

## The Photodimerization Characteristics of Anthracene Pendants within Amphiphilic Polymer Micelles in Aqueous Solution

### Supporting Information

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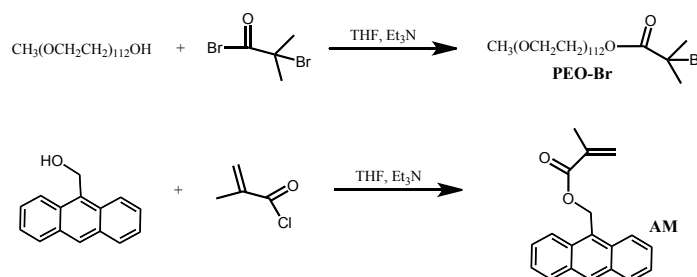
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### Experimental Details

#### Materials

Dioxane and THF were purified by distillation from sodium with benzophenone. Catalyst Cu(I)Br was washed repeatedly with acetic acid and ether, then dried and stored under nitrogen. 2-Bromo-2-methylpropionyl bromide, methylacryloyl chloride, 1-pyrenemethanol, *N, N, N', N', N''*-pentamethyldiethylenetriamine (PMDETA) and triethylamine were purchased from Aladdin and used without further purification. DMF received was of spectroscopic grade and used for optical experiments. Ultrapure water for this study was prepared using a FDY-1002-UV-P purification system. Poly(ethylene glycol) methyl ether with number-average molecular weight about 5000 g/mol (from Aldrich) were used to prepare poly(ethylene oxide) (PEO) macroinitiator.<sup>1</sup> The anthracene methyl methacrylate (AM) was synthesized by esterification reaction.<sup>2</sup>



#### Methods

**<sup>1</sup>H-NMR** (400 MHz) spectra were investigated by a Bruker spectrometer with CDCl<sub>3</sub> as solvent.

**GPC** was performed using a Waters system equipped with a refractive index and a photodiode array detector; with THF as eluent (0.5 mL/min) and polystyrene standards used for calibration.

**FTIR spectra** were measured with a Nicolet Avatar 360 spectrometer at frequencies ranging from 4000 to 400 cm<sup>-1</sup> adopting KBr compression method.

**Fluorescence spectra** were recorded on a PTI fluorescence master system. All spectra were taken at room temperature with an integration time of 0.1 s. The slit width was set at 4 nm for excitation and 3 nm for emission, respectively. Emission spectra were obtained from 380 to 680 nm with excitation at 353 nm.

**Absorbance spectra** at room temperature were collected on UV-6100S spectrophotometer (Shanghai Meipuda Instrument Co., Ltd.).

**Dynamic light scattering (DLS) measurements** were performed with a Malvern Nano-ZS90 instrument (Malvern, U.K.). Samples were sealed in quartz cells, which were soaked overnight in refluxed acetone and thoroughly cleaned with ultrapure water. Measurements were taken three times at 25 °C in order to check their reproducibility.

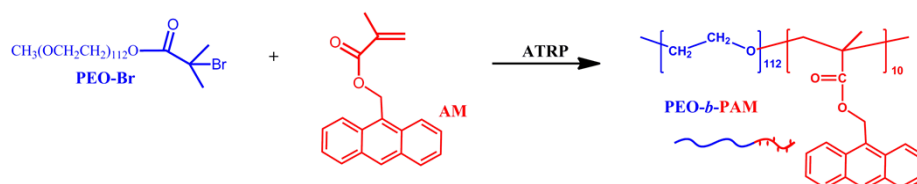
**AFM** images of assemblies were obtained using a CSPM5500A scanning probe microscope system (Beijing Benyuan Nanometer Instrument Co., Ltd.). The samples were prepared by dropping the solution of micelles (0.015 mg/mL) onto mica sheet, and dried at room temperature overnight. The surface morphologies of samples were acquired in tapping mode.

**The light irradiation** experiments of anthracene pendants in polymer micelle was carried out by an adjustable double grating monochromator of Omni-λ1805i equipped with a broadband laser-driven light source of EQ-1500

LDLST<sup>TM</sup> and a set of six optical filters, which can afford narrow band wavelength of light between 250-950 nm intervals. The wavelength of light range from 100-600 nm and 550-1000 nm were generated by grating one and grating two, respectively. And the different optical filter was applied to the selected narrow band of light in order to eliminate the influence of other stray light.

Filter type	wavelength rage (nm)	Transmission performance (%)
No filter	190-1500	100
ZJB280	350-440	89.5
ZJB360	440-650	87
CB550	650-800	88.7
HB720	800-1100	80
HWB3	>1100	75

### Polymer synthesis

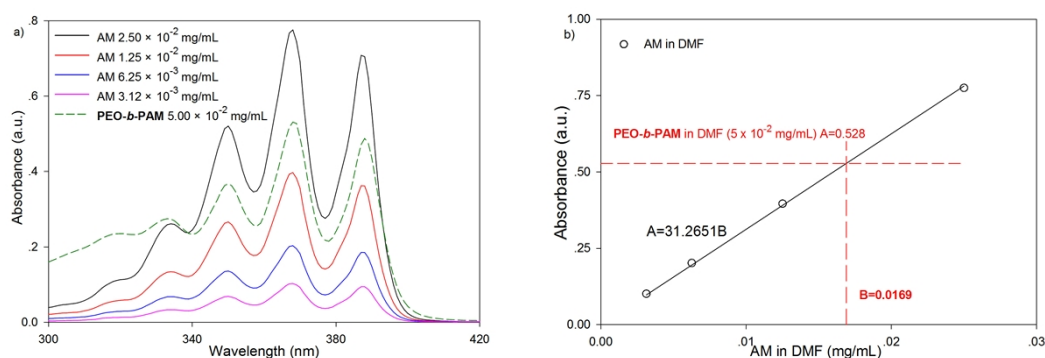


In the polymerization, PEO-Br macroinitiator (3 g, 0.6 mmol), AM (2.99 g, 10.8 mmol), CuBr (0.1735 g, 1.2 mmol), PMDETA (0.2168 g, 1.2 mmol) and dioxane (10 mL) were quickly added into a 25 mL ampoule. Then, the mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the ampoule was placed in a preheated oil bath (95 °C) for 30 h. The solution was passed through a neutral Al<sub>2</sub>O<sub>3</sub> column with chloroform as eluent to remove the catalyst. The amphiphilic polymer was collected by precipitation twice into diethyl ether. The pale yellow white powder was dried under vacuum at 30 °C to constant weight. Yield: 70%. Mn=7.80×10<sup>3</sup> g/mol. Mw/Mn=1.20 (GPC).

The composition of the polymer was also analyzed according to the calibration curve of the anthracene in DMF.

### Calibration curve of the anthracene pendants

A standard solution of AM in DMF was prepared at the concentration of 0.1 mg/mL. Then, the solution was diluted to 1.00×10<sup>-1</sup>, 5.00×10<sup>-2</sup>, 2.50×10<sup>-2</sup>, 1.25×10<sup>-2</sup>, 6.25×10<sup>-3</sup> and 3.125×10<sup>-3</sup> mg/mL with DMF and scanned by the UV-vis instrument. And polymer was also dissolved in DMF (5.00×10<sup>-2</sup> mg/mL) and checked by UV-vis instrument.



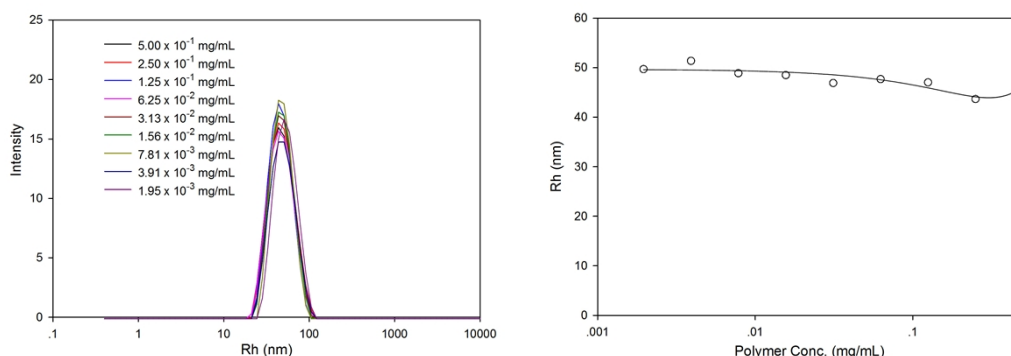
S1. a) UV spectra of AM and polymer in DMF. b) The standard line of AM fit according to absorbance intensities at 368 nm and the estimated anthracene content in **PEO-*b*-PAM**.

As shown in S1, AM show a series of vibrationally spaced absorption structures at 317, 334, 350, 368 and 388 nm (finger like absorption bands), and the absorbance intensity at 368 nm displayed a good linearity in the DMF (S2), resulted in a standard line of  $A = 31.2651B$  and the estimation of 10 units of anthracene pendants in **PEG-*b*-PAM** and the average Mn of 7.77×10<sup>3</sup> g/mol.

### ***Preparation of amphiphilic polymer micelle.***

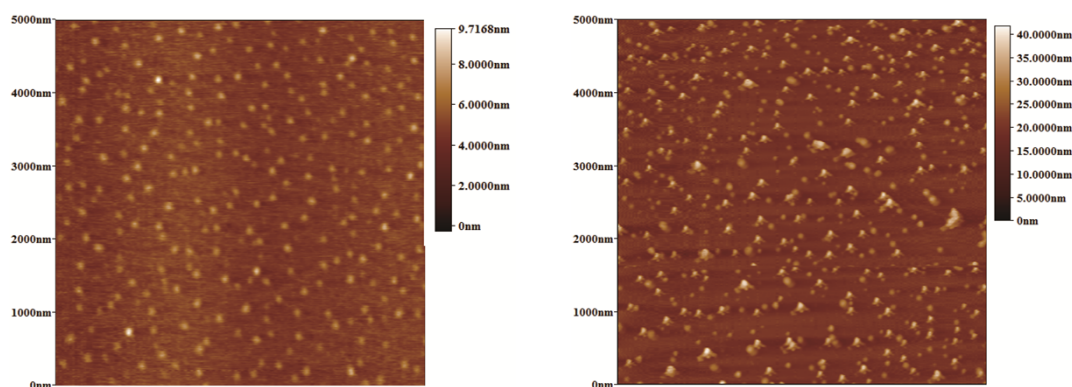
The polymer micelle in aqueous solution was expected to be composed of confined micellar core with high concentration of anthracene pendants. The micelle was prepared by dropwisely adding ultrapure water to the homogeneous DMF solution of **PEG-*b*-PAM** (5.0 mg/mL×10 mL) at 25 °C under vigorous stirring. When the water content reached 70%, the mixed solution was stirred for 12 h. Then, the micellar solution was dialyzed against ultrapure water (Spectrum, MW cutoff 3,500) while stirring for three days; water was frequently refreshed (every 2 h during day time). Finally, the amphiphilic polymer micelle was diluted to 1.0 mg/mL.

### ***Determination of critical micelle concentration***



**S2.** Size distributions of **PEO-*b*-PAM** in aqueous solution (left) and the average size dependence as a function of concentration (right).

A series of micelle solutions ranging from 0.5 mg/mL to  $1 \times 10^{-4}$  mg/mL was measured by fluorescence spectroscopy and dynamic light scattering. The setup temperature was kept at 25 °C. The DLS examinations (S2) show narrow size distributions around 50 nm above  $2.00 \times 10^{-3}$  mg/mL and no effective size distributions were found below this concentration. Which is very consistent with the CMC value obtained by FL analysis. The nanostructures of polymer micelles before and after photodimerization were also visualized by AFM images with uniformly spherical micelles.



**S3.** AFM images for polymer micelles before (left) and after light irradiation (right).

### ***Selected narrow band light irradiations in the UV-Vis-NIR region***

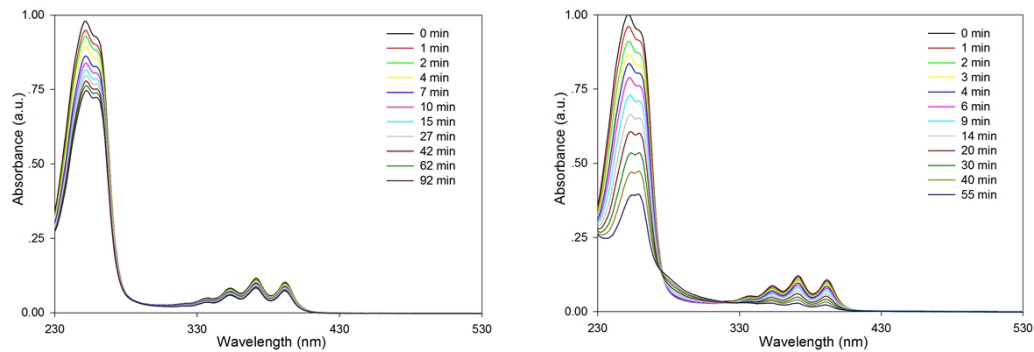
In order to better understand the photodimerization kinetics dependency of irradiation conditions, according to the characteristic absorbance bands of anthracene pendants in aqueous solution, six narrow band UV light of 261, 300, 338, 353, 371 and  $392 \pm 5$  nm and four Vis-NIR light of 416, 550, 700 and  $900 \pm 5$  nm were chosen as the irradiation light. The polymer micelles ( $0.015$  mg/mL×1 mL) were sealed in the fluorescence cuvette and irradiated directly by selected narrow band of light derived from the monochromator with the optical filter of each and in-situ traced with UV-vis instrument. The illumination intensities at the cuvette surface were measured by a CEL-NP 2000 optical power meter.

And because of its linear degradation and higher signal-to-noise ratio, the absorption band intensity at 371 nm was

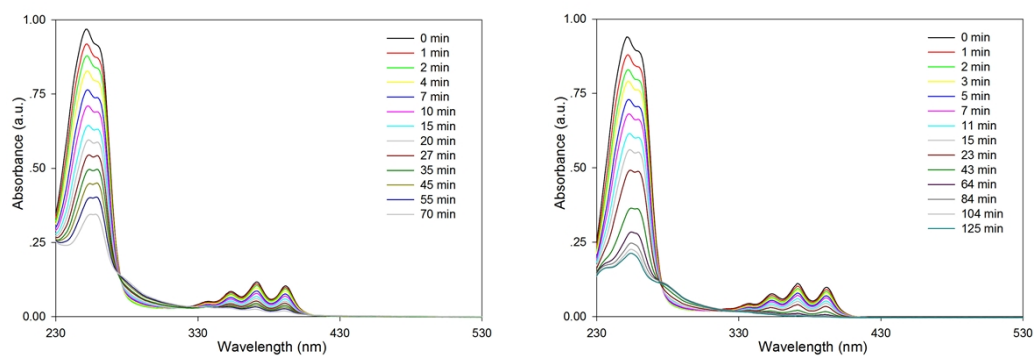
used as the baseline to measure the time-dependent photodimerization changes, resulting in the definition of photodimerization degree (PD) by comparing the peak absorption at 371 nm. The time-dependant PD values for anthracene pendants upon those narrow band light irradiations are fit reasonably with a biexponential equation:

$$PD(t) = X_1(1 - e^{-k_1 t}) + X_2(1 - e^{-k_2 t}) \quad (1)$$

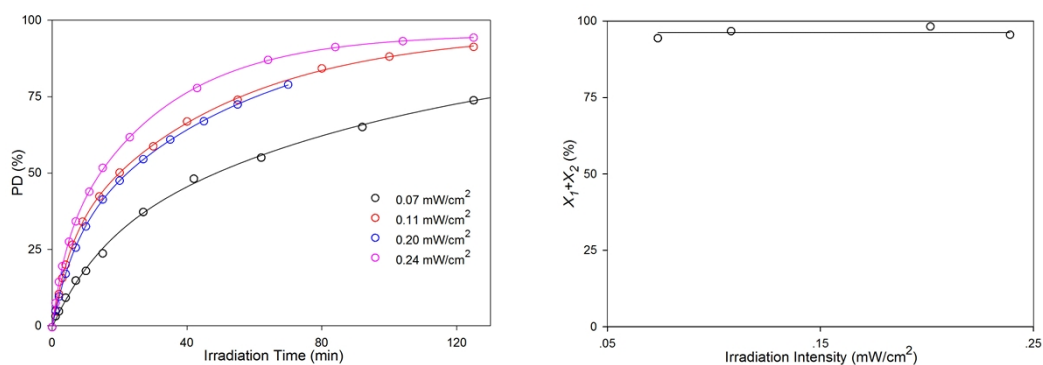
where  $PD(t)$  corresponds to the time-dependent photodimerization degree,  $k_1$  and  $k_2$  are rate constants,  $X_1$  and  $X_2$  are the relative weighting fractions. And the sum of  $X_1$  and  $X_2$  were used to determine the maximum photodimerization extent ( $PD_{max}$ ) that the anthracene pendants could reach after long enough irradiation time.



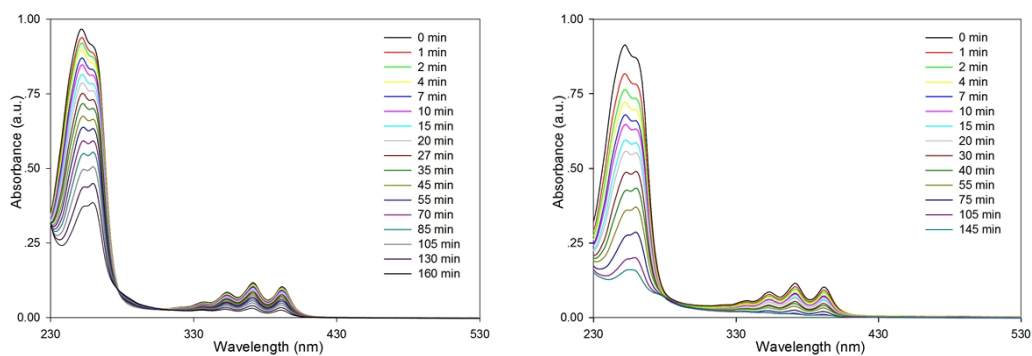
**S4.** UV-vis spectra changes anthracene pendants upon  $261 \pm 5$  nm light irradiation (left for  $0.07 \text{ mW/cm}^2$ , right for  $0.11 \text{ mW/cm}^2$ ).



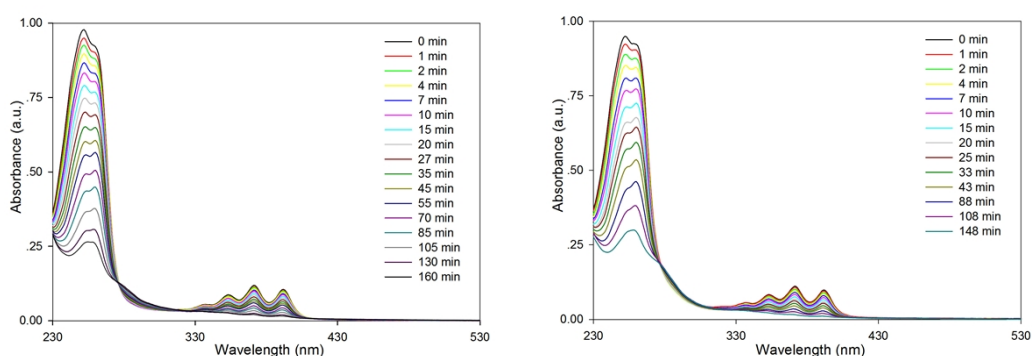
**S5.** UV-vis spectra changes of anthracene pendants upon  $261 \pm 5$  nm light irradiation (left for  $0.20 \text{ mW/cm}^2$ , right for  $0.24 \text{ mW/cm}^2$ ).



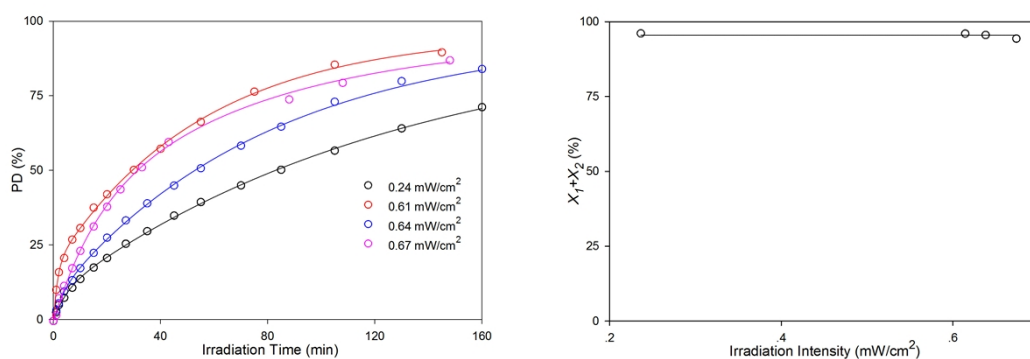
**S6.** Left: the time-dependent PD of anthracenes upon  $261 \pm 5$  nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1 + X_2$  values.



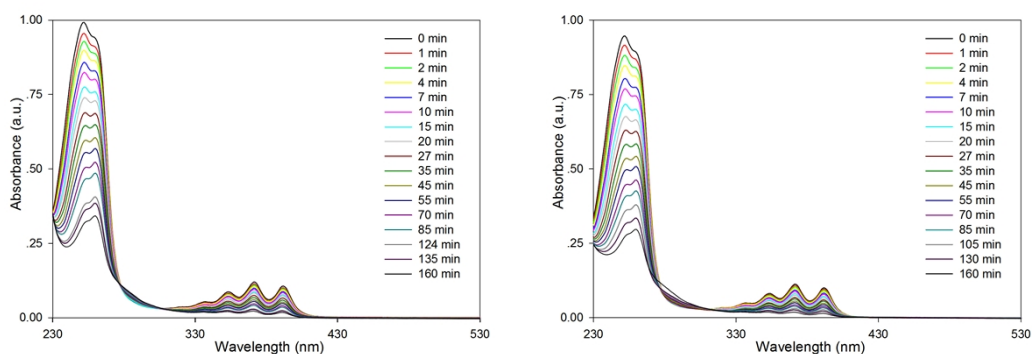
**S7.** UV-vis spectra changes of anthracene pendants upon 300±5 nm light irradiation (left for 0.24 mW/cm<sup>2</sup>, right for 0.61 mW/cm<sup>2</sup>).



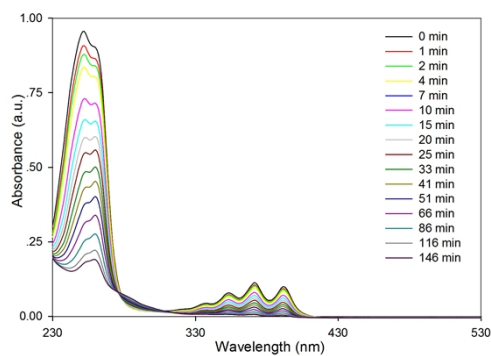
**S8.** UV-vis spectra changes of anthracene pendants upon 300±5 nm light irradiation (left for 0.64 mW/cm<sup>2</sup>, right for 0.67 mW/cm<sup>2</sup>).



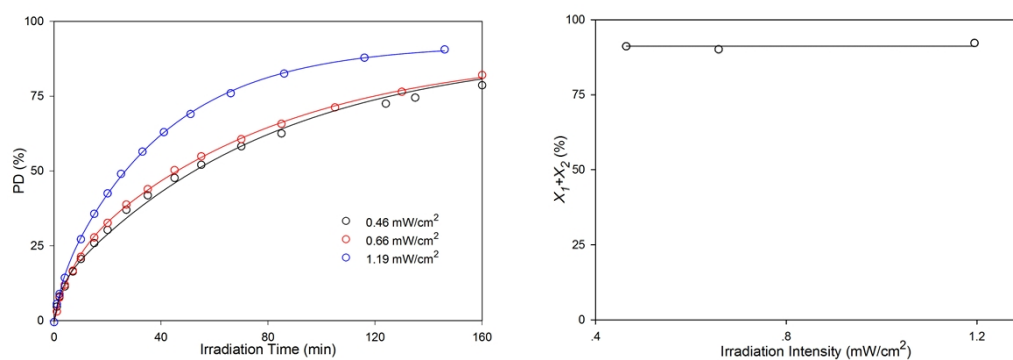
**S9.** Left: the time-dependent PD of anthracenes upon 300±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.



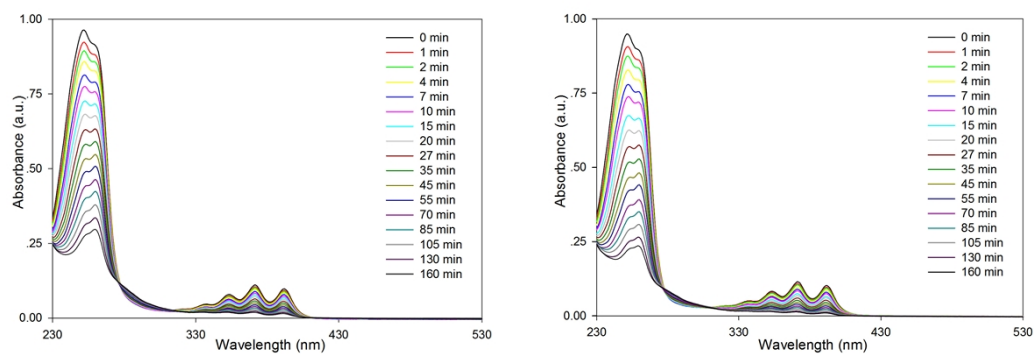
**S10.** UV-vis spectra changes of anthracene pendants upon 338±5 nm light irradiation (left for 0.46 mW/cm<sup>2</sup>, right for 0.66 mW/cm<sup>2</sup>).



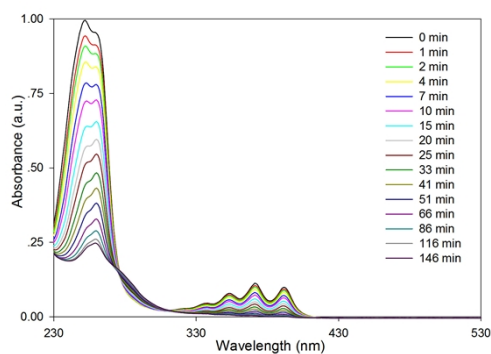
**S11.** UV-vis spectra changes of anthracene pendants upon  $338\pm 5$  nm light irradiation ( $1.19 \text{ mW/cm}^2$ ).



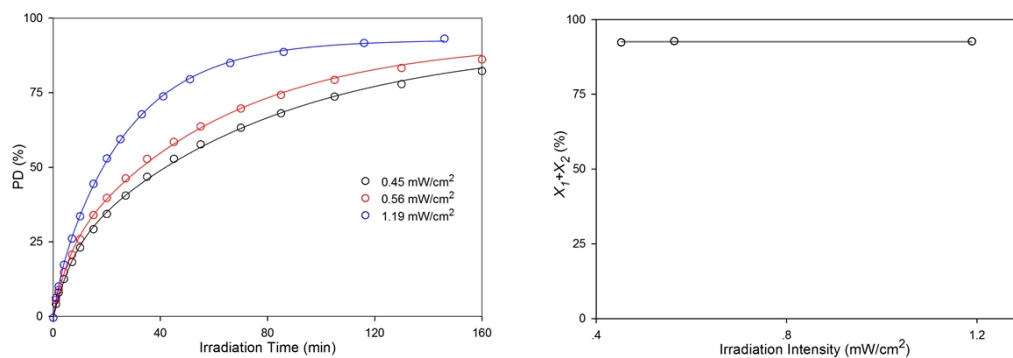
**S12.** Left: the time-dependent PD of anthracenes upon  $338\pm 5$  nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.



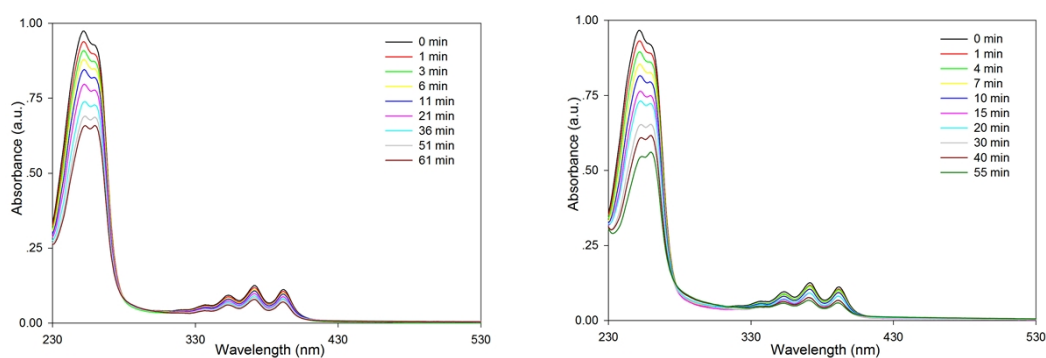
**S13.** UV-vis spectra changes of anthracene pendants upon  $353\pm 5$  nm light irradiation (left for  $0.45 \text{ mW/cm}^2$ , right for  $0.56 \text{ mW/cm}^2$ ).



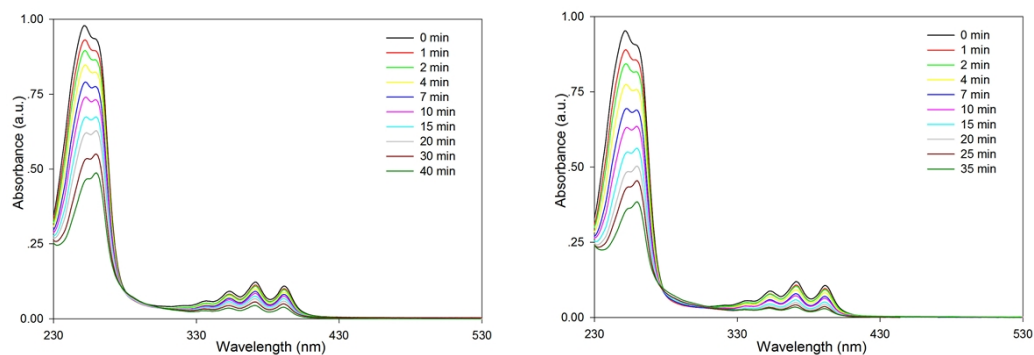
**S14.** UV-vis spectra changes of anthracene pendants upon  $353\pm 5$  nm light irradiation ( $1.19 \text{ mW/cm}^2$ ).



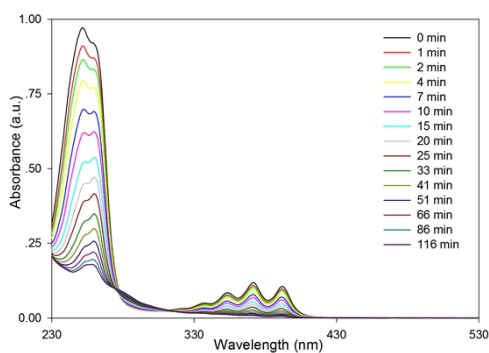
**S15.** Left: the time-dependent PD of anthracenes upon  $353 \pm 5$  nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1 + X_2$  values.



**S16.** UV-vis spectra changes of anthracene pendants upon  $371 \pm 5$  nm light irradiation (left for 0.13 mW/cm², right for 0.25 mW/cm²).

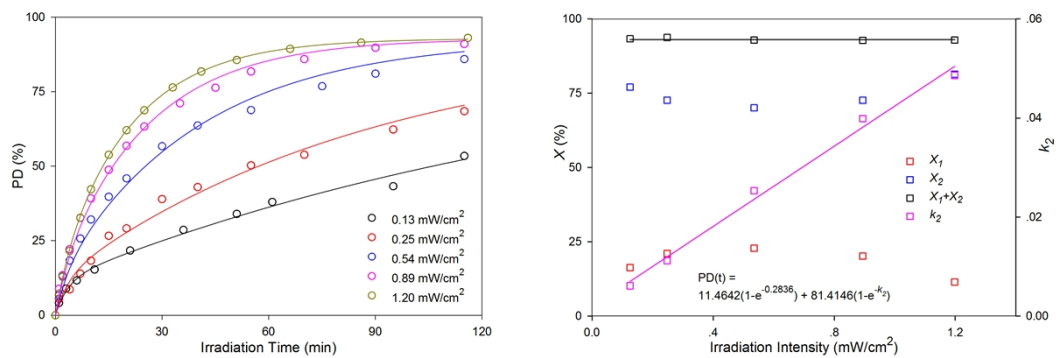


**S17.** UV-vis spectra changes of anthracene pendants upon  $371 \pm 5$  nm light irradiation (left for 0.54 mW/cm², right for 0.89 mW/cm²).

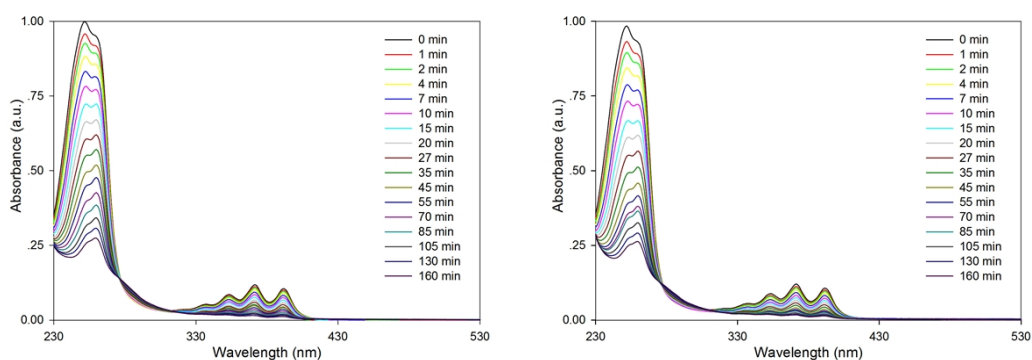


**S18.** UV-vis spectra changes of anthracene pendants upon  $371 \pm 5$  nm light irradiation (1.20 mW/cm²).

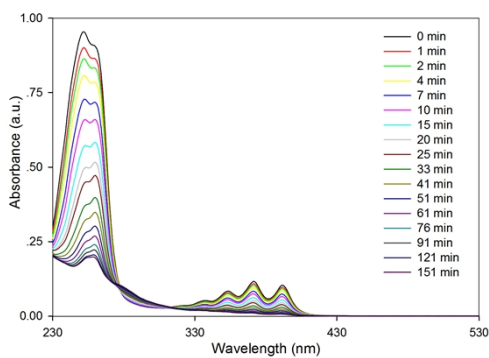




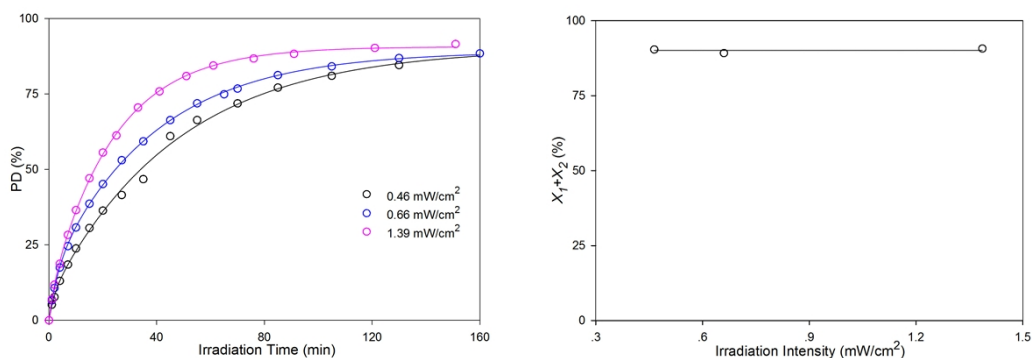
**S19.** Left: the time-dependent PD of anthracenes upon 371±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.



**S20.** UV-vis spectra changes of anthracene pendants upon 392±5 nm light irradiation (left for 0.46 mW/cm², right for 0.66 mW/cm²).

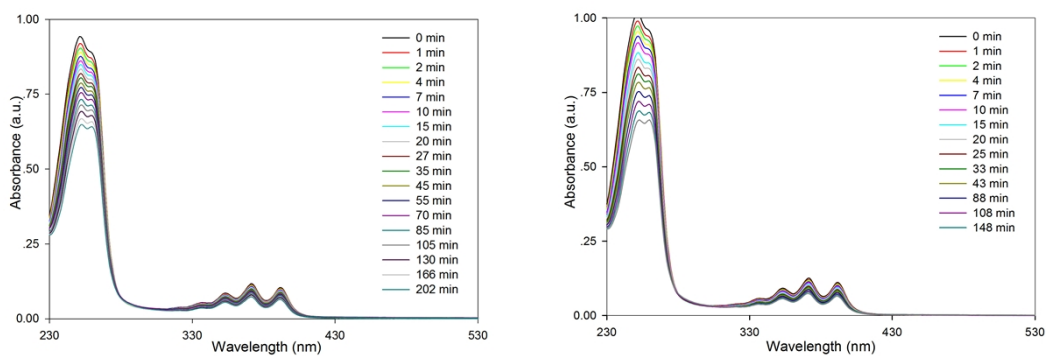


**S21.** UV-vis spectra changes of anthracene pendants upon 392±5 nm light irradiation (1.39 mW/cm²).

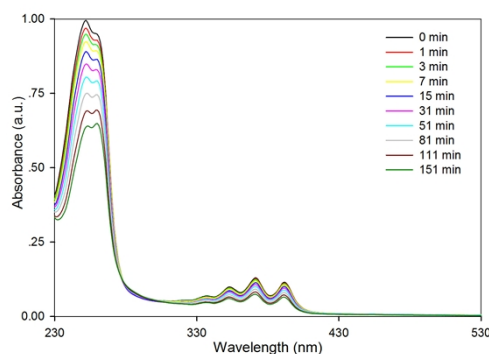


**S22.** Left: the time-dependent PD of anthracenes upon 392±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.

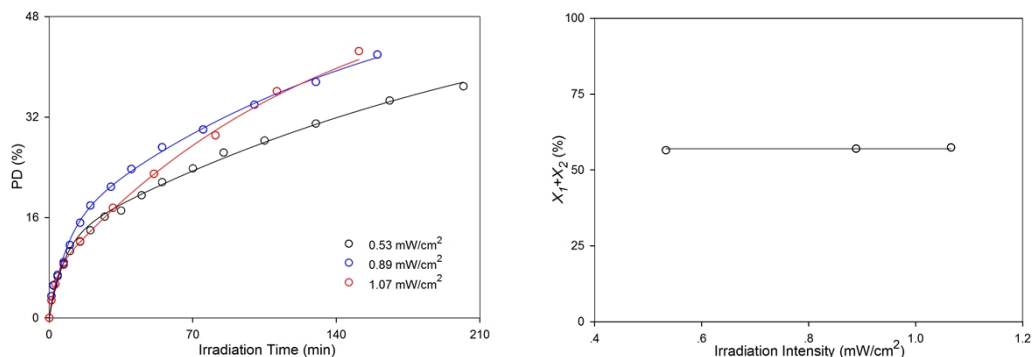




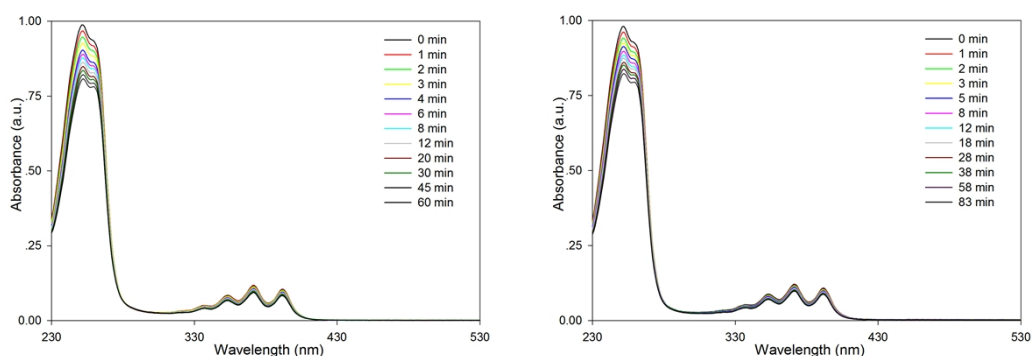
**S23.** UV-vis spectra changes of anthracene pendants upon 416±5 nm light irradiation (left for 0.53 mW/cm<sup>2</sup>, right for 0.89 mW/cm<sup>2</sup>).



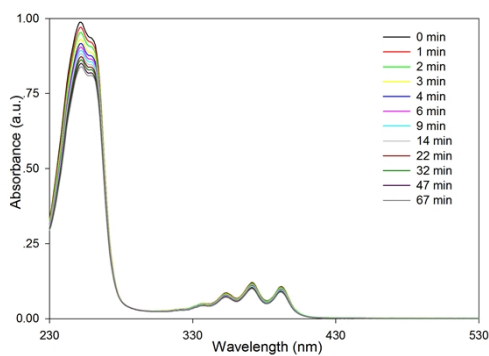
**S24.** UV-vis spectra changes of anthracene pendants upon 416±5 nm light irradiation (1.07 mW/cm<sup>2</sup>).



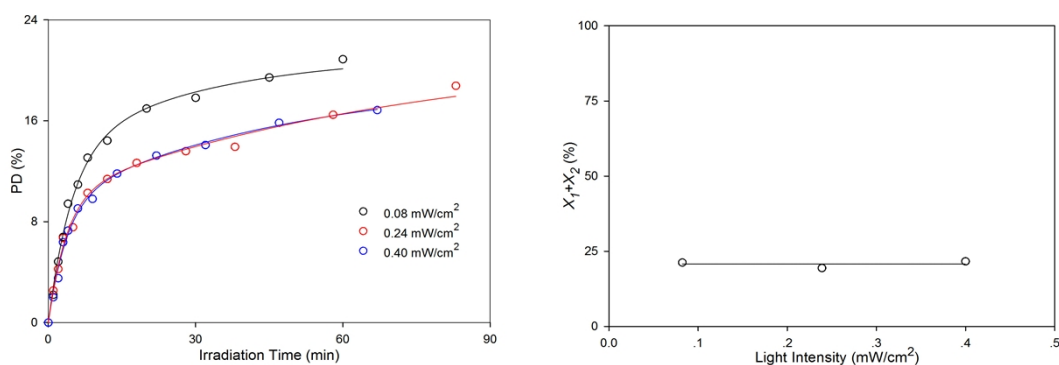
**S25.** Left: the time-dependent PD of anthracenes upon 416±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.



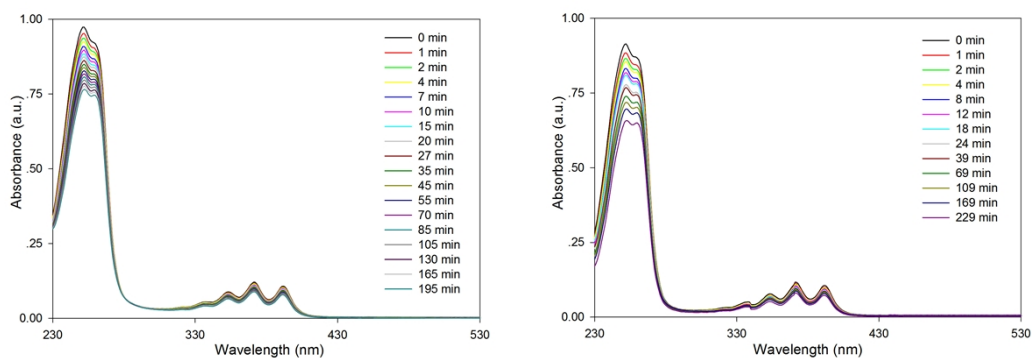
**S26.** UV-vis spectra changes of anthracene pendants upon 550±5 nm light irradiation (left for 0.08 mW/cm<sup>2</sup>, right for 0.24 mW/cm<sup>2</sup>).



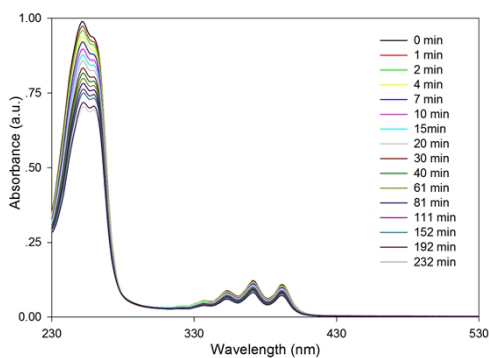
**S27.** UV-vis spectra changes of anthracene pendants upon  $550\pm 5$  nm light irradiation ( $0.40\text{mW}/\text{cm}^2$ ).



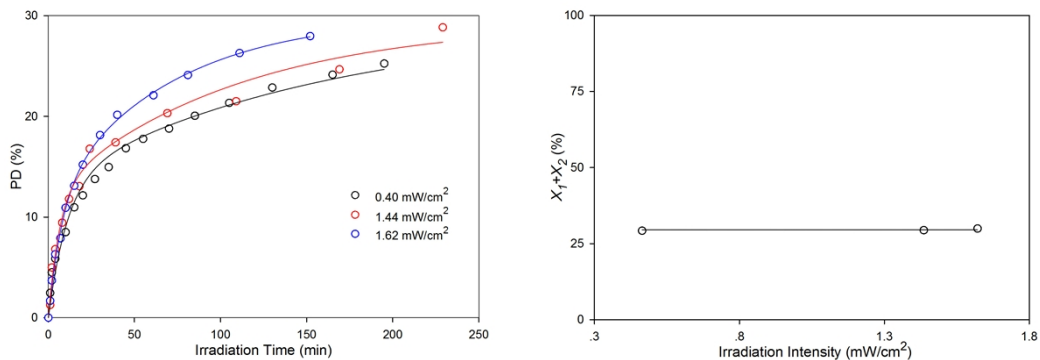
**S28.** Left: the time-dependent PD of anthracenes upon  $550\pm 5$  nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1+X_2$  values.



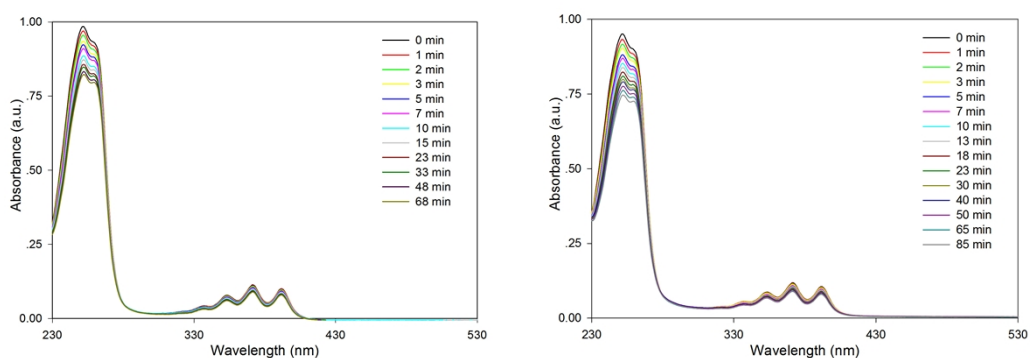
**S29.** UV-vis spectra changes of anthracene pendants upon  $700\pm 5$  nm light irradiation (left for  $0.40\text{ mW}/\text{cm}^2$ , right for  $1.44\text{ mW}/\text{cm}^2$ ).



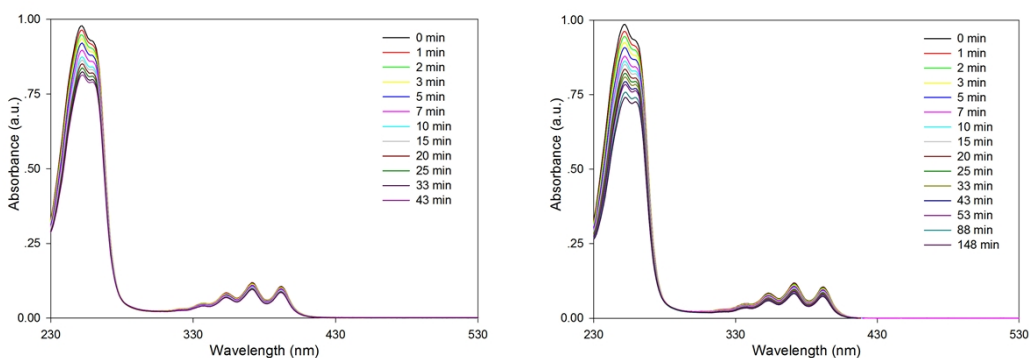
**S30.** UV-vis spectra changes of anthracene pendants upon  $700\pm 5$  nm light irradiation ( $1.62\text{ mW}/\text{cm}^2$ ).



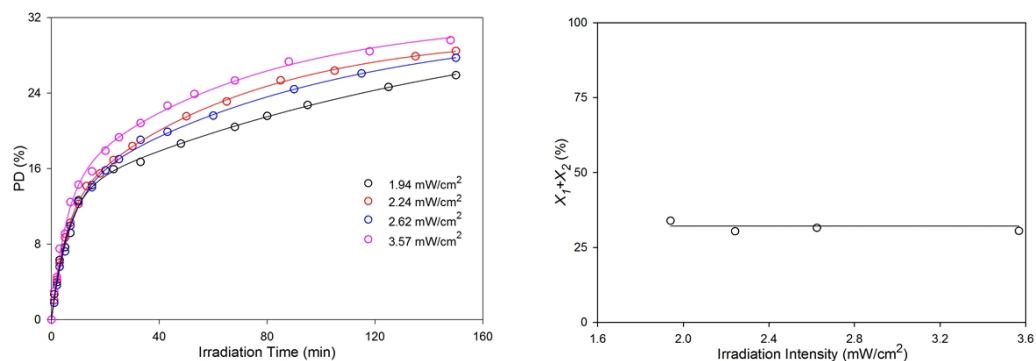
**S31.** Left: the time-dependent PD of anthracenes upon 700±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1 + X_2$  values.



**S32.** UV-vis spectra changes of anthracene pendants upon 900±5 nm light irradiation (left for 1.94 mW/cm², right for 2.24 mW/cm²).



**S33.** UV-vis spectra changes of anthracene pendants upon 900±5 nm light irradiation (left for 2.62 mW/cm², right for 3.57 mW/cm²).



**S34.** Left: the time-dependent PD of anthracenes upon 900±5 nm light irradiation and their biexponential fits to eq 1. Right: the obtained intensity-independence of  $X_1 + X_2$  values.

- 1 J.-Q. Jiang, X. Tang, Y. Zhao, *J. Am. Chem. Soc.*, 2005, **127**, 8290-8291.
- 2 E.-H. Sarah, D. Vincent, G. Xavier, L. Jean-Philippe, N. Benjamin, C. Jean, *Adv. Func. Mater.*, 2011, **21**, 3321-3330.