

Supporting Information

1. Photopolymerization setup

Photopolymerization was carried out in a geometry illustrated below. The reaction is irradiated with RY-5050 green LED lights (5 W/m, $\lambda_{\text{max}} = 535$ nm). The distance of the reaction to LED light was 5 cm. The light intensity (3600 lm/m²) reaching the reaction was measured by Smart Sensor AR823 luminometer (ARCO, Beijing, China).



2. Materials

Dicyclohexylcarbodiimide (DCC, 99%), 4-dimethylaminopyridine (DMAP, 99%) and N,N-dimethylacrylamide (DMA, 98%) were purchased from Aladdin. Poly (ethylene glycol) methyl ether methacrylate (PEGMA, $M_n = 500$ g/mol) and poly (ethylene glycol) methyl ether acrylate (PEGA, $M_n = 480$ g/mol) were purchased from Sigma-Aldrich. Cucurbit[7]uril (CB[7], 99%) was purchased from Shanghai BioChem Partner. The inhibitors contained in all monomers were removed by passing the monomers through Al₂O₃ columns prior to use. Triethanolamine (TEOA, 98%) and Poly (ethylene glycol) monomethyl ether (PEG₈-OH, M_n

= 350 g/mol) were purchased from Energy Chemical. 4-Cyano-4-(ethylthiocarbonothioylthio)pentanoic acid was synthesized as previously reported.¹ The chain transfer agent (CTA) used in polymerization was synthesized according to a previously reported procedure.² Perylene diimide (PDI) was synthesized according to the work previously reported.³

3. Characterization

Nuclear Magnetic Resonance (NMR) spectroscopy was carried out with a JEOL resonance ECZ400S 400 MHz spectrometer using D₂O or CDCl₃ as the solvent. All chemical shifts are reported in ppm (δ), referenced to the chemical shifts of residual solvent resonances.

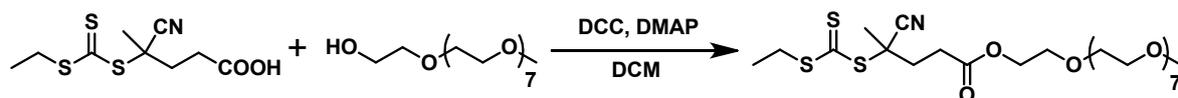
Gel Permeation Chromatography (GPC) was analyzed on a Waters Alliance e2695 GPC system equipped with a Styragel guard column (WAT054415, 30 \times 4.6 mm), two Org separation columns D2500 (300 \times 8 mm) and D5000 (300 \times 8 mm). Detection was made with a 2414 refractive index detector (Waters Alliance) and a Viscotek TDA 305-020 LALS/RALS detector (Malvern Instruments). DMF (HPLC grade, 1.75 mg/mL LiBr) was used as the eluent at a flow rate of 0.7 mL/min.

UV-Vis absorption spectroscopy was acquired on a Hitachi U-3010 UV-Vis photospectrometer. The path length was 10 mm, slit width was 2 nm, and scan speed was 1200 nm/min.

Fluorescence spectroscopy was recorded on a Hitachi U-3010 spectrophotometer. The excitation wavelength was 510 nm, slit width was 5.0 nm, and scanning rate was 1200 nm/min, voltage was 500 V.

Cyclic Voltammetry (CV) was performed using 0.1 M NaCl as the supporting electrolyte with a standard three-electrode system. A platinized carbon electrode (diameter: 3 mm, CHI104, CH Instruments) was used as the working electrode, a platinum wire (CHI115, CH Instruments.) was used as the counter electrode, and a saturated calomel electrode (CHI150, CH Instruments) was used as the reference electrode. The scan rate was 0.05 V/s. All electrochemical measurements were carried out using an electrochemical working station (CHI760E, Shanghai, China) at room temperature.

4. Synthesis of chain transfer agent (CTA)



The chain transfer agent (CTA) was synthesized according to a reported protocol.² 4-Cyano-4-(ethylthiocarbonothioylthio) pentanoic acid (0.8637 g, 3.28 mmol), PEG₈-OH (1.2630 g, 3.61 mmol), and DMAP (0.0801 g, 0.66 mmol) were added into a glass vial and dissolved in 25 mL CH₂Cl₂. After the solution was stirred for 10 min, DCC (0.8789 g, 4.26 mmol) dissolved in 6 mL CH₂Cl₂ was dropwise added via a syringe pump. After stirring at room temperature for 24 h, the reaction mixture was filtered to remove the white precipitate, then washed with saturated NaCl solution (4 × 100 mL) and dried over anhydrous MgSO₄. The solvent was removed via rotary evaporation to obtain an oil, which was further purified by column chromatography (methanol/CH₂Cl₂ = 2/98) to afford PEG₈-CTA (1.6 g, 85% yield). The ¹H NMR spectrum in D₂O and ¹³C NMR spectrum in CDCl₃ are shown in **Figure S1** and **Figure S2**.

¹H NMR (400 MHz, D₂O): δ ppm 4.11 (t, 2H), 3.55 (m, 30 H), 3.27 (t, 2H), 3.24 (s, 3H), 2.56 (t, 2H), 2.43 (t, 2H), 1.77 (s, 3H), 1.23 (t, 3H).

¹³C NMR (100 MHz, CDCl₃): δ ppm 216.84, 171.49, 119.03, 71.93, 70.61, 68.97, 64.18, 59.05, 46.35, 33.76, 31.38, 29.70, 24.82, 12.82.

5. General procedure for the synthesis of homopolymers via RAFT photopolymerization using PDI/TEOA

All polymerizations were conducted in H₂O at room temperature under green LED light (5 W, λ_{max} = 535 nm) at a monomer concentration of 10% w/v. The synthesis of PDMA₂₀₀ is given as a representative procedure as follows. A solution consisting of CTA (0.0088 g, 0.0148 mmol), DMA (0.2913 g, 2.939 mmol), TEOA (0.0022 g, 0.0015 mmol), PDI (0.032 mg, 0.037 μmol) and 3 mL water was prepared in a 20 mL glass vial. The glass vial was sealed and degassed with nitrogen for at least 30 minutes and then exposed to green LED light (5 W, 535 nm) at a stirring rate of 500 rpm. After 4 hours, the light was switched off and the

solution was exposed to air. The monomer conversion was analyzed by ^1H NMR spectroscopy. The theoretical molecular weight was calculated using the following equation: $M_{n,\text{th}} = [\text{M}]_0/[\text{CTA}]_0 \times M_w(\text{M}) \times \alpha(\text{NMR}) + M_w(\text{CTA})$, where $[\text{M}]_0$, $[\text{CTA}]_0$, $M_w(\text{M})$, $\alpha(\text{NMR})$ and $M_w(\text{CTA})$ correspond to the monomer and CTA concentration, molar mass of the monomer, conversion determined by ^1H NMR and the molar mass of CTA, respectively. The molecular weights and dispersities were determined by DMF GPC.

6. General procedure for kinetic studies of RAFT photopolymerization

The polymerizations were conducted in H_2O at room temperature under green LED light (5 W, $\lambda_{\text{max}} = 535 \text{ nm}$), 10% w/v monomer concentration. The synthesis of PDMA₂₀₀ at a molar ratio of $[\text{DMA}]/[\text{CTA}]/[\text{PDI}]/[\text{TEOA}] = 200/1/0.0025/0.1$ is given as a representative procedure as follows. A solution consisting of CTA (0.0088 g, 0.0148 mmol), DMA (0.2913 g, 2.939 mmol), TEOA (0.0022 g, 0.0015 mmol), PDI (0.032 mg, 0.037 μmol), and 3 mL water was prepared in a 20 mL glass vial. The glass vial was sealed and degassed with nitrogen for at least 30 minutes and then exposed to green LED light (5 W, 535 nm) at a stirring rate of 500 rpm. Aliquots were withdrawn at predetermined time intervals for ^1H NMR and GPC measurements. After the polymerization was complete, the light was switched off and the resulting mixture was exposed to air. The monomer conversion was determined by ^1H NMR spectroscopy. The theoretical molecular weight was calculated using the following equation: $M_{n,\text{th}} = [\text{M}]_0/[\text{CTA}]_0 \times M_w(\text{M}) \times \alpha(\text{NMR}) + M_w(\text{CTA})$, where $[\text{M}]_0$, $[\text{CTA}]_0$, $M_w(\text{M})$, $\alpha(\text{NMR})$ and $M_w(\text{CTA})$ correspond to the monomer and CTA concentration, molar mass of the monomer, conversion measured by ^1H NMR and the molar mass of CTA, respectively. The molecular weights and dispersities were determined by DMF GPC.

7. Synthesis of PDMA multiblock homopolymers via successive chain extensions using supramolecular photocatalyst

The following conditions were used: $[\text{DMA}]/[\text{CTA}]/[\text{PDI}]/[\text{CB}[7]]/[\text{TEOA}] = 100/1/0.005/0.01/0.1$, monomer concentration 10% w/v. The multiblock homopolymer was synthesized without intermediate isolation and purification. No additional PDI, CB[7], and TEOA were added for each of the chain extensions. In the synthesis of the first block, CTA

(0.0170 g, 0.029 mmol), DMA (0.2830 g, 2.9 mmol), TEOA (0.43 mg, 0.0029 mmol), PDI (0.13 mg, 0.145 μmol), and CB [7] (0.35 mg, 0.29 μmol) were mixed in a 20 mL glass tube with 3 mL water and degassed with nitrogen for 30 minutes. Then the glass tube was irradiated with green LED light at a stirring rate of 500 rpm. After 4 hours, a PDMA₁₀₀ was obtained with $\sim 100\%$ conversion. Then a certain amount of a DMA solution (10% w/v, degassed with nitrogen for 30 min) was added to the first block solution, and polymerization continued by light exposure for another 4 hours to result in the formation of the diblock PDMA₁₀₀-PDMA₁₀₀ with $\sim 100\%$ monomer conversion. The third and the fourth block each with a target DP of 100 were synthesized following the same protocol. At the end of each of the polymerizations, a small aliquot was withdrawn for ¹H NMR and GPC measurements.

8. Synthesis of diblock copolymers of different monomer families using supramolecular photocatalyst

The synthesis of diblock copolymers of different monomer families was conducted in H₂O at room temperature under green LED light (5 W, $\lambda_{\text{max}} = 535 \text{ nm}$) at a molar ratio of [CTA]/[PDI]/[CB[7]]/[TEOA] = 1/0.01/0.02/0.1. The first blocks of PDMA₁₀₀, PPEGA₂₀₀ and PPEGMA₂₀₀ were synthesized via the procedure described for homopolymer synthesis. After the polymerization of the first block was complete, a solution of the second monomer was added and chain extension was conducted without purification and isolation of the first block. No additional PDI, CB[7], and TEOA were added for chain extension experiments. The synthesis of PPEGMA₂₀₀-PDMA₂₀₀ is given as a representative procedure for the preparation of diblock copolymers as follows. A solution consisting of CTA (0.0018 g, 0.0030 mmol), PEGMA (0.2982 g, 0.5964 mmol), TEOA (0.0449 mg, 0.3 μmol), PDI (0.0262 mg, 0.03 μmol), CB[7] (0.0698 mg, 0.06 μmol), and 3 mL water was prepared in a 20 mL glass vial. The glass vial was sealed and degassed with nitrogen for 30 minutes and then exposed to green LED light (5 W, 535 nm) at a stirring rate of 500 rpm at room temperature. After polymerization for 8 h, 100 μL of the polymerization solution was taken out for ¹H NMR and GPC measurement. For chain extension, the PPEGMA₂₀₀ polymer solution and 10% w/v DMA (0.0572 g, 0.577 mmol) solution were respectively degassed with nitrogen for 30 min. Then the DMA solution was injected into the PPEGMA₂₀₀ solution and exposed to green LED

light (5 W, 535 nm) at a stirring rate of 500 rpm at room temperature for another 6 h. The theoretical molecular weight of second block was calculated using the following equation: $M_{n,th} = M_{n,th}(B1) + [(M2)]_0/[CTA]_0 \times M_w(M2) \times \alpha(NMR)$, where $[M2]_0$, $[CTA]_0$, $M_{n,th}(B1)$, $M_w(M2)$ and $\alpha(NMR)$ correspond to the second monomer and CTA concentration, the theoretical molecular weight of the first block and the molar mass of the second monomer, and the monomer conversion measured by 1H NMR. The molecular weights and dispersities were determined by GPC.

9. Supplementary data and analysis

9.1. NMR data of CTA

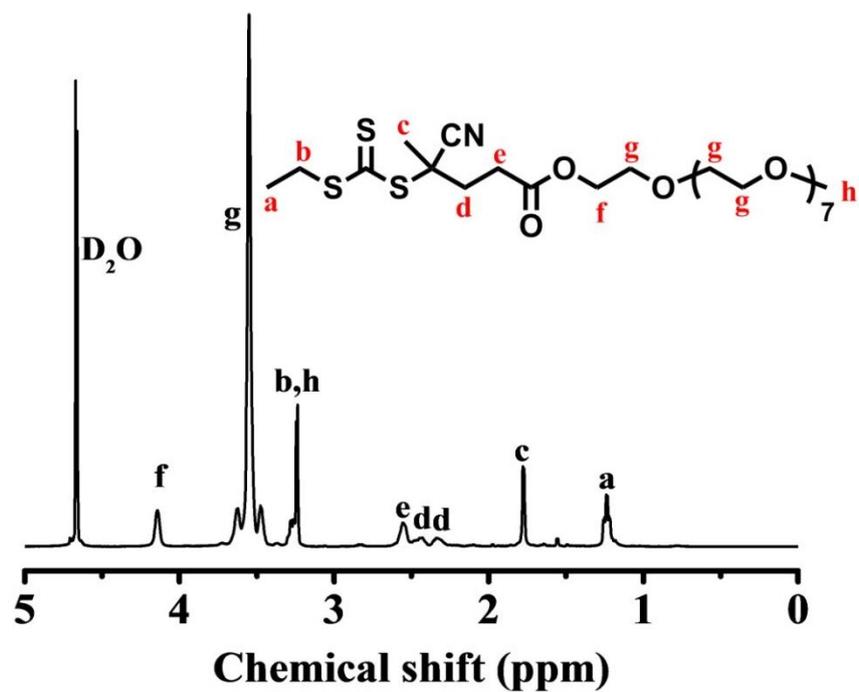


Figure S1. ¹H NMR spectrum of CTA in D₂O.

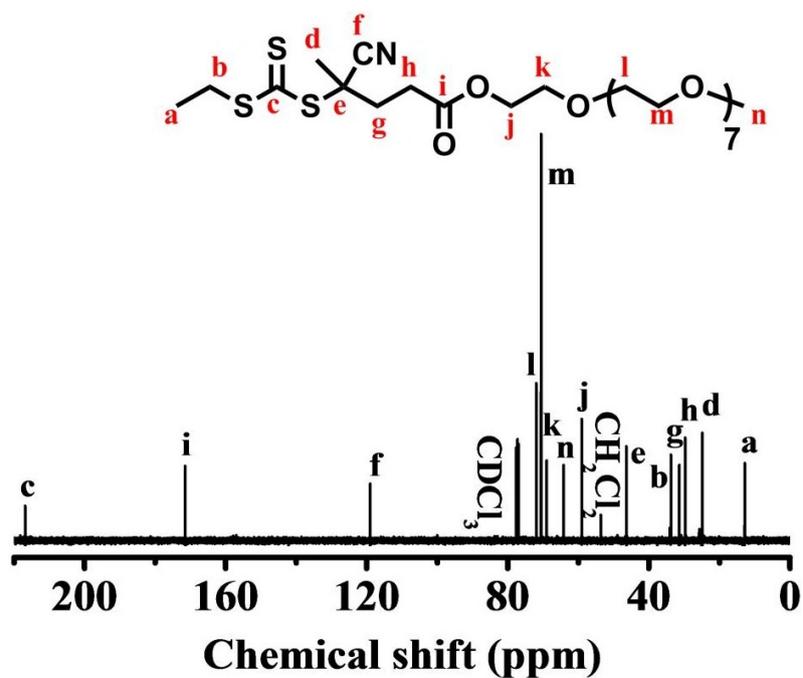


Figure S2. ¹³C NMR spectrum of CTA in CDCl₃.

9.2. UV-Vis absorption and fluorescence spectroscopic studies of PDI/CB[7] complexation

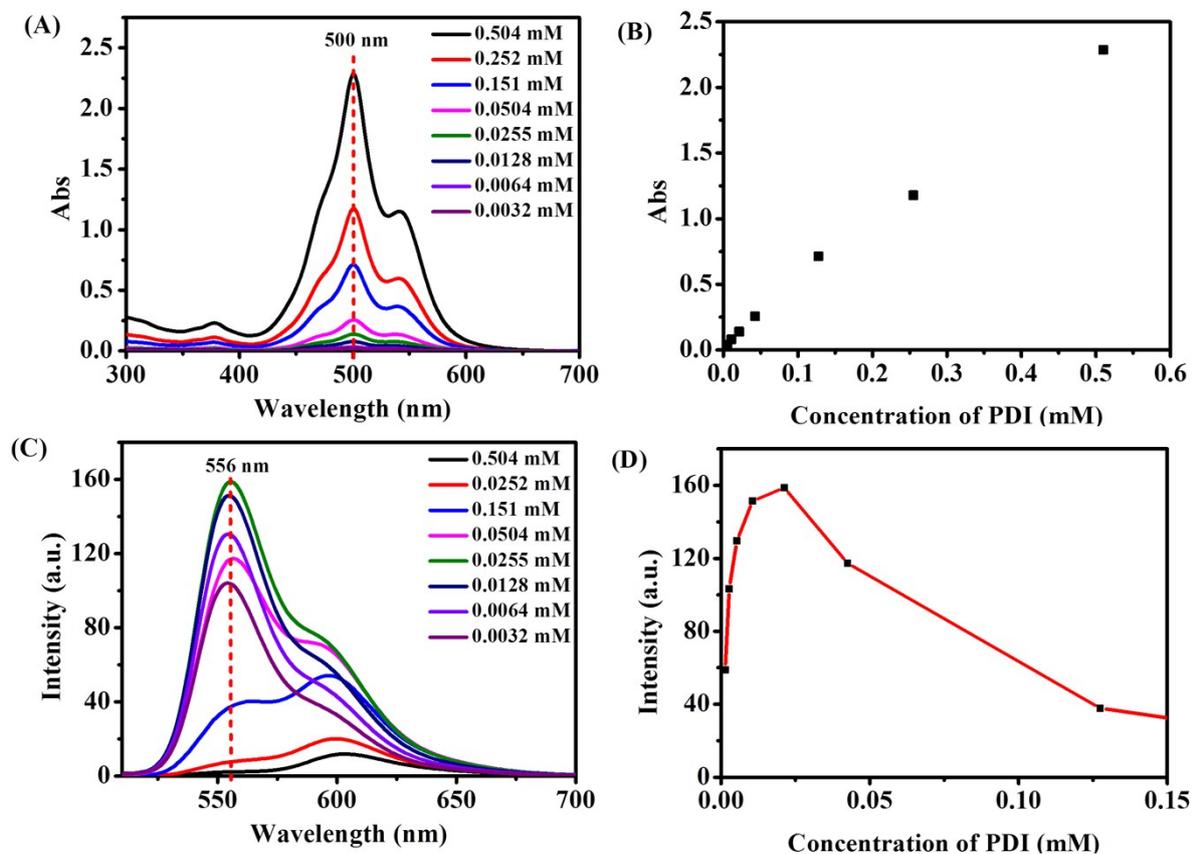


Figure S3. UV-Vis absorption spectra of PDI in **water** (A) and the corresponding dependence of absorbance (measured at 500 nm) on PDI concentration (B); fluorescence spectra of PDI in **water** (C) and the corresponding dependence of fluorescence intensity (measured at 556 nm) on PDI concentration (D).

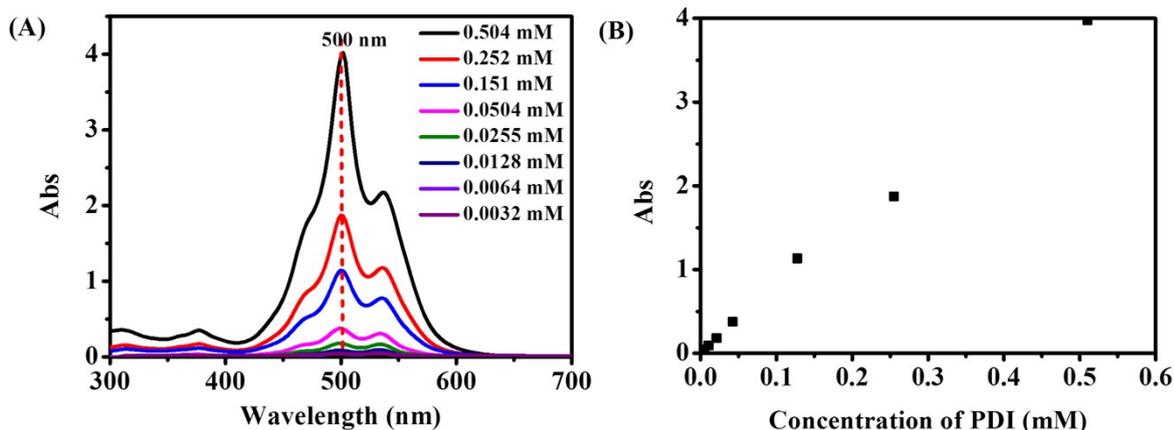


Figure S4. UV-Vis absorption spectra of PDI in **DMA solution** (10% w/v) (A) and the corresponding dependence of absorbance (measured at 500 nm) on PDI concentration (B).

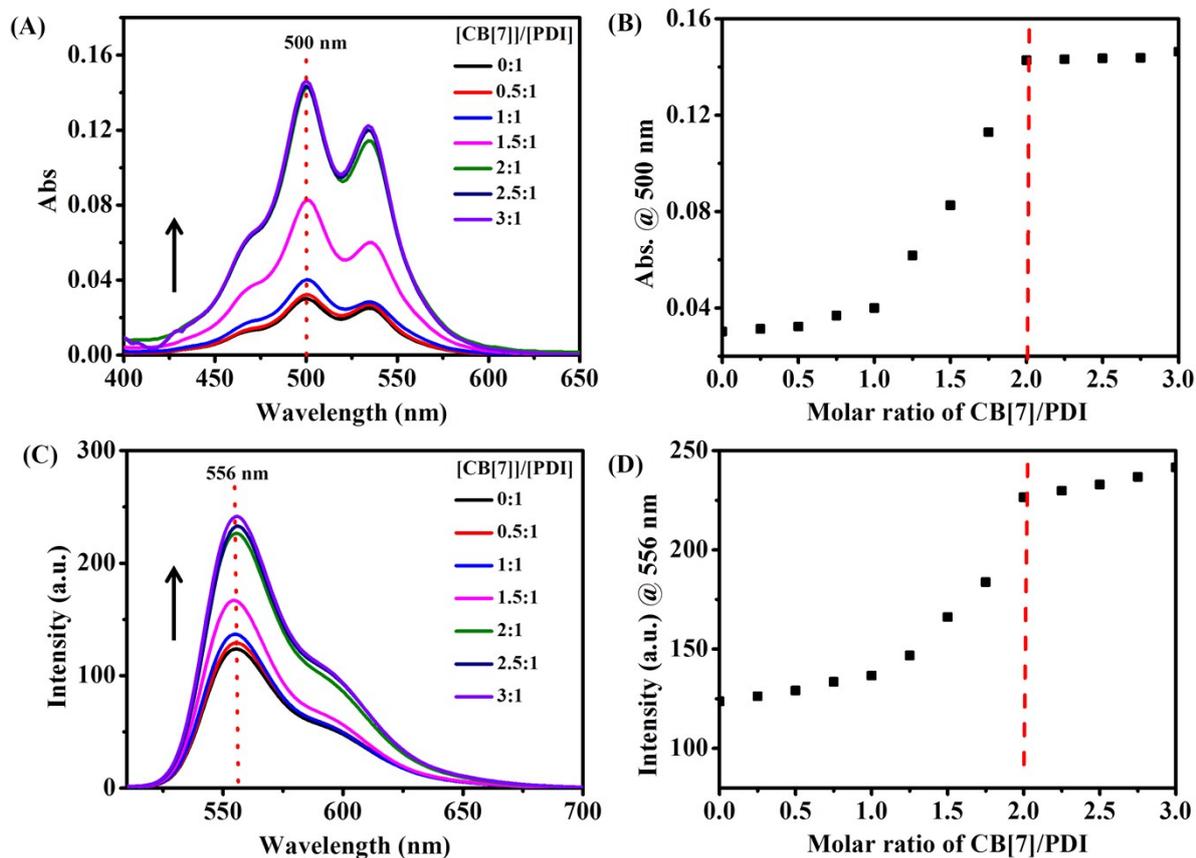


Figure S5. UV-Vis absorption spectra of PDI in **water** (0.0128 mM) with added CB[7] (A) and the corresponding dependence of absorbance (measured at 500 nm) on the molar ratio of CB[7]/PDI (B); fluorescence spectra of PDI in **water** (0.0128 mM) with added CB[7] (C) and the corresponding dependence of fluorescence intensity (measured at 556 nm) on the molar ratio of CB[7]/PDI (D).

9.3. Redox potentials of PDI, CTA, and TEOA

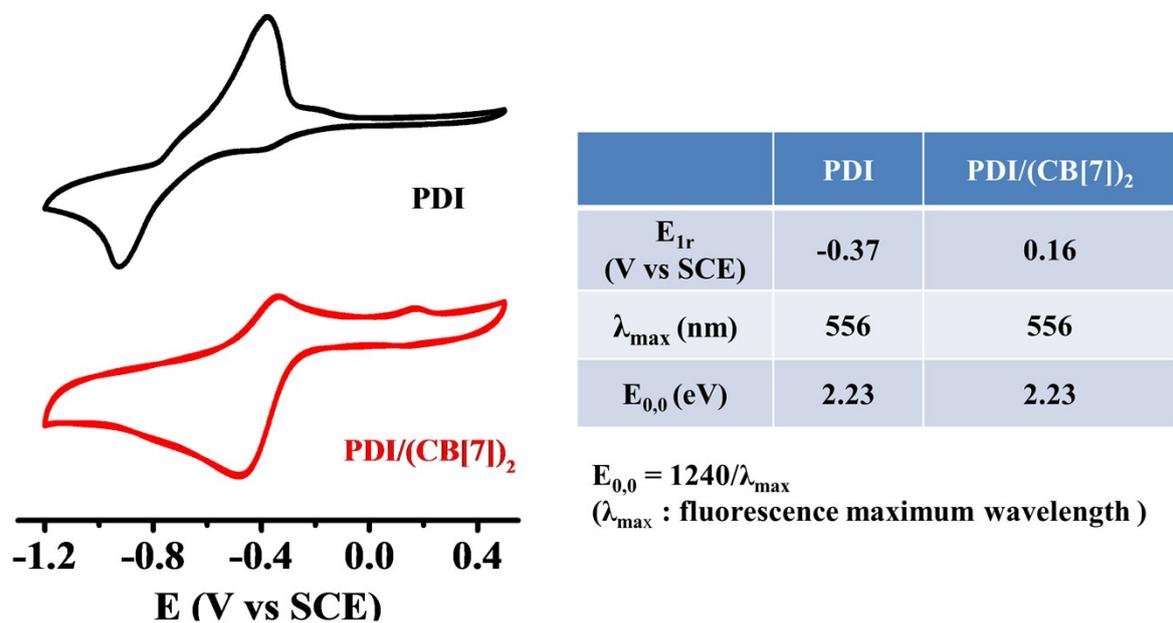


Figure S6. Cyclic voltammograms and tabulated data for one-electron reduction potentials and optical energy gaps of PDI and PDI/(CB[7])₂.

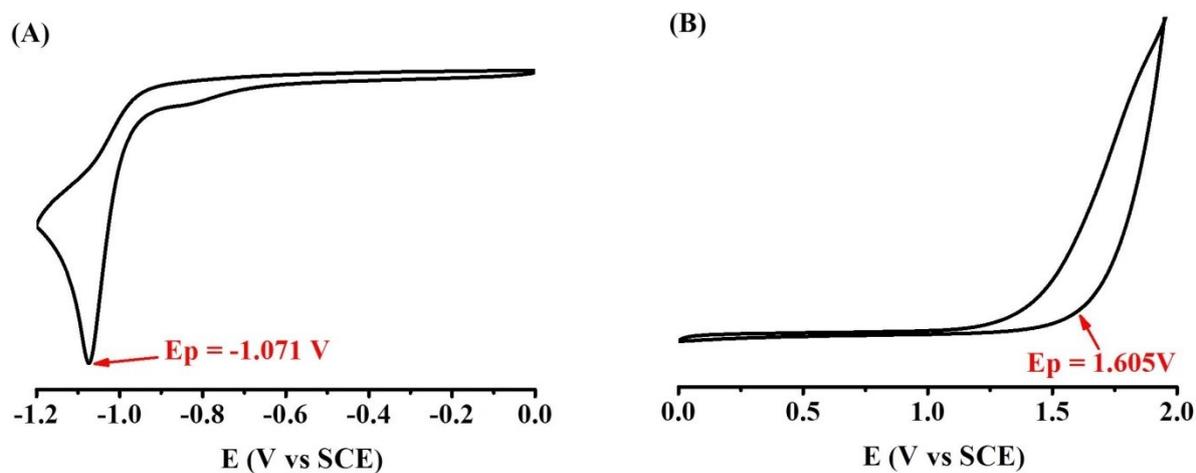


Figure S7. Cyclic voltammograms of CTA.

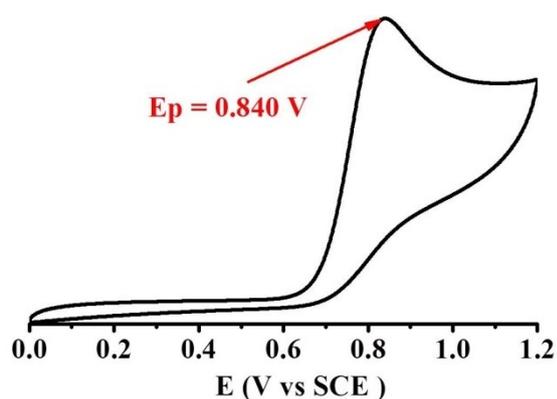


Figure S8. Cyclic voltammograms of TEOA.

9.4. Analysis of excited-state redox potentials of PDI

(1) Reductive quenching pathway:



$$\begin{aligned} E_{\text{ox}}^*(\text{PDI}^{\bullet+}/\text{PDI}^*) &= E_{\text{ox}}(\text{PDI}^{\bullet+}/\text{PDI}) - E_{0,0} \\ &= 1.67 \text{ V} - 2.23 \text{ V} \\ &= -0.45 \text{ V} \end{aligned}$$

Note: $E_{\text{ox}}(\text{PDI}^{\bullet+}/\text{PDI})$ (1.67 V) was taken from ref. 66

(2) Oxidative quenching pathway:



$$\begin{aligned} E_{\text{red}}^*(\text{PDI}^*/\text{PDI}^{\bullet-}) &= E_{\text{red}}(\text{PDI}/\text{PDI}^{\bullet-}) + E_{0,0} \\ &= -0.37 \text{ V} + 2.23 \text{ V} \\ &= 1.86 \text{ V} \end{aligned}$$

9.5. UV-Vis and fluorescence spectroscopic studies of PDI: effect of DMA, CTA, and TEOA

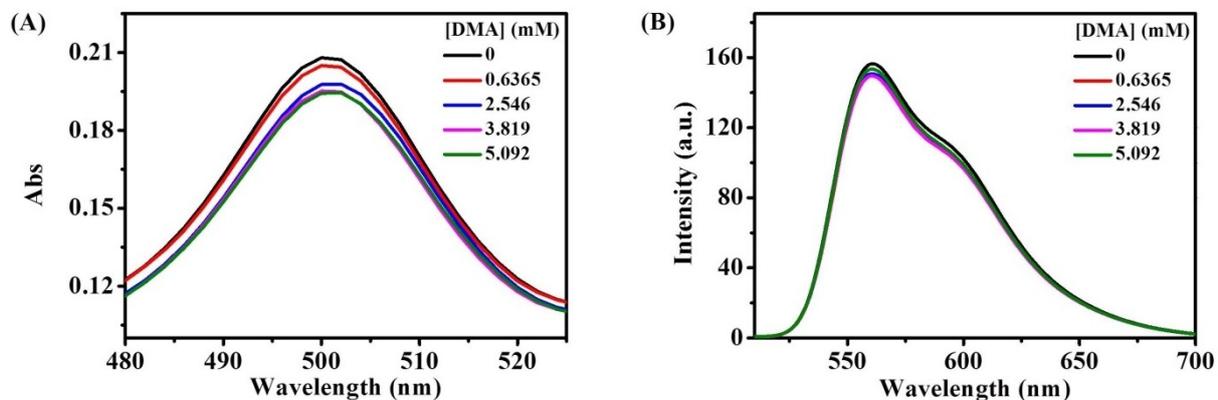


Figure S9. UV-Vis absorption spectra (A) and fluorescence spectra (B) of PDI aqueous solution (0.0255 mM) in the presence of different concentrations of DMA.

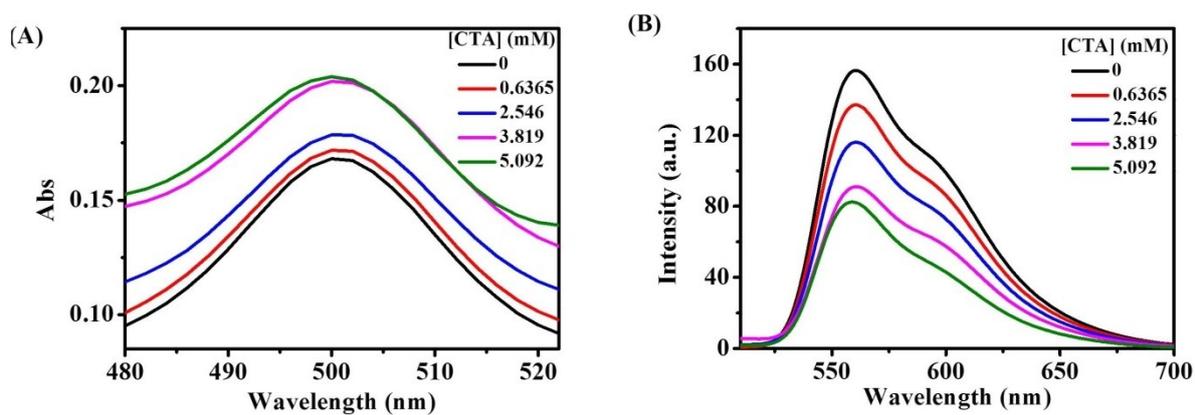


Figure S10. UV-Vis absorption spectra (A) and fluorescence spectra (B) of PDI in water (0.0255 mM) in the presence of different concentrations of CTA.

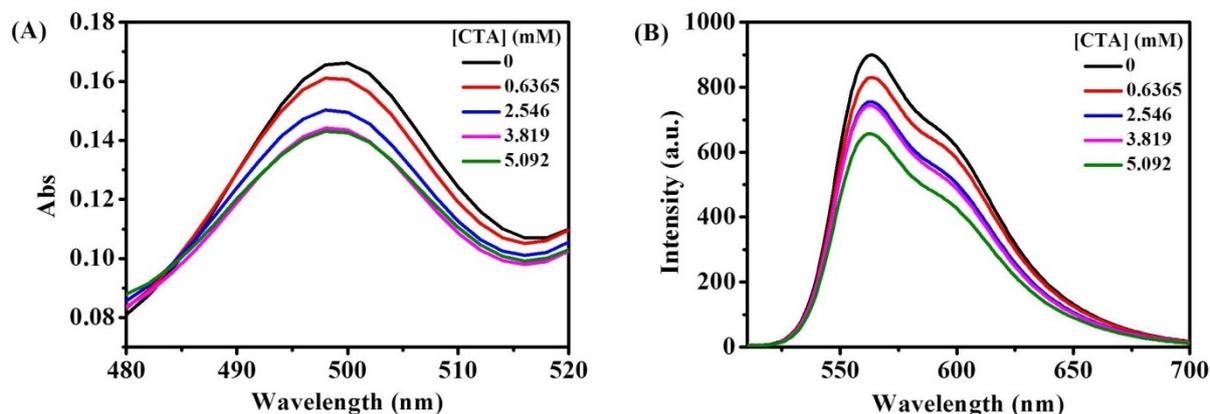


Figure S11. UV-Vis absorption spectra (A) and fluorescence spectra (B) of PDI in **DMA solution (10% w/v)** (0.0255 mM) in the presence of different concentrations of CTA.

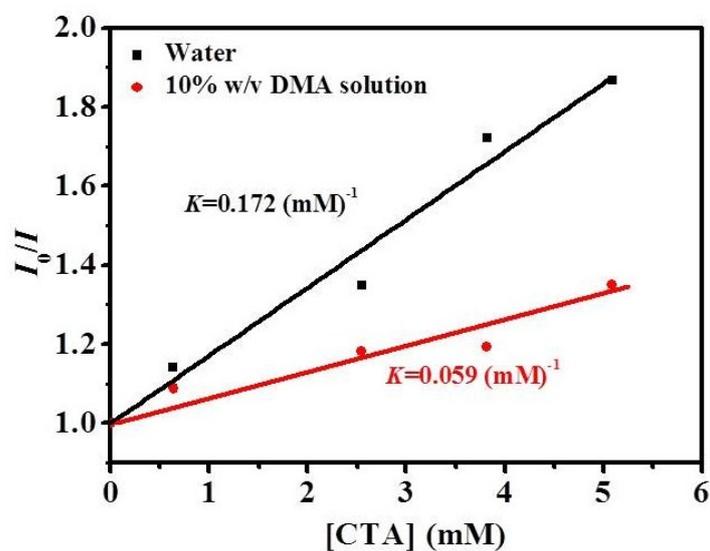


Figure S12. Stern-Volmer plots for PDI fluorescence quenching in **water** and **DMA solution (10% w/v)** (0.0255 mM) in the presence of different concentrations of CTA.

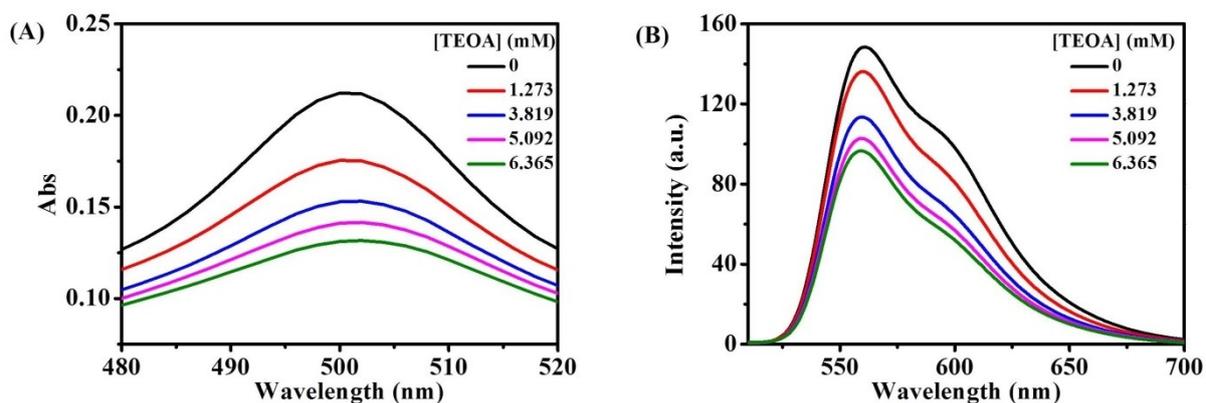


Figure S13. UV-Vis absorption spectra (A) and fluorescence spectra (B) of PDI in **water** (0.0255 mM) in the presence of different concentrations of TEOA.

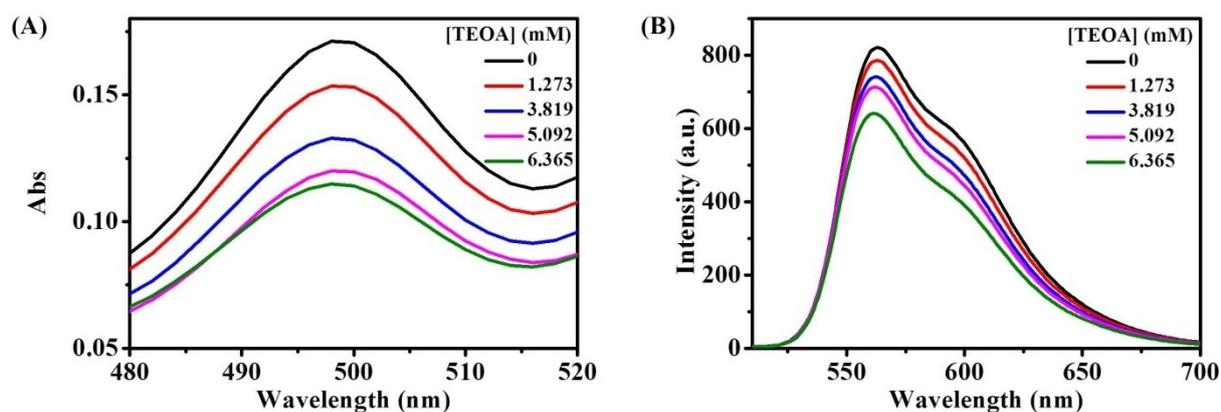


Figure S14. UV-Vis absorption spectra (A) and fluorescence spectra (B) of PDI in **DMA solution** (10% w/v) (0.0255 mM) in the presence of different concentrations of TEOA.

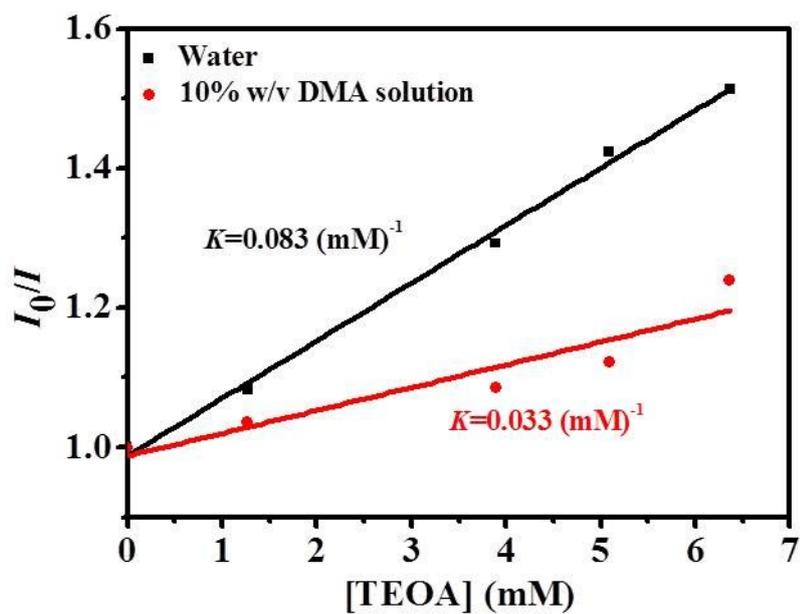
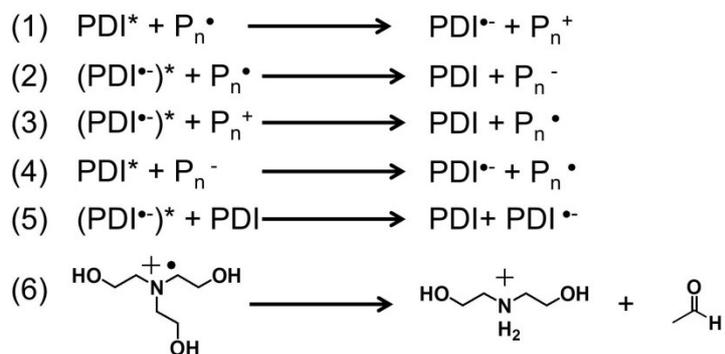


Figure S15. Stern-Volmer plots for PDI fluorescence quenching in **water** and **DMA solution (10% w/v)** (0.0255 mM) in the presence of different concentrations of TEOA.

9.6. Additional possible redox reactions during the polymerization



9.7. Additional GPC traces and table for polymer synthesis

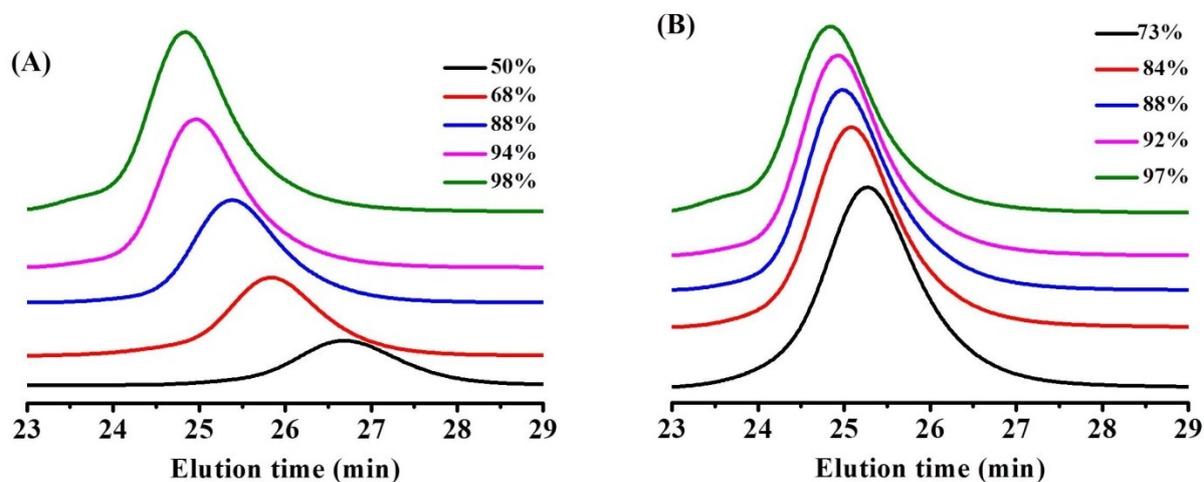


Figure S16. GPC traces for RAFT photopolymerizations conducted in water using 0.3 (A) and 0.5 equivalents of TEOA (B), $[\text{DMA}] = 10\%$ w/v, $[\text{DMA}]/[\text{CTA}]/[\text{PDI}] = 200/1/0.005$, green light (5 W, $\lambda_{\text{max}} = 535$ nm).

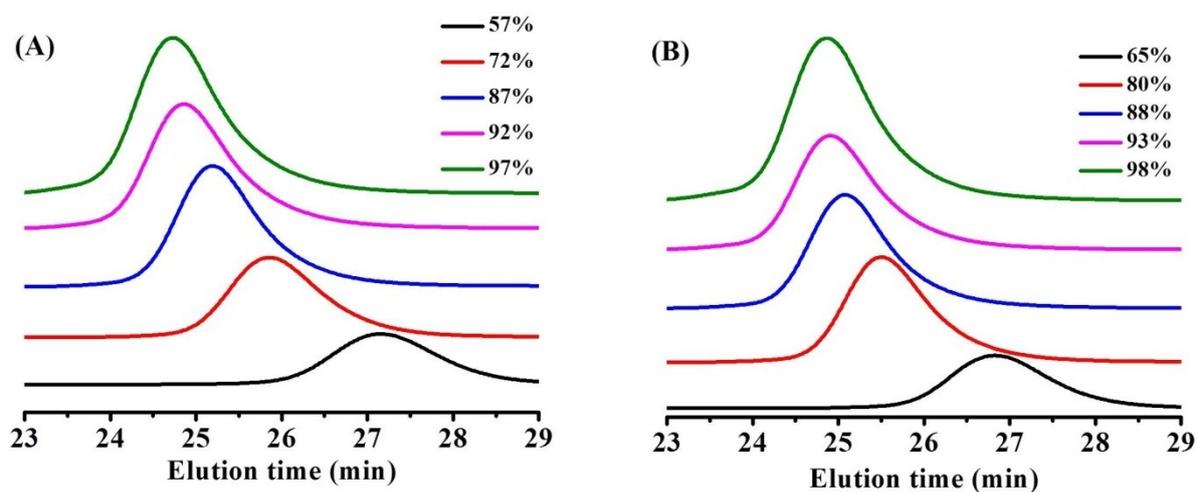


Figure S17. GPC traces for RAFT photopolymerizations conducted in water using 0.005 (A) and 0.01 equivalents of PDI (B), $[\text{DMA}] = 10\%$ w/v, $[\text{DMA}]/[\text{CTA}]/[\text{TEOA}] = 200/1/0.1$, green light (5 W, $\lambda_{\text{max}} = 535$ nm).

Table S1. Summary of PPEGA and PPEGMA synthesized using supramolecular PDI/CB[7] photocatalyst. ^a

polymer	target DP	time (h)	conv. (%)	$M_{n,th}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	\bar{D}
PPEGA	100	8	>99	48.6	46.4	1.15
PPEGMA	100	8	>99	50.6	56.7	1.15

^a[M]/[CTA]/[PDI]/[CB[7]]/[TEOA] = 100/1/0.005/0.01/0.1, green LED light (5 W, λ_{max} = 535 nm).

Table S2. Summary of PDMA multiblock homopolymers synthesized via successive chain extensions using supramolecular PDI/CB[7] photocatalyst. ^a

block #	DMA (w/v %)	conv. (%)	time (h)	$M_{n,th}$ (kg/mol)	$M_{n,GPC}$ (kg/mol)	\bar{D}
1	10	>99	4	10.5	10.8	1.19
2	10	>99	4	20.4	21.2	1.18
3	10	>99	4	30.4	32.1	1.06
4	10	>99	4	40.2	40.7	1.17

^a[CTA]/[PDI]/[CB[7]]/[TEOA] = 1/0.005/0.01/0.1, green LED light (5 W, λ_{max} = 535 nm), the target DP for each block is 100.

10. References

1. S. H. Thang, Y. K. Chong, R. T. A. Mayadunne, G. Moad and E. Rizzardo, *Tetrahedron Lett.*, 1999, **40**, 2435-2438.
2. W. Shen, Q. Qiu, Y. Wang, M. Miao, B. Li, T. Zhang, A. Cao and Z. An, *Macromol. Rapid Commun.*, 2010, **31**, 1444-1448.
3. Y. Jiao, K. Liu, G. Wang, Y. Wang and X. Zhang, *Chem. Sci*, 2015, **6**, 3975-3980.