

## Supporting Information

### **An Aqueous Photo-Controlled Polymerization under NIR Wavelengths: Synthesis of Polymeric Nanoparticles through Thick Barriers**

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## EXPERIMENTAL SECTION

### Materials

*N,N*-dimethylacrylamide (DMA, 99%), *N,N*-diethylacrylamide (DEA, 99%), 2-hydroxyethyl acrylate (HEA, 96%), oligo(ethylene glycol) methyl ether acrylate (OEGA, 99%) ( $M_n = 480 \text{ g mol}^{-1}$ ), and oligo(ethylene glycol) methyl ether methacrylate (OEGMA, 99%) ( $M_n = 300 \text{ g mol}^{-1}$ ) were all purchased from Aldrich and deinhhibited by passing through a basic alumina column (Ajax Chemical, AR). 2-Hydroxypropyl methacrylate (HPMA, 97%) was purchased from Aldrich and purified by silica column chromatography using ethyl acetate/hexane (1/8) as the eluent. Zinc tetrasulfonated phthalocyanine ( $\text{ZnPcS}_{4-}$ , 95%) was obtained from phthalocyanine tetrasulfonic acid (Frontier Scientific) neutralized with quantitative sodium bicarbonate ( $\text{NaHCO}_3$ , AR). Thiocarbonylthio compounds (RAFT agents), including 4-cyano-4-[(dodecylsulfanylthiocarbonyl)sulfanyl] pentanoic acid (CDTPA, 97%), 4-(((2-carboxyethyl)thio)carbonothioyl)thio)-4-cyanopentanoic acid (CTCPA, 95%), 2-(Butylthiocarbonothioylthio)propanoic acid (BTPA, 95%) were purchased from Boron Molecular while 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT, 97%) were purchased from Aldrich. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt% in  $\text{H}_2\text{O}$ ) was purchased from Chem-Supply. 9,10-Dimethylantracene (9,10-DMA, 99%), nitrotetrazolium blue chloride (NBT, 90%), triethanolamine (TEOA, 99%), poly(ethylene glycol) methyl ether ( $\text{PEG}_{113}$ ,  $M_n = 5,000 \text{ g mol}^{-1}$ ), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), and 4-(dimethylamino)pyridine (DMAP, 99%) were all purchased from Aldrich and used as received. Zinc meso-tetra(*N*-methyl-4-pyridyl) porphine tetrachloride ( $\text{ZnTMPyP}$ ) was purchased from Frontier Scientific.

### Instrumentation

Gel Permeation Chromatography (GPC) was used to characterize synthesized polymer (MWDs,  $M_n$ , and  $D$ ) with dimethylacetamide (DMAc) as the eluent. The GPC instrument was comprised of a Shimadzu modular system with an autoinjector, a Phenomenex 5.0  $\mu\text{M}$  bead size guard column ( $50 \times 7.5 \text{ mm}$ ) followed by four Phenomenex 5.0  $\mu\text{M}$  bead size columns ( $10^5$ ,  $10^4$ ,  $10^3$ , and  $10^2 \text{ \AA}$ ), and a differential refractive-index detector. The GPC system was calibrated based on the narrow molecular weight distribution of PMMA standards with molecular weights of 200 to  $10^6 \text{ g mol}^{-1}$ .

Nuclear Magnetic Resonance (NMR) spectroscopy was carried out with Bruker Avance III HD 400 MHz NMR for  $^1\text{H}$  using  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  as solvent. Tetramethylsilane (TMS) was used as a reference. The data was reported as chemical shift ( $\delta$ ) measured in ppm downfield from TMS.

Online Fourier Transform Near-Infrared (FTNIR) was used for monitoring monomer conversion by

calculating the decrement of the vinylic C-H stretching overtone of the monomer at  $\sim 6200\text{ cm}^{-1}$ . A Bruker IFS 66/S Fourier transform spectrometer equipped with a tungsten halogen lamp, a CaF<sub>2</sub> beam splitter, and liquid nitrogen cooled InSb detector was used. The prepared sample was placed in an FTNIR glass cuvette (1 cm  $\times$  2 mm) and polymerized under NIR ( $\lambda_{\text{max}} = 730\text{ nm}$ ) LED light irradiation. The sample was manually placed into the cuvette holder, with each spectrum comprising 16 scans with a resolution of  $4\text{ cm}^{-1}$  in the region of  $8000\text{-}4000\text{ cm}^{-1}$ . The measurement time per spectrum was around 10 seconds, and the results from FTNIR were analyzed with OPUS software.

UV-vis Spectroscopy was measured using a CARY 300 spectrophotometer (Varian) using a quartz cuvette (1 cm  $\times$  1 cm).

Dynamic Light Scattering (DLS) measurements were performed using a Malvern Zetasizer Ultra and analyzed by ZS Xplorer software. A 4 mW He-Ne laser operating at a wavelength of 633 nm and an avalanche photodiode (APD) detector were used. The scattered light was detected at an angle of  $173^\circ$ .

Transmission Electron Microscopy (TEM) studies of self-assembled block copolymers were conducted at an accelerating voltage of 100 kV (JEOL-1400). The polymerization dispersions were diluted with water to give 0.2 - 0.5 wt% dispersions and deposited onto carbon-coated copper grids. Uranyl acetate staining was applied to all samples.

Photopolymerizations were performed in quartz cuvettes (1 cm  $\times$  2 mm) or 2 ml glass vials where the prepared mixtures were irradiated by NIR ( $\lambda_{\text{max}} = 730\text{ nm}$ ), violet ( $\lambda_{\text{max}} = 405\text{ nm}$ ), and green ( $\lambda_{\text{max}} = 530\text{ nm}$ ) LEDs. The light intensity was quantified by Newport 843-R Power Meter.

### **Synthesis of PEG<sub>113</sub>-CDTPA macroRAFT agent**

CDTPA (0.97 g, 2.4 mmol) in DCM (20 mL) was added to a flask containing PEG<sub>113</sub> (6 g, 1.2 mmol) and a stirrer bar. Then a solution of DCC (0.5 g, 2.4 mmol) and DMAP (0.029 g, 0.24 mmol) in DCM (10 mL) was added dropwise to the reaction mixture at  $0\text{ }^\circ\text{C}$ . The flask was sealed with a rubber septum and purged with nitrogen for 30 min at  $0\text{ }^\circ\text{C}$ . The esterification reaction was allowed to proceed with stirring at room temperature for 48 hours. PEG<sub>113</sub>-CDTPA macroRAFT agent was collected by filter and repeated precipitation of the reaction mixture in cold diethyl ether.

### **Experiments of quenching singlet oxygen ( $^1\text{O}_2$ ) and superoxide ( $\text{O}_2^{\cdot-}$ )**

Experiments of quenching singlet oxygen ( $^1\text{O}_2$ ) by 9,10-dimethylanthracene

As an example, experiments of quenching  $^1\text{O}_2$  with a stoichiometry of  $[\text{ZnPcS}_4^-]:[9,10\text{-DMA}]:[\text{TEOA}] = 0.002:0.02:1$  was conducted as follows: A reaction solution consisting of DMF (190  $\mu\text{L}$ ), water (170  $\mu\text{L}$ ),  $\text{ZnPcS}_4^-$  (17  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0194  $\mu\text{mol}$ ), 9,10-dimethylantracene (9,10-DMA) (10  $\mu\text{L}$  of 19.4 mM 9,10-DMA in DMF stock solution, 0.194  $\mu\text{mol}$ ), and TEOA (13  $\mu\text{L}$  of 750 mM TEOA in water stock solution, 9.70  $\mu\text{mol}$ ) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. Under the irradiation of NIR light ( $\lambda_{\text{max}} = 730$  nm;  $I = 12$  mW  $\text{cm}^{-2}$ ), the characteristic peak of 9,10-DMA (absorption at  $\sim 379$  nm) was monitored by UV-vis spectroscopy at designated time points. Decreasing absorption of 9,10-DMA reflected the successful  $^1\text{O}_2$  trapping (**Scheme S1A**). In the presence of higher concentrations of TEOA, slower decreasing rates of 9,10-DMA absorption were observed, indicating  $^1\text{O}_2$  was also quenched by TEOA.

#### Experiments of quenching superoxide ( $\text{O}_2^{\bullet-}$ ) by nitrotetrazolium blue chloride

As an example, experiments of quenching  $\text{O}_2^{\bullet-}$  by nitrotetrazolium blue chloride (NBT) with a stoichiometry of  $[\text{ZnPcS}_4^-]:[\text{TEOA}]:[\text{NBT}] = 0.002:4:0.05$  was conducted as follows: A reaction solution consisting of water (131  $\mu\text{L}$ ),  $\text{ZnPcS}_4^-$  (17  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0194  $\mu\text{mol}$ ), TEOA (52  $\mu\text{L}$  of 750 mM TEOA in water stock solution, 38.8  $\mu\text{mol}$ ), and NBT (200  $\mu\text{L}$  of 2.43 mM NBT in DMF stock solution, 0.485  $\mu\text{mol}$ ) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. Under the irradiation of NIR light ( $\lambda_{\text{max}} = 730$  nm;  $I = 12$  mW  $\text{cm}^{-2}$ ), generated  $\text{O}_2^{\bullet-}$  was quenched by NBT, forming monoformazan (MF; absorption at  $\sim 525$  nm) and diformazan (DF; absorption at  $\sim 740$  nm) (**Scheme S1B**). MF and DF. Therefore, increasing absorption of MF and DF reflected the  $\text{O}_2^{\bullet-}$  trapping. In the presence of TEOA, increasing absorption at  $\sim 525$  nm and  $\sim 740$  were observed, indicating  $\text{O}_2^{\bullet-}$  was generated by TEOA.

### **Homogenous photo-RAFT polymerization**

#### General procedure for aqueous photo-RAFT polymerizations mediated by $\text{ZnPcS}_4^-$ in the absence of oxygen under NIR LED light (PET-RAFT via an oxidative quenching pathway (OQP))

As an example, PET-RAFT polymerization with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{ZnPcS}_4^-] = 200:1:0.01$  was conducted as follows: A reaction solution consisting of water (113  $\mu\text{L}$ ), *N,N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ), and  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. After deoxygenation for 15 mins, the cuvette was placed under a NIR ( $\lambda_{\text{max}} = 730$  nm;  $I = 60$  mW  $\text{cm}^{-2}$ ) LED light at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100-6220  $\text{cm}^{-1}$ ) at designated time points. After reaching a certain

monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

General procedure for aqueous photo-RAFT polymerizations mediated by  $\text{ZnPcS}_4^-$  in the absence of oxygen under NIR LED light (PET-RAFT via a reductive quenching pathway (RQP))

As an example, PET-RAFT polymerization with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  was conducted as follows: A reaction solution consisting of water (108  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer), and TEOA (5.2  $\mu\text{L}$ , 38.80  $\mu\text{mol}$ ) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. After deoxygenation for 15 mins, the cuvette was placed under a NIR ( $\lambda_{\text{max}} = 730$  nm;  $I = 60$  mW  $\text{cm}^{-2}$ ) LED light at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100-6220  $\text{cm}^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

General procedure for aqueous photo-RAFT polymerizations mediated by  $\text{ZnPcS}_4^-$  in the presence of TEOA and oxygen under NIR LED light (via an oxygen-mediated photoinitiation (O-PI))

As an example, photo-RAFT polymerization with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  was conducted as follows: A reaction solution consisting of water (108  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer), and TEOA (5.2  $\mu\text{L}$ , 38.80  $\mu\text{mol}$ ) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. After that, the cuvette was placed without deoxygenation under a NIR ( $\lambda_{\text{max}} = 730$  nm;  $I = 60$  mW  $\text{cm}^{-2}$ ) LED light at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100-6220  $\text{cm}^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

Procedure for aqueous photo-RAFT polymerizations mediated by  $\text{ZnPcS}_4^-$  in the presence of  $\text{H}_2\text{O}_2$  without deoxygenation under NIR LED light

As an example, photo-RAFT polymerization with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{H}_2\text{O}_2]:[\text{ZnPcS}_4^-] = 200:1:1:0.01$  was conducted as follows: A reaction solution consisting of water (103  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer),  $\text{H}_2\text{O}_2$  (10  $\mu\text{L}$  of 970 mM  $\text{H}_2\text{O}_2$  in water stock solution, 9.70  $\mu\text{mol}$ ), and DMF (1.89 mg, 2  $\mu\text{L}$ , 0.066 mmol, added as a  $^1\text{H}$  NMR internal standard) was prepared in a quartz cuvette (1 cm  $\times$  2

mm) and sealed with a rubber septum. After that, the cuvette was placed without deoxygenation under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer ( $6100\text{-}6220 \text{ cm}^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

#### General procedure for chain extension mediated by $\text{ZnPcS}_4^-$ in presence of TEOA and oxygen under NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ) in an aqueous solution

In general, the homopolymer was synthesized similarly to the general procedure outlined above. The  $\text{DP}_{\text{target}}$  was reduced to 100 using the first block with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 100:1:2:0.005$ . As an example, a PDMA macroRAFT agent was first synthesized in a cuvette containing water (108  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (5.96 mg, 19.40  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer), and TEOA (5.2  $\mu\text{L}$ , 38.80  $\mu\text{mol}$ ). After that, the cuvette was placed without deoxygenation under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light at room temperature for 6 hours. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer ( $6100\text{-}6220 \text{ cm}^{-1}$ ). The polymerization was stopped and removed for  $^1\text{H}$  NMR (93 % monomer conversion) and GPC ( $M_n = 9900$ ,  $D = 1.12$ ) analyses.

A degree of polymerization (DP) of 400 monomer units was targeted to observe a clear shift in molecular weight distributions (MWDs). For example, for the chain extension of the above PDMA macroRAFT agent with DMA, a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 400:1:8:0.02$  was used. The reaction solution consisted of water (8  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), above crude PDMA macroRAFT agent water solution (100  $\mu\text{L}$ , 4.85  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer), and TEOA (5.2  $\mu\text{L}$ , 38.80  $\mu\text{mol}$ ). After that, the cuvette was placed without deoxygenation under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light at room temperature for 4 hours. The polymerization was stopped and removed for  $^1\text{H}$  NMR (83 % monomer conversion) and GPC ( $M_n = 38900$ ,  $D = 1.11$ ) analyses.

#### General procedure for aqueous photo-RAFT polymerizations mediated by $\text{ZnPcS}_4^-$ in the presence of TEOA and oxygen under NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ) passing through different barriers

As an example, photo-RAFT polymerization with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  was conducted as follows: A reaction solution consisting of water (108  $\mu\text{L}$ ), *N, N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ),  $\text{ZnPcS}_4^-$  (87  $\mu\text{L}$  of 1.113 mM  $\text{ZnPcS}_4^-$  in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer), and TEOA (5.2  $\mu\text{L}$ , 38.80  $\mu\text{mol}$ ) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. Photopolymerization through barriers was performed by warping the cuvette

with appropriate barriers (**Figure S14**) with the thickness measured by a set of calipers. The barriers used in this test include print paper ( $\sim 0.10$  mm), and pig skin (from pig leg with the extra fat removed). Thereafter, the reaction was placed under a NIR ( $\lambda_{\max} = 730$  nm;  $I = 60$  mW cm $^{-2}$ ) LED light without deoxygenation at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100-6220 cm $^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

General procedure for aqueous photo-RAFT polymerizations mediated by ZnTMPyP in the presence of oxygen under violet ( $\lambda_{\max} = 405$  nm) or green ( $\lambda_{\max} = 530$  nm) LED light

As an example, photo-RAFT polymerization with a reaction stoichiometry of [DMA]:[CTCPA]:[ZnPcS $_4^-$ ] = 200:1:0.01 was conducted as follows: A reaction solution consisting of water (109  $\mu\text{L}$ ), *N,N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ), and ZnTMPyP (86  $\mu\text{L}$  of 1.131 mM ZnTMPyP in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. Subsequently, the cuvette was placed without deoxygenation under a violet ( $\lambda_{\max} = 405$  nm;  $I_0 = 45$  mW cm $^{-2}$ ) or a green ( $\lambda_{\max} = 530$  nm;  $I_0 = 72$  mW cm $^{-2}$ ) LED light at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100–6220 cm $^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

General procedure for aqueous photo-RAFT polymerizations mediated by ZnTMPyP in the presence of oxygen under violet ( $\lambda_{\max} = 405$  nm) or green ( $\lambda_{\max} = 530$  nm) LED light passing through 3.0 mm pig skin

As an example, photo-RAFT polymerization with a reaction stoichiometry of [DMA]:[CTCPA]:[ZnPcS $_4^-$ ] = 200:1:0.01 was conducted as follows: A reaction solution consisting of water (109  $\mu\text{L}$ ), *N,N*-dimethylacrylamide (DMA, 200  $\mu\text{L}$ , 1.941 mmol, 50 vol%), CTCPA (2.98 mg, 9.70  $\mu\text{mol}$ ), and ZnTMPyP (86  $\mu\text{L}$  of 1.131 mM ZnTMPyP in water stock solution, 0.0970  $\mu\text{mol}$ ; 50 ppm relative to monomer) was prepared in a quartz cuvette (1 cm  $\times$  2 mm) and sealed with a rubber septum. Photopolymerization through barriers was performed by warping the cuvette with 3.0 mm pig skin. Thereafter, the reaction was placed under a violet ( $\lambda_{\max} = 405$  nm;  $I_0 = 45$  mW cm $^{-2}$ ) or a green ( $\lambda_{\max} = 530$  nm;  $I_0 = 72$  mW cm $^{-2}$ ) LED light without deoxygenation at room temperature. The monomer conversion was monitored by online FTNIR by calculating the decrement of the vinylic C-H stretching overtone of the monomer (6100-6220 cm $^{-1}$ ) at designated time points. After reaching relatively high monomer conversion, the cuvette was removed from the light source, and aliquots were removed for GPC (DMAc) and  $^1\text{H}$  NMR analyses.

## Photo-RAFT dispersion polymerization

### Kinetic studies of photo-RAFT dispersion polymerization of HPMA mediated by $\text{ZnPcS}_4^-$ in the presence of TEOA and oxygen under NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ )

For example, kinetics of the photo-RAFT dispersion polymerization of HPMA with a reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 350:1:4:0.02$  at a total solids content of 20 wt% was conducted as follows: A reaction solution consisting of PEG<sub>113</sub>-CDTPA (21.61 mg, 4.01  $\mu\text{mol}$ ), HPMA (190  $\mu\text{L}$ , 202.54 mg, 1.40 mmol),  $\text{ZnPcS}_4^-$  (72.10  $\mu\text{g}$ , 0.080  $\mu\text{mol}$ , 72.1  $\mu\text{L}$  of a 1 mg  $\text{mL}^{-1}$  aqueous stock solution), DMF (9.44 mg, 10  $\mu\text{L}$ , 0.13 mmol, added as the  $^1\text{H}$  NMR internal standard), TEOA (2.1  $\mu\text{L}$ , 16.05  $\mu\text{mol}$ ) and water (725.8  $\mu\text{L}$ ) were prepared in a 2 mL glass vial. A stirrer bar was added to the vial, and the vial was sealed with a cap. After that, the reaction was placed under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light without deoxygenation on a mixing plate at room temperature. Aliquots were taken for analysis by  $^1\text{H}$  NMR, GPC, and TEM at determined time points. Monomer conversions were calculated using  $^1\text{H}$  NMR ( $d_6$ -DMSO) relative to DMF as an internal standard. Molecular weight values ( $M_{n, \text{GPC}}$ ) and polymer dispersity ( $\mathcal{D}$ ) were characterized by GPC (DMAc, PMMA standards). Morphologies of synthesized polymeric nanoparticles were characterized by TEM.

### Photo-RAFT dispersion polymerization of HPMA mediated by $\text{ZnPcS}_4^-$ in the presence of TEOA and oxygen under NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ )

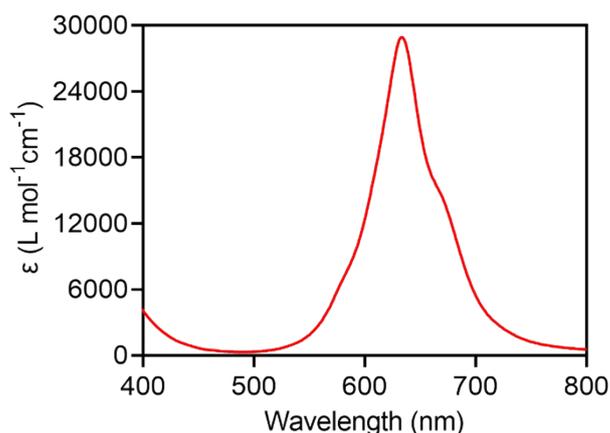
For example, photo-RAFT dispersion polymerization of HPMA with a reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 300:1:4:0.02$  at a total solids content of 10 wt% was conducted as follows: A reaction solution consisting of PEG<sub>113</sub>-CDTPA (12.48 mg, 2.32  $\mu\text{mol}$ ), HPMA (94  $\mu\text{L}$ , 100.20 mg, 0.70 mmol),  $\text{ZnPcS}_4^-$  (41.6  $\mu\text{g}$ , 0.046  $\mu\text{mol}$ , 41.6  $\mu\text{L}$  of a 1 mg  $\text{mL}^{-1}$  aqueous stock solution), DMF (9.44 mg, 10  $\mu\text{L}$ , 0.13 mmol, added as a  $^1\text{H}$  NMR internal standard), TEOA (1.2  $\mu\text{L}$ , 9.27  $\mu\text{mol}$ ) and water (853.2  $\mu\text{L}$ ) were prepared in a 2 mL glass vial. A stirrer bar was added to the vial, and the vial was sealed with a cap. After that, the reaction was placed under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light without deoxygenation on a mixing plate at room temperature. After 24 hours, the reaction was removed from the light source, and aliquots were removed for  $^1\text{H}$  NMR, GPC (DMAc), and TEM analyses.

### Photo-RAFT dispersion polymerization of HPMA mediated by $\text{ZnPcS}_4^-$ under NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ) passing through 6.0 mm pig skin

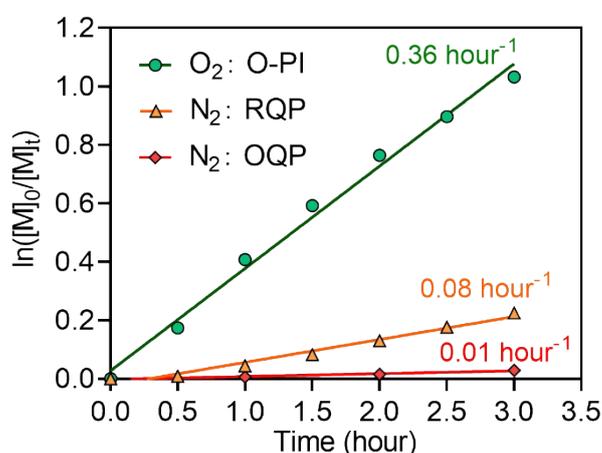
Kinetics of the photo-RAFT dispersion polymerization of HPMA with a reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 350:1:4:0.02$  at a total solids content of 20 wt% was conducted as follows: A reaction solution consisting of PEG<sub>113</sub>-CDTPA (21.61 mg, 4.01  $\mu\text{mol}$ ), HPMA (190  $\mu\text{L}$ , 202.54 mg, 1.40 mmol),  $\text{ZnPcS}_4^-$  (72.10  $\mu\text{g}$ , 0.080  $\mu\text{mol}$ , 72.1  $\mu\text{L}$  of a 1 mg  $\text{mL}^{-1}$  aqueous stock solution), DMF (9.44 mg, 10  $\mu\text{L}$ , 0.13 mmol, added as a  $^1\text{H}$  NMR internal standard), TEOA (2.1  $\mu\text{L}$ , 16.05  $\mu\text{mol}$ ) and water (725.8  $\mu\text{L}$ ) were prepared in a 2 mL glass vial. A stirrer bar was added to the vial, and the

vial was sealed with a cap. Photopolymerization through barriers was performed by warping the vial with 6.0 mm pig skin (**Figure 7A**) (the thickness was measured by a set of calipers). After that, the reaction was placed under a NIR ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) LED light without deoxygenation on a mixing plate at room temperature. At predetermined time points, aliquots were taken for analysis by  $^1\text{H}$  NMR, GPC, and TEM. Monomer conversions were calculated using  $^1\text{H}$  NMR ( $d_6$ -DMSO) relative to DMF as an internal standard. Molecular weight values ( $M_{n, \text{GPC}}$ ) and polymer dispersity ( $\mathcal{D}$ ) were characterized by GPC (DMAc, PMMA standards). Morphologies of synthesized polymeric nanoparticles were characterized by TEM.

## ADDITIONAL RESULTS



**Figure S1.** UV-vis spectrum of zinc tetrasulfonated phthalocyanine ( $\text{ZnPcS}_4^-$ ) in water.



**Figure S2.** Comparison of the kinetics of photo-RAFT polymerization via three pathways, including PET-RAFT via an oxidative quenching pathway (OQP), PET-RAFT via a reductive quenching pathway (RQP) and an oxygen-mediated photoinitiation (O-PI).

### Experimental conditions:

PET-RAFT polymerization via OQP was performed at room temperature under the irradiation of NIR light  $c$  after deoxygenation in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{ZnPcS}_4^-] = 200:1:0.01$  was used.

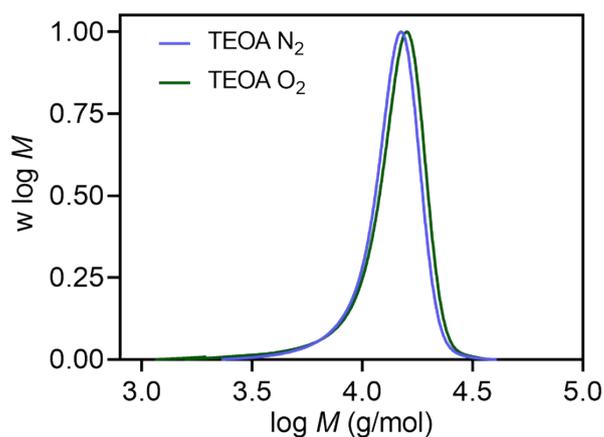
PET-RAFT polymerization via RQP was performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) after deoxygenation in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  was used.

Photo-RAFT polymerization via O-PI was performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) without deoxygenation in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  was used.

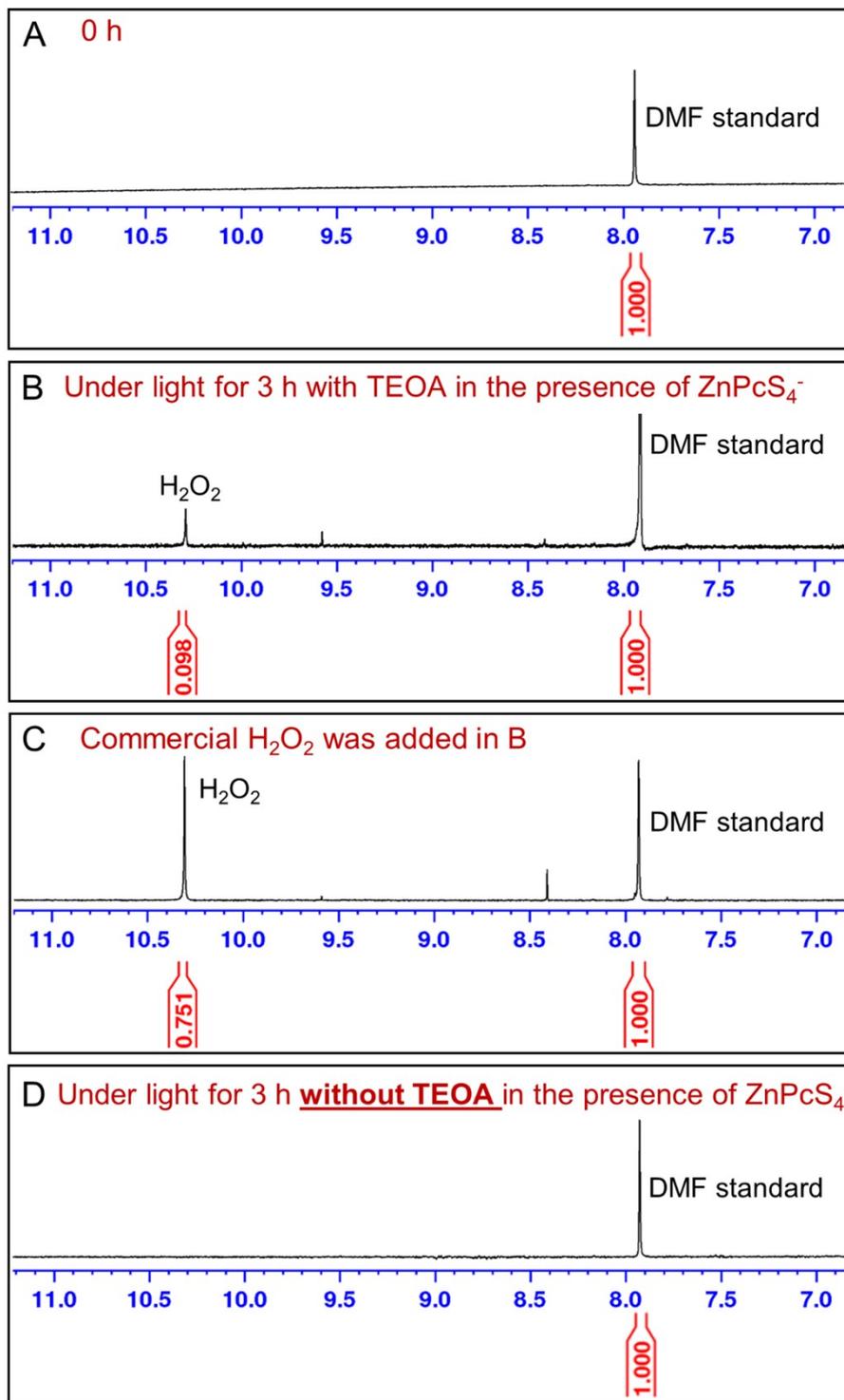
**Table S1.** Comparison of  $\text{ZnPcS}_4^-$  mediated photo-RAFT polymerization in the presence and absence of oxygen under NIR light irradiation.

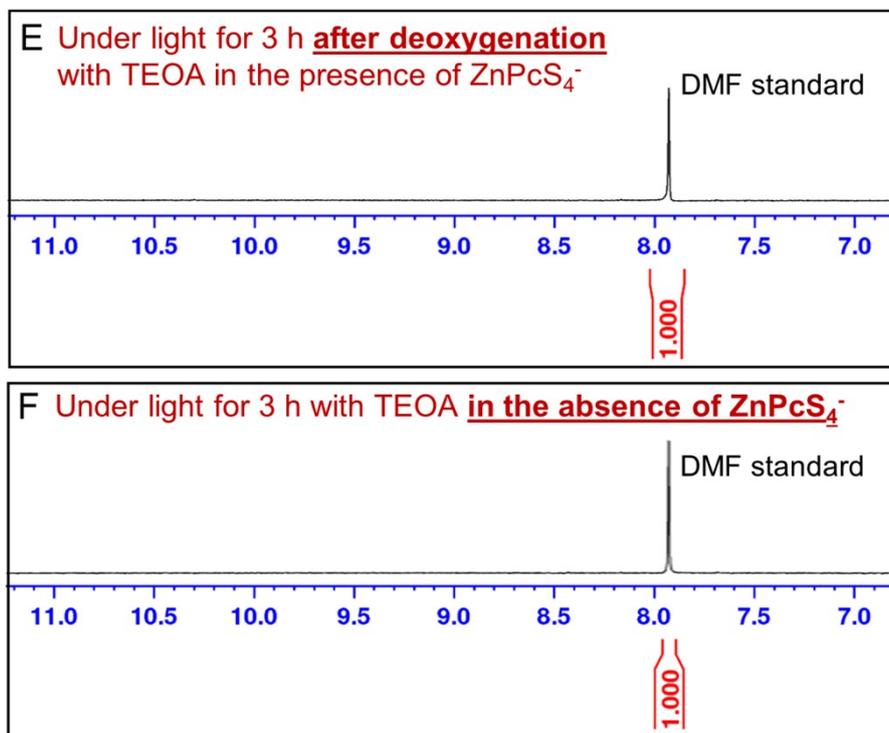
#	Deoxygenation	Time (hour)	$\alpha$ (%)	$k_p^{\text{app}}$ ( $\text{hour}^{-1}$ )	$M_{n, \text{theo}}$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{GPC}}$ ( $\text{g mol}^{-1}$ )	$\bar{D}$
1	yes	15	64	0.07	13000	13100	1.10
2	no	3	65	0.36	13200	13000	1.09

*Note:* Reactions were performed at room temperature under NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  (50 ppm relative to monomer) was used.

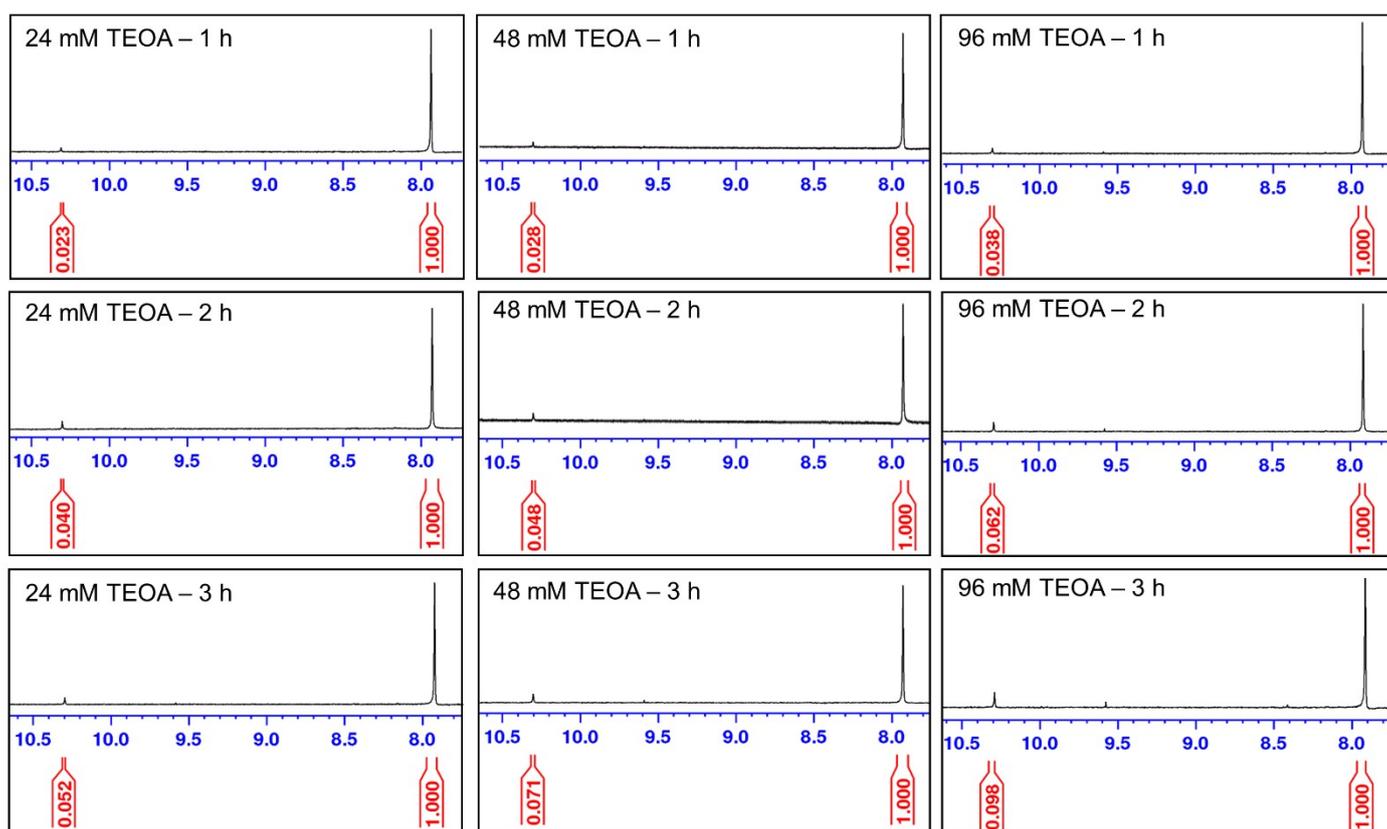


**Figure S3.** Comparison of MWDs of synthesized PDMA in the presence and absence of oxygen. Reactions were conducted under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) without (green line) and with deoxygenation (blue line) using a fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$ .

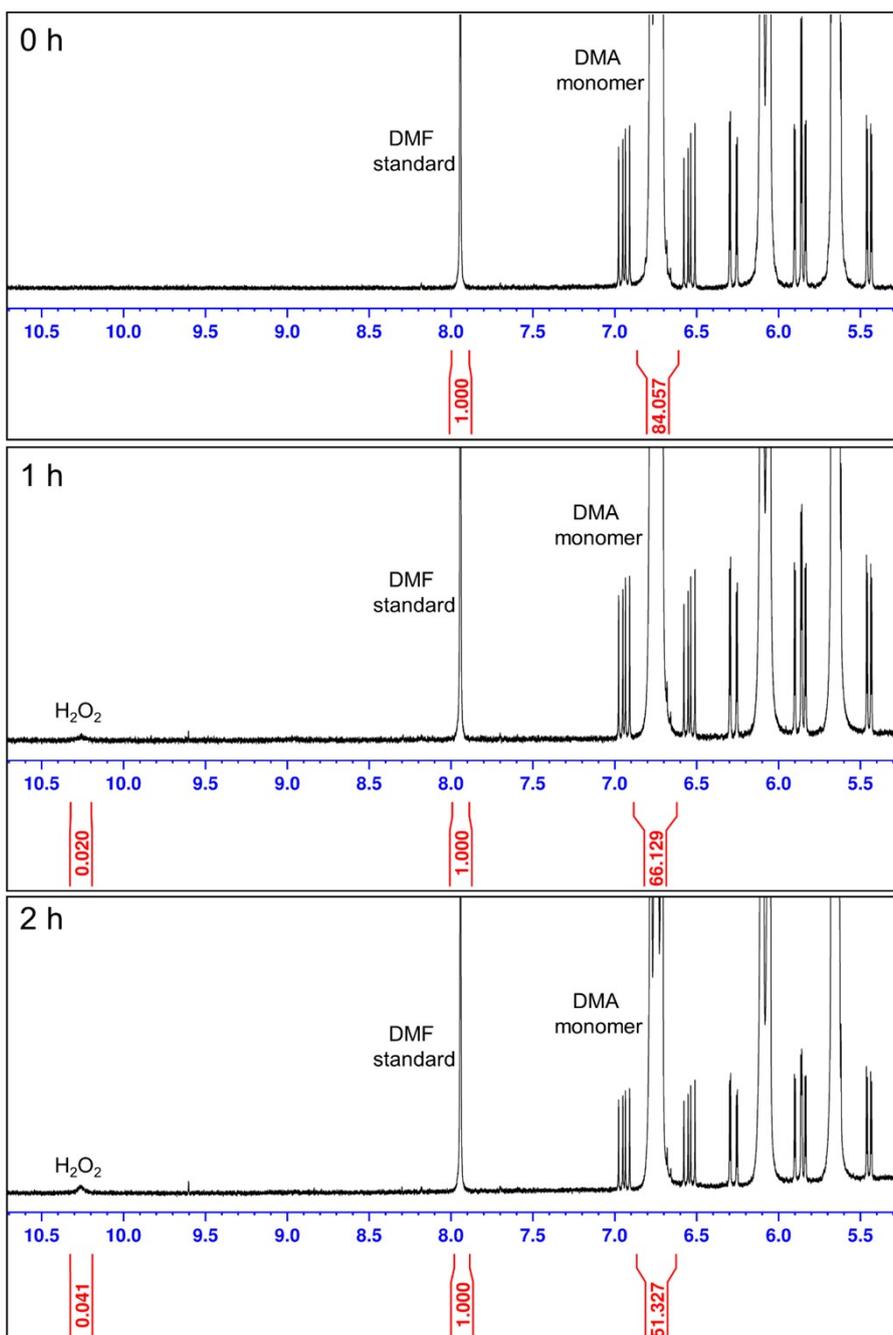


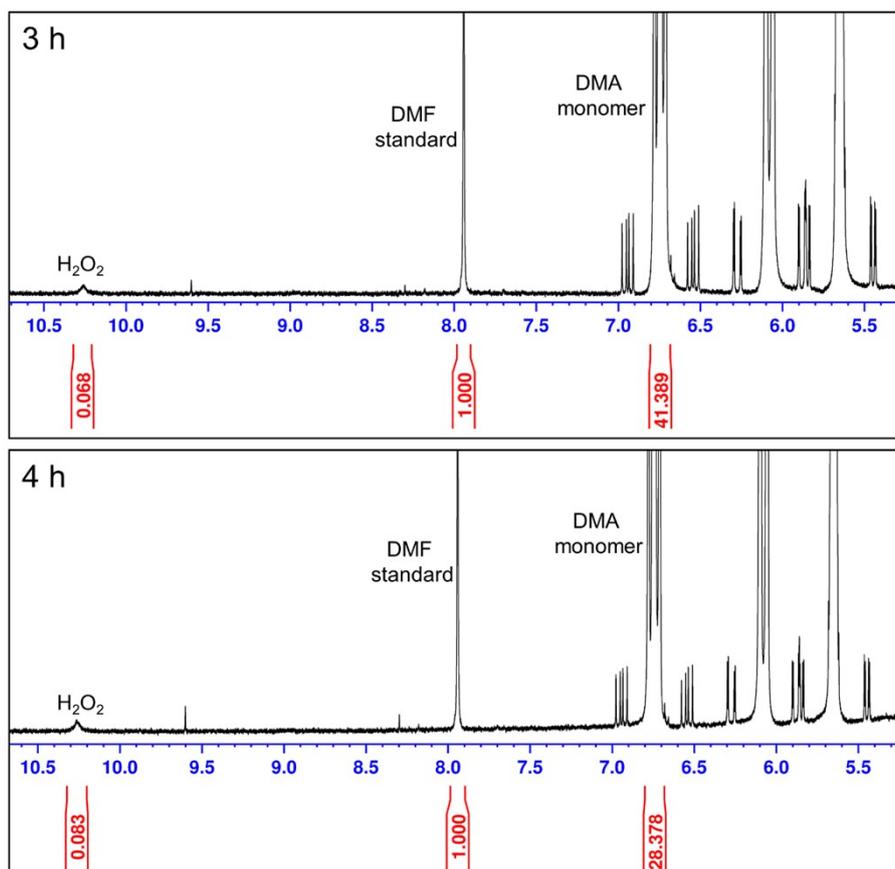


**Figure S4.** (A and B) The formation of  $\text{H}_2\text{O}_2$  as indicated by  $^1\text{H}$  NMR spectra ( $d_6$ -DMSO) with increasing irradiation time in the reaction consisting of 0.24 mM  $\text{ZnPcS}_4^-$  and 96 mM TEOA without deoxygenation. Reaction was performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 3 hours without deoxygenation. 0.24 mM  $\text{ZnPcS}_4^-$  and 97 mM TEOA were used, and 64.6 mM DMF was added as the internal standard. (C) 16 mM commercial  $\text{H}_2\text{O}_2$  was added in (B) to identify the formatting compound at  $\sim 10.3 \text{ ppm}$ . (D) A control experiment in the absence of TEOA but in the presence of  $\text{ZnPcS}_4^-$  without deoxygenation indicated the absence of  $\text{H}_2\text{O}_2$  formation under light irradiation for 3 hours. (E) A control experiment in the absence of  $\text{O}_2$  (after deoxygenation) but in the presence of  $\text{ZnPcS}_4^-$  and TEOA indicated the absence of  $\text{H}_2\text{O}_2$  formation under light irradiation for 3 hours. (F) A control experiment in the absence of  $\text{ZnPcS}_4^-$  but in the presence of TEOA and without deoxygenation indicated the absence of  $\text{H}_2\text{O}_2$  formation under light irradiation for 3 hours.

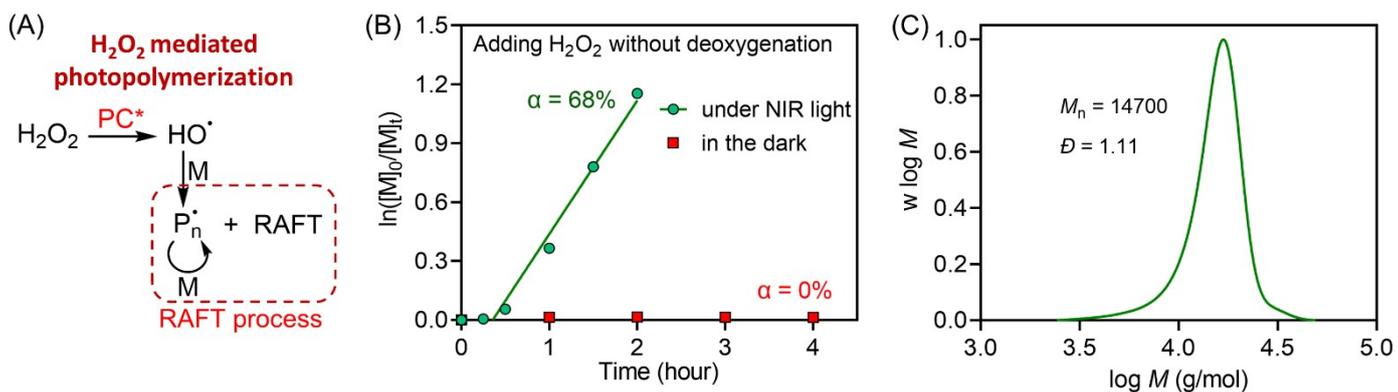


**Figure S5.** The formation of H<sub>2</sub>O<sub>2</sub> was detected by <sup>1</sup>H NMR spectra (d<sub>6</sub>-DMSO) with increasing irradiation time (1, 2, and 3 hours) in the presence of different concentrations of TEOA (24, 48, and 96 mM) without deoxygenation. Reactions consisting of 0.24 mM of ZnPcS<sub>4</sub><sup>-</sup> and TEOA were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) without deoxygenation in water, and 64.6 mM of DMF was used as internal standard.

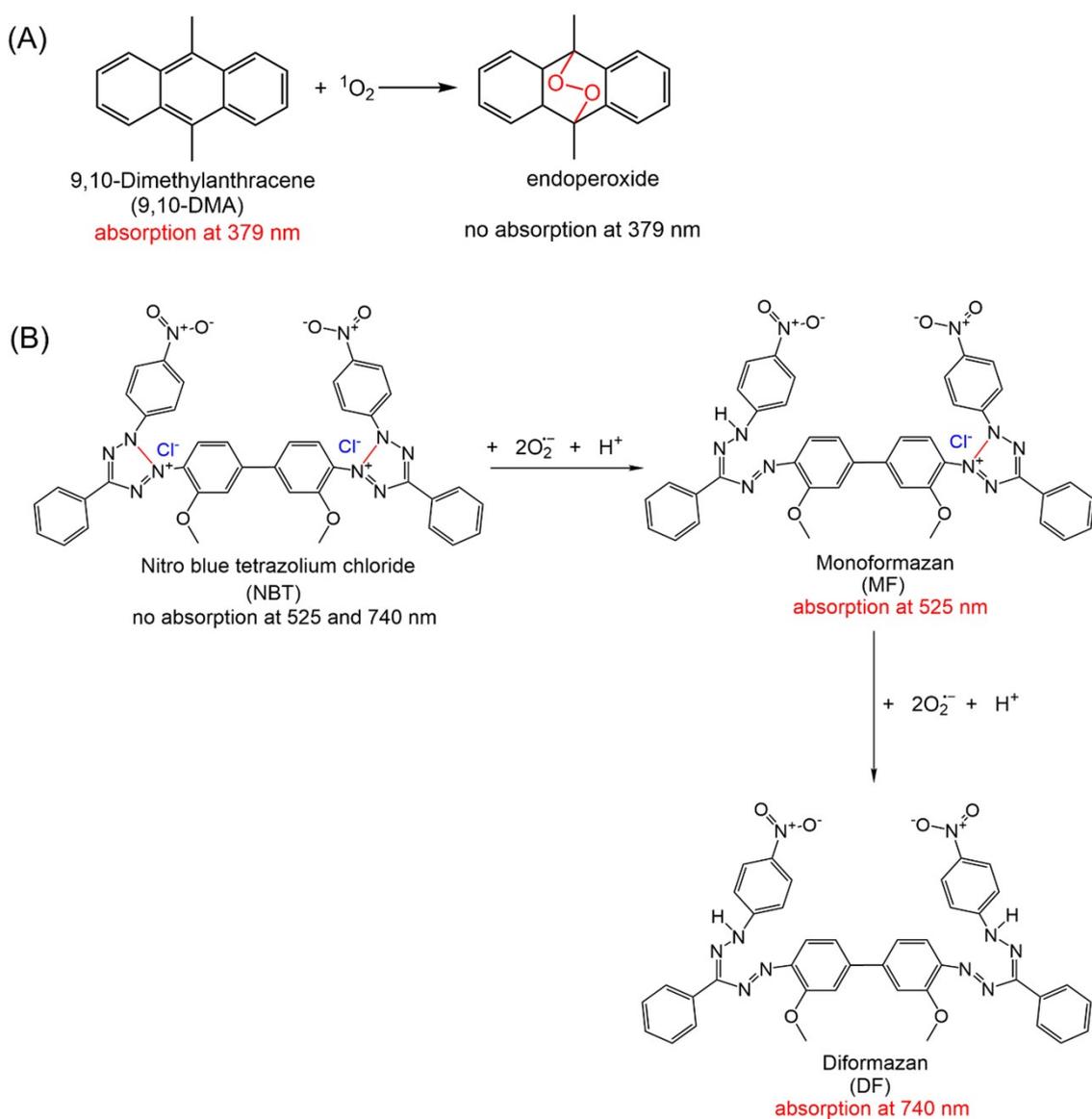




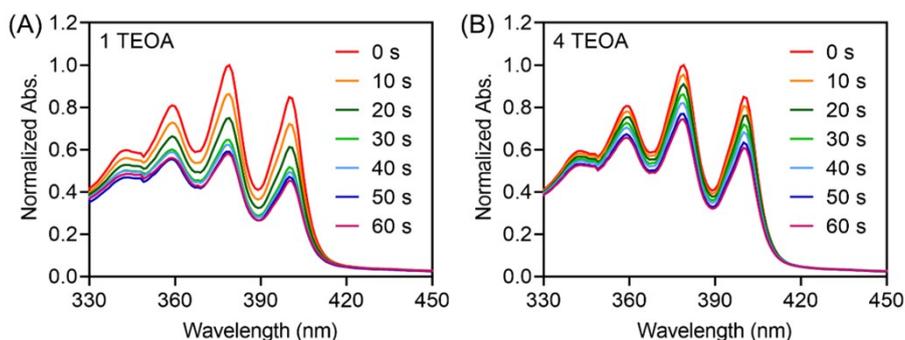
**Figure S6.** The formation of H<sub>2</sub>O<sub>2</sub> was detected by <sup>1</sup>H NMR spectra (d<sub>6</sub>-DMSO) with increasing irradiation time for ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization in the presence of TEOA without deoxygenation. Photo-RAFT polymerization was performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) without deoxygenation in water at [DMA]/[water] = 50/50 (v/v) and 64.6 mM DMF was used as internal standard. A fixed reaction stoichiometry of [DMA]:[CTCPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 200:1:4:0.01 was used.



**Figure S7.** Aqueous photo-RAFT polymerization mediated by  $\text{ZnPcS}_4^-$  in the presence of 24.3 mM  $\text{H}_2\text{O}_2$  without deoxygenation under the irradiation of NIR LED light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ). Polymerization using a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{H}_2\text{O}_2]:[\text{ZnPcS}_4^-] = 200:1:1:0.01$  was conducted in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v).

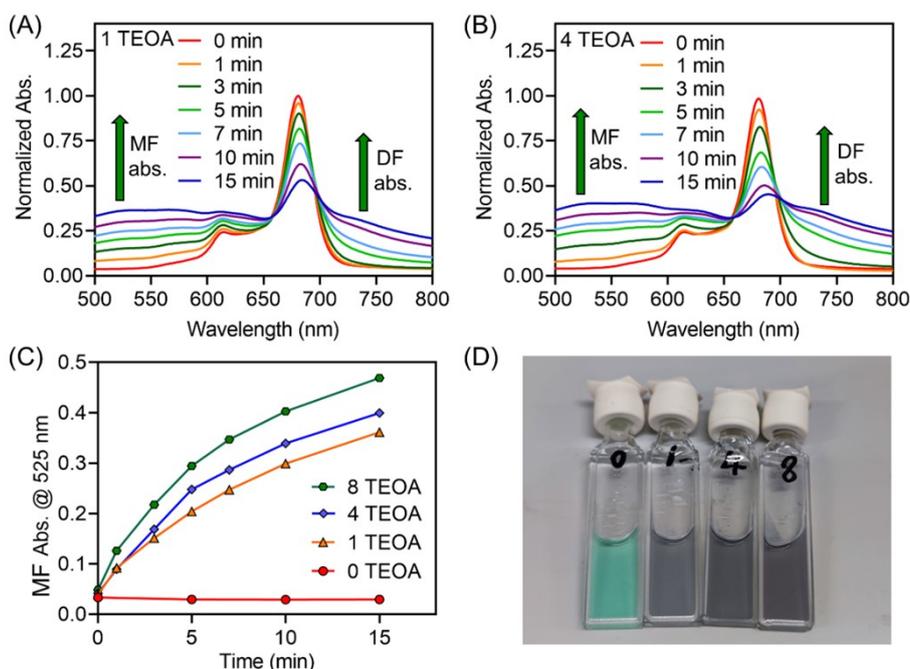


**Scheme S1.** (A) 9,10-Dimethylanthracene (9,10-DMA; absorption at  $\sim 379$  nm) reacts with singlet oxygen ( $^1\text{O}_2$ ), generating the corresponding endoperoxide.<sup>1</sup> (B) Nitrotetrazolium blue chloride (NBT) reacts with superoxide ( $\text{O}_2^-$ ), generating monoformazan (MF; absorption at  $\sim 525$  nm) and diformazan (DF); absorption at  $\sim 740$  nm).<sup>2</sup>



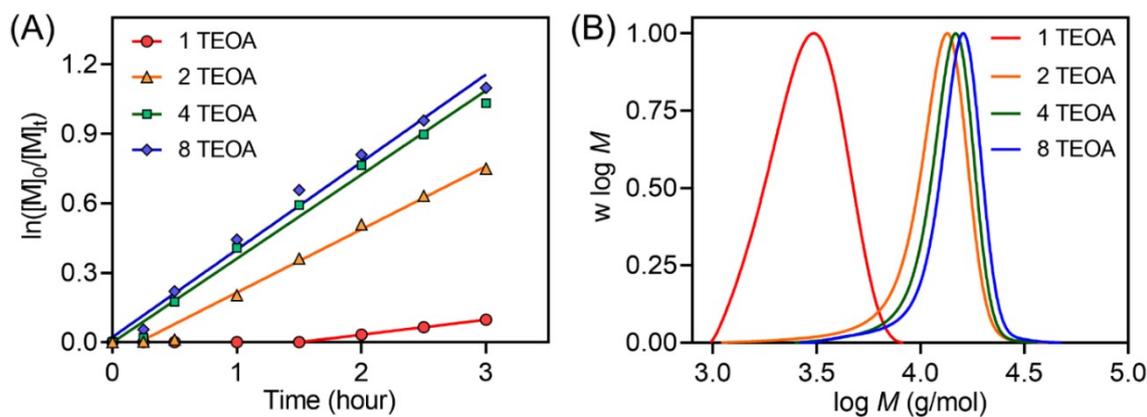
**Figure S8.** Experiments of quenching singlet oxygen ( $^1\text{O}_2$ ) by 0.485 mM 9,10-dimethylanthracene (9,10-DMA) in the presence of different ratios of TEOA using a stoichiometry of  $[\text{ZnPcS}_4^-]:[9,10\text{-DMA}]:[\text{TEOA}] = 0.002:0.02:(1 \text{ and } 4)$  in water/DMF at 50/50 (v/v) under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 12 \text{ mW cm}^{-2}$ )

Additional discussion: Decreased absorption of 9,10-DMA (at  $\sim 379 \text{ nm}$ ) reflected the successful  $^1\text{O}_2$  trapping (**Scheme S1A**).



**Figure S9.** (A–B) Experiments of quenching superoxide ( $\text{O}_2^{\bullet-}$ ) by 1.215 mM nitrotetrazolium blue chloride (NBT) in the presence of different ratios of TEOA using a stoichiometry of  $[\text{ZnPcS}_4^-]:[\text{TEOA}]:[\text{NBT}] = 0.002:(1 \text{ and } 4):0.05$  in water/DMF at 50/50 (v/v) under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 12 \text{ mW cm}^{-2}$ ); (C) Kinetics of generating MF absorption at  $\sim 525 \text{ nm}$  in the presence of different ratios of TEOA. (D) Digital photos of  $\text{O}_2^{\bullet-}$  quenching experiments with different ratios of TEOA under the irradiation of NIR light for 15 mins (the appearance of dark color indicated the formation of MF and DF).

Additional discussion: Generated  $\text{O}_2^{\bullet-}$  was quenched by NBT, to yield monoformazan (MF; absorption at  $\sim 525 \text{ nm}$ ) and diformazan (DF; absorption at  $\sim 740 \text{ nm}$ ) (**Scheme S1B**).

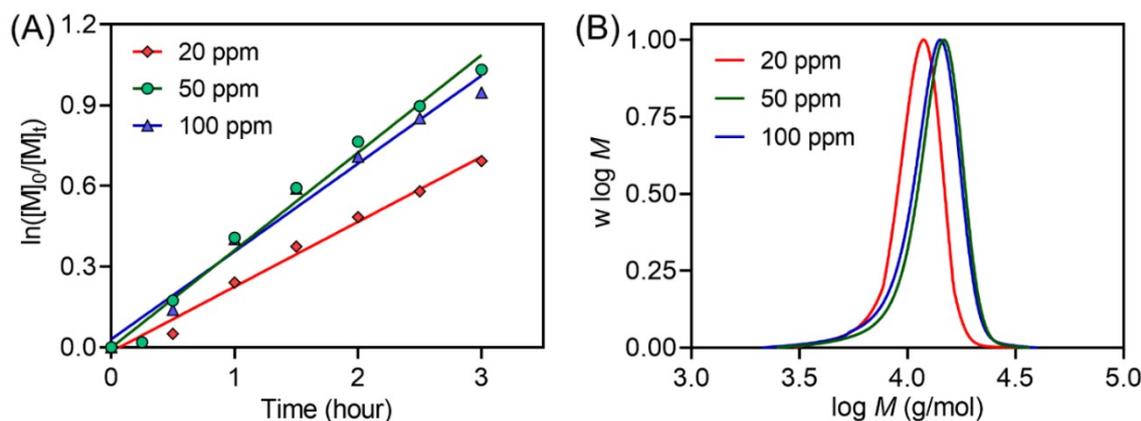


**Figure S10.** (A) Kinetics and (B) MWDs of ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization using various ratios (1, 2, 4, and 8) of TEOA related to RAFT agent under NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 3 hours.

**Table S2.** Photo-RAFT polymerization mediated by ZnPcS<sub>4</sub><sup>-</sup> with various ratios of TEOA.

#	[TEOA]:[CTCPA]	$\alpha$ (%)	Induction period (min)	$k_p^{\text{app}}$ (hour <sup>-1</sup> )	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\mathcal{D}$
1	1:1	9	~90	0.06	2100	2700	1.15
2	2:1	53	~30	0.27	10800	11300	1.13
3	4:1	65	~15	0.36	13200	13000	1.09
4	8:1	67	~15	0.38	13600	13600	1.13

*Note:* Reactions were performed at room temperature under NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 3 hours without prior deoxygenation in water at [DMA]/[water] = 50/50 (v/v). A fixed reaction stoichiometry of [DMA]:[CTCPA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 200:1:0.01 (50 ppm relative to monomer) was used.

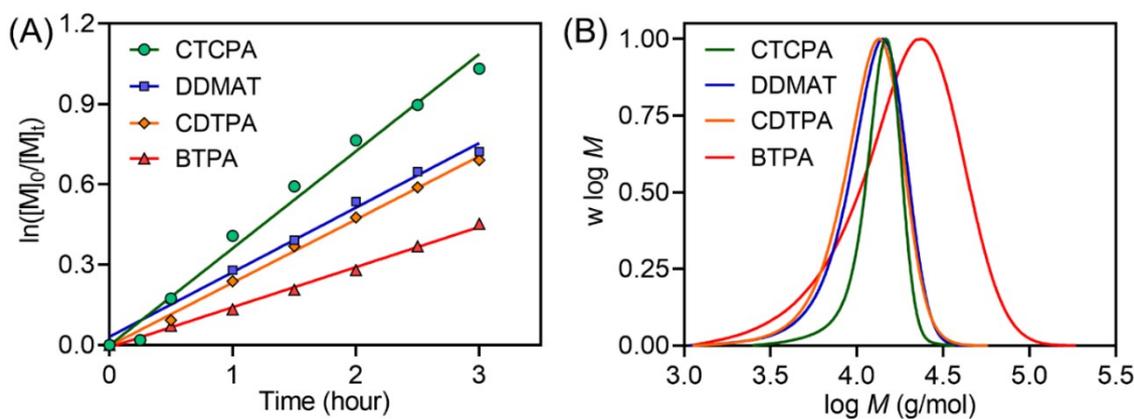


**Figure S11.** (A) Kinetics and (B) MWDs of  $\text{ZnPcS}_4^-$  mediated photo-RAFT polymerization with different PC concentrations (20, 50, and 100 ppm related to monomer) under NIR light irradiation.

**Table S3.**  $\text{ZnPcS}_4^-$  mediated photo-RAFT polymerization with different PC concentrations under 730 nm light.

#	PC concentration (ppm)	$\alpha$ (%)	$k_p^{\text{app}}$ ( $\text{hour}^{-1}$ )	$M_{n, \text{theo}}$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{GPC}}$ ( $\text{g mol}^{-1}$ )	$\mathcal{D}$
1	20	50	0.24	10200	10800	1.07
2	50	65	0.36	13200	13000	1.09
3	100	61	0.33	12400	12300	1.10

*Note:* were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 3 hours without prior deoxygenation in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}] = 200:1:4$  was used.

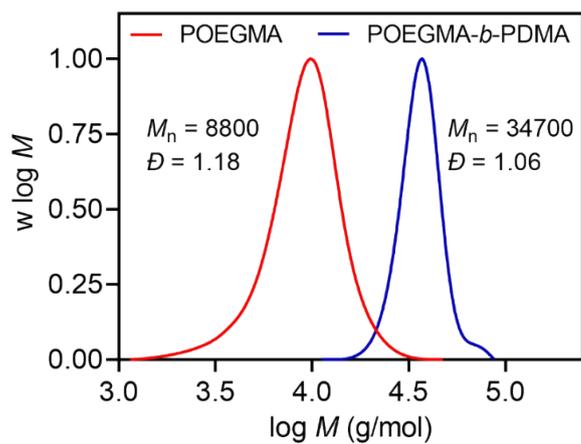


**Figure S12.** (A) Kinetics and (B) MWDs of  $\text{ZnPcS}_4^-$  mediated photo-RAFT polymerization with different RAFT agents under NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ).

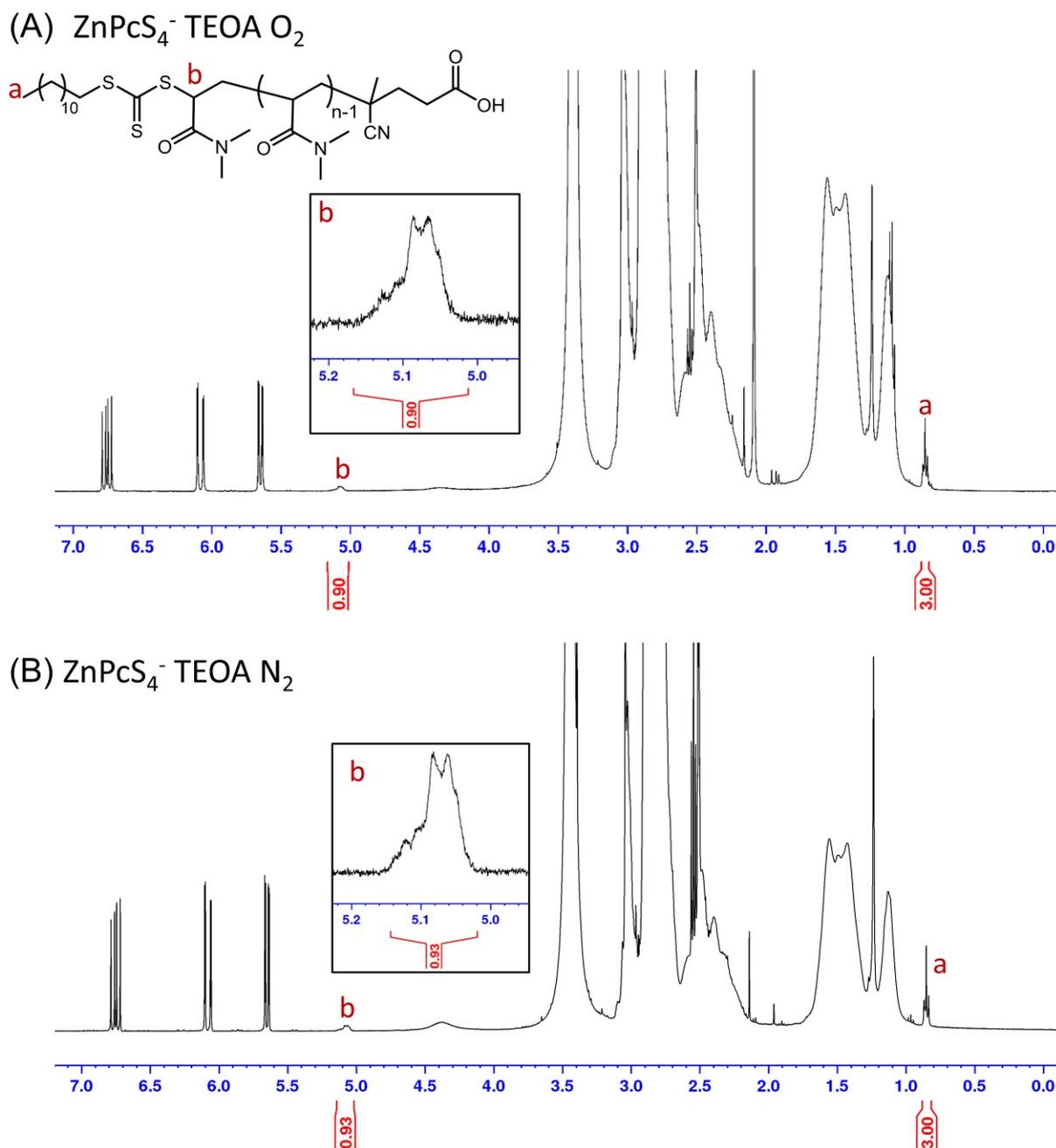
**Table S4.**  $\text{ZnPcS}_4^-$  mediated photo-RAFT polymerization using different RAFT agents under NIR light.

#	RAFT agent	$\alpha$ (%)	$k_p^{\text{app}}$ ( $\text{hour}^{-1}$ )	$M_{n, \text{theo}}$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{GPC}}$ ( $\text{g mol}^{-1}$ )	$\mathcal{D}$
1	CTCPA	65	0.36	13200	13000	1.09
2	CDTPA	50	0.23	10300	11000	1.20
3	DDMAT	51	0.24	10500	11400	1.20
4	BTPA	36	0.15	7400	15000	1.59

*Note:* Reactions were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 3 hours without prior deoxygenation in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v). A fixed reaction stoichiometry of  $[\text{DMA}]:[\text{RAFT agent}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  (50 ppm relative to monomer) was used.



**Figure S13.** Normalized MWDs of POEGMA and its chain extension with DMA using a reaction stoichiometry of [DMA]:[macroRAFT agent]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 400:1:4:0.02 in water under the NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ).

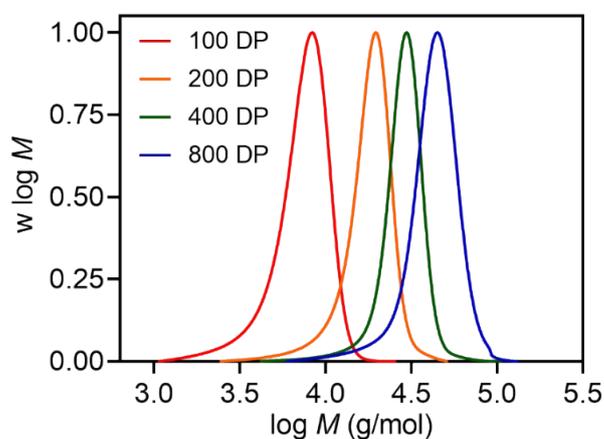


**Figure S14.**  $^1\text{H}$  NMR spectroscopy of PDMA synthesized using CDTPA as the RAFT agent. Reactions were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) (A) without prior deoxygenation (monomer conversion = 95%) and (B) after deoxygenation (monomer conversion = 93%) in water at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v) using a fixed reaction stoichiometry of  $[\text{DMA}]:[\text{CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 100:1:4:0.005$  (50 ppm relative to monomer).

**Table S5.** ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization with different targeted DPs under the NIR light irradiation.

	DP	$\alpha$ (%)	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\mathcal{D}$
1	100	68	7000	7000	1.14
2	200	84	17000	16800	1.11
3	400	80	32000	26700	1.09
4	800	57	45500	38400	1.13

*Note:* Reactions were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730$  nm;  $I = 60$  mW cm<sup>-2</sup>) for 5 hours without prior deoxygenation in water at [DMA]/[water] = 50/50 (v/v). A fixed reaction stoichiometry of [CTCPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 1:4:0.01 (50 ppm relative to monomer) was used.



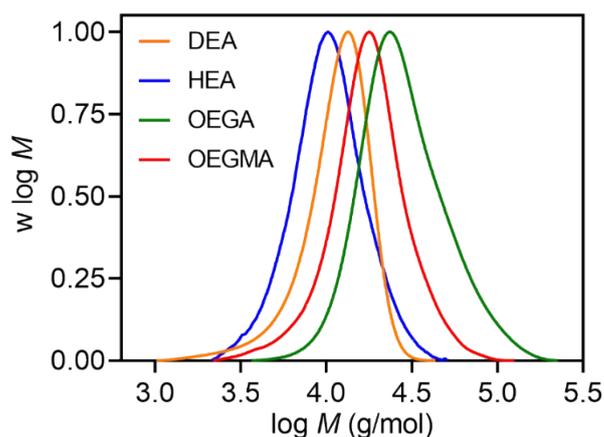
**Figure S15.** MWDs of ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization with different targeted DPs (100, 200, 400, and 800) under the NIR light irradiation for 5 hours.

**Table S6.** ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization with various monomers.

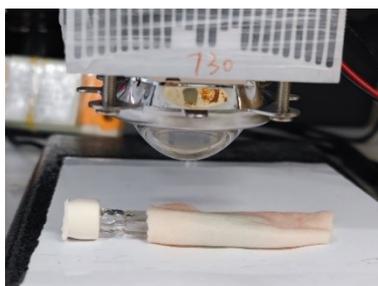
#	Monomer	$\alpha$ (%)	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\bar{D}$
1	DEA	53	13800	10600	1.21
2	HEA	51	12100	9500	1.25
3 <sup>a</sup>	OEGA	77	37300	23600	1.33
4 <sup>a</sup>	OEGMA	72	21900	16100	1.26

*Note:* *N,N*-diethylacrylamide (DEA), 2-hydroxyethyl acrylate (HEA), Oligo(ethylene glycol) methyl ether acrylate (OEGA,  $M_n = 300$  g mol<sup>-1</sup>) and Oligo(ethylene glycol) methyl ether methacrylate (OEGMA,  $M_n = 480$  g mol<sup>-1</sup>) were used as monomers in this work. Reactions were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730$  nm;  $I = 60$  mW cm<sup>-2</sup>) for 3 hours without prior deoxygenation in water at [monomer]/[water] = 50/50 (v/v). A fixed reaction stoichiometry of [monomer]:[CTCPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 200:1:4:0.01 (50 ppm relative to monomer) was used.

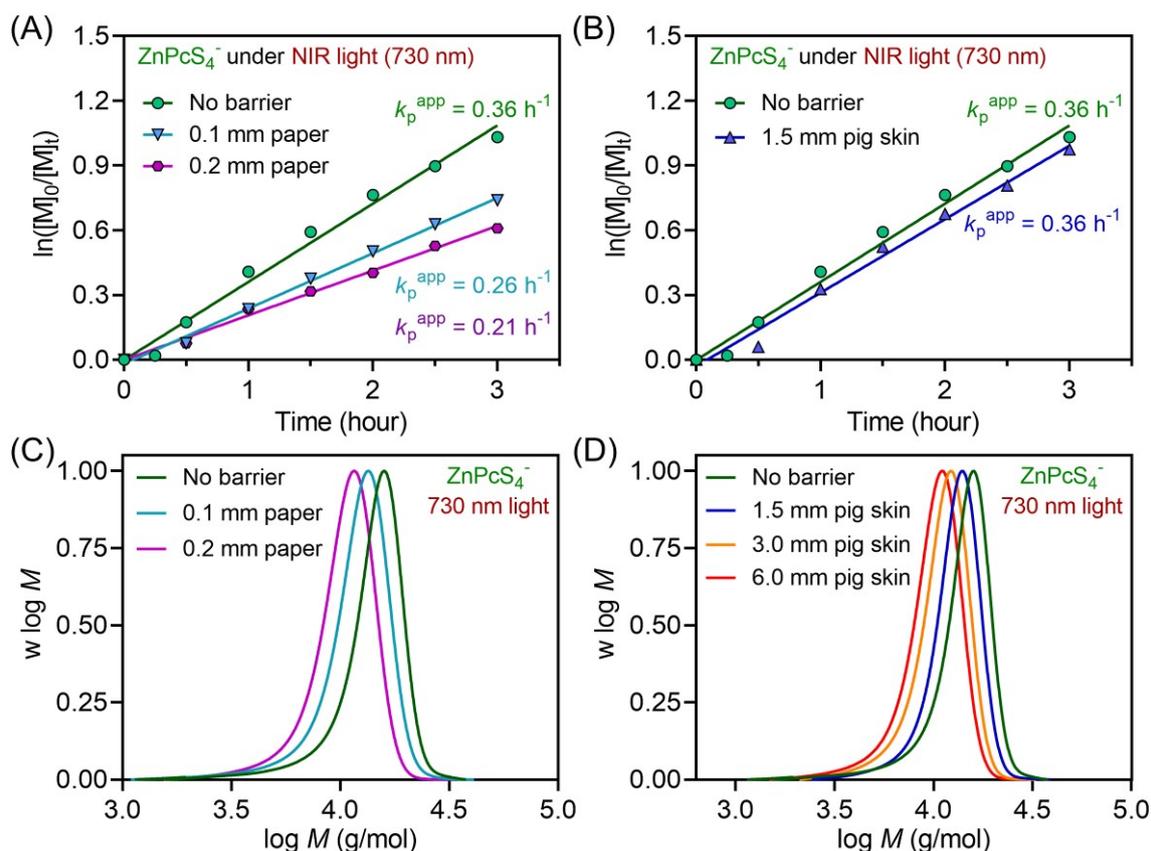
<sup>a</sup>A reaction stoichiometry of [monomer]:[CTCPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 100:1:2:0.05 (50 ppm relative to monomer) was used.

**Figure S16.** Normalized MWDs of ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization using various monomers, including acrylamide, acrylate, and methacrylate.

*Note:* *N,N*-diethylacrylamide (DEA), 2-hydroxyethyl acrylate (HEA), oligo(ethylene glycol) methyl ether acrylate (OEGA,  $M_n = 300$  g mol<sup>-1</sup>) and oligo(ethylene glycol) methyl ether methacrylate (OEGMA,  $M_n = 480$  g mol<sup>-1</sup>).



**Figure S17.** Experimental set-up of photo-RAFT polymerization catalyzed by  $\text{ZnPcS}_4^-$  under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) irradiation passing through 1.5 mm pig skin.

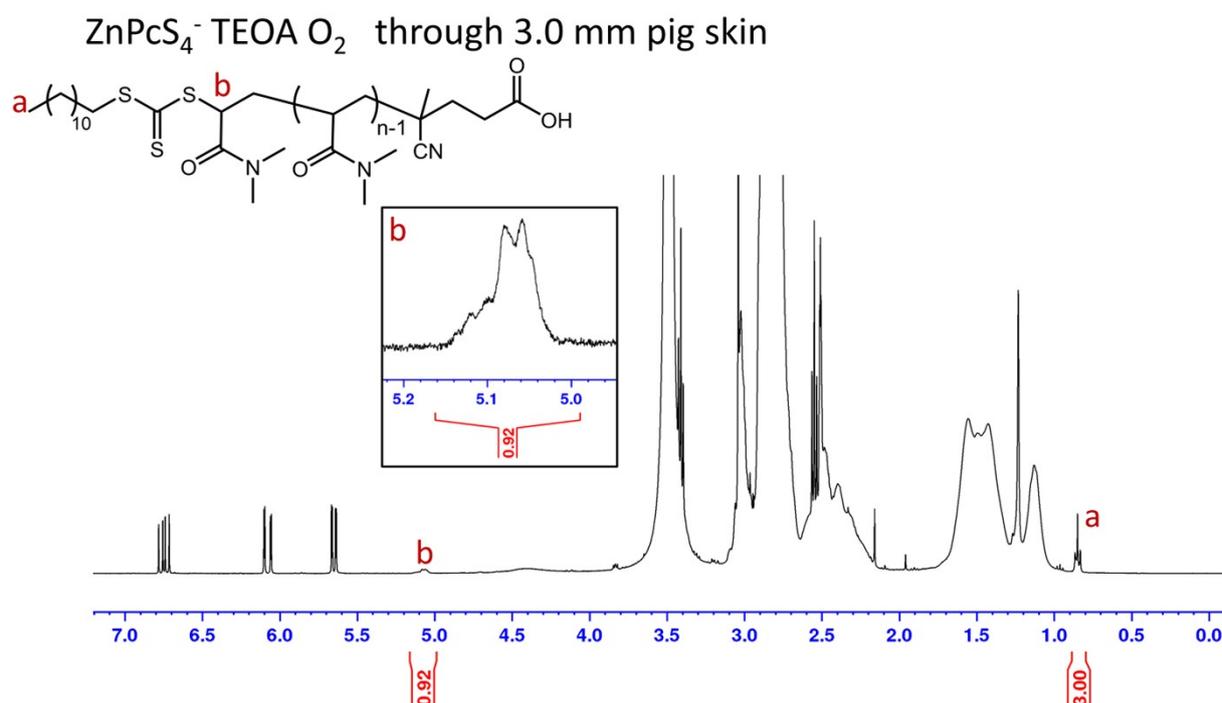


**Figure S18.** (A–B)  $\ln([M]_0/[M]_t)$  versus irradiation time plots of  $\text{ZnPcS}_4^-$  mediated photo-RAFT under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) irradiation passing through various thicknesses of (A) paper and (B) pig skin with a reaction stoichiometry of  $[\text{DMA}]:[\text{CTCPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 200:1:4:0.01$  at  $[\text{DMA}]/[\text{water}] = 50/50$  (v/v) without deoxygenation. (C–D) MWDs of synthesized PDMA by  $\text{ZnPcS}_4^-$  mediated photo-RAFT under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) irradiation for 3 hours passing through various thicknesses of (C) paper and (D) pig skin.

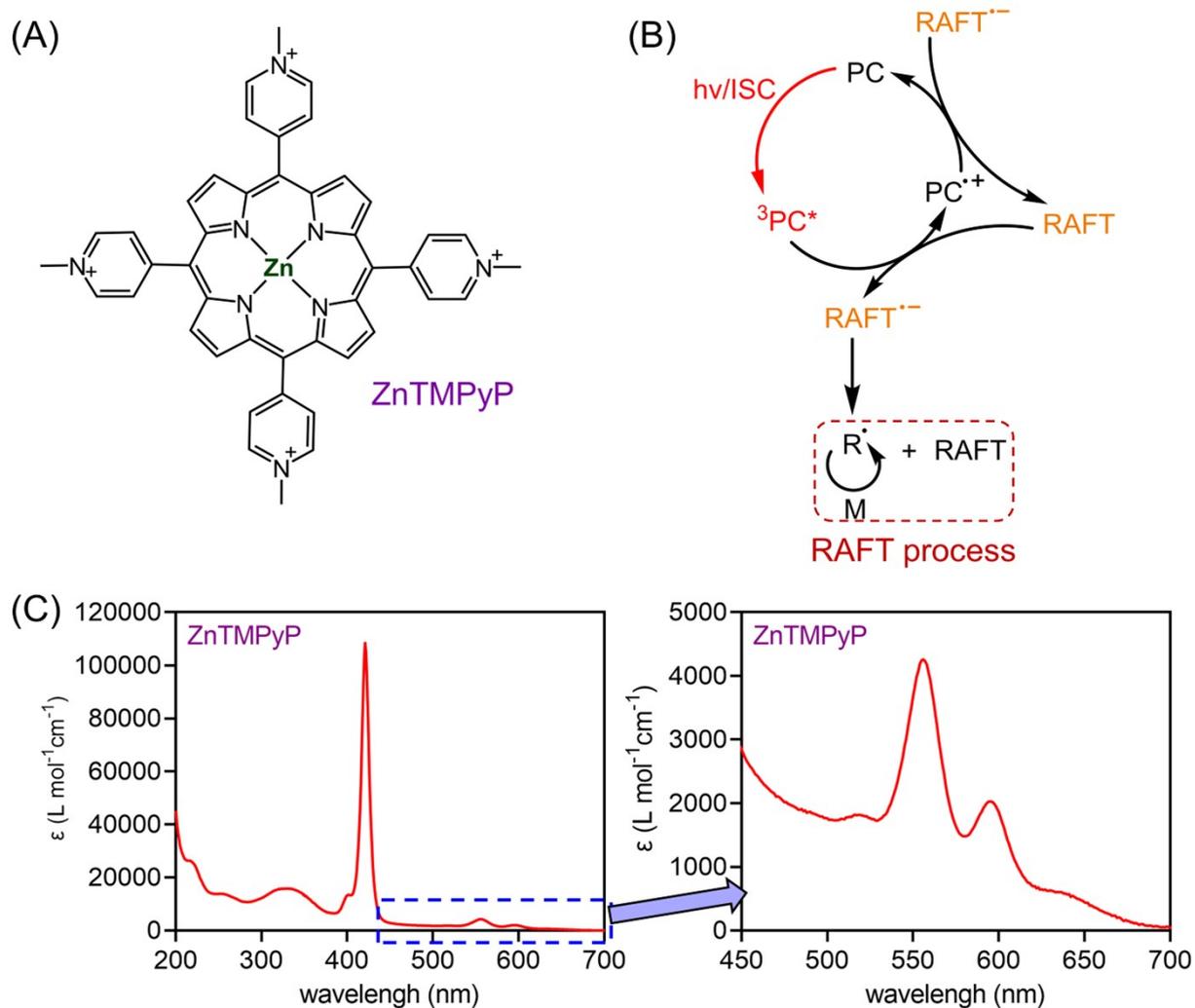
**Table S7.** ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT polymerization under the NIR light irradiation passing through various barriers.

#	Barrier	$\alpha$ (%)	$k_p^{\text{app}}$ (hour <sup>-1</sup> )	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\bar{D}$
1	no	65	0.36	13200	13000	1.09
2	0.1 mm paper	51	0.26	10400	10900	1.13
3	0.2 mm paper	44	0.21	9000	9600	1.12
4	1.5 mm pig skin	62	0.34	12600	12300	1.09
5	3.0 mm pig skin	53	0.27	10800	10600	1.10
6	6.0 mm pig skin	45	0.21	9200	9100	1.11

*Note:* Reactions were irradiated by NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) passing through various barriers for 3 hours at room temperature without prior deoxygenation in water at [DMA]/[water] = 50/50 (v/v). A fixed reaction stoichiometry of [DMA]:[CTCPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 200:1:4:0.01 (50 ppm relative to monomer) was used.



**Figure S19.** <sup>1</sup>H NMR spectroscopy of PDMA synthesized using CDTPA as the RAFT agent. Reactions were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) passing through 3.0 mm pig skin (A) without prior deoxygenation (monomer conversion = 96%) in water at [DMA]/[water] = 50/50 (v/v) using a fixed reaction stoichiometry of [DMA]:[CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 100:1:4:0.005 (50 ppm relative to monomer).

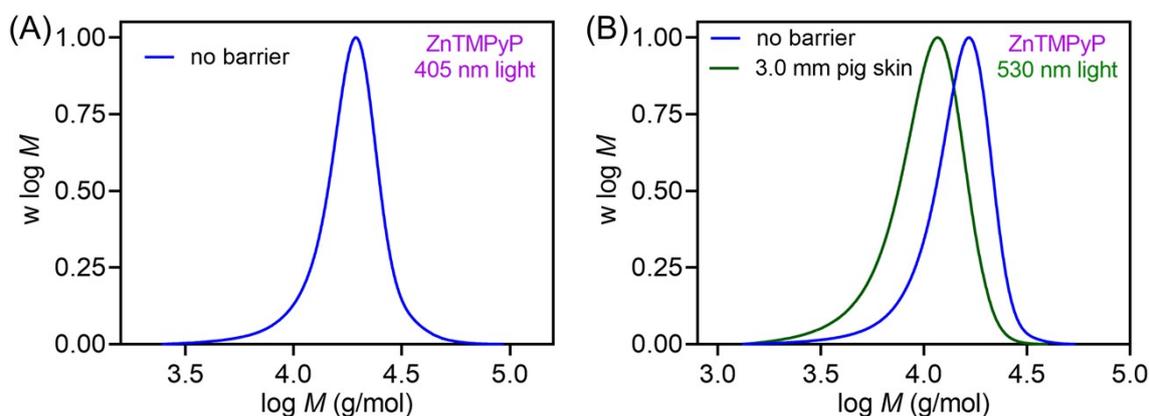


**Figure S20.** (A) Chemical structure of zinc meso-tetra(*N*-methyl-4-pyridyl) porphine tetrachloride (ZnTMPyP) (B) Mechanism of PET-RAFT polymerization via an oxidative quenching pathway (OQP) using ZnTMPyP as the PC. (C) UV-vis spectrum of ZnTMPyP in water.

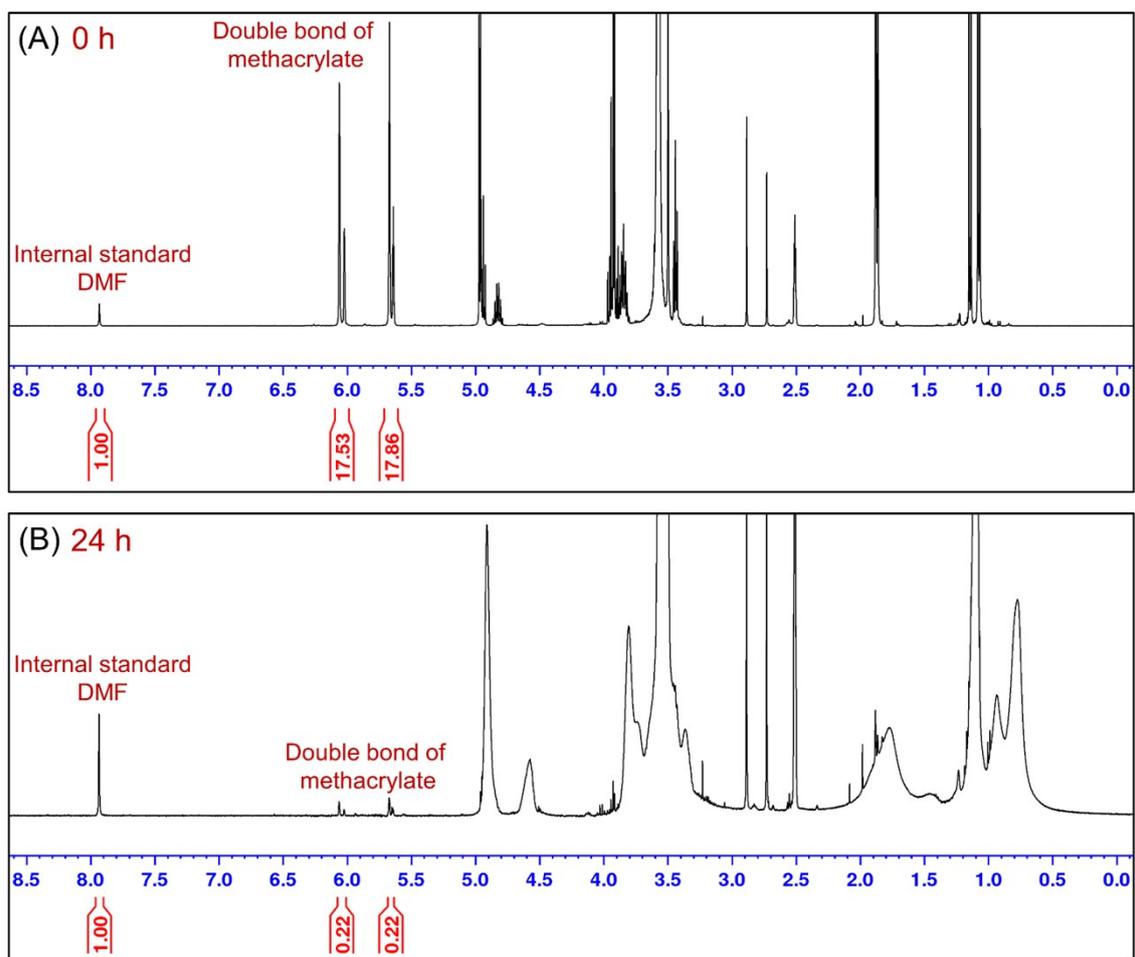
**Table S8.** ZnTMPyP mediated photo-RAFT polymerization under the violet and green light irradiation passing through 3.0 mm pig skin.

#	Light irradiation wavelength (nm)	3.0 mm pig skin barrier	$k_p^{\text{app}}$ (hour <sup>-1</sup> )	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\mathcal{D}$
1	Violet (405 nm)	no	6.30	14200	16100	1.13
2	Violet (405 nm)	yes	0	-	-	-
3	Green (530 nm)	no	0.93	13400	13600	1.15
4	Green (530 nm)	yes	0.07	9000	9600	1.18

*Note:* Reactions were irradiated by violet ( $\lambda_{\text{max}} = 405 \text{ nm}$ ;  $I_0 = 45 \text{ mW cm}^{-2}$ ) and green light ( $\lambda_{\text{max}} = 530 \text{ nm}$ ;  $I_0 = 72 \text{ mW cm}^{-2}$ ) passing through 3.0 mm pig skin for at room temperature without prior deoxygenation in water at [DMA]/[water] = 50/50 (v/v). A fixed reaction stoichiometry of [DMA]:[CTCPA]:[ZnTMPyP] = 200:1:0.01 (50 ppm relative to monomer) was used.



**Figure S21.** MWDs of synthesized PDMA by ZnTMPyP mediated photo-RAFT under violet ( $\lambda_{\text{max}} = 405 \text{ nm}$ ;  $I_0 = 45 \text{ mW cm}^{-2}$ ) and green ( $\lambda_{\text{max}} = 530 \text{ nm}$ ;  $I_0 = 72 \text{ mW cm}^{-2}$ ) light irradiation in the (A) absence and (B) presence of 3.0 mm pig skin barrier.

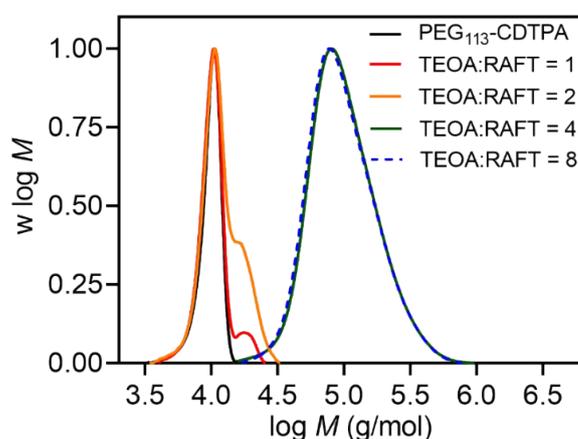


**Figure S22.**  $^1\text{H}$  NMR spectra of crude photo-RAFT dispersion polymerization at different time points. Monomer conversions of dispersion photopolymerizations of HPMA were determined by  $^1\text{H}$  NMR spectroscopy using DMF as the internal standard. Polymerizations were performed under the irradiation of NIR light for 24 hours without prior deoxygenation in water with a fixed reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 350:1:4:0.02$  and a total solids content of 20 wt%.

**Table S9.** Photo-RAFT dispersion polymerization catalyzed by  $\text{ZnPcS}_4^-$  with various ratios of TEOA.

#	[TEOA]:[RAFT]	$\alpha$ (%)	$M_{n, \text{theo}}$ ( $\text{g mol}^{-1}$ )	$M_{n, \text{GPC}}$ ( $\text{g mol}^{-1}$ )	$\mathcal{D}$
1	1	4	7400	10100	1.07
2	2	8	10800	11300	1.12
3	4	99	55300	73100	1.37
4	8	99	55300	74000	1.39

*Note:* Dispersion photopolymerizations were performed at room temperature under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $I = 60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation using HPMA as the monomer at a total solids content of 20 wt% in water. A fixed reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 350:1:4:0.02$  was used.

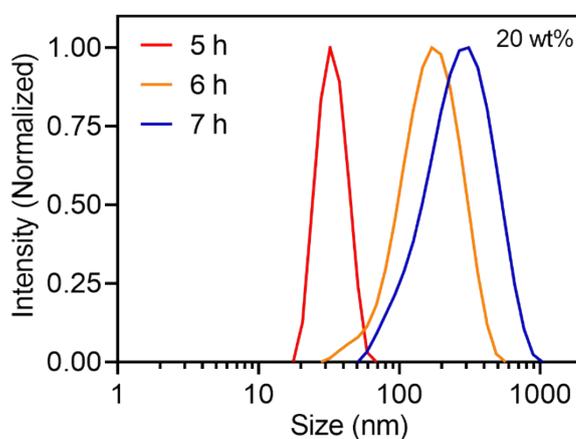


**Figure S23.** MWDs of synthesized  $\text{PEG}_{113}\text{-}b\text{-PHPMA}$  in the optimization experiments with various ratios (1, 2, 4, and 8) of TEOA related to RAFT agent using  $\text{ZnPcS}_4^-$  as the photocatalyst. Polymerizations were performed under NIR light for 24 hours without prior deoxygenation in water with a fixed reaction stoichiometry of  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{ZnPcS}_4^-] = 350:1:0.02$  and a total solids content of 20 wt%.

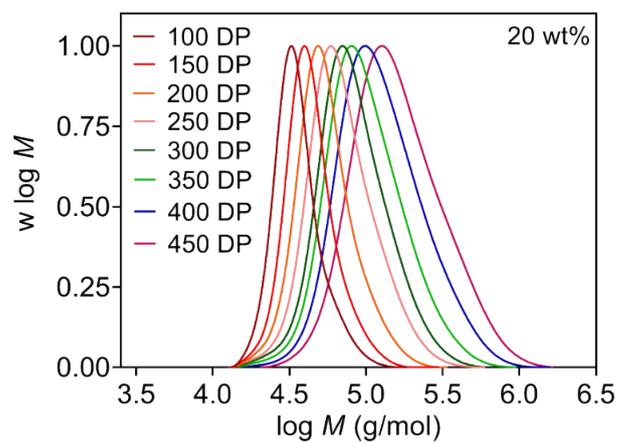
**Table S10.** Evolution of DLS data of self-assembled PEG<sub>113</sub>-*b*-PHPMA polymeric nanoparticles synthesized by ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization.

#	Irradiation time (hour)	Monomer conversion (%)	DLS D <sub>h</sub> (nm)	DLS PDI
1	5	43	34	0.22
2	6	78	147	0.19
3	7	92	229	0.22

*Note:* Polymerizations were performed under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation using a fixed reaction stoichiometry of [HPMA]:[PEG<sub>113</sub>-CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 350:1:4:0.02 in water and a total solids content of 20 wt%.



**Figure S24.** DLS derived intensity-based size distributions of self-assembled PEG<sub>113</sub>-*b*-PHPMA at different irradiation times (5, 6, and 7 hours) in **Table S8**.

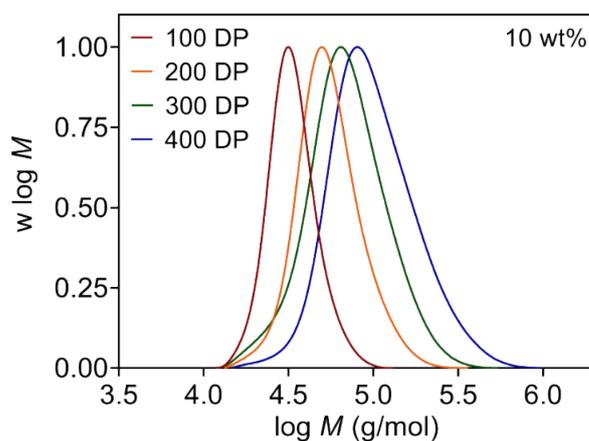


**Figure S25.** MWDs of PEG<sub>113</sub>-*b*-PHPMA synthesized by ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization of HPMA. Polymerizations were conducted under NIR light irradiation ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation in water with a fixed reaction stoichiometry of [PEG<sub>113</sub>-CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 1:4:0.02 and a total solids content of 20 wt%.

**Table S11.** ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization of HPMA with varying targeted DPs at a total solids content of 10 wt%.

#	DPs	$\alpha$ (%)	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\mathcal{D}$	Morphology (Major/Minor)
1	100	99	19700	26000	1.11	S
2	200	96	33100	42700	1.19	S
3	300	94	46000	55800	1.33	S
4	400	91	57900	69800	1.39	S

*Note:* Polymerizations were conducted under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation in water with a fixed reaction stoichiometry of [PEG<sub>113</sub>-CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 1:4:0.02 and a total solids content of 10 wt%.

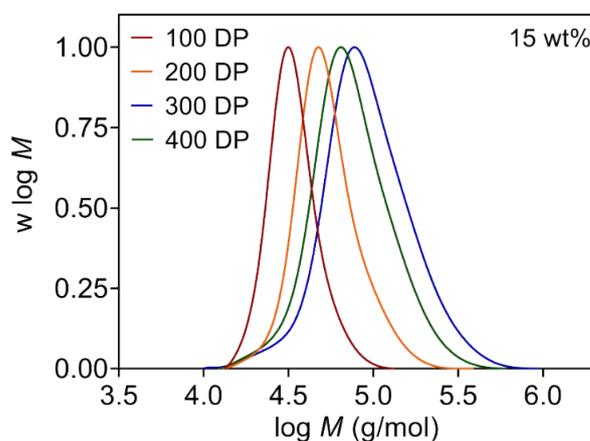


**Figure S26.** MWDs of PEG<sub>113</sub>-*b*-PHPMA with various DPs synthesized by ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization of HPMA at a total solids content of 10 wt%.

**Table S12.** ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization of HPMA with varying target DPs at a total solids content of 15 wt%.

#	DPs	$\alpha$ (%)	$M_{n, \text{theo}}$ (g mol <sup>-1</sup> )	$M_{n, \text{GPC}}$ (g mol <sup>-1</sup> )	$\mathcal{D}$	Morphology (Major/Minor)
1	100	100	19800	26200	1.11	S/W
2	200	98	33600	41700	1.19	W/S
3	300	96	46900	59800	1.32	W/S
4	400	92	58400	70500	1.41	V

*Note:* Polymerizations were conducted under the irradiation of NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation in water with a fixed reaction stoichiometry of [PEG<sub>113</sub>-CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 1:4:0.02 and a total solids content of 15 wt%.

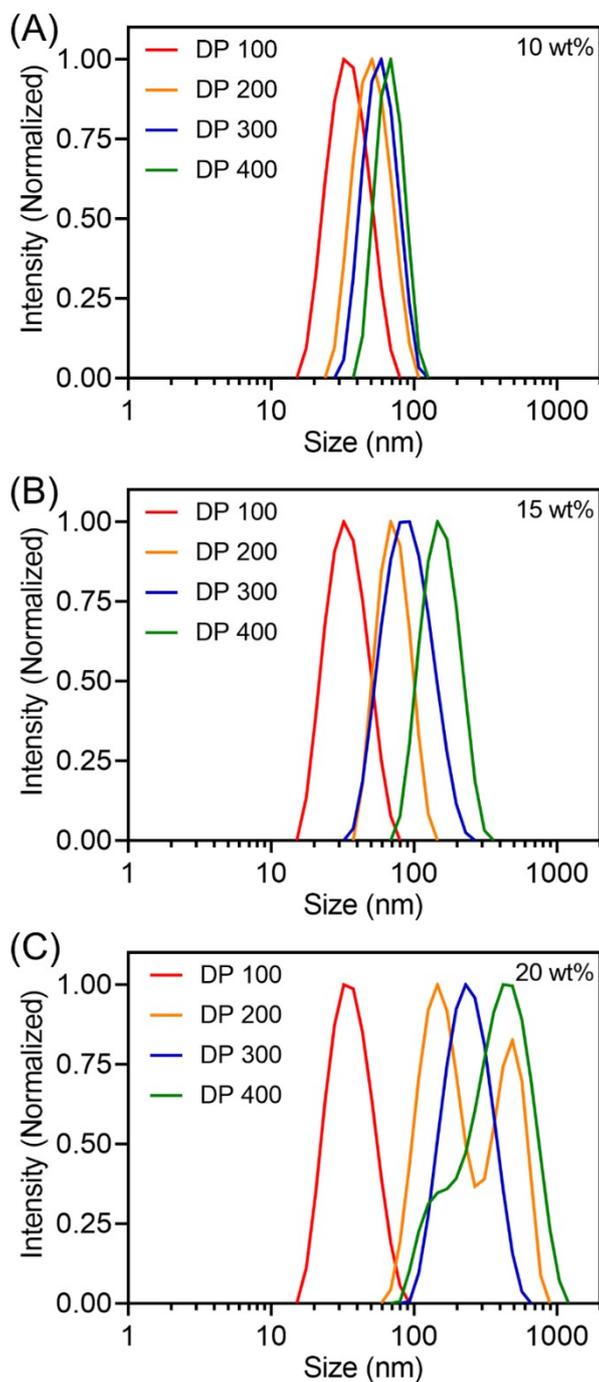


**Figure S27.** MWDs of PEG<sub>113</sub>-*b*-PHPMA with various DPs synthesized by ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization of HPMA at a total solids content of 15 wt%.

**Table S13.** DLS analyses of self-assembled PEG<sub>113</sub>-*b*-PHPMA polymeric nanoparticles synthesized by ZnPcS<sub>4</sub><sup>-</sup> mediated photo-RAFT dispersion polymerization.

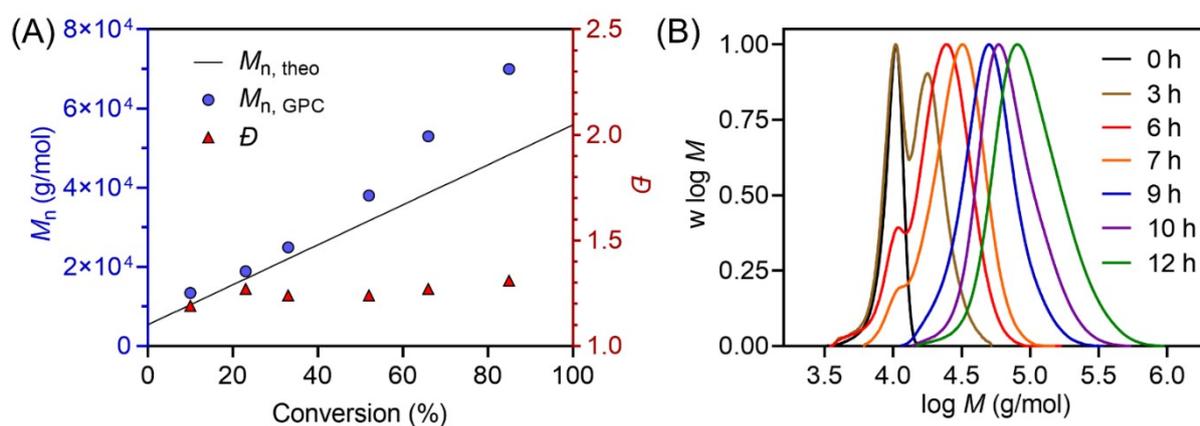
#	Solid contents (wt%)	DPs	DLS D <sub>h</sub> (nm)	DLS PDI	Morphology (Major/Minor)
1	10	100	36	0.12	S
2	10	200	52	0.08	S
3	10	300	59	0.05	S
4	10	400	69	0.01	S
5	15	100	35	0.14	S/W
6	15	200	74	0.04	W/S
7	15	300	95	0.13	W/S
8	15	400	158	0.06	V
9	20	100	38	0.21	S/W
10	20	200	156	0.52	W/S
11	20	300	252	0.23	W/V
12	20	400	408	0.23	V

*Note:* Polymerizations were performed under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) for 24 hours without prior deoxygenation using a fixed reaction stoichiometry of [PEG<sub>113</sub>-CDTPA]:[TEOA]:[ZnPcS<sub>4</sub><sup>-</sup>] = 1:4:0.02 in water. 10, 15, and 20 wt% solid contents were used in the reaction with various targeted DPs including 100, 200, 300, and 400.



**Figure S28.** DLS derived intensity-based size distributions of self-assembled PEG<sub>113</sub>-*b*-PHPMA in **Table S11** with different solid contents including (A) 10, (B) 15, and (C) 20 wt%.

Note: DLS was only used as an indicative measurement for non-spherical particles as DLS is only appropriate to be employed for spherical nanoparticles.



**Figure S29.** (A) Evolution of  $M_n$  and  $\bar{D}$  versus monomer conversion obtained from  $\text{ZnPcS}_4^-$  mediated photo-RAFT dispersion polymerization of HPMA under NIR light ( $\lambda_{\text{max}} = 730 \text{ nm}$ ;  $60 \text{ mW cm}^{-2}$ ) irradiation passing through 6.0 mm pig skin using  $[\text{HPMA}]:[\text{PEG}_{113}\text{-CDTPA}]:[\text{TEOA}]:[\text{ZnPcS}_4^-] = 350:1:4:0.02$  at a total solids content of 20 wt%. (B) Evolution of normalized MWDs versus irradiation time from the reaction in (A).

## DFT CALCULATIONS

### Coordinates and energies of photocatalysts

The coordinates of photocatalysts are optimized at B3LYP-GD3BJ/6-311G\* with the SMD-water solvation model (for C H N elements) and B3LYP-GD3BJ/LANL2TZ with the SMD-water solvation model (for Zn). All coordinates are exhibited as XYZ Cartesian coordinates. Single-point energy calculations were performed at B3LYP-GD3BJ/6-311+G\*\* with the SMD-DMSO solvation model using the optimized coordinates. Zinc tetrasulfonated phthalocyanine ( $\text{ZnPcS}_4^-$ ) was simplified to zinc phthalocyanine. All geometry optimizations and energies were calculated using the GAUSSIAN 09 D01 software package installed in the Katana high-performance computing clusters at the University of New South Wales.

### PC

*Ground state (PC) (-3447.155599)*

C	1.11848300	2.78888400	0.08358300
N	0.00000000	2.01280400	0.18278000
C	-1.11848300	2.78888400	0.08358300
C	-0.70615900	4.18549900	-0.05540100
C	0.70615900	4.18549900	-0.05540100
N	-2.38834600	2.38834600	0.06253600
C	-2.78888400	1.11848300	0.08358300
N	-2.01280400	0.00000000	0.18278000
C	-2.78888400	-1.11848300	0.08358300
C	-4.18549900	-0.70615900	-0.05540100
C	-4.18549900	0.70615900	-0.05540100
N	2.38834600	2.38834600	0.06253600
C	4.18549900	0.70615900	-0.05540100
C	4.18549900	-0.70615900	-0.05540100
C	2.78888400	-1.11848300	0.08358300
N	2.01280400	0.00000000	0.18278000
C	2.78888400	1.11848300	0.08358300
N	2.38834600	-2.38834600	0.06253600
N	0.00000000	-2.01280400	0.18278000
C	1.11848300	-2.78888400	0.08358300
C	0.70615900	-4.18549900	-0.05540100
C	-0.70615900	-4.18549900	-0.05540100
C	-1.11848300	-2.78888400	0.08358300
N	-2.38834600	-2.38834600	0.06253600
Zn	0.00000000	0.00000000	0.70585600
C	5.37222400	1.42203600	-0.19095400
C	6.55846600	0.70203900	-0.31863500
C	6.55846600	-0.70203900	-0.31863500
C	5.37222400	-1.42203600	-0.19095400
C	-1.42203600	-5.37222400	-0.19095400
C	-0.70203900	-6.55846600	-0.31863500
C	0.70203900	-6.55846600	-0.31863500
C	1.42203600	-5.37222400	-0.19095400
C	-5.37222400	1.42203600	-0.19095400
C	-6.55846600	0.70203900	-0.31863500

C	-6.55846600	-0.70203900	-0.31863500
C	-5.37222400	-1.42203600	-0.19095400
C	1.42203600	5.37222400	-0.19095400
C	0.70203900	6.55846600	-0.31863500
C	-0.70203900	6.55846600	-0.31863500
C	-1.42203600	5.37222400	-0.19095400
H	5.37448300	2.50597800	-0.19589600
H	5.37448300	-2.50597800	-0.19589600
H	-2.50597800	-5.37448300	-0.19589600
H	2.50597800	-5.37448300	-0.19589600
H	-5.37448300	2.50597800	-0.19589600
H	-5.37448300	-2.50597800	-0.19589600
H	2.50597800	5.37448300	-0.19589600
H	-2.50597800	5.37448300	-0.19589600
H	-7.49850300	1.23263300	-0.42123100
H	-7.49850300	-1.23263300	-0.42123100
H	-1.23263300	7.49850300	-0.42123100
H	1.23263300	7.49850300	-0.42123100
H	7.49850300	1.23263300	-0.42123100
H	7.49850300	-1.23263300	-0.42123100
H	1.23263300	-7.49850300	-0.42123100
H	-1.23263300	-7.49850300	-0.42123100

*Triplet state ( $\beta$ PC\*) (-3447.116532)*

C	2.77802300	1.18208300	0.08434100
N	1.41519100	1.43113200	0.18921100
C	1.17911900	2.75742500	0.09076300
C	2.46521500	3.45660600	-0.04991000
C	3.46672900	2.46072200	-0.05055800
N	0.00000000	3.39889600	0.08192700
C	-1.17911900	2.75742500	0.09076300
N	-1.41519100	1.43113200	0.18921100
C	-2.77802300	1.18208300	0.08434100
C	-3.46672900	2.46072200	-0.05055800
C	-2.46521500	3.45660600	-0.04991000
N	3.38431300	0.00000000	0.05644000
C	3.46672900	-2.46072200	-0.05055800
C	2.46521500	-3.45660600	-0.04991000
C	1.17911900	-2.75742500	0.09076300
N	1.41519100	-1.43113200	0.18921100
C	2.77802300	-1.18208300	0.08434100
N	0.00000000	-3.39889600	0.08192700
N	-1.41519100	-1.43113200	0.18921100
C	-1.17911900	-2.75742500	0.09076300
C	-2.46521500	-3.45660600	-0.04991000
C	-3.46672900	-2.46072200	-0.05055800
C	-2.77802300	-1.18208300	0.08434100
N	-3.38431300	0.00000000	0.05644000
Zn	0.00000000	0.00000000	0.64379300
C	4.80891000	-2.80302300	-0.18410500
C	5.13155300	-4.15608200	-0.30833800
C	4.13694200	-5.14244500	-0.30761800
C	2.78741700	-4.80037100	-0.18196900

C	-4.80891000	-2.80302300	-0.18410500
C	-5.13155300	-4.15608200	-0.30833800
C	-4.13694200	-5.14244500	-0.30761800
C	-2.78741700	-4.80037100	-0.18196900
C	-2.78741700	4.80037100	-0.18196900
C	-4.13694200	5.14244500	-0.30761800
C	-5.13155300	4.15608200	-0.30833800
C	-4.80891000	2.80302300	-0.18410500
C	4.80891000	2.80302300	-0.18410500
C	5.13155300	4.15608200	-0.30833800
C	4.13694200	5.14244500	-0.30761800
C	2.78741700	4.80037100	-0.18196900
H	5.58346800	-2.04493200	-0.18942800
H	2.01761200	-5.56326200	-0.18667100
H	-5.58346800	-2.04493200	-0.18942800
H	-2.01761200	-5.56326200	-0.18667100
H	-2.01761200	5.56326200	-0.18667100
H	-5.58346800	2.04493200	-0.18942800
H	5.58346800	2.04493200	-0.18942800
H	2.01761200	5.56326200	-0.18667100
H	-4.41890200	6.18438500	-0.40800800
H	-6.17056700	4.44950400	-0.40873900
H	4.41890200	6.18438500	-0.40800800
H	6.17056700	4.44950400	-0.40873900
H	6.17056700	-4.44950400	-0.40873900
H	4.41890200	-6.18438500	-0.40800800
H	-4.41890200	-6.18438500	-0.40800800
H	-6.17056700	-4.44950400	-0.40873900

*Anionic radical (PC<sup>•-</sup>) (-3447.280044)*

C	2.76906200	1.18352000	0.07339200
N	1.43616600	1.42122500	0.15458000
C	1.18558700	2.78269500	0.07037700
C	2.45948100	3.46922000	-0.04445500
C	3.46145300	2.46536700	-0.04446000
N	0.00000000	3.38548400	0.04739100
C	-1.18558700	2.78269500	0.07037700
N	-1.43616600	1.42122500	0.15458000
C	-2.76906200	1.18352000	0.07339200
C	-3.46145300	2.46536700	-0.04446000
C	-2.45948100	3.46922000	-0.04445500
N	3.40429300	0.00000000	0.06363300
C	3.46145300	-2.46536700	-0.04446000
C	2.45948100	-3.46922000	-0.04445500
C	1.18558700	-2.78269500	0.07037700
N	1.43616600	-1.42122500	0.15458000
C	2.76906200	-1.18352000	0.07339200
N	0.00000000	-3.38548400	0.04739100
N	-1.43616600	-1.42122500	0.15458000
C	-1.18558700	-2.78269500	0.07037700
C	-2.45948100	-3.46922000	-0.04445500
C	-3.46145300	-2.46536700	-0.04446000
C	-2.76906200	-1.18352000	0.07339200

N	-3.40429300	0.00000000	0.06363300
Zn	0.00000000	0.00000000	0.57038200
C	4.81087700	-2.80050500	-0.15751300
C	5.15198700	-4.14574800	-0.26362600
C	4.15882300	-5.14319200	-0.26360300
C	2.81075800	-4.81773500	-0.15815000
C	-4.81087700	-2.80050500	-0.15751300
C	-5.15198700	-4.14574800	-0.26362600
C	-4.15882300	-5.14319200	-0.26360300
C	-2.81075800	-4.81773500	-0.15815000
C	-2.81075800	4.81773500	-0.15815000
C	-4.15882300	5.14319200	-0.26360300
C	-5.15198700	4.14574800	-0.26362600
C	-4.81087700	2.80050500	-0.15751300
C	4.81087700	2.80050500	-0.15751300
C	5.15198700	4.14574800	-0.26362600
C	4.15882300	5.14319200	-0.26360300
C	2.81075800	4.81773500	-0.15815000
H	5.57624400	-2.03220000	-0.16114700
H	2.05227800	-5.59285700	-0.16177100
H	-5.57624400	-2.03220000	-0.16114700
H	-2.05227800	-5.59285700	-0.16177100
H	-2.05227800	5.59285700	-0.16177100
H	-5.57624400	2.03220000	-0.16114700
H	5.57624400	2.03220000	-0.16114700
H	2.05227800	5.59285700	-0.16177100
H	-4.45316300	6.18392300	-0.34851100
H	-6.19450800	4.43246000	-0.34885400
H	4.45316300	6.18392300	-0.34851100
H	6.19450800	4.43246000	-0.34885400
H	6.19450800	-4.43246000	-0.34885400
H	4.45316300	-6.18392300	-0.34851100
H	-4.45316300	-6.18392300	-0.34851100
H	-6.19450800	-4.43246000	-0.34885400

*Cationic radical (PC<sup>•+</sup>) (-3446.975349)*

C	1.11544400	2.78176600	0.09685700
N	0.00000000	2.00628500	0.21504400
C	-1.11544400	2.78176600	0.09685700
C	-0.70424200	4.18211900	-0.06245200
C	0.70424200	4.18211900	-0.06245200
N	-2.38612500	2.38612500	0.07370400
C	-2.78176600	1.11544400	0.09685700
N	-2.00628500	0.00000000	0.21504400
C	-2.78176600	-1.11544400	0.09685700
C	-4.18211900	-0.70424200	-0.06245200
C	-4.18211900	0.70424200	-0.06245200
N	2.38612500	2.38612500	0.07370400
C	4.18211900	0.70424200	-0.06245200
C	4.18211900	-0.70424200	-0.06245200
C	2.78176600	-1.11544400	0.09685700
N	2.00628500	0.00000000	0.21504400
C	2.78176600	1.11544400	0.09685700

N	2.38612500	-2.38612500	0.07370400
N	0.00000000	-2.00628500	0.21504400
C	1.11544400	-2.78176600	0.09685700
C	0.70424200	-4.18211900	-0.06245200
C	-0.70424200	-4.18211900	-0.06245200
C	-1.11544400	-2.78176600	0.09685700
N	-2.38612500	-2.38612500	0.07370400
Zn	0.00000000	0.00000000	0.76920800
C	5.35815700	1.42282800	-0.21325600
C	6.54763400	0.69882100	-0.35562900
C	6.54763400	-0.69882100	-0.35562900
C	5.35815700	-1.42282800	-0.21325600
C	-1.42282800	-5.35815700	-0.21325600
C	-0.69882100	-6.54763400	-0.35562900
C	0.69882100	-6.54763400	-0.35562900
C	1.42282800	-5.35815700	-0.21325600
C	-5.35815700	1.42282800	-0.21325600
C	-6.54763400	0.69882100	-0.35562900
C	-6.54763400	-0.69882100	-0.35562900
C	-5.35815700	-1.42282800	-0.21325600
C	1.42282800	5.35815700	-0.21325600
C	0.69882100	6.54763400	-0.35562900
C	-0.69882100	6.54763400	-0.35562900
C	-1.42282800	5.35815700	-0.21325600
H	5.36009200	2.50616700	-0.21874200
H	5.36009200	-2.50616700	-0.21874200
H	-2.50616700	-5.36009200	-0.21874200
H	2.50616700	-5.36009200	-0.21874200
H	-5.36009200	2.50616700	-0.21874200
H	-5.36009200	-2.50616700	-0.21874200
H	2.50616700	5.36009200	-0.21874200
H	-2.50616700	5.36009200	-0.21874200
H	-7.48498600	1.23079200	-0.46953300
H	-7.48498600	-1.23079200	-0.46953300
H	-1.23079200	7.48498600	-0.46953300
H	1.23079200	7.48498600	-0.46953300
H	7.48498600	1.23079200	-0.46953300
H	7.48498600	-1.23079200	-0.46953300
H	1.23079200	-7.48498600	-0.46953300
H	-1.23079200	-7.48498600	-0.46953300

### Coordinates and energies of RAFT agent, TEOA, and O<sub>2</sub>

The coordinates of RAFT agent, TEOA, and O<sub>2</sub> are optimized at B3LYP-GD3BJ/6-311G\* with the SMD-water solvation model exhibited as XYZ Cartesian coordinates. Single-point energy calculations were performed at B3LYP-GD3BJ/6-311+G\*\* with the SMD-water solvation model using the optimized coordinates. All geometry optimizations and energies were calculated using the GAUSSIAN 09 D01 software package installed in the Katana high-performance computing clusters at the University of New South Wales.

#### CTCPA

*Ground state (CTCPA) (-1939.523066)*

S	-0.33247500	0.31936600	1.30579300
S	0.61714400	-1.77126900	-0.71970000
C	2.31159700	-1.28619900	-0.10000100
C	2.37177600	-1.47294200	1.34852000
N	2.50562700	-1.67637400	2.47724700
C	3.23755300	-2.32814700	-0.75902400
H	3.21625200	-2.20359600	-1.84221100
H	4.25957200	-2.17926600	-0.41147000
H	2.93955300	-3.34595700	-0.50559900
C	2.65799900	0.15068000	-0.53271100
H	2.64972300	0.16509600	-1.62359100
H	1.88431500	0.83379400	-0.18984100
C	-0.55338900	-0.64585700	-0.00638500
C	4.01165700	0.62192800	-0.00979500
H	4.07244700	0.53833500	1.07973800
H	4.83695000	0.02581000	-0.40572400
C	4.27971800	2.05916100	-0.36144100
O	3.52704700	2.79797200	-0.96117600
O	5.48946800	2.45774300	0.08020200
H	5.61946200	3.39021300	-0.15781100
S	-2.03020700	-0.78751900	-0.95164700
C	-3.25354800	0.15070300	0.03733700
H	-3.28926600	-0.28289700	1.03430400
H	-2.91294200	1.18161800	0.10812600
C	-4.59707400	0.05130400	-0.67628100
H	-4.92877700	-0.99005600	-0.74255500
H	-4.53882400	0.42526000	-1.70043000
C	-5.71887900	0.80676700	-0.00753800
O	-6.77109600	1.06291200	-0.55345700
O	-5.45503000	1.15017700	1.26409700
H	-6.22681400	1.61221200	1.63179200

*Anionic radical (CTCPA<sup>•-</sup>) (-1939.636429)*

S	1.39017800	-2.39571200	1.62770700
S	2.57029500	-1.04783400	-0.84787100
C	2.30080900	0.82629100	-0.43368800
C	2.95663300	1.07431800	0.83898100
N	3.48539800	1.28319300	1.84772600

C	3.00669500	1.59767900	-1.55191300
H	2.46962200	1.44619400	-2.48932100
H	3.03268100	2.66729100	-1.33249700
H	4.03638700	1.25729100	-1.67863000
C	0.79878400	1.11325900	-0.33308500
H	0.33923800	0.81337000	-1.27579700
H	0.37768700	0.47843700	0.44485900
C	1.29773500	-1.92500300	-0.02028700
C	0.46955700	2.57128400	-0.03044700
H	0.98964200	2.92130200	0.86851100
H	0.77972300	3.23936000	-0.83667400
C	-1.00009000	2.78331800	0.20891000
O	-1.83675200	1.91311800	0.33797600
O	-1.30910000	4.09419300	0.28474700
H	-2.26036400	4.18139700	0.46024600
S	-0.14637900	-2.25921900	-1.02649300
C	-1.55931700	-1.73607000	0.04307900
H	-1.94714500	-2.59794800	0.58358500
H	-1.16308800	-1.03017700	0.76844200
C	-2.63410400	-1.09229700	-0.82192900
H	-3.03979900	-1.80198200	-1.54944400
H	-2.21535000	-0.26877900	-1.40545100
C	-3.81673000	-0.51745300	-0.08453900
O	-4.75140300	0.03031100	-0.63432700
O	-3.75261200	-0.65798600	1.25156700
H	-4.54342900	-0.25290600	1.64441000

### TEOA

*Ground state (TEOA)(-518.276192)*

N	-0.00575100	-0.00285000	0.30768300
C	0.52997100	-1.31047300	0.70983700
C	0.85766100	1.10777700	0.73298900
C	-1.39819600	0.18075000	0.73804800
C	1.47383600	-1.93385200	-0.29828600
C	0.95775100	2.23027800	-0.27869800
C	-2.42251400	-0.28292500	-0.27636600
H	-0.30172600	-2.00465000	0.82127200
H	1.02568200	-1.25208100	1.69216100
H	1.86905000	0.72932500	0.87454100
H	0.53432700	1.51252100	1.70493500
H	-1.57707800	1.24372900	0.89417300
H	-1.58526900	-0.31392900	1.70449000
H	0.96712000	-2.01594500	-1.26643300
H	1.31603100	1.82425000	-1.23153300
H	-2.24400900	0.23166300	-1.22732900
O	-2.33878400	-1.70381200	-0.46027900
H	-2.96634100	-1.94758900	-1.15049000
H	-3.42346000	-0.00944200	0.08165800
H	1.73179500	-2.94607000	0.03906400
O	2.66531300	-1.14444500	-0.43076500
H	3.19236200	-1.52640800	-1.14213700
O	-0.31992200	2.85804500	-0.46116600

H	-0.23223700	3.50107700	-1.17418400
H	1.69010000	2.96585700	0.07857200

*Cationic radical (TEOA<sup>•+</sup>) (-518.094921)*

N	-0.00111800	0.00123800	0.89780300
C	-1.34468400	0.53601600	0.87610900
H	-1.90553800	0.06579400	1.68906200
H	-1.28590700	1.60609900	1.05397000
C	0.20958600	-1.42855700	0.86927000
H	0.89636000	-1.68397200	1.68099500
H	-0.74593500	-1.91689000	1.04022600
C	1.12984400	0.90000900	0.89521800
H	0.98349800	1.62670500	1.69920800
H	2.02854900	0.32200300	1.09267300
C	0.81738000	-1.96504800	-0.45082800
H	0.27034100	-1.57436300	-1.31052900
C	1.32319600	1.68638800	-0.42609800
H	1.31371800	1.00625900	-1.27886600
C	-2.12229000	0.28865400	-0.43988900
H	-1.51153000	0.56861500	-1.29943100
H	-2.98148300	0.96032300	-0.38935200
H	2.31752600	2.13015200	-0.34433400
H	0.67202600	-3.04635600	-0.40751800
O	-2.61706500	-1.03279100	-0.56775200
H	-2.03271700	-1.54109900	-1.14034600
O	0.38983400	2.73786300	-0.60013400
H	-0.28660600	2.46531300	-1.22972500
O	2.20766600	-1.72083600	-0.57193000
H	2.35385400	-0.97591500	-1.16482500

Oxygen

*Triplet state (O<sub>2</sub>) (-150.371874)*

O	0.00000000	0.00000000	0.60227800
O	0.00000000	0.00000000	-0.60227800

*Singlet state (<sup>1</sup>O<sub>2</sub>) (-150.312597)*

O	0.00000000	0.00000000	0.60251800
O	0.00000000	0.00000000	-0.60251800

*Anionic radical (O<sub>2</sub><sup>•-</sup>) (-150.519608)*

O	0.00000000	0.00000000	0.67344900
O	0.00000000	0.00000000	-0.67344900

## REFERENCES

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2. R.-h. Liu, S.-y. Fu, H.-y. Zhan and L. A. Lucia, *Ind. Eng. Chem. Res.*, 2009, **48**, 9331-9334.