-state UV-vis absorption and photoluminescence spectra were respectively measured on a V-750 spectrometer (JASCO, Tokyo, Japan) and an FP-8500 fluorescence spectrometer (JASCO, Tokyo, Japan) using  $1.0 \times 1.0 \text{ cm}^2$  or  $0.2 \times 1.0 \text{ cm}^2$  cuvettes. The samples were prepared by diluting a 10 mM DMSO stock solution with DMSO or a 1.0 mM phosphate buffer solution (pH 7.4). The DMSO contents of all the samples were kept below 0.1 vol% except for the experiments using DMSO as a solvent. The spectra were recorded within 3 h of sample preparation at room temperature. The excitation wavelengths used in the PL spectroscopy are mentioned in the figure captions.

### **Phosphorescence spectroscopy**

A 5.0  $\mu\text{M}$  **DiI-C18** solution was frozen at 77 K and the phosphorescence spectrum was recorded using the FluoroMax-3 instrument (HORIBA). The excitation wavelength was 530 nm.

### **DLS measurements**

The sample solutions used for DLS measurements were prepared using the same method as that used for preparing the samples for UV-vis and PL spectroscopy. The sample solutions were then filtered through a PTFE membrane filter (pore size: 450 nm, ADVANTEC DISMIC-25JP) to remove contaminants that hinder DLS measurements. The samples were poured into plastic cuvettes, and DLS measurements were performed at room temperature at a scattering angle of  $90^\circ$  and a laser wavelength of 633 nm.

### **TEM observations**

The hydrophilic treatment of the formvar support film-coated Cu grid (*Cu 200* mesh covered with a formvar membrane, JEOL) was performed using a JEOL HDT-400 for 60 s. The sample solutions (50  $\mu\text{M}$ , 5.0  $\mu\text{L}$ ) were dropped onto the hydrophilic-treated formvar membrane-coated Cu grid on filter paper for rapid removal of solvent. The Cu grid were dried in *vacuo* for 12 h. The obtained samples were observed using a JEOL ARM200F instrument at an accelerating potential of 200 kV.

### **Examination of photocatalytic activity of rhodamine derivatives toward HITCI**

A **HITCI** stock solution in DMSO (10 mM, 1.5  $\mu\text{L}$ ) was added to the prepared sample solutions (3.0 mL) in  $1.0 \times 1.0 \text{ cm}^2$  cuvettes. The mixtures were then irradiated using a Xe lamp (300 W) with a band-pass filter (520 nm, FWHM: 10 nm) with continuous stirring to initiate the photoreaction. To monitor the course of the reaction, UV-vis spectra were recorded every 10 s for 60 s.

### **ESR experiments using spin-trapping reagents**

The prepared sample solutions ( $[\text{DiI-C2}] = [\text{DiI-C18}] = 30 \mu\text{M}$ ,  $[\text{4-OH-TEMP}] = 100 \text{ mM}$ ,  $[\text{CPH}] = 25 \text{ mM}$ ) were poured into quartz capillary tubes ( $\varphi$ : 2 mm, kk-agri) and irradiated with a Xe lamp for 3 min. The distance between the sample and the light source was 2.0 cm. After photoirradiation, the ESR spectra were immediately recorded with a center field of 3415 G, sweep width of 100 G, and microwave power of 1.0 mW at room temperature.

### **Low-temperature ESR measurement**

The prepared sample solution ( $[\text{DiI-C18}] = 50 \mu\text{M}$ ) was poured into quartz capillary tubes ( $\varphi = 4 \text{ mm}$ , NORELL). Then, the solution was cooled and frozen using liquid nitrogen and placed in the ESR cavity at 173 K. ESR measurements were conducted after photoirradiation with a Xe lamp (300 W, 3 min).

### **Redox potential measurements**

CV and SHACV were performed using a three-electrode setup in a 100  $\mu\text{M}$  KCl aqueous solution ( $[\text{DiI-C2}] = 50 \mu\text{M}$ ,  $[\text{DiI-C18}] = 10 \mu\text{M}$ ) in the potential range of at 50 and 4.0 mV/s, respectively, using a carbon working electrode, a platinum wire counter electrode, and an Ag/AgCl reference electrode.

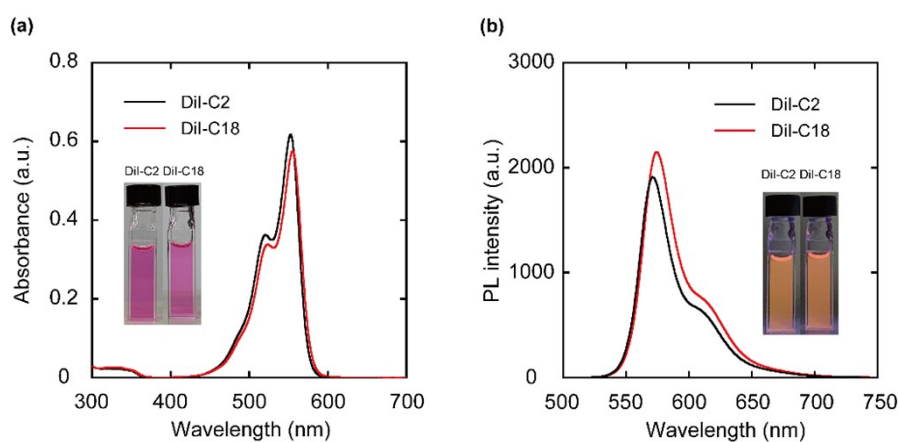
### **ns-TA spectra measurements**

Deaerated or oxygen-saturated 1.0 mM phosphate buffer solutions (pH 7.4) of **DiI-C2** and **DiI-C18** were placed in  $1.0 \times 1.0 \text{ cm}^2$  cuvettes (3.0 mL,  $[\text{DiI-C2}] = 10 \mu\text{M}$ ,  $[\text{DiI-C18}] = 30 \mu\text{M}$ ) and excited by a Nd:YAG laser (Continuum, SLII-10, 10 ns) at  $\lambda = 532 \text{ nm}$  with a power of 20 mJ per pulse. The output from the samples was recorded using a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). The transient spectra were recorded using fresh solutions for each laser excitation at 298 K.

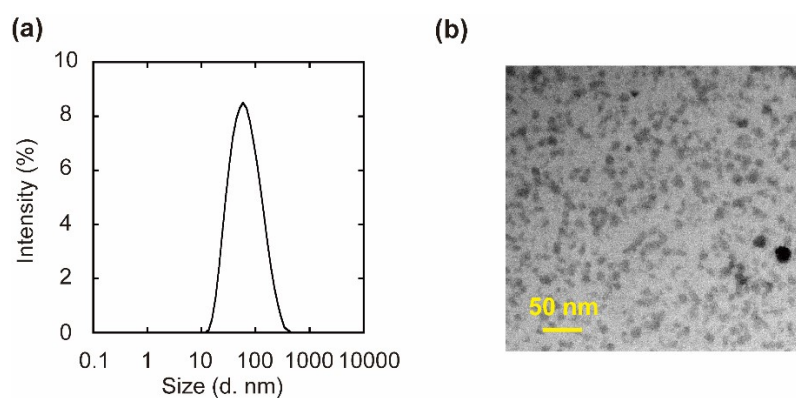
### **Photocatalytic reaction of hydrophobic aromatic compounds in water and the HPLC analyses**

The 1.0  $\mu\text{L}$  DMSO stock solutions of hydrophobic aromatic compounds (anthracene, 9,10-dimethylanthracene (**DMA**), 9,10-diphenylanthracene (**DPA**), and acenaphthylene, concentration: 10 mM), and 5.0  $\mu\text{L}$  **DiI-C2** or **DiI-C18** DMSO stock solution (10 mM) were poured into 1.0 mL aqueous solutions of **DiI-C2** or **DiI-C18** in sample tubes ( $[\text{DiI-C2}] = [\text{DiI-C18}] = 50 \mu\text{M}$ , [aromatic compounds] = 10  $\mu\text{M}$ ). After 20 min photoirradiation, acetonitrile (1.0 mL) was added to the samples, and the resultant solutions were subjected to reversed-phase HPLC analysis (column: Ascentis<sup>®</sup> C18, detection wavelength: 254 or 280 nm, eluent linear gradient; A:B = 60:40 to 100:0 for 40 min (anthracene), 80:20 to 100:0 for 20 min (**DMA**, **DPA**), 10:90 to 50:50 for 40 min, and 100:0 for 5 min (1-naphthol, 2-naphthol), A: acetonitrile, B: 10 mM ammonium acetate aqueous solution).

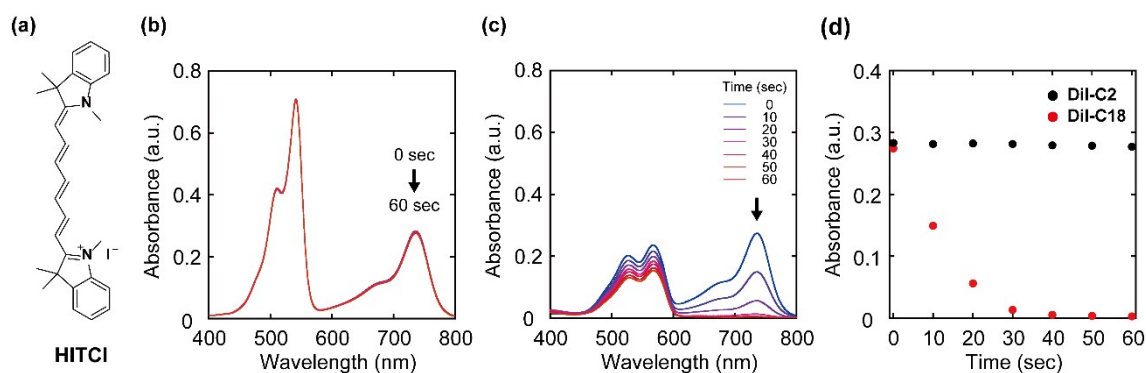
### 3. Supplementary Figures



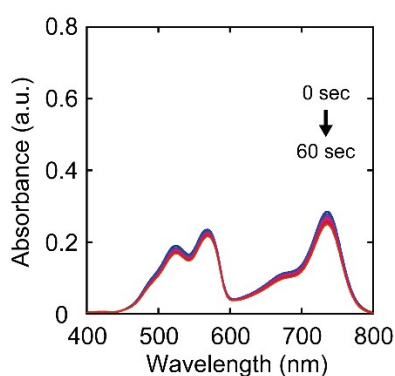
**Figure S1.** (a) UV-vis and (b) PL spectra of **DiI-C2** and **DiI-C18** in DMSO. Experimental conditions:  $[\text{DiI-C2}] = [\text{DiI-C18}] = 5.0 \mu\text{M}$ , rt, DMSO, Excitation wavelength: 500 nm. Insets: Optical photos of **DiI-C2** and **DiI-C18** in DMSO under (a) daylight and (b) UV light (365 nm).



**Figure S2.** (a) Size distributions of **DiI-C18** supramolecular assemblies determined by DLS (average particle diameter: 48 nm, polydispersity index: 0.315). (b) TEM image of **DiI-C18** supramolecular assemblies. Scale bar: 50 nm. (c,d) Experimental conditions:  $[\text{DiI-C18}] = 50 \mu\text{M}$ , rt, 1.0 mM phosphate buffer (pH 7.4).

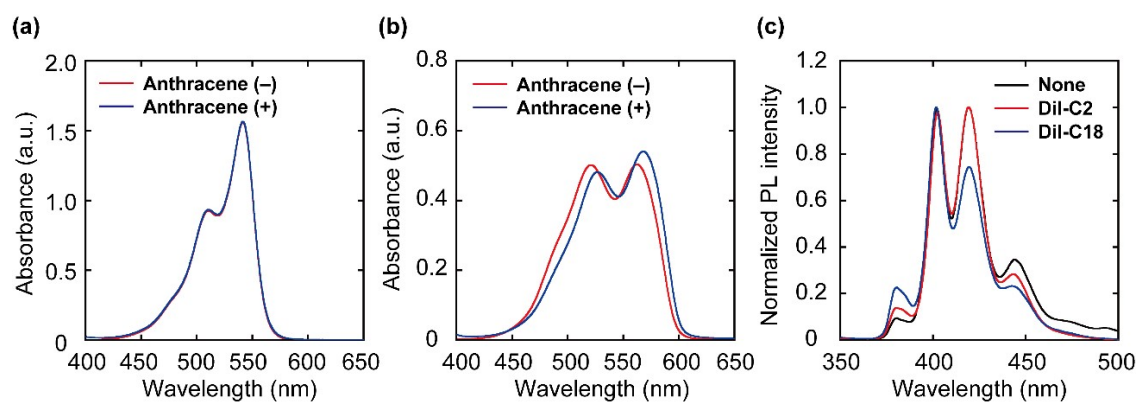
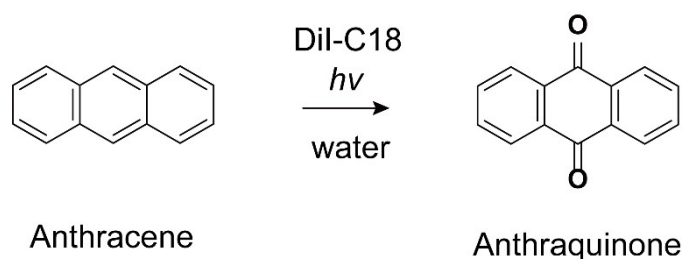


**Figure S3.** (a) Chemical structure of 1,1',3,3,3',3'-hexamethylindotricarbocyanine iodide (**HITCI**). (b,c) UV-vis spectra of a (b) **DiI-C2/HITCI** and (c) **DiI-C18/HITCI** mixtures during photoirradiation for 60 sec. (d) Time-courses of the absorbance ( $\lambda_{\text{abs}} = 735 \text{ nm}$ ) of **DiI-C2/HITCI** (black) and **DiI-C18/HITCI** (red) mixtures after photoirradiation. Experimental conditions:  $[\text{DiI-C2}] = [\text{DiI-C18}] = 5.0 \mu\text{M}$ ,  $[\text{HITCI}] = 2.5 \mu\text{M}$ , 1.0 mM phosphate buffer (pH 7.4), rt, irradiation wavelength: 520 nm (Xe lamp, 300 W, FWHM: 10 nm).

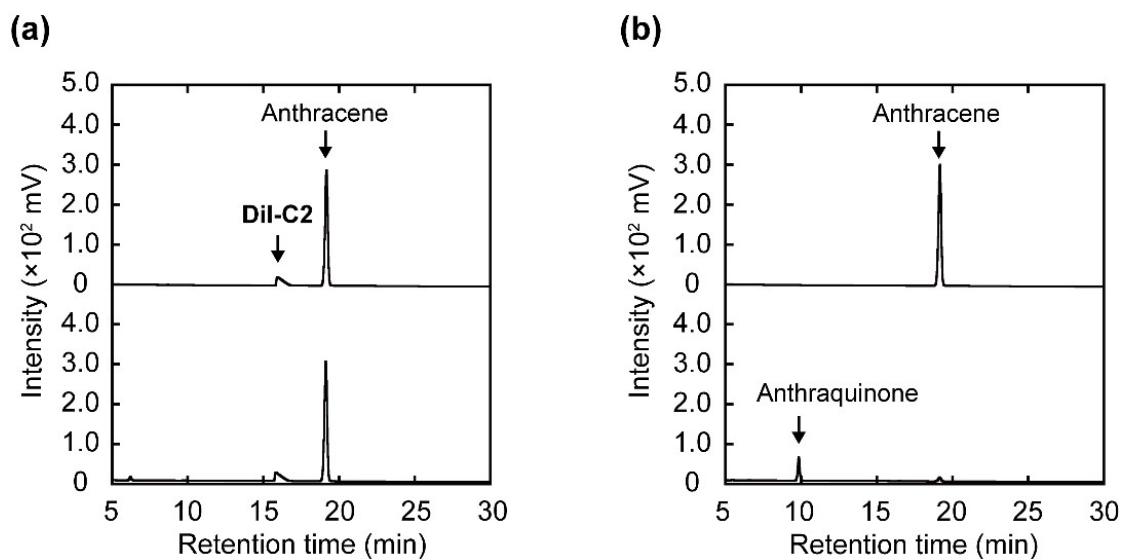


**Figure S4.** UV-vis spectra of a **DiI-C18/HITCI** mixture during photoirradiation for 60 sec under deaerated conditions. Experimental conditions:  $[\text{DiI-C2}] = [\text{DiI-C18}] = 5.0 \mu\text{M}$ ,  $[\text{HITCI}] = 2.5 \mu\text{M}$ , 1.0 mM phosphate buffer (pH 7.4), rt, Irradiation wavelength: 520 nm (Xe lamp, 300 W, FWHM: 10 nm).

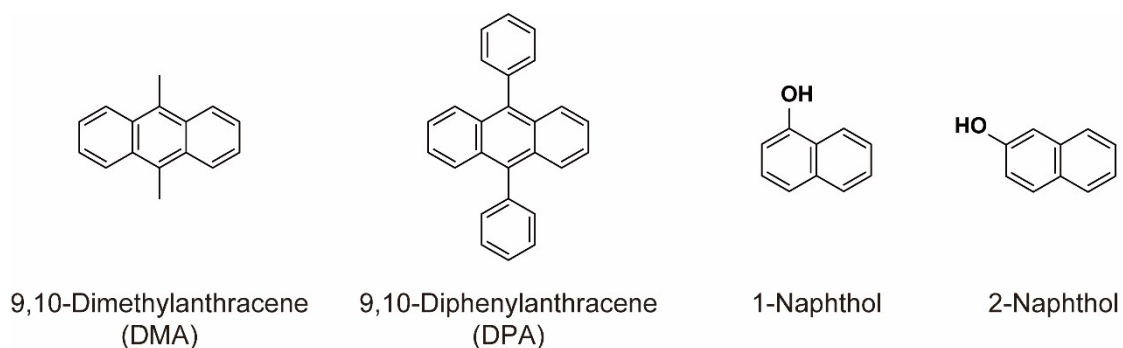
**Scheme S1.** Photo-oxidation of anthracene.



**Figure S5.** (a,b) UV-vis spectra of (a) **DiI-C2** and (b) **DiI-C18** with (blue) or without (red) anthracene. (c) PL spectra of anthracene with **DiI-C2** (red) and **DiI-C18** (blue) and no additive (black). Experiment conditions: [**DiI-C2**] = [**DiI-C18**] = 50  $\mu\text{M}$ , [Anthracene] = 10  $\mu\text{M}$ , 1.0 mM phosphate buffer (pH 7.4), rt. UV-vis spectra (optical pass length: 0.2 cm), PL spectra (excitation wavelength: 340 nm).

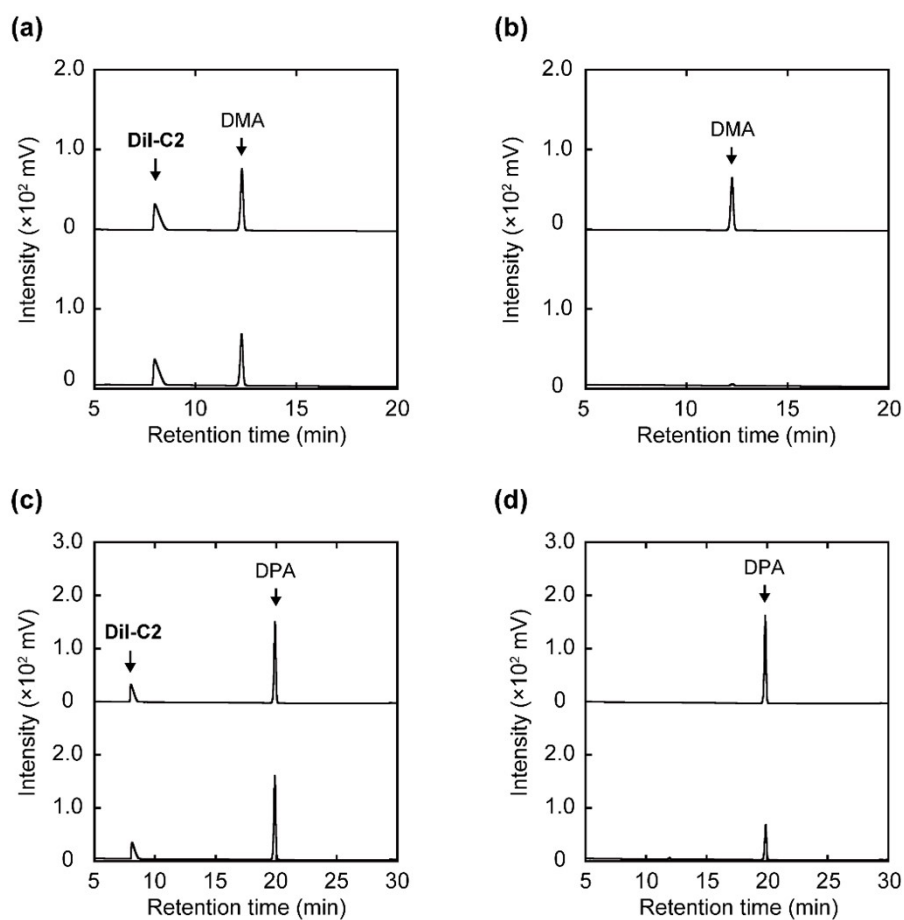


**Figure S6.** HPLC charts of anthracene mixtures with (a) **DiI-C2** and (b) **DiI-C18** before (upper) and after (lower) 20 min photoirradiation. Experiment conditions:  $[\text{DiI-C2}] = [\text{DiI-C18}] = 50 \mu\text{M}$ ,  $[\text{Anthracene}] = 10 \mu\text{M}$ , 1.0 mM phosphate buffer (pH 7.4), rt. Irradiation light: 520 nm (Xe lamp, 300 W, FWHM: 10 nm).

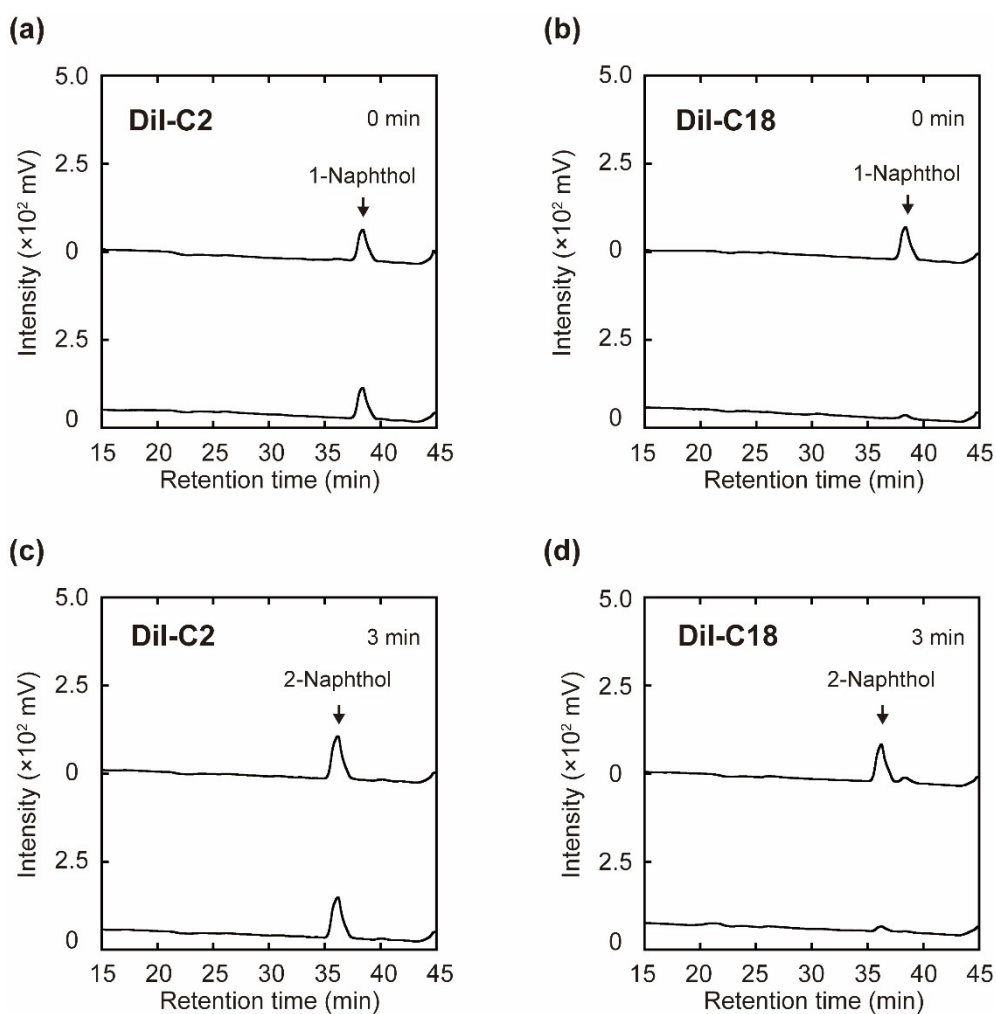


**Figure S7.** Chemical structures of hydrophobic aromatic compounds (9,10-Dimethylantracene (**DMA**), 9,10-Diphenylantracene (**DPA**), 1-Naphthol, and 2-Naphthol) employed in this work.

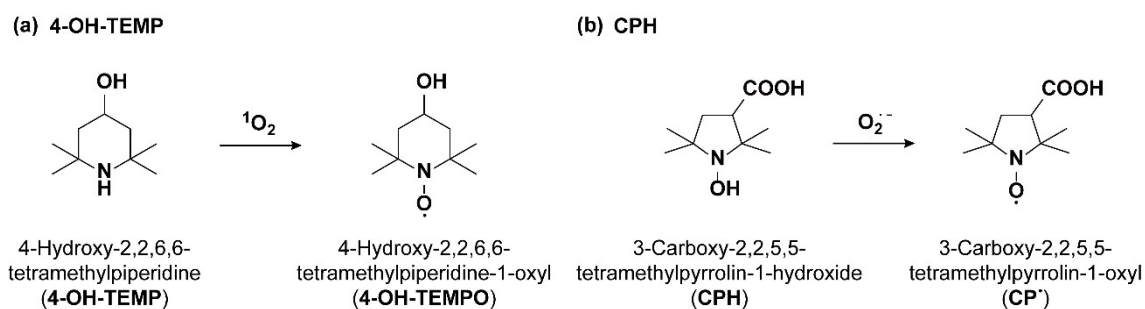




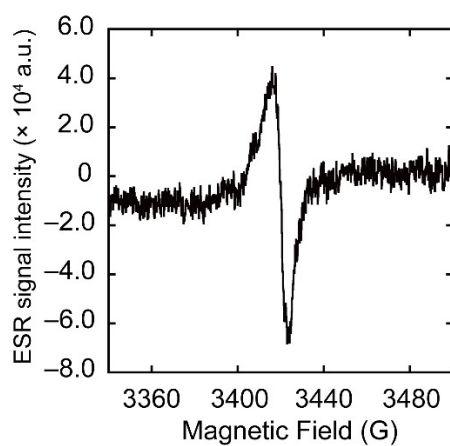
**Figure S8.** HPLC charts of (a,c) **DiI-C2** and (b,d) **DiI-C18** mixtures with (a,b) **DMA**, (c,d) **DPA** before (upper) and after (lower) 20 min photoirradiation. Experiment conditions:  $[\text{DiI-C2}] = [\text{DiI-C18}] = 50 \mu\text{M}$ ,  $[\text{DMA}] = [\text{DPA}] = 10 \mu\text{M}$ , 1.0 mM phosphate buffer (pH 7.4), rt. Irradiation light: 520 nm (Xe lamp, 300 W, FWHM: 10 nm).



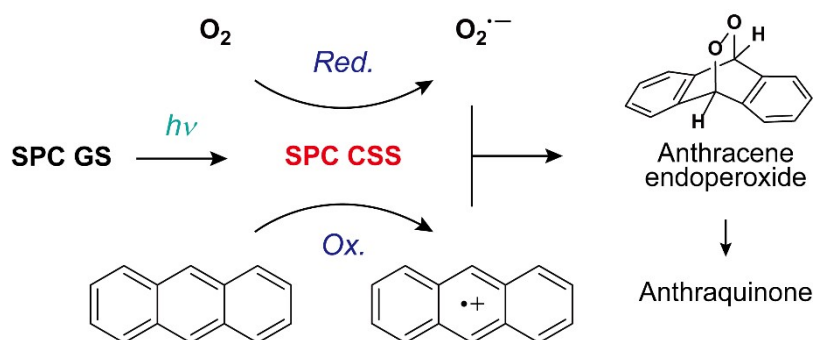
**Figure S9.** HPLC charts of (a,c) **DiI-C2** and (b,d) **DiI-C18** mixtures with (a,b) 1-Naphthol, (c,d) 2-Naphthol, before (upper) and after (lower) 20 min photoirradiation. Experiment conditions: [**DiI-C2**] = [**DiI-C18**] = 50  $\mu$ M, [1-naphthol] = [2-naphthol] = 10  $\mu$ M, 1.0 mM phosphate buffer (pH 7.4), rt. Irradiation light: 520 nm (Xe lamp, 300 W, FWHM: 10 nm).



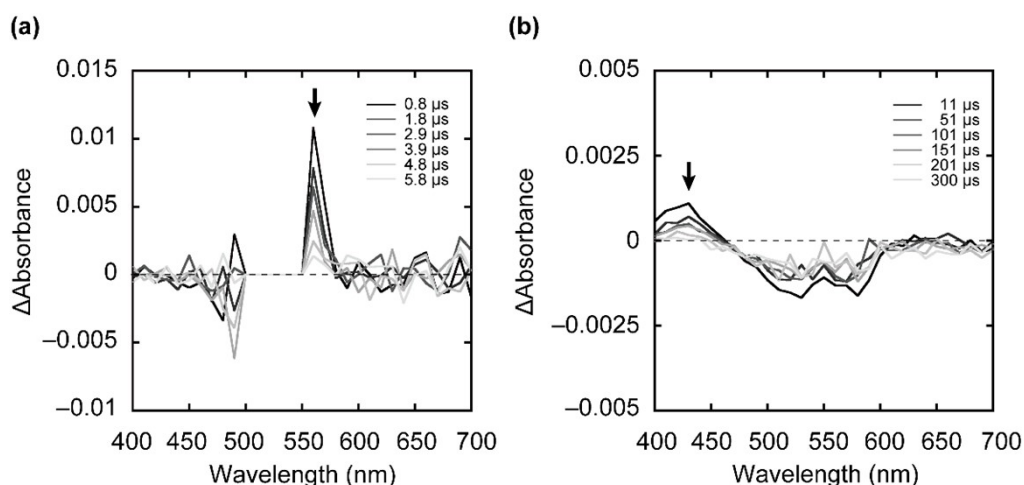
**Figure S10.** (a,b) Chemical structures of (a) 4-OH-TEMP and (b) CPH, and the reactions with singlet oxygen and superoxide, respectively.



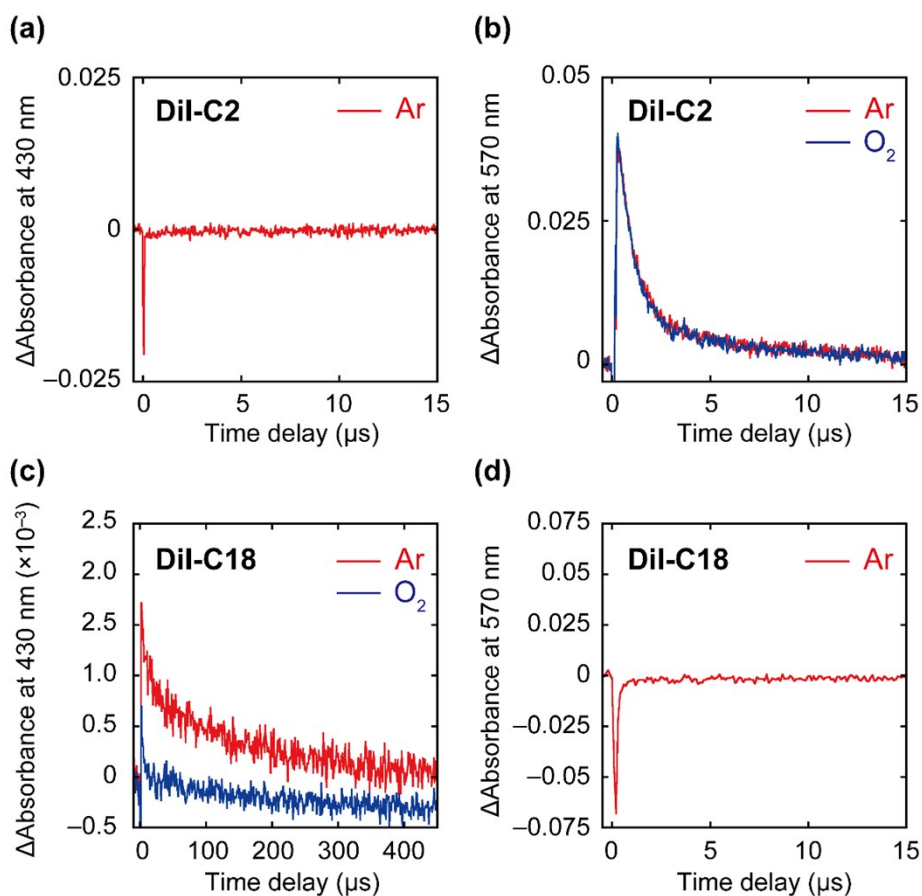
**Figure S11.** ESR signal of photo-irradiated **DiI-C18** supramolecular assembly. Experimental conditions: [**DiI-C18**] = 50  $\mu\text{M}$ , solvent: 1.0 mM phosphate buffer (pH 7.4), 173 K, Photoirradiation: Xe lamp, 300 W, 3 min.



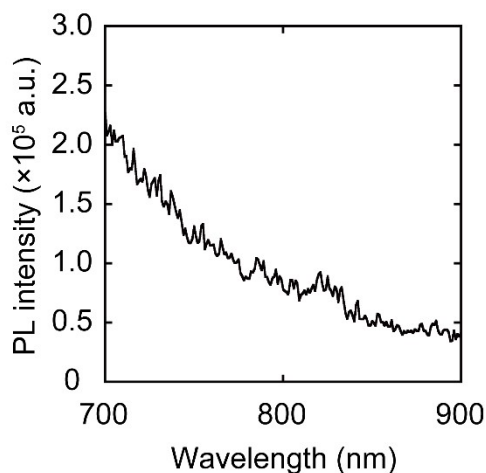
**Figure S12.** Assumed reaction mechanism of photocatalytic oxidation of anthracene using **DiI-C18** in water. GS: ground state, CSS: charge separated state.



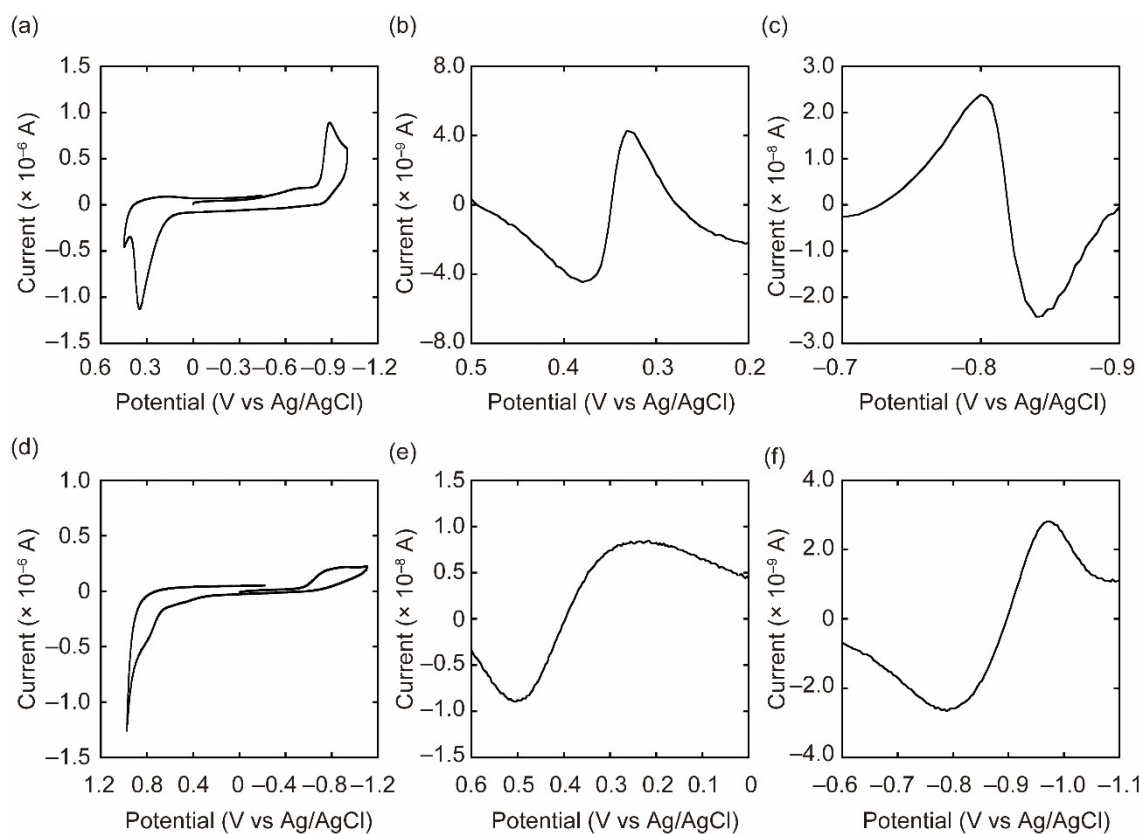
**Figure S13.** Transient absorption spectra of (a) **DiI-C2** and (b) **DiI-C18** excited at 532 nm with 10 ns laser pulses, respectively. Experimental conditions: [**DiI-C2**] = 10  $\mu$ M, [**DiI-C18**] = 30  $\mu$ M, 1.0 mM phosphate buffer (pH 7.4), rt, Argon atmosphere.



**Figure S14.** Transient absorption (TA) decay profiles of (a,b) **DiI-C2** and (c,d) **DiI-C18** at (a,c) 430 and (b,d) 570 nm. Red and blue lines are TA decay profiles under Ar and O<sub>2</sub> atmospheres, respectively. Experimental conditions: [**DiI-C2**] = 10  $\mu$ M, [**DiI-C18**] = 30  $\mu$ M, 1.0 mM phosphate buffer solution (pH 7.4), rt. Excitation light: 532 nm (10 ns).



**Figure S15.** Phosphorescence spectrum of **DiI-C18**. Experiment conditions: [**DiI-C18**] = 5.0  $\mu$ M, solvent: 1.0 mM phosphate buffer (pH 7.4), 77 K, excitation wavelength: 530 nm.



**Figure S16.** (a,d) Cyclic voltammogram (CV) and (b,c,e,f) second harmonic alternating current voltammogram (SHACV) of (a-c) **DiI-C2** and (d-f) **DiI-C18**. Experiment conditions: [**DiI-C2**] = 50  $\mu$ M, [**DiI-C18**] = 10  $\mu$ M, [KCl] = 100  $\mu$ M, water, rt.

**Table S1.** Estimated optical and electrochemical properties of **DiI-C2** and **DiI-C18** (supramolecular assembly) in water.

Compound	$E_{\text{ox}}(\text{DiI}^{\bullet 2+}/\text{DiI}^+)$ (V vs SHE)	$E_{\text{red}}(\text{DiI}^+/\text{DiI}^{\bullet})$ (V vs SHE)	$E_{\text{ox}}(\text{DiI}^{\bullet 2+}/\text{DiI}^{\bullet*})$ (V vs SHE)	$E_{\text{red}}(\text{DiI}^{\bullet*}/\text{DiI}^{\bullet})$ (V vs SHE)	$S_1$ (eV)	$T_1$ (eV)	$\Delta E_{\text{es}}$ (eV)
<b>DiI-C2</b>	+0.35	-0.82	-2.55	+1.38	2.20	-	1.17
<b>DiI-C18</b>	+0.40	-0.90	-2.43	+1.13	2.03	1.51	1.30