

## Supplementary Information

# Simultaneously Recorded Photochemical Action Plots Reveal Orthogonal Reactivity

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## 1 General

### 1.1 1D NMR Spectroscopy Measurements

$^1\text{H}$ - and  $^{13}\text{C}$ -spectra were recorded on a *Bruker* Avance III HD 600 MHz spectrometer, equipped with a BBO-Probe (5 mm) with z-gradient ( $^1\text{H}$  600.13 MHz,  $^{13}\text{C}$ : 150.90 MHz). All measurements were carried out in deuterated solvents. The chemical shift ( $\delta$ ) is reported in parts per million (ppm) relative to the residual solvent protons. The measured coupling constants were calculated in Hertz (Hz). MESTRENOVA 11.0 software was used to analyze the spectra. The signals were designated as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, q=quartet and m = multiplet.

### 1.2 UV-Vis Spectroscopy

UV-vis absorbance spectra were recorded on a *Shimadzu* UV-2700 spectrophotometer equipped with a CPS-100 electronic temperature control cell positioner. Samples were measured at ambient temperature in *Hellma Analytics* quartz high precision cells with a path length of 10 mm.

### 1.3 Size Exclusion Chromatography

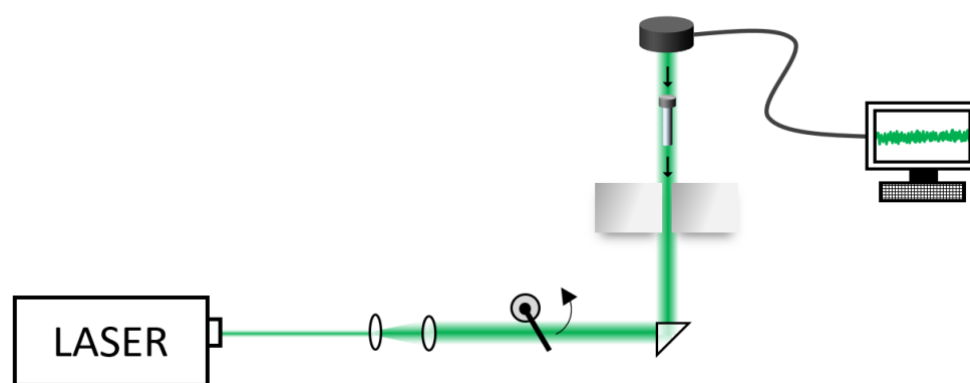
The SEC measurements were conducted on a *PSS* SECurity<sup>2</sup> system consisting of a *PSS* SECurity Degasser, *PSS* SECurity TCC6000 Column Oven (35 °C), *PSS* SDV Column Set (8x150 mm 5  $\mu\text{m}$  Precolumn, 8x300 mm 5  $\mu\text{m}$  Analytical Columns, 100000 Å, 1000 Å and 100 Å) and an *Agilent* 1260 Infinity Isocratic Pump, *Agilent* 1260 Infinity Standard Autosampler, *Agilent* 1260 Infinity Diode Array and Multiple Wavelength Detector (A: 254 nm, B: 360 nm), *Agilent* 1260 Infinity Refractive Index Detector (35 °C). HPLC grade THF, stabilized with BHT, is used as eluent at a flow rate of 1 mL·min<sup>-1</sup>. Narrow disperse linear poly(styrene) ( $M_n$  266 g·mol<sup>-1</sup> to 2.52x10<sup>6</sup> g·mol<sup>-1</sup>) and poly(methyl methacrylate) ( $M_n$  202 g·mol<sup>-1</sup> to 2.2x10<sup>6</sup> g·mol<sup>-1</sup>) standards (*PSS* ReadyCal) were used as calibrants. All samples were passed over 0.22  $\mu\text{m}$  PTFE membrane filters. Molecular weight and dispersity analysis was performed in *PSS* WinGPC UniChrom software (version 8.2).

### 1.4 LC-MS Measurements<sup>1</sup>

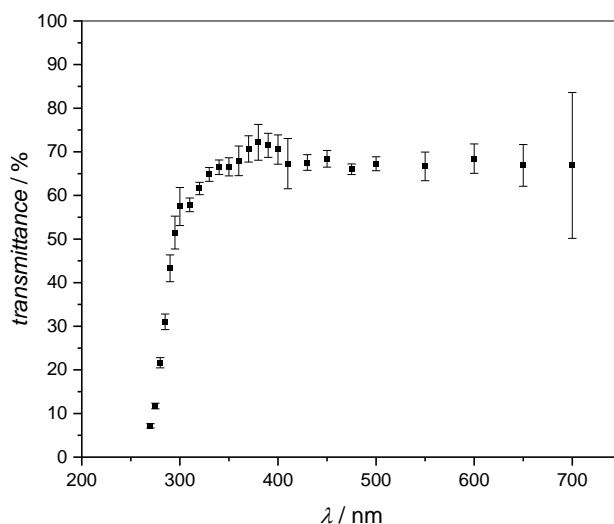
LC-MS measurements were performed on an UltiMate 3000 UHPLC system (*Dionex*, Sunnyvale, CA, USA) consisting of a pump (LPG 3400SZ, autosampler WPS 3000TSL) and a temperature-controlled column compartment (TCC 3000). Separation was performed on a C18 HPLC-column (*Phenomenex* Luna 5 $\mu\text{m}$ , 100 Å, 250 x 2.0 mm) operating at 40 °C. A gradient of ACN:H<sub>2</sub>O 10:90  $\rightarrow$  80:20 v/v (additive 10 mmol L<sup>-1</sup> NH<sub>4</sub>CH<sub>3</sub>CO<sub>2</sub>) at a flow rate of 0.20 mL min<sup>-1</sup> during 15 min was used as the eluent. The flow was split in a 9:1 ratio, where 90 % (0.18 mL min<sup>-1</sup>) of the eluent was directed through the UV-detector (VWD 3400, *Dionex*, detector wavelengths 215, 254, 280, 360 nm) and 10 % (0.02 mL min<sup>-1</sup>) was infused into the electrospray source. Spectra were recorded on a LTQ Orbitrap Elite mass spectrometer (*Thermo Fisher Scientific*, San Jose, CA, USA) equipped with an HESI II probe. The instrument was calibrated in the  $m/z$  range 74-1822 using premixed calibration solutions (*Thermo Scientific*). A constant spray voltage of 3.5 kV, a dimensionless sheath gas and a dimensionless auxiliary gas flow rate of 5 and 2 were applied, respectively. The capillary temperature was set to 300 °C, the S-lens RF level was set to 68, and the aux gas heater temperature was set to 125 °C.

## 1.5 Tunable Laser Studies<sup>2</sup>

All laser experiments were conducted using the apparatus shown in **Figure S1**. The light source was an Oportek Opolette 355 OPO, producing 7 ns, 20 Hz pulses. The output beam was initially passed through a beam expander (-50 mm and 100 mm lens combination) to ensure it was large enough to uniformly irradiate the entire sample volume. The beam then passed through an electronic shutter and was directed upwards using a UV silica right angle prism. Finally, the beam entered the sample, suspended in an aluminum block, from below. The laser energy deposited into the sample was measured above the aluminum block before and after experiments using a Coherent EnergyMax thermopile sensor (J-25MB-LE) to account for any power fluctuations during irradiation.



**Figure S1.** Schematic diagram of apparatus used for laser experiments.



**Figure S2.** Transmittance of the bottom of the glass vials used in this study. The transmittance values shown and used here were obtained analogously to a method reported previously.<sup>3</sup> The glass vials were cut at a height of 3 mm.

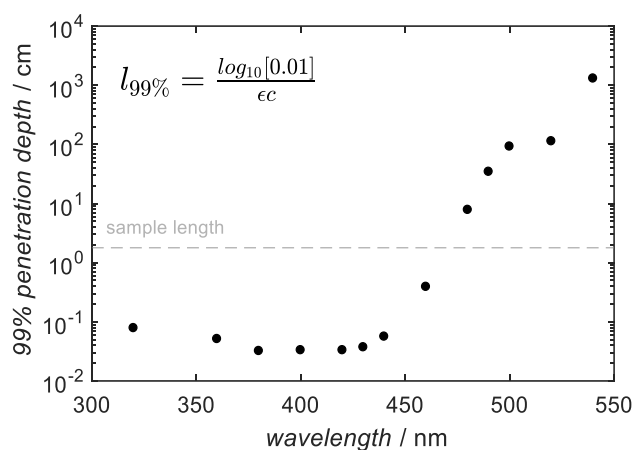
For laser measurements, all samples were prepared in a 0.7 mL glass crimp vials (ID 6.2 mm) capped with a rubber/PTFE septum. The wavelength dependent glass transmittance, essential for quantitative

measurements, is presented in **Figure S2**. Precise photons numbers were determined from the laser pulse energy using the following relation

$$N_p = \frac{E_{pulse} \lambda f_{rep} t}{hc [T_\lambda/100]} \quad (1)$$

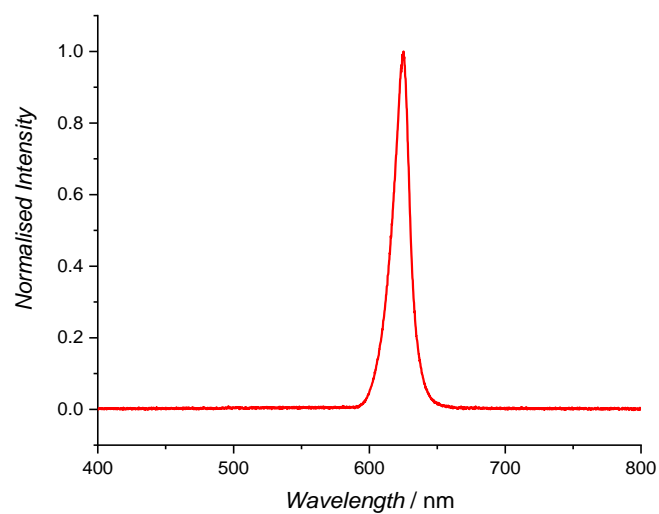
where  $E_{pulse}$  is the measured pulse energy above the aluminum block,  $\lambda$  is the wavelength of the incident radiation,  $f_{rep}$  is the laser repetition rate,  $t$  is the irradiation time,  $h$  is Planck's constant,  $c$  is the speed of light and  $T_\lambda$  is the wavelength dependent glass transmittance presented in **Figure S2**. Once an initial measurement was completed and the photon number was known, the required energies at other wavelengths can be found by rearranging Equation 1 to give

$$E_{pulse} = \frac{N_p hc [T_\lambda/100]}{\lambda f_{rep} t} \quad (2)$$



**Figure S3.** Wavelength dependent penetration depth, at which 99% of the incident light is absorbed. Calculated using the molar absorptivities at each wavelength investigated and a sample concentration of 1 mmol L<sup>-1</sup>.

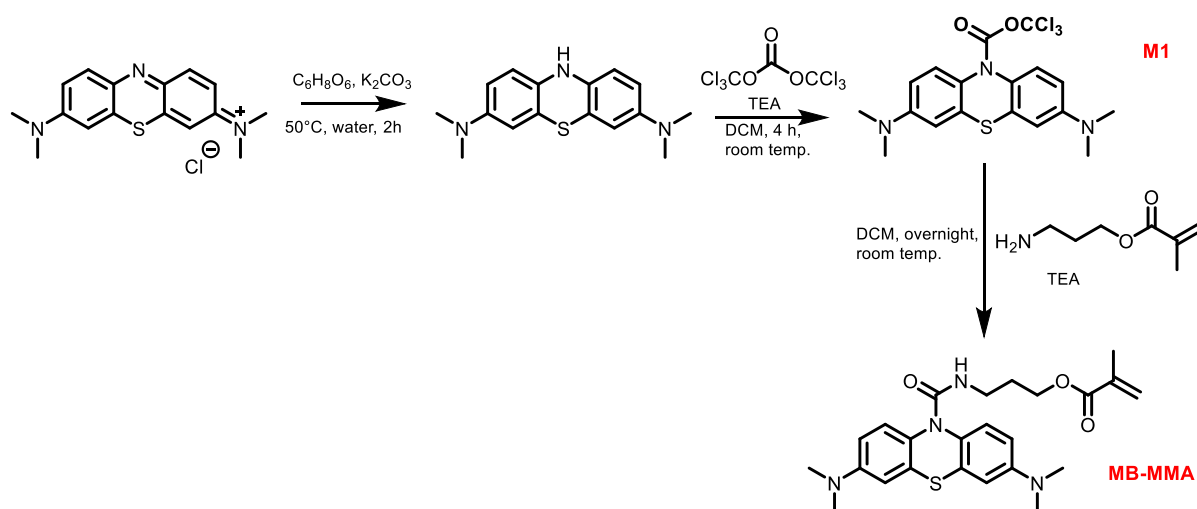
## 1.6 Emission Spectrum of 625 nm LED



**Figure S4.** Emission spectrum of the commercially available 625 nm LED (10 W) from *ELE Doctor* used for irradiation experiments.

## 2 Experimental Data

### 2.1 Synthesis of MB-MMA



**M1** and **MB-MMA** were synthesized by adapting two previously published procedures.<sup>4,5</sup>

#### **M1 (trichloromethyl 3,7-bis(dimethylamino)-10H-phenothiazine-10-carboxylate):**

Methylene blue (3 g, 9.38 mmol, 1 eq.) was dissolved in water (200 mL) and the flask was flushed with argon. To this solution, ascorbic acid (3.3 g, 18.7 mmol, 2 eq.) was added, followed by  $K_2CO_3$  (5.19 g, 37.5 mmol, 4 eq.). The solution was stirred at 50 °C overnight under an argon atmosphere upon which the solution turns turbid. The turbid mixture was filtered and the aqueous filtrate was clear and brown. The cloudy blue residue was transferred to a separating funnel and washed with DCM 5 times, with 200–300 mL each time. The organic phase was dark blue.

The DCM phase was concentrated to around 150 mL and cooled in an ice bath. Triphosgene (2.78 g, 9.38 mmol, 1 eq.) and triethylamine (2.85 g, 28.1 mmol, 3 eq.) were added to the cooled solution and allowed to stir overnight while gradually warming up to room temperature. The solution was then washed with saturated bicarbonate solution twice, 0.01 M HCl twice and brine once. The organic solvent was then evaporated to leave behind a pale blue-green solid, which was recrystallized in acetonitrile. **M1** was then isolated as a pale green solid and immediately used in the next step.

#### **MB-MMA (3-(3,7-bis(dimethylamino)-10H-phenothiazine-10-carboxamido)propyl methacrylate):**

**M1** (1.40 g, 3.1 mmol, 1 eq.) was dissolved in DCM (50 mL) and to this solution, N-(3-aminopropyl)methacrylamide hydrochloride (2.24 g, 12.5 mmol, 4 eq.) and triethylamine (1.9 g, 18.8 mmol, 6 eq.) were added. The solution was stirred in the dark at ambient temperature overnight. The solution was then washed with saturated sodium bicarbonate solution thrice, water thrice and brine thrice before being adsorbed onto celite. The crude product was purified by column chromatography eluting with hexane: ethyl acetate (v/v = 1:1) → hexane: ethyl acetate: acetone (v/v = 5:5:1) → hexane: ethyl acetate: acetone (v/v = 1:1:1) to afford the product as white powder (yield = 77% (1.1 g, 2.4 mmol)).

$^1\text{H}$  NMR (600 MHz, Acetonitrile- $d_3$ )  $\delta$  7.29 (d,  $J = 8.8$  Hz, 2H), 6.96 (s, 1H), 6.75 (d,  $J = 2.8$  Hz, 2H), 6.69 (dd,  $J = 8.9, 2.9$  Hz, 2H), 5.64 – 5.58 (m, 2H), 5.28 (p,  $J = 1.6$  Hz, 1H), 3.22 – 3.16 (m, 2H), 3.14 (q,  $J = 6.2$  Hz, 2H), 2.92 (s, 12H), 1.87 (dd,  $J = 1.6, 1.0$  Hz, 3H), 1.59 – 1.48 (m, 2H).

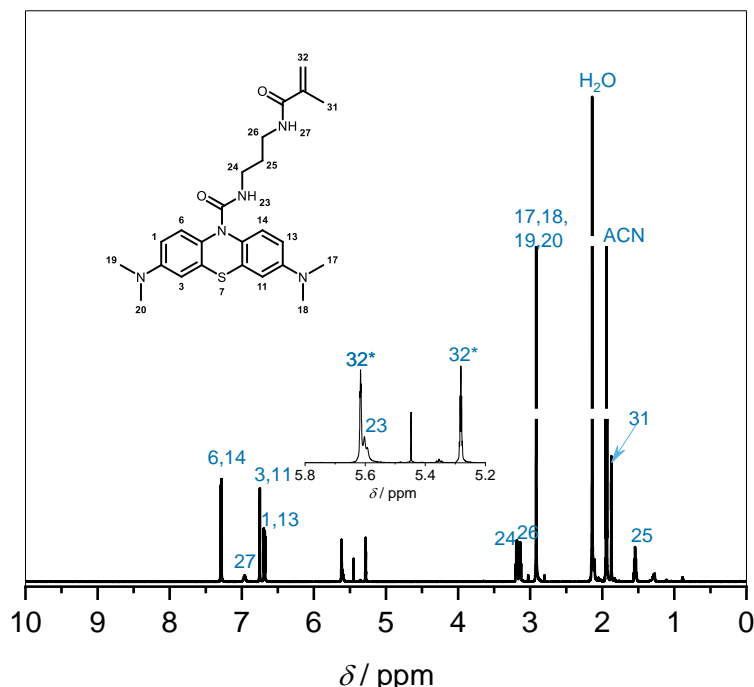
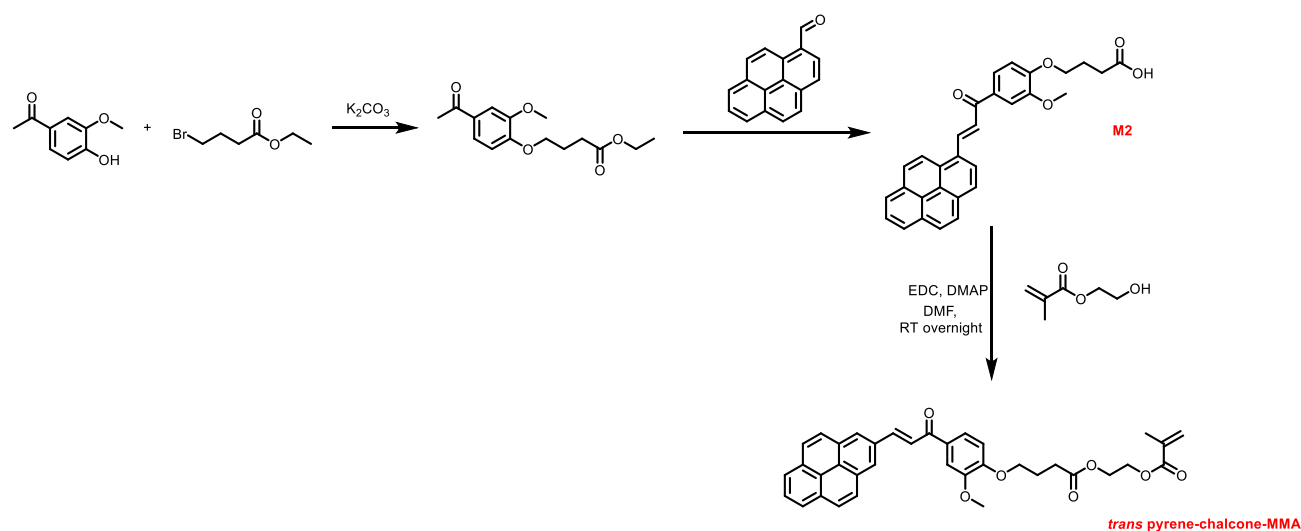


Figure S5.  $^1\text{H}$  NMR spectrum of MB-MMA in deuterated ACN (600 MHz).

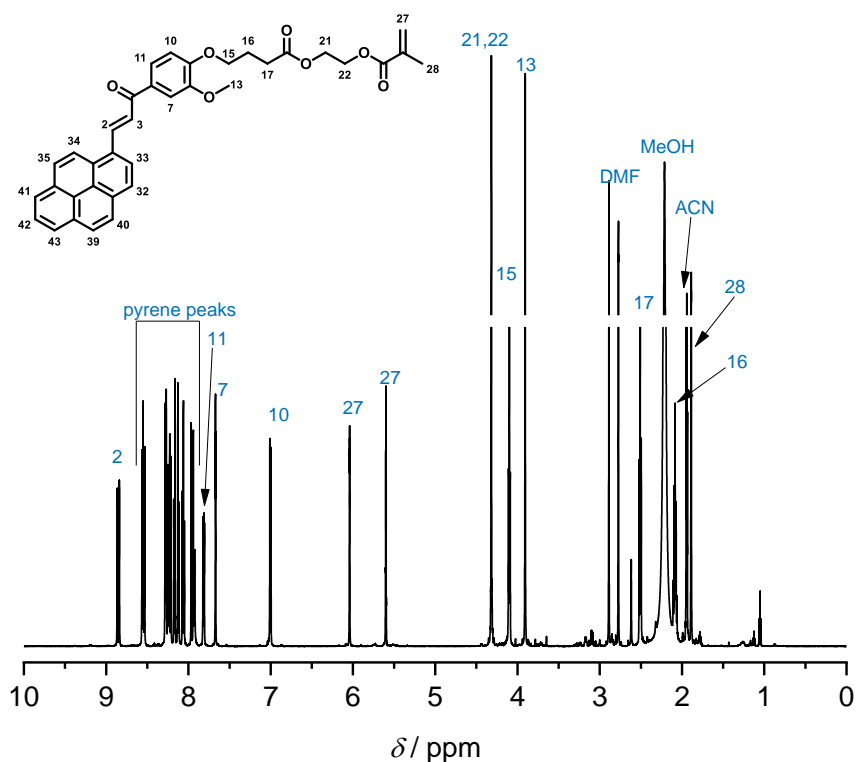
## 2.2 Synthesis of *trans* pyrene-chalcone-MMA



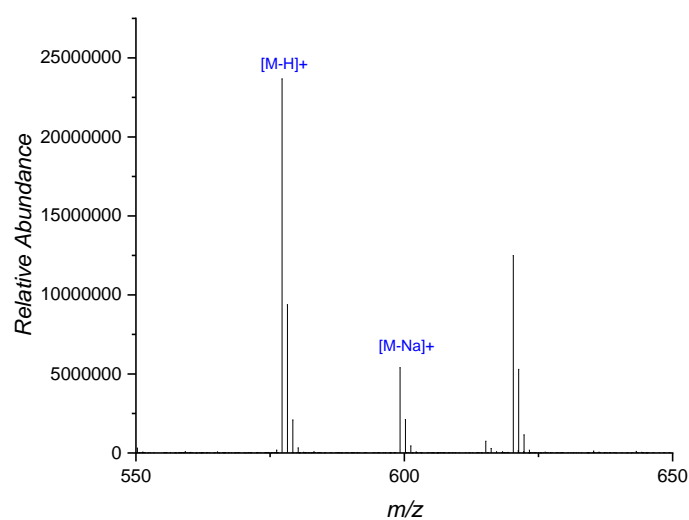
**M2** was synthesized according to previously published procedures.<sup>6</sup> **M2** (1.0 g, 2.15 mmol, 1 eq.), 4-dimethylaminopyridine (DMAP) (26 mg, 215  $\mu\text{mol}$ , 0.1 eq.), and hydroxyethyl methacrylate (HEMA) (336 mg, 2.58 mmol, 1.2 eq.) were dissolved in 40 mL DMF and cooled in an ice bath while stirring. N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl) (454 mg, 2.37 mmol, 1.1 eq.) was added to the cooled mixture and the solution was stirred overnight in the dark and gradually allowed to warm up to room temperature. The product was then precipitated in 1L of cooled methanol

and the product was filtered out and washed well with cold methanol before being dried in an oven at a 40°C.

$^1\text{H}$  NMR (600 MHz, Acetonitrile- $d_3$ )  $\delta$  8.85 (d,  $J = 15.3$  Hz, 1H), 8.55 (dd,  $J = 11.0, 8.7$  Hz, 2H), 8.31 – 8.26 (m, 2H), 8.23 (dd,  $J = 14.5, 8.7$  Hz, 2H), 8.19 – 8.11 (m, 2H), 8.06 (t,  $J = 7.6$  Hz, 1H), 7.95 (d,  $J = 15.3$  Hz, 1H), 7.81 (dd,  $J = 8.4, 2.1$  Hz, 1H), 7.67 (d,  $J = 2.1$  Hz, 1H), 7.00 (d,  $J = 8.4$  Hz, 1H), 6.04 (m,  $J = 2.0, 1.0$  Hz, 1H), 5.60 (m,  $J = 1.6$  Hz, 1H), 4.32 (s, 4H), 4.10 (t,  $J = 6.3$  Hz, 2H), 3.90 (s, 3H), 2.51 (t,  $J = 7.3$  Hz, 2H), 2.12 – 2.04 (p, 2H), 1.90 – 1.87 (m, 3H).



**Figure S6.**  $^1\text{H}$  NMR spectrum of *trans* pyrene-chalcone-MMA in deuterated ACN (600 MHz).



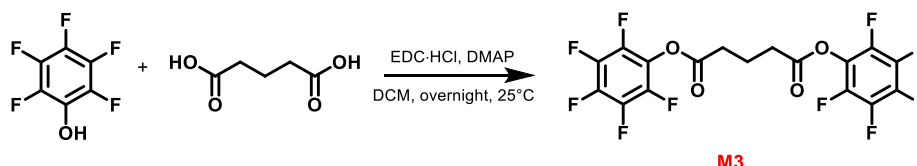
**Figure S7.** Mass spectrum of *trans* pyrene-chalcone-MMA.



**Table 1.** Summary of the experimental and theoretical  $m/z$  values of *trans* pyrene-chalcone-MMA

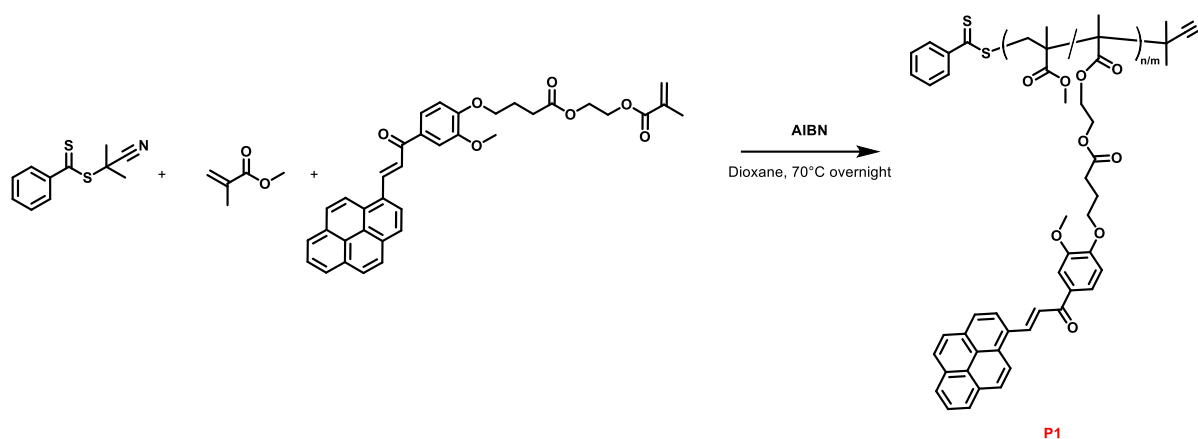
Symbol	$m/z_{exp}$	$m/z_{theor}$	$\Delta_{ppm}$	Composition
$[M+H]^+$	577.2229	577.2221	1.39	$C_{36}H_{32}O_7H^+$
$[M+Na]^+$	599.2048	599.2040	1.34	$C_{36}H_{32}O_7Na^+$

### 2.3 Synthesis of M3 (PFP-glutaric acid crosslinker)



**M3** was synthesized according to previously published literature.<sup>4</sup>

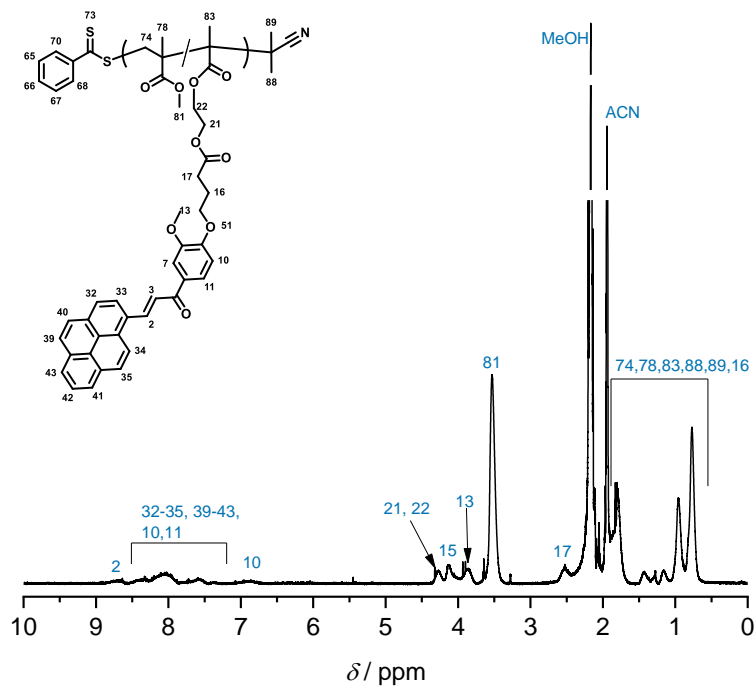
### 2.4 P1



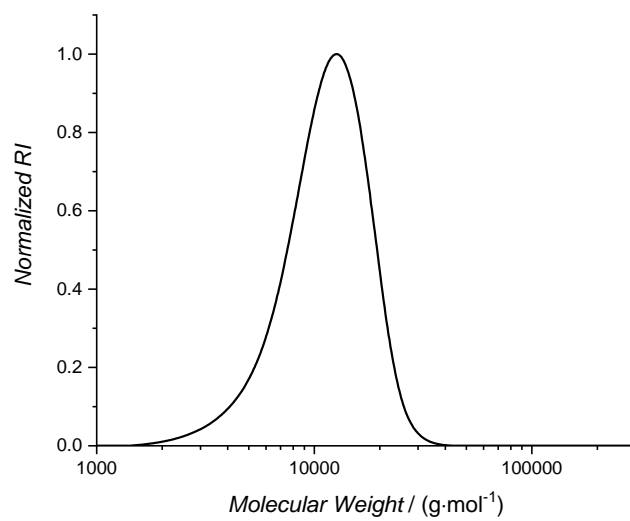
MMA was passed through a short alumina column to remove the inhibitor before being utilized in the polymerization. MMA (481  $\mu$ L, 200 eq., 4.5 mmol), *trans* pyrene-chalcone-MMA (390 mg, 30 eq., 678  $\mu$ mol), 2-cyano-2-propyl benzodithioate (5 mg, 1 eq., 23  $\mu$ mol) and AIBN (0.9 mg, 0.25 eq., 5.6  $\mu$ mol) were dissolved in 5 mL dioxane and deoxygenated via sparging with argon for 20 min in a crimped vial. The mixture was subsequently heated at 70 °C for 18 h, before being quenched by exposure to ambient air. The polymer was purified by precipitation into methanol four times over and drying overnight in a vacuum oven at 40°C. Each polymer chain was calculated to have approximately 6 chalcone units per polymer chain according to the method described in literature, using the resonances of the protons representing the CH group of the chalcone at  $\delta=8.8$  ppm and  $CH_3$  of the MMA at  $\delta=3.5$  ppm.<sup>7</sup>

$^1H$  NMR (600 MHz, Acetonitrile- $d_3$ )  $\delta$  8.84 – 8.60 (m, 1H), 8.31 (m, 2H), 8.25 – 7.87 (m, 4H), 7.81 – 7.47 (m, 2H), 6.89 (s, 1H), 4.34 – 4.19 (s, 1H), 4.19 – 3.98 (s, 3H), 3.96 – 3.76 (s, 3H), 3.53 (s, 28H), 2.60 – 2.41 (m, 4H), 1.89–1.68 (m, 15H), 1.39 (d, 2H), 1.16 (s, 2H), 0.95 (s, 12H), 0.77 (s, 20H).

SEC (THF)  $M_n=9.9$  kg·mol<sup>-1</sup> |  $M_w=12.2$  kg·mol<sup>-1</sup> |  $D=1.2$

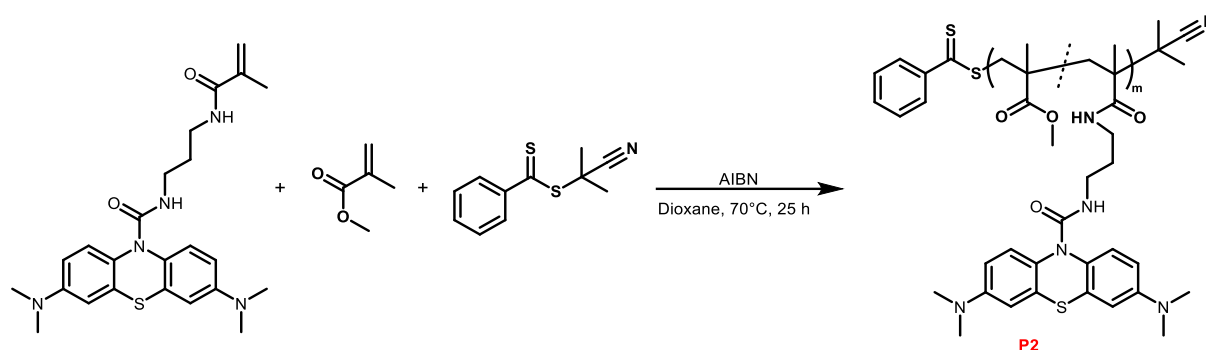


**Figure S8.**  $^1\text{H}$  NMR spectrum of **P1** in deuterated ACN (600 MHz).



**Figure S9.** SEC of **P1** in THF.

## 2.5 P2



MMA was passed through a short alumina column to remove the inhibitor before being utilized in the polymerization. MMA (962  $\mu\text{L}$ , 200 eq., 9 mmol), **MB-MMA** (614 mg, 30 eq., 1.36 mmol), 2-cyano-2-propyl benzodithioate (10 mg, 1 eq., 45  $\mu\text{mol}$ ) and AIBN (1.4 mg, 0.2 eq., 9  $\mu\text{mol}$ ) were dissolved in 5.5 mL dioxane and deoxygenated via sparging with argon for 20 min in a crimped vial. The mixture was subsequently heated at 70  $^{\circ}\text{C}$  for 18 h, before being quenched by exposure to ambient air. The polymer was purified by precipitation into cold methanol thrice over and dried overnight in a vacuum oven at 40 $^{\circ}\text{C}$ . Each polymer chain was calculated to have approximately 11 **MB-MMA** units per polymer chain according to the method described in literature, using the resonances of the protons representing the  $\text{CH}_3$  group of the **MB-MMA** at  $\delta=2.94$  ppm and  $\text{CH}_3$  of the MMA at  $\delta=3.59$  ppm.<sup>7</sup>

$^1\text{H}$  NMR (600 MHz, Chloroform-*d*)  $\delta$  7.38 – 7.30 (m, 2H), 6.85 (s, 1H), 6.68 (d,  $J = 40.3$  Hz, 4H), 5.17 – 5.07 (m, 1H), 3.59 (s, 32H), 3.34 – 3.11 (m, 4H), 2.94 (d,  $J = 10.1$  Hz, 12H), 2.10 – 1.75 (m, 16H), 1.58 – 1.30 (m, 4H), 1.02 (s, 12H), 0.84 (d,  $J = 10.9$  Hz, 22H).

SEC (THF)  $M_n = 16.9$  kg $\cdot\text{mol}^{-1}$  |  $M_w = 19.6$  kg $\cdot\text{mol}^{-1}$  |  $D = 1.2$

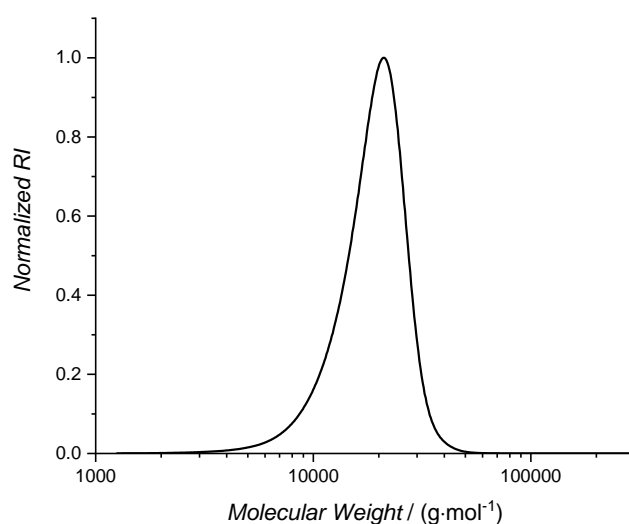
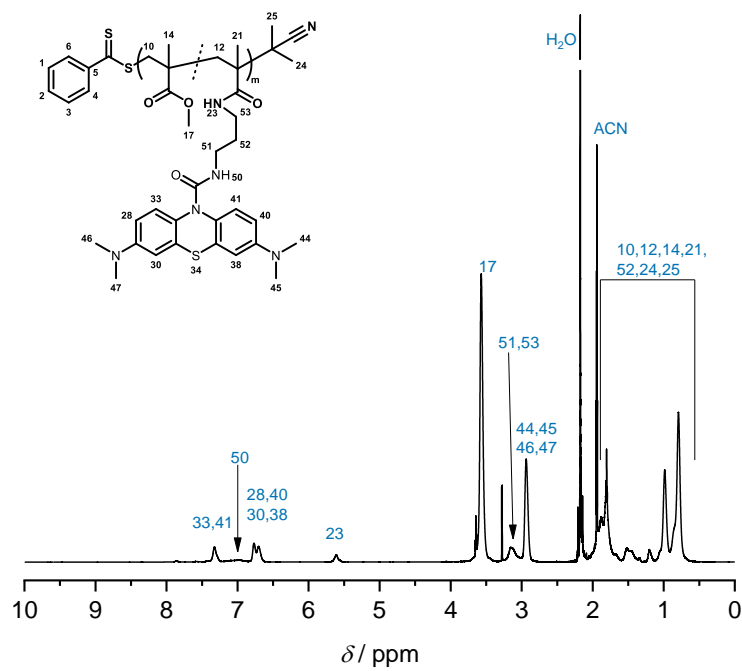


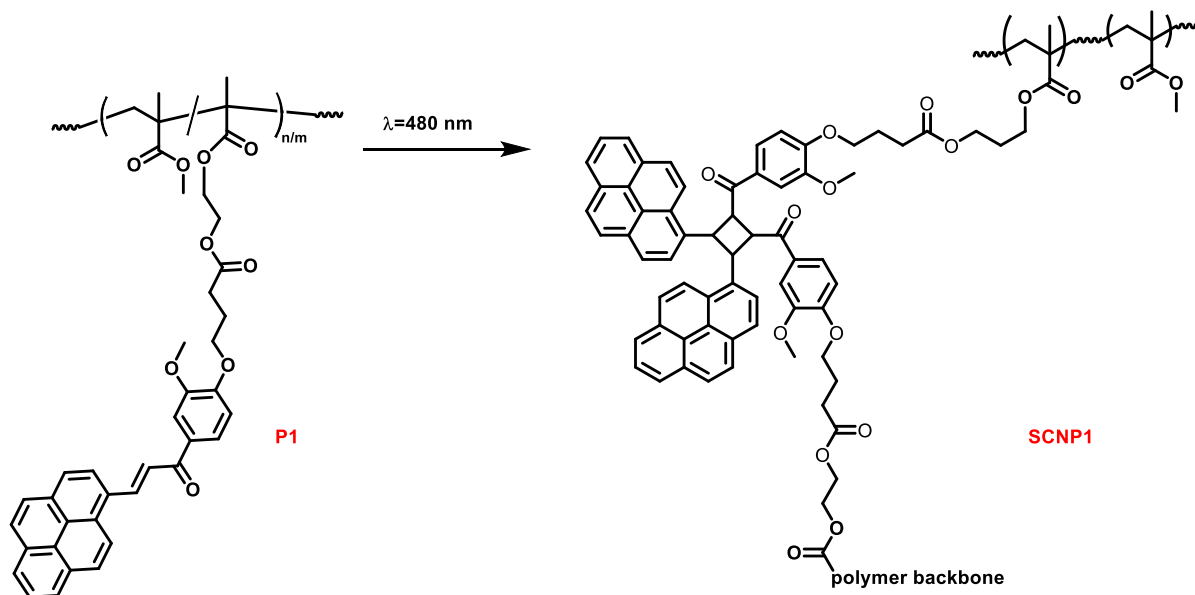
Figure S10. SEC of P2 in THF.



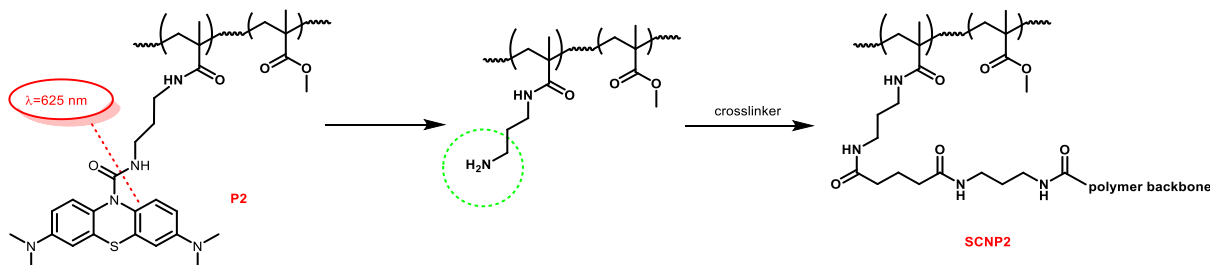
**Figure S11.**  $^1\text{H}$  NMR spectrum of **P2** in deuterated ACN (600 MHz)

### 3 Irradiation experiments

The general reaction for the folding of **P1** into **SCNP1** via the [2+2] photodimerization reaction of the chalcone is as follows:



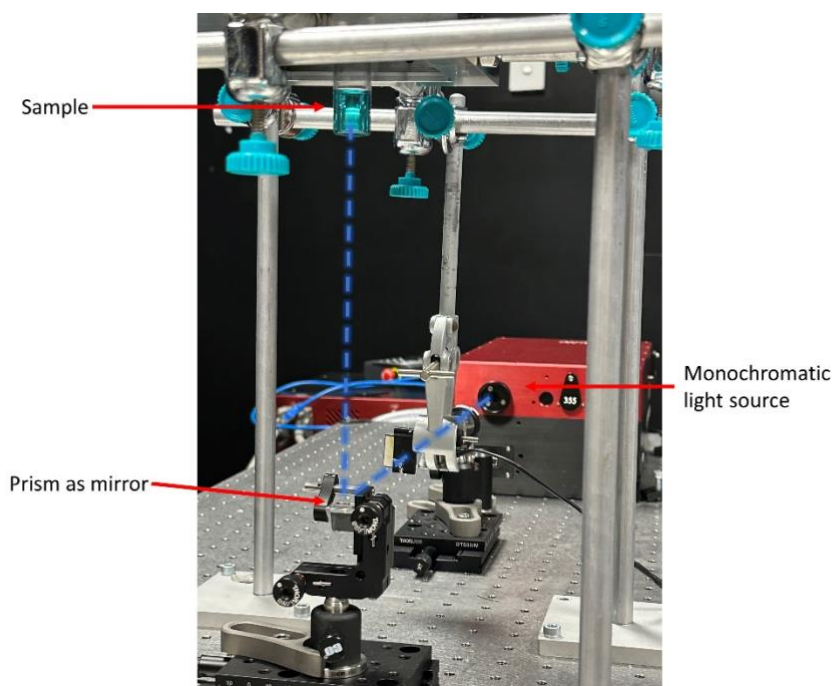
The general reaction for the photodeprotection of **P2** and subsequent intramolecular crosslinking to form **SCNP2** is as follows:



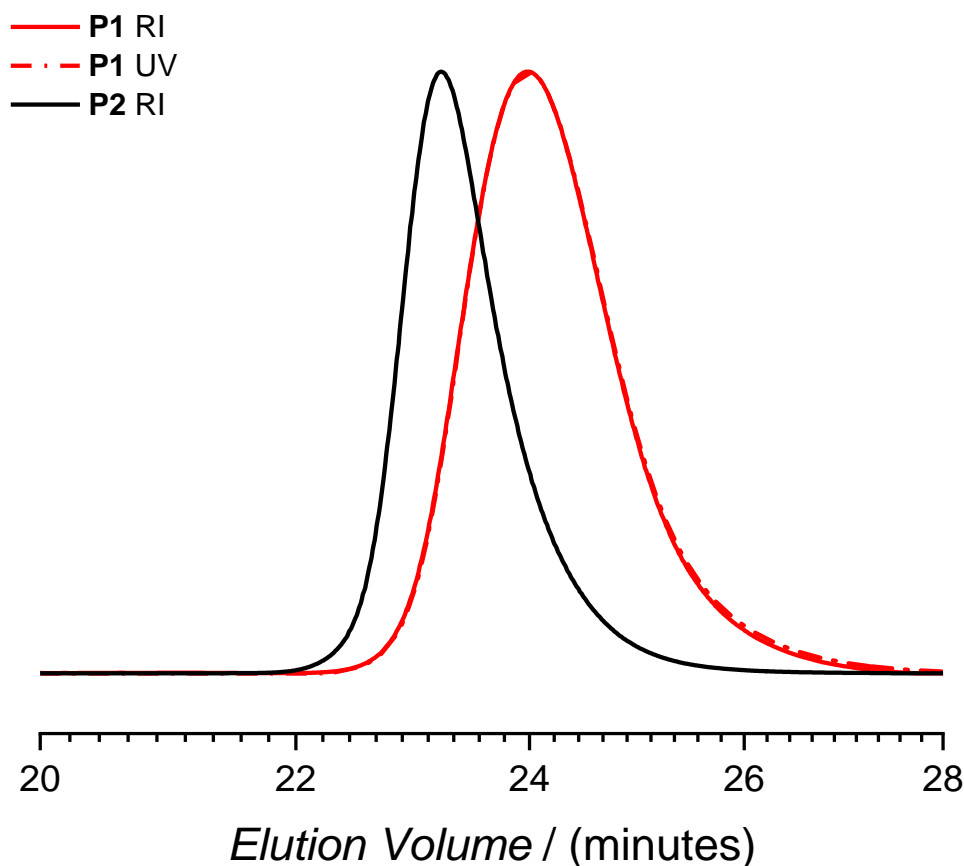
All samples utilized the red-light LED ( $\lambda_{\text{max}} = 625 \text{ nm}$ ) described in section 1.6 while placed at a distance of 1 cm from the LED for red light irradiations, and were irradiated bottom-up with a laser beam for blue light irradiations. The samples were placed in 12 mL clear glass vials (Labtek Screw Neck Vial 19x65mm, clear, flat bottom, finish 15-425) for irradiation experiments. (see figures S12 and S13).



**Figure S12.** Setup used for LED irradiations at  $\lambda_{\text{max}} = 625 \text{ nm}$



**Figure S13.** Setup used for laser irradiations at  $\lambda = 480 \text{ nm}$



**Figure S14.** SECs of **P1** and **P2** measured separately and overlaid. The UV signal was set to read at  $\lambda=360$  nm which is the isosbestic point of the chalcone and its dimer.

### 3.1 Folding of **P1** and **P2** with blue light, then red light (480nm $\rightarrow$ 625 nm)

**P1** (5.0 mg, 0.51  $\mu\text{mol}$ ), **P2** (3.0 mg, 0.17  $\mu\text{mol}$ , 1 eq.) **M3** (1.5 mg, 8.7  $\mu\text{mol}$ , 49.5 eq.) and 4-dimethylaminopyridine (0.1 mg, 1.8  $\mu\text{mol}$ , 10 eq.) were dissolved in 20 mL acetonitrile and 9 mL of the solution was transferred into a clear glass vial for irradiation experiments.

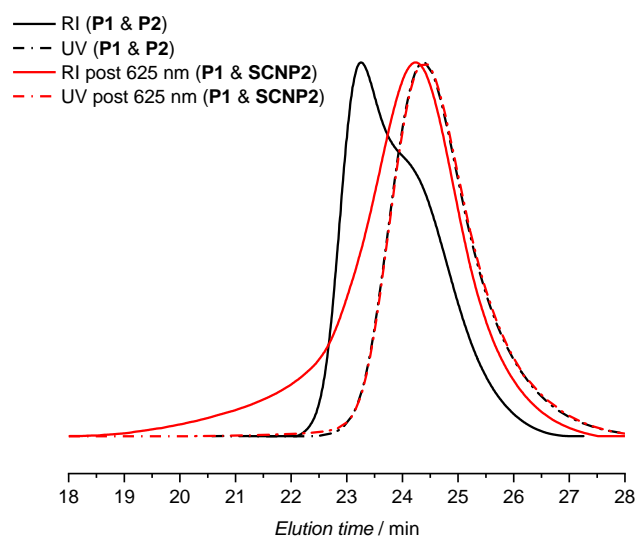
The clear vial was irradiated with light at 480 nm (630  $\mu\text{J}$ ) for 15 min and a 3 mL aliquot was removed to measure SEC of the mixture. The remainder 6 mL of solution was irradiated with a red-light LED ( $\lambda_{\text{max}}=625$  nm) for 1.5 h (placed 1 cm from the sample) allowed to stir in the dark for 2 days before measuring SEC. All SEC measurements had the UV detection set to  $\lambda=360$  nm which is the isosbestic point of the chalcone and its dimer. This UV absorbance measurement is taken to be representative of **P1** as the RI trace is dominated by **P2**.

### 3.2 Folding of **P1** and **P2** with red light, then blue light (625 nm $\rightarrow$ 480 nm)

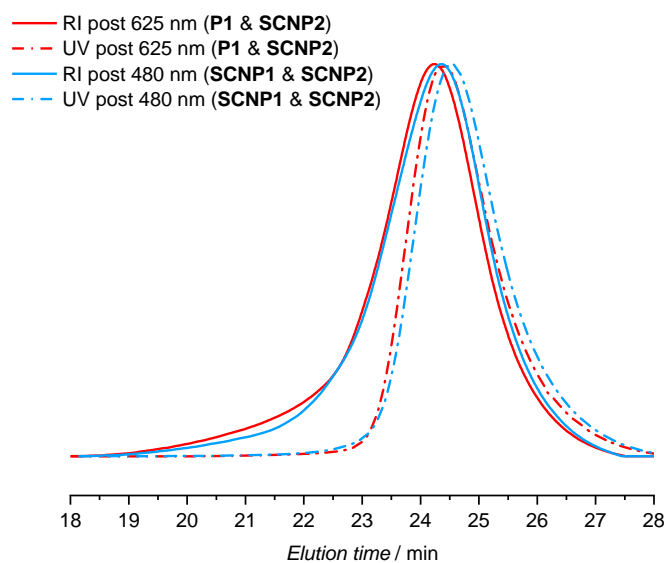
**P1** (5.0 mg, 0.51  $\mu\text{mol}$ ), **P2** (3.0 mg, 0.17  $\mu\text{mol}$ , 1 eq.) **M3** (1.5 mg, 8.7  $\mu\text{mol}$ , 49.5 eq.) and 4-dimethylaminopyridine (0.1 mg, 1.8  $\mu\text{mol}$ , 10 eq.) were dissolved in 20 mL acetonitrile and 9 mL of the solution was transferred into a clear vial for irradiation experiments.

The clear vial was irradiated with a red-light LED ( $\lambda_{\text{max}}=625$  nm) for 1.5 h (placed 1 cm away from the sample) and the solution was allowed to stir in the dark for 2 days, before a 3 mL aliquot was removed

to measure SEC. The remaining solution was irradiated at 480 nm (630  $\mu$ ) for 15 minutes and SEC of the mixture was then measured. measurements had the UV absorbance measurement set to  $\lambda=360$  nm which is the isosbestic point of the chalcone and its dimer. This UV absorbance measurement is taken to be representative of **P1** as the RI trace is dominated by **P2**.



**Figure S15** SEC and UV trace (UV detection set to  $\lambda=360$  nm) of **P1** and **P2** before irradiation, and **P1** and **SCNP2** after irradiation at  $\lambda_{\text{max}} = 625$  nm, and stirring in the dark for 2 days



**Figure S16** SEC and UV trace (UV detection set to  $\lambda=360$  nm) of **SCNP1** and **SCNP2** after irradiation with  $\lambda=480$  nm following the initial irradiation at  $\lambda_{\text{max}} = 625$  nm.



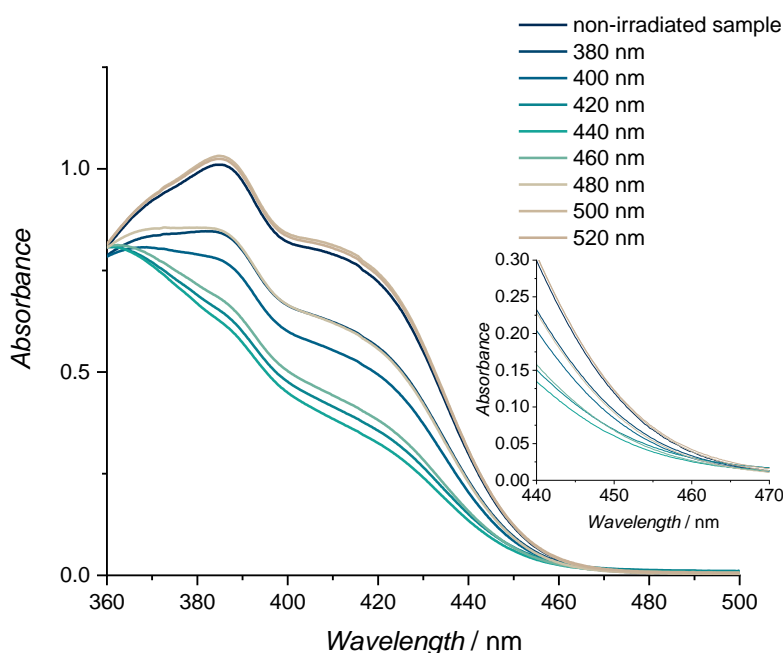
## 4 Supplementary Results

### 4.1 UV-Vis absorption spectra for the dual Action Plot of MB-MMA and *trans* pyrene-chalcone-MMA

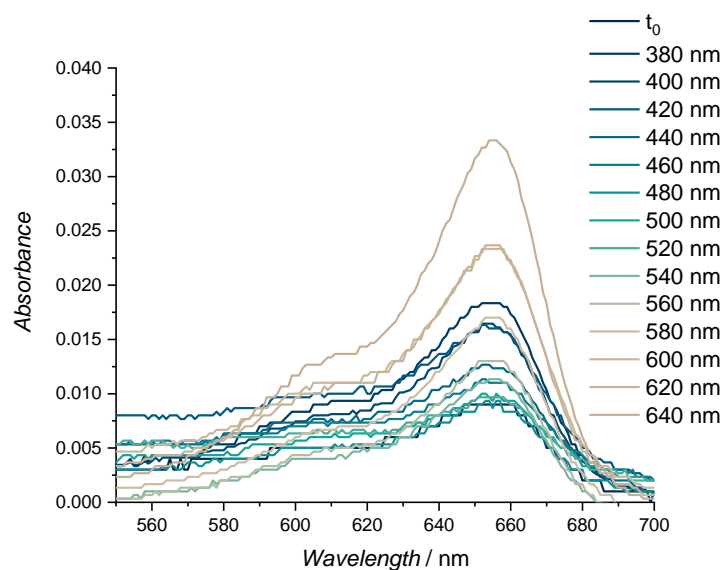
**MB-MMA** and *trans* pyrene-chalcone-MMA were dissolved in an equimolar ratio in acetonitrile ( $5.5 \times 10^{-11} \text{ mol}\cdot\text{L}^{-1}$ ) and irradiated with  $7.7 \mu\text{mol}$  of photons at a range of wavelengths from  $\lambda = 380 \text{ nm}$  to  $640 \text{ nm}$ . Each irradiation event was repeated across 3 samples and the UV-Vis absorbance spectrum of each sample was measured after each irradiation event. For each wavelength the average UV-Vis absorbance across the 3 samples was used to determine the conversion.

The change in absorbance at  $450 \text{ nm}$  was determined to be representative of the depletion of *trans* pyrene-chalcone-MMA as neither **MB-MMA** nor any of the photoproducts possess significant absorbance at  $450 \text{ nm}$ , while the *trans* pyrene-chalcone-MMA has significant absorbance.<sup>6</sup> As *trans* pyrene-chalcone-MMA was progressively consumed, the absorbance at  $450 \text{ nm}$  would decrease (Figure S19).

The change in absorbance at  $655 \text{ nm}$  is representative of the depletion of **MB-MMA** as the absorbance at  $655 \text{ nm}$  would increase when the caged amine was deprotected and free methylene blue was released into the solution.<sup>4,5</sup> (Figure S20).



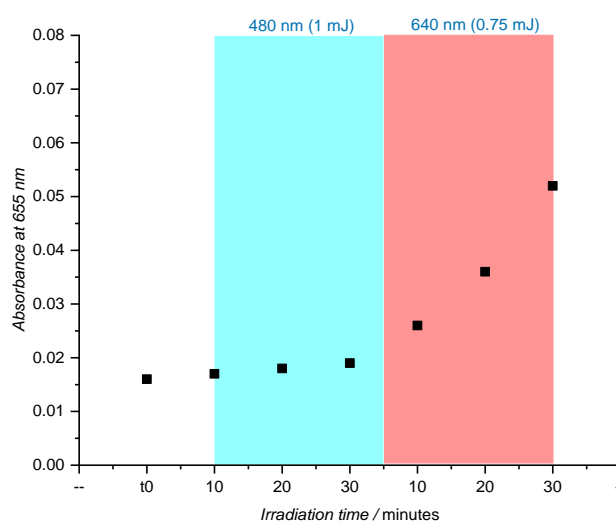
**Figure S17.** Average UV-Vis absorption spectra of *trans* pyrene-chalcone-MMA in acetonitrile after irradiation at each wavelength with a tunable laser ( $7.7 \mu\text{mol}$  of photons at each wavelength) at a concentration of  $5.5 \times 10^{-11} \text{ mol}\cdot\text{dm}^{-3}$ . The change in absorbance at  $450 \text{ nm}$  was used to track the depletion of *trans* pyrene-chalcone-MMA. Note that the slight increase in the UV-vis of the samples at  $500 \text{ nm}$  and  $520 \text{ nm}$  compared to the non-irradiated sample is likely due to slight concentration differences arising from transfer of solution from the laser vial to cuvette, and sample storage.



**Figure S18.** Average UV-Vis absorption spectra of **MB-MMA** in acetonitrile after irradiation at each wavelength with a tunable laser ( $7.7 \mu\text{mol}$  of photons at each wavelength) at a concentration of  $5.5 \times 10^{-11} \text{ mol}\cdot\text{dm}^{-3}$ . The change in absorbance at  $655 \text{ nm}$  was used to track the depletion of **MB-MMA**.

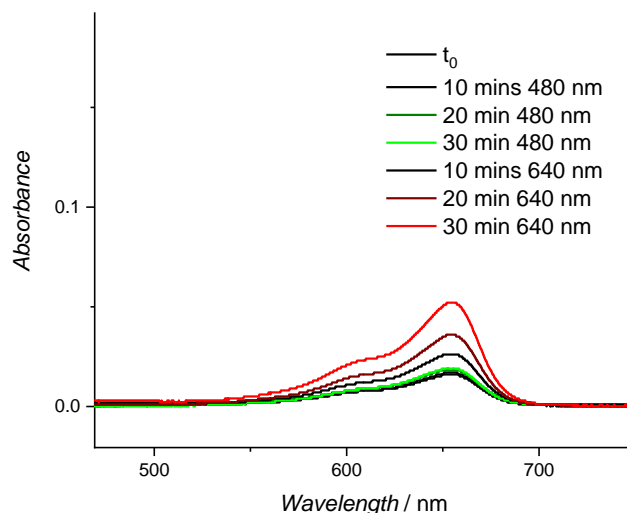
## 4.2 Kinetic experiments of MB-MMA at 480 nm and 640 nm

$2.93 \text{ mg}$  of **MB-MMA** was dissolved in  $1 \text{ mL}$  ACN and  $300 \mu\text{L}$  of the solution was added to  $3 \text{ mL}$  of acetonitrile ( $0.27 \text{ mg mL}^{-1}$ ,  $0.59 \text{ mmol L}^{-1}$ ) and placed in a quartz cuvette before it was irradiated (bottom up) with monochromatic light at  $480 \text{ nm}$  ( $1 \text{ mJ}$ ) from a laser for  $30 \text{ minutes}$  and the UV-Vis absorbance was measured every  $10 \text{ minutes}$  during the irradiation period. Then the same sample was irradiated with monochromatic light at  $640 \text{ nm}$  ( $0.75 \text{ mJ}$ ) from the laser for a further  $30 \text{ minutes}$ , and the absorbance was measured every  $10 \text{ minutes}$ . The number of photons was kept identical at both wavelengths ( $1.98 \times 10^{19}$  photons every  $10 \text{ minutes}$ ), and the energy was adjusted accordingly.



**Figure S19.** A solution of **MB-MMA** ( $0.27 \text{ mg mL}^{-1}$ ,  $0.59 \text{ mmol L}^{-1}$ ) was irradiated with monochromatic light at  $480 \text{ nm}$  ( $1 \text{ mJ}$ ) for  $30 \text{ minutes}$ , followed by monochromatic light at  $640 \text{ nm}$  ( $0.75 \text{ mJ}$ ) for  $30 \text{ minutes}$ , and the UV-Vis absorbance of the solution was measured at regular time intervals of  $10 \text{ minutes}$ .  $1.98 \times 10^{19}$  photons were supplied

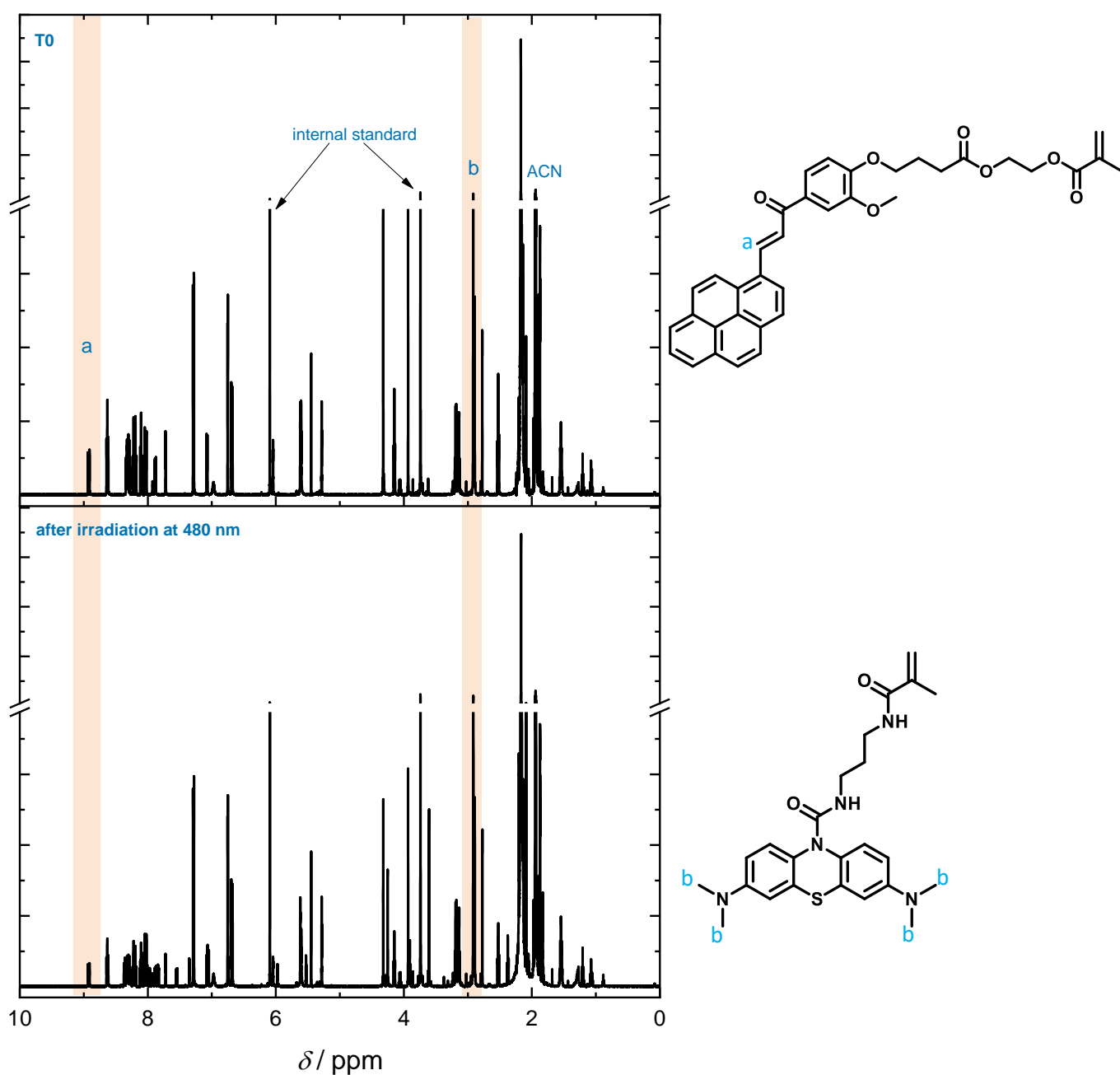
to the solution over each 10 minute period at both wavelengths. This graph depicts the absorbance of the product mixture at 655 nm over the course of irradiation as the increase in absorbance at 655 nm is correlated to the photoinduced cleavage reaction of **MB-MMA**.



**Figure S20** UV-Vis spectrum of the product mixture after irradiating a solution of **MB-MMA** with monochromatic light at 480 nm (1 mJ) for 30 minutes, followed by monochromatic light at 640 nm (0.75 mJ) for 30 minutes. The UV-Vis absorbance of the solution was measured at regular intervals of 10 minutes.  $1.98 \times 10^{19}$  photons were supplied to the solution over each 10 minute period at both wavelengths.

### 4.3 $^1\text{H}$ NMR spectrum of irradiation of **MB-MMA** and *trans* pyrene-chalcone-MMA at 480 nm

An equimolar solution of **MB-MMA** and *trans* pyrene-chalcone-MMA ( $1.47 \times 10^{-10}$  mol L $^{-1}$ ), along with an internal standard of 1,3,5-trimethoxybenzene in deuterated acetonitrile was placed in a laser vial and irradiated with monochromatic light at 480 nm (580  $\mu\text{J}$  for 595 seconds, 19 mmol of photons), and the  $^1\text{H}$  NMR of the sample was then measured. The resonance at  $\delta = 2.91$  ppm representative of the  $\text{CH}_3$  groups of **MB-MMA** and the resonance at  $\delta = 8.92$  ppm representative of the CH group of *trans* pyrene-chalcone-MMA were used to calculate the conversion of both species before and after irradiation. According to the  $^1\text{H}$  NMR spectrum, *trans* pyrene-chalcone-MMA was subjected to a conversion of 47% while **MB-MMA** only saw a conversion of 1.7%.

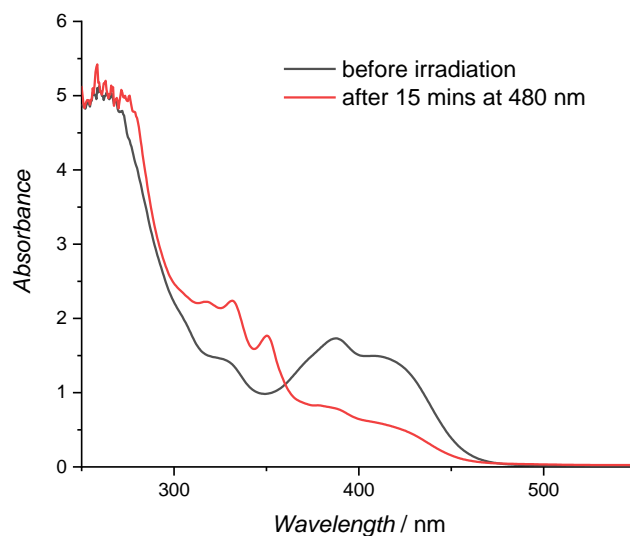


**Figure S21**  $^1\text{H}$  NMR spectra of an equimolar solution of MB-MMA and *trans* pyrene-chalcone-MMA ( $1.47 \times 10^{-10} \text{ mol L}^{-1}$ ) in deuterated ACN measured at 600 MHz, measured before and after irradiation at 480 nm (19 mmol of photons). An internal standard of 1,3,5-trimethoxybenzene was used and the resonances at  $\delta = 8.92 \text{ ppm}$  and  $2.91 \text{ ppm}$  were taken to represent *trans* pyrene-chalcone-MMA and MB-MMA respectively.

#### 4.4 UV-Vis spectrum of P1 and P2 after irradiation

**P1** (5.0 mg, 0.51  $\mu\text{mol}$ ), **P2** (3.0 mg, 0.17  $\mu\text{mol}$ , 1 eq.) **M3** (1.5 mg, 8.7  $\mu\text{mol}$ , 49.5 eq.) and 4-dimethylaminopyridine (0.1 mg, 1.8  $\mu\text{mol}$ , 10 eq.) were dissolved in 20 mL acetonitrile ( $0.25 \text{ mg mL}^{-1}$ ),

and 3 mL of the solution was transferred to a quartz cuvette with a clear bottom. The solution was irradiated with monochromatic light at 480 nm for 15 mins. mins (700  $\mu$ J, 23  $\mu$ mol of photons). And the UV-Vis absorbance spectrum of the solution was measured before and after irradiation (Figure S22).



**Figure S22.** UV-vis spectrum of a solution of **P1**, **P2**, **M3** and DMAP in ACN, before and after irradiation at 480 nm for 15 mins (23  $\mu$ mol of photons).

## 5 Materials

Unless stated otherwise, all chemicals and solvents were used as received from the supplier without further purification.

2-cyano-2-propyl benzodithioate (Sigma Aldrich), methyl methacrylate (Sigma Aldrich, after passing through a short plug of basic alumina), 2,2'-azobis(2-methylpropionitrile) (AIBN, Sigma Aldrich, recrystallized), dichloromethane (DCM, Thermo Fisher Scientific), tetrahydrofuran (THF, Thermo Fisher Scientific), acetonitrile (Thermo Fisher Scientific), methanol (Thermo Fisher Scientific), deuterated acetonitrile- $d_3$  ( $CD_3CN$ , Novachem), deuterated chloroform- $d_1$  ( $CDCl_3$ , Sigma Aldrich), triethylamine (Sigma Aldrich) sodium carbonate (anhydrous, Sigma Aldrich), hydrochloric acid 32% (Thermo Fisher Scientific), hexane (Thermo Fischer Scientific), methylene blue (ChemSupply), ascorbic acid (Sigma Aldrich), acetovanillone (Merck), dimethylformamide (Thermo Fisher Scientific), ethyl acetate (Thermo Fisher Scientific), diethyl ether (Thermo Fisher Scientific), triphosgene (Sigma Aldrich), 4-dimethylaminopyridine (DMAP, Sigma Aldrich), potassium carbonate (ChemSupply); sodium bicarbonate (Merck), N-(3-aminopropyl)methacrylamide hydrochloride (Combiblocks), acetone (Thermo Fischer Scientific), 3-bromopropanol (Sigma Aldrich), 1-pyrenecarboxaldehyde (Merck), anhydrous magnesium sulfate (Merck), sodium hydroxide (ChemSupply), ethanol (Thermo Fisher Scientific), ethyl 4-bromobutyrate (Merck), 4'-methoxyacetophenone (Merck), N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC·HCl) (Sigma Aldrich), 2-hydroxyethyl methacrylate (Sigma Aldrich), pentafluorophenol (Sigma Aldrich), glutaric acid (Sigma Aldrich), dioxane (Sigma Aldrich).

## 6 References

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