

Supporting Information

An Environmentally Benign and pH Sensitive Photocatalyst with Surface-Bound Metalloporphyrin for Heterogeneous Catalysis of Controlled Radical Polymerization

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Experiment Section

Materials

Ammonium hydroxide solution (28.0~30.0 wt% NH₃ basis), tetraethyl orthosilicate (TEOS, 98%), [3-(methacryloyloxy)propyl]trimethoxysilane (MPS, 98%), sodium azide (NaN₃, ≥99.5%), ammonium chloride (NH₄Cl, ≥99.5%), *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DDMAT, 98%) and methoxy poly(ethylene glycol) *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetate)trithiocarbonate (PEG-DDMAT, M_n = 1100 g/mol) were purchased from Sigma-Aldrich Chem. Co. and used as received unless otherwise noted. All liquid monomers including methacrylic acid (MAA, 99%), glycidyl methacrylate (GMA, ≥97%), 2-hydroxyethyl methacrylate (HEMA, ≥99%), ethylene glycol dimethacrylate (EGDMA, 98%), methyl acrylate (MA, 99%), *N,N*-dimethylacrylamide (DMA, 99%), styrene (St, ≥99%), *n*-butyl acrylate (*n*BA, ≥99%), *N*-(2-hydroxypropyl) methacrylate (HPMA, 99%), diethylacrylamide (DEA, 99%) and poly(ethylene glycol) methyl ether methacrylate (PEGMA, M_n = 500 g/mol) were purchased from Sigma-Aldrich Chem. Co. and purified by percolating over an inhibitor-removal column prior to use. *N*-isopropylacrylamide (NIPAM, 97%) was recrystallized twice from toluene/hexane (7:3, v/v). The synthesis of 5-(4'-propargyloxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine zinc (ZnTPP-Pra) was performed following the previously reported method.¹⁻³

Instrumentation

The absorbance spectra of different samples were measured by UV-vis photospectrometer (Lambda Bio40, PerkinElmer, USA) equipped with a temperature controller. Fourier transform infrared spectroscopy (FTIR) analysis was detected by a Bio-Rad FTS 135 Fourier transform infrared spectrophotometer, and the diffuse

reflectance spectra were scanned within the range from 4000 to 400 cm^{-1} . The thermal stability of the microspheres was investigated by thermogravimetric analysis (TGA). The samples were heated from 25 $^{\circ}\text{C}$ to around 700 $^{\circ}\text{C}$ with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under a dry nitrogen atmosphere in a thermal analyzer (TGS-II, PerkinElmer). Surface compositions of the microspheres were analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al $\text{K}\alpha$ X-ray source (1468.71 eV photons). The dynamic laser scattering (DLS) were performed on a Brookhaven 90 plus laser light scattering spectrometer at the scattering angle $\theta = 90^{\circ}$. The hydrodynamic diameter (D_h) was obtained by averaging the values from five measurements.

Nuclear magnetic resonance (NMR) spectroscopy and gel permeation chromatography (GPC) were used to characterize the molecular weights and chemical structures of the synthesized polymers. ^1H NMR spectroscopy were recorded on a Bruker ARX operating at 400 MHz for ^1H using CDCl_3 , D_2O and $\text{DMSO-}d_6$ as solvents and internal reference with chemical shifts (δ) reported in ppm. GPC profiles were conducted on a Waters GPC system equipped with an isocratic pump model 1515, a differential refractometer model 2414, a dual-wavelength UV detector model 2487 and Styragel columns. The number-average molecular weight ($M_{n,\text{GPC}}$) and polydispersity index ($D = M_{w,\text{GPC}}/M_{n,\text{GPC}}$) were measured with narrow molecular weight distribution poly(methyl methacrylate) (PMMA) as the standards and tetrahydrofuran (THF) or *N,N*-dimethylformamide (DMF) as the eluent at a flow rate of 1.0 mL/min.

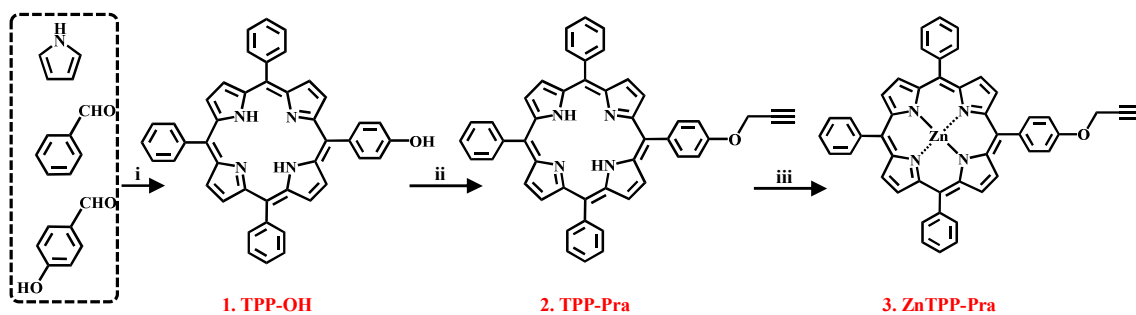
Synthesis of SiO₂@PGM-N₃ Hybrid Microspheres

Typically, TEOS (9.0 mL) was added dropwise to a mixture of ethanol (150 mL), deionized water (15 mL) and ammonium hydroxide solution (3.0 mL, 28~30 wt% NH₃ basis). The mixture was stirred vigorously at room temperature for 12 h. Afterward, MPS (2.0 mL, 8.4 mmol) was slowly dosed to the reaction suspension and the reaction was allowed to proceed for another 12 h. Finally, the raw product was purified by five cycles of centrifugation/redispersion/washing in excessive ethanol and deionized water. The SiO₂-MPS microspheres were centrifuged and stored in ethanol prior to use.

The SiO₂@PGM core-shell microspheres were prepared by distillation-precipitation polymerization of MAA and GMA in acetonitrile using EGDMA as a crosslinker.^{4,5} Briefly, about 200 mg of SiO₂-MPS microspheres were dispersed into acetonitrile (80 mL) by ultrasonication for 30 min. A mixture of MAA (0.41 mL, 50 mmol), GMA (0.68 mL, 50 mmol), EGDMA (0.28 mL, 15 mmol) and AIBN (20 mg) was then dosed to the reaction flask to initiate the polymerization. The polymerization was conducted under reflux condition for 2 h and stopped by quenching the reaction flask in ice water. The resultant SiO₂@PGM core-shell microspheres were purified by extraction with acetonitrile and ethanol five times to remove the unreacted monomers and oligomers. The SiO₂@PGM core-shell microspheres were centrifuged and stored in ethanol prior to use.

The ring opening reaction of oxirane groups by sodium azide and ammonium chloride gave rise to the surface tethering of “clickable” azide groups and hydroxyl groups.⁶ About 200 mg of SiO₂@PGM core-shell microspheres were dispersed into DMF (30 mL) by ultrasonication for 0.5 h. Excess sodium azide (130 mg, 2.0 mmol) and NH₄Cl (107

mg, 2.0 mmol) were added to the reaction mixture. The reaction was allowed to perform at 50 °C for 12 h under vigorous stirring. After the reaction, the purification of SiO₂@PGM-N₃ core-shell microspheres was done by five cycles of centrifugation/redispersion/washing in a mixed solution of ethanol and deionized water (1:1, v/v). The SiO₂@PGM-N₃ core-shell microspheres were centrifuged and stored in ethanol prior to use.



Scheme S1. Synthesis of ZnTPP-Pra metalloporphyrin. Reagents and conditions: (i) propionic acid, 135 °C, 4 h; (ii) propargyl bromide, K₂CO₃, anhydrous DMF, Ar, RT, 24 h; (iii) Zn(II) acetate, CHCl₃/CH₃OH, RT, 12 h.

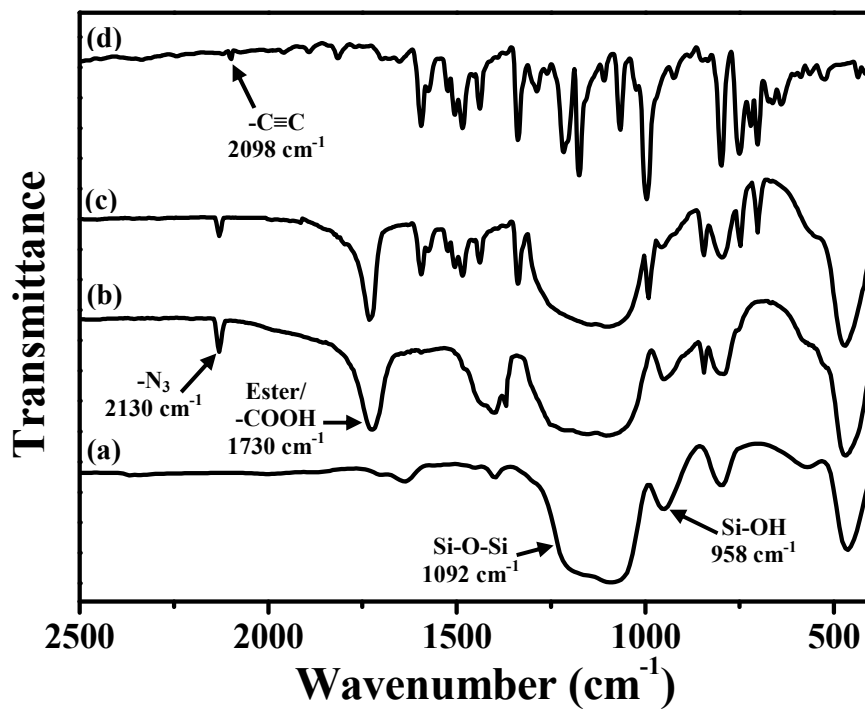


Figure S1. FTIR spectra of the (a) SiO₂-MPS, (b) SiO₂@PGM-N₃, (c) SiO₂@PGM-ZnTPP microspheres and (d) ZnTPP-Pra.

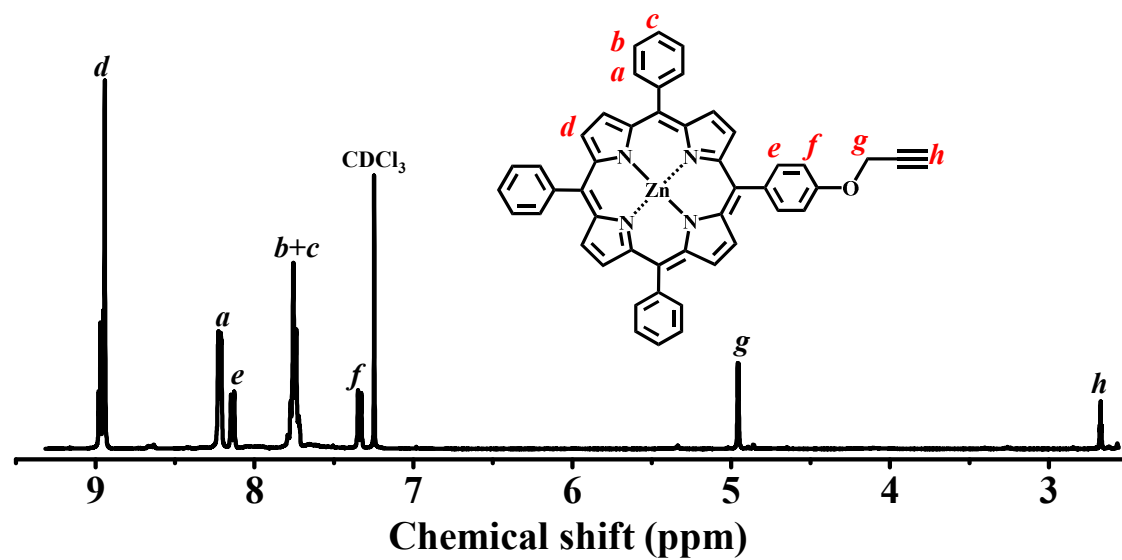


Figure S2. ^1H NMR spectrum of the ZnTPP-Pra in CDCl_3 .

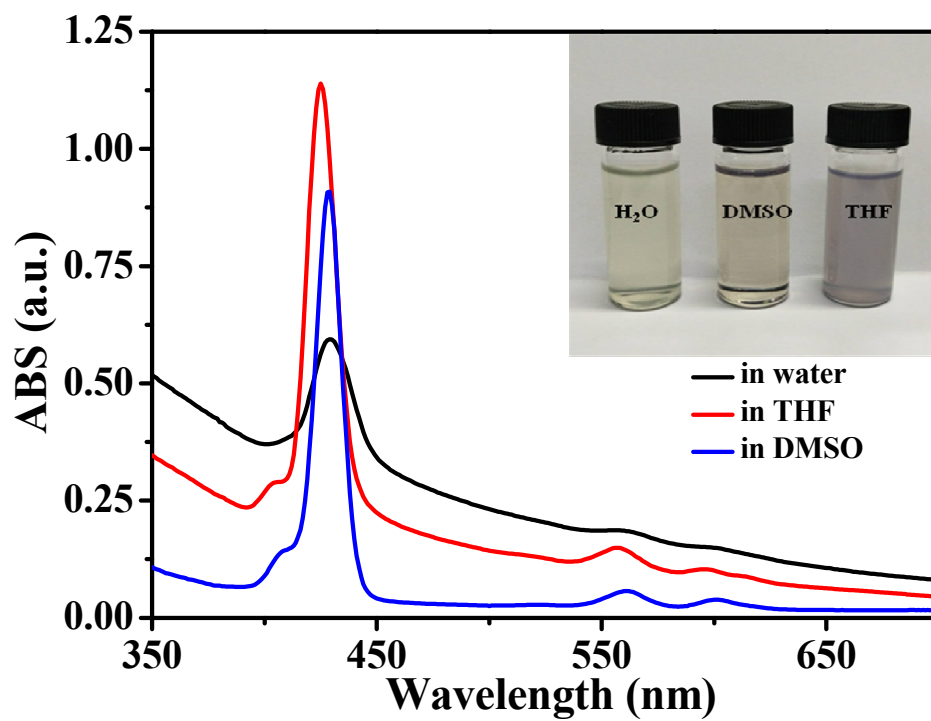


Figure S3. UV-vis absorption spectrum of *h*PGM-ZnTPP microspheres dispersed in different solvents.

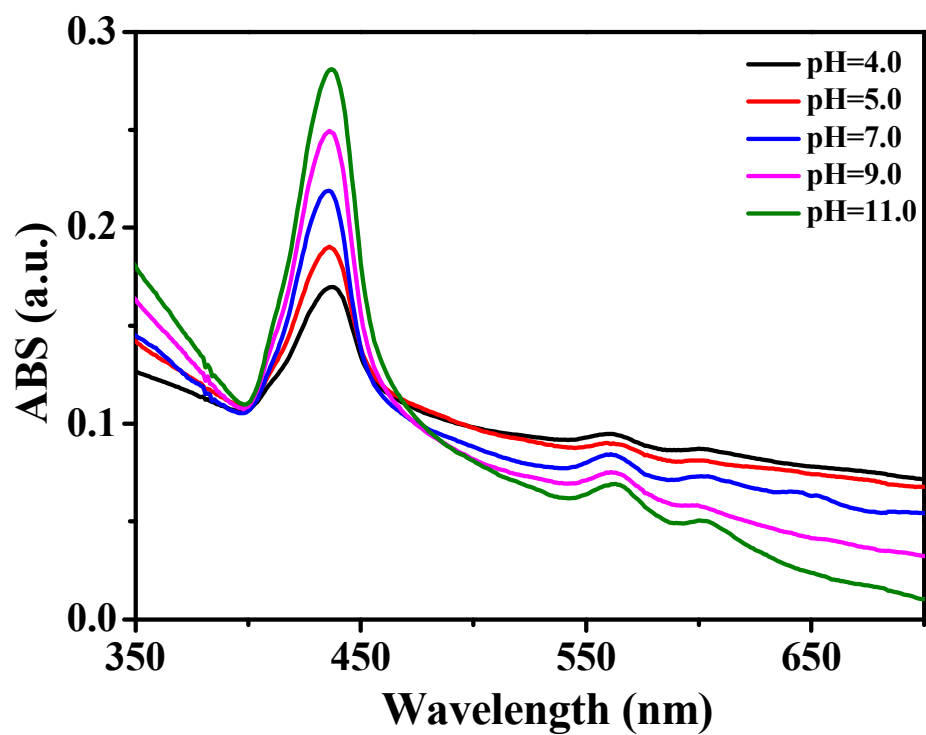


Figure S4. UV-vis absorption spectrum of *h*PGM-ZnTPP microspheres dispersed in ultrapure water at different pH values.

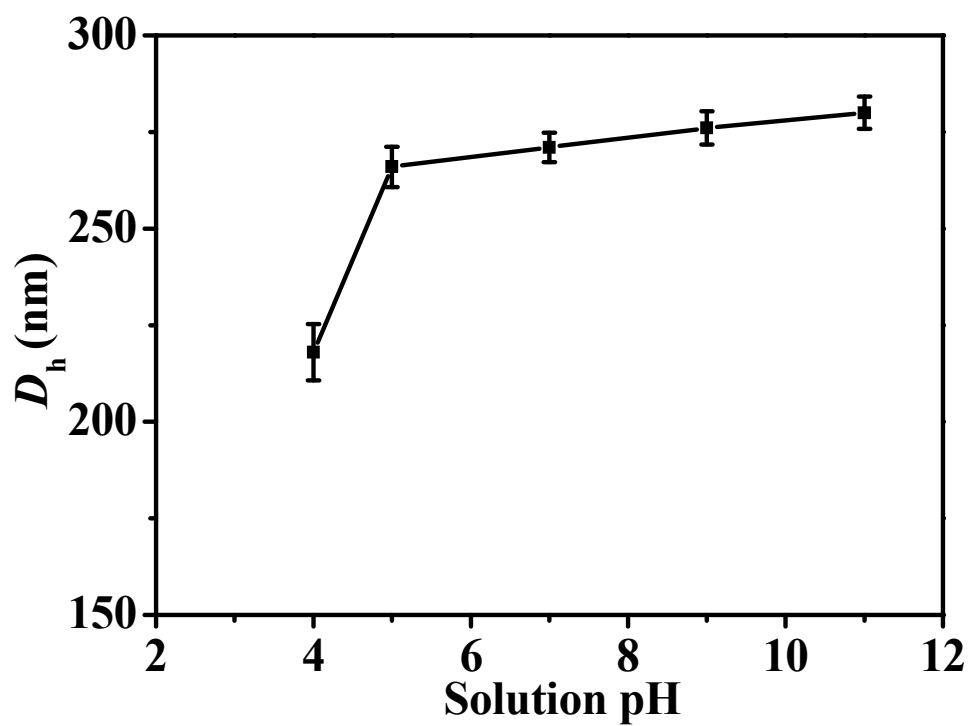


Figure S5. Influence of increasing solution pH on the hydrodynamic diameters (D_h) of the hPGM-ZnTPP microspheres in aqueous media.

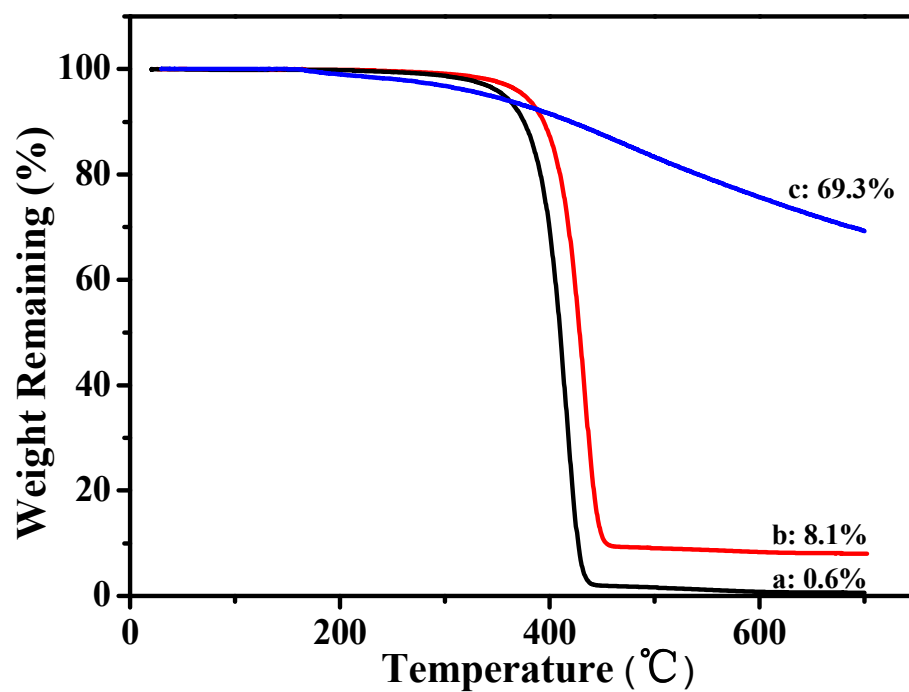


Figure S6. TGA curves of the (a) *h*PGM-N₃, (b) *h*PGM-ZnTPP microspheres and (c) ZnTPP-Pra.

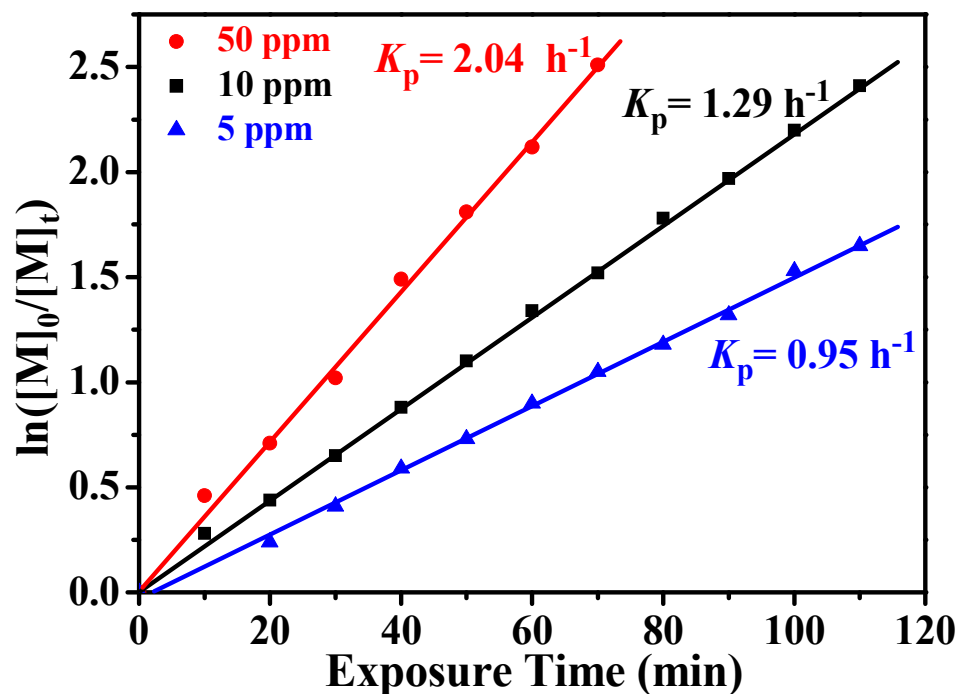


Figure S7. Kinetic analysis of PET-RAFT polymerization of MA with different concentration of ZnTPP-Pra precursors in DMSO with prior deoxygenation at 25 °C under green LED light irradiation (5 W, $\lambda_{\text{max}} = 520 \text{ nm}$, 1.2 mW/cm^2) with DDMAT as the CTA ($[MA]/[DDMAT] = 200:1$). Plot of $\ln([M]_0/[M]_t)$ versus exposure time t at different catalyst concentrations in reference to monomer concentration.

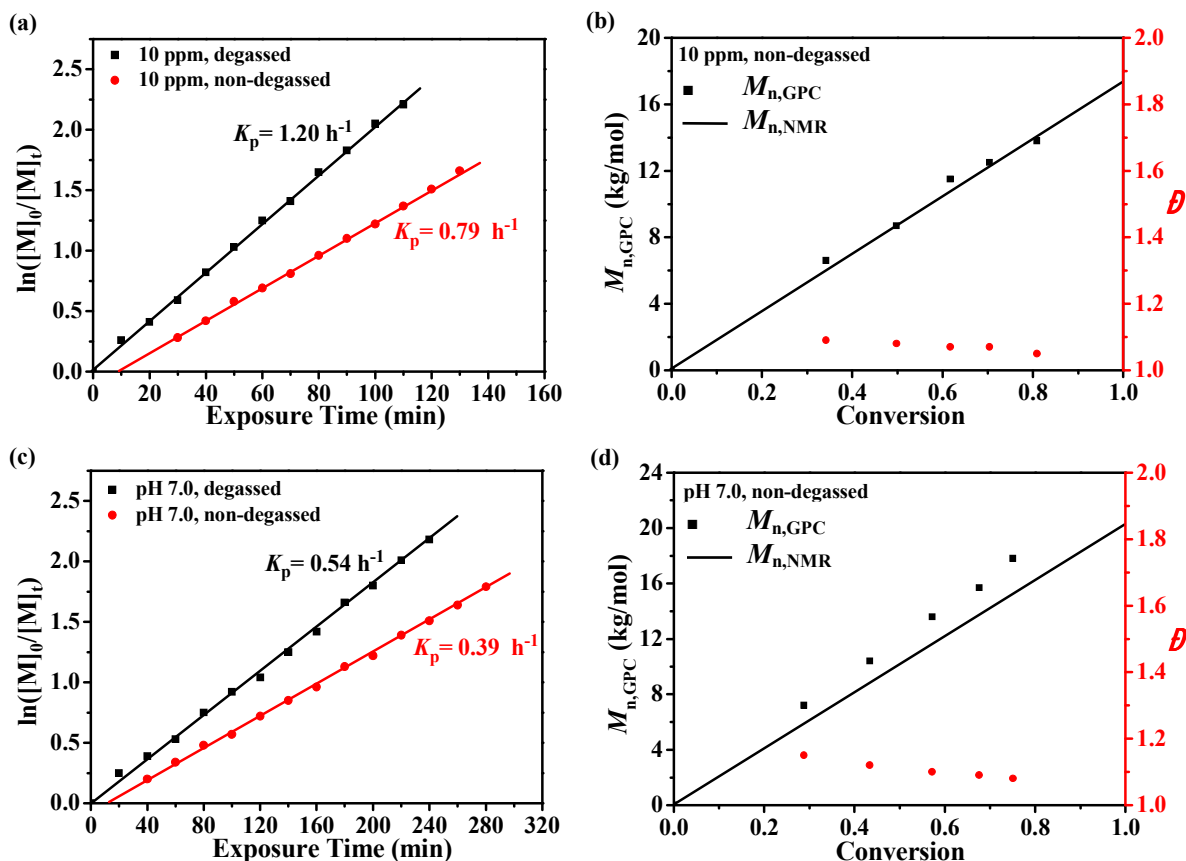


Figure S8. Kinetic analysis of PET-RAFT polymerization of MA or DMA with 10 ppm *h*PGM-ZnTPP microspheres with and without prior deoxygenation at 25 °C under green LED light irradiation (5 W, $\lambda_{\text{max}} = 520 \text{ nm}$, 1.2 mW/cm^2) with DDMAT as the CTA ($[\text{MA}(\text{DMA})]/[\text{DDMAT}] = 200:1$). (a) Plot of $\ln([M]_0/[M]_t)$ versus exposure time t in reference to monomer concentration; and (b) $M_{n,NMR}$, $M_{n,GPC}$ and \bar{D} versus monomer conversion for the PET-RAFT polymerization of MA; (c) plot of $\ln([M]_0/[M]_t)$ versus exposure time t of solution pH 7.0 in reference to monomer concentration; and (d) $M_{n,NMR}$, $M_{n,GPC}$ and \bar{D} versus monomer conversion for the PET-RAFT polymerization of DMA.

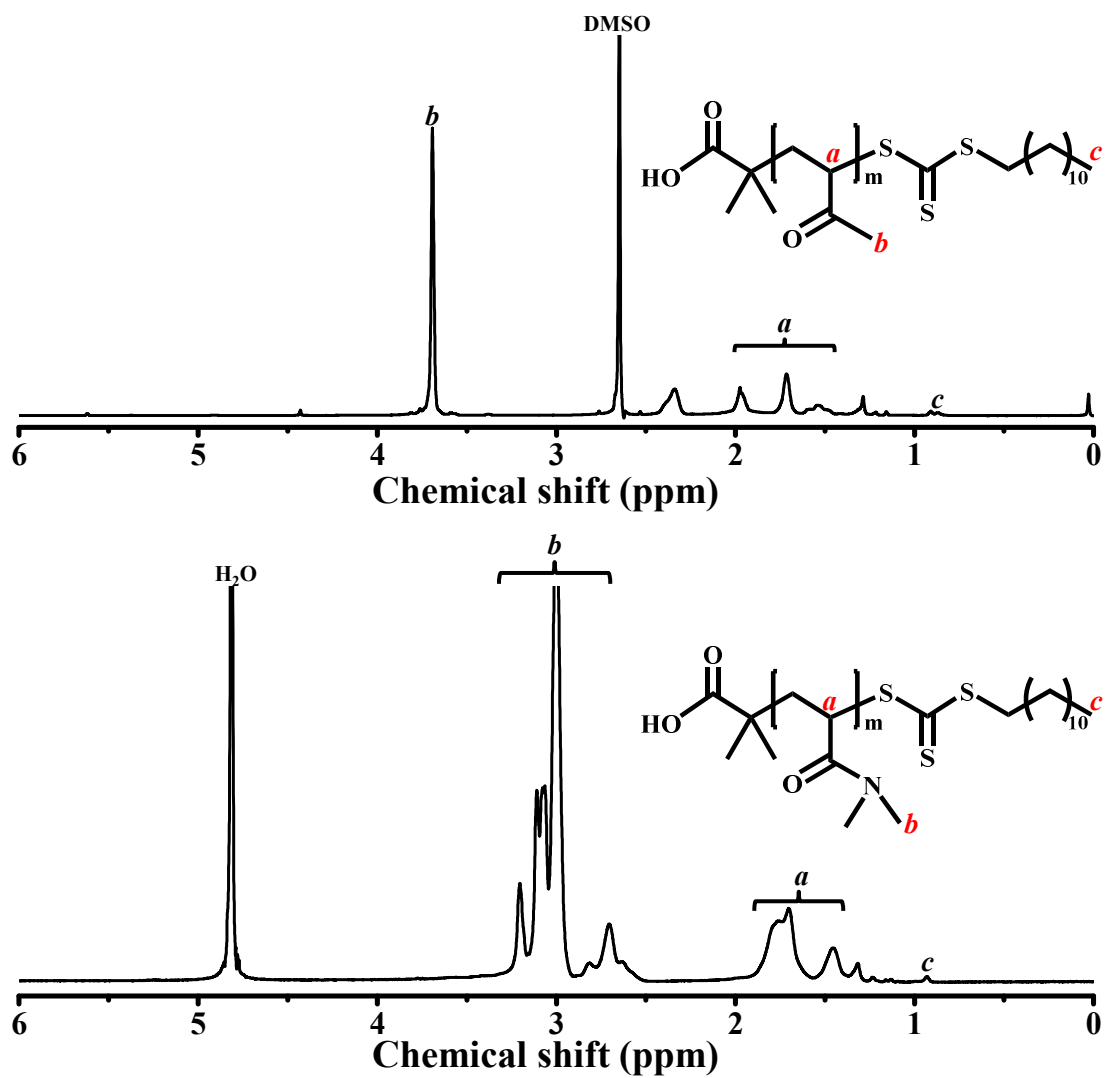


Figure S9. ^1H NMR spectra of the PMA-DDMAT macroinitiator in CDCl_3 and PDMA-DDMAT macroinitiator in D_2O .

Table S1. PET-RAFT Polymerization of Different Monomers Using *h*PGM-ZnTPP Microspheres as Photocatalysts

Entry	Photocatalyst	Monomer	CTA	Solvent	[PC]/[M] ^a (ppm)	time (h)	α^b (%)	$M_{n,NMR}^b$ (kg/mol)	$M_{n,GPC}^c$ (kg/mol)	\bar{D}^c
1 ^d	<i>h</i> PGM-ZnTPP	<i>n</i> BA	DDMAT	DMSO	10	12	94	24.4	27.5	1.05
2	<i>h</i> PGM-ZnTPP	HEMA	DDMAT	DMSO	10	12	72	19.1	23.8	1.23
3	<i>h</i> PGM-ZnTPP	NIPAM	DDMAT	DMSO	10	2	96	22.1	28.2	1.06
4	<i>h</i> PGM-ZnTPP	HPMA	DDMAT	DMSO	10	12	64	18.7	24.1	1.26
5	<i>h</i> PGM-ZnTPP	St	DDMAT	DMSO	10	24	68	14.5	19.5	1.12
6	<i>h</i> PGM-ZnTPP	MA	DDMAT	DMSO	10	6	92	16.2	17.4	1.04
7	<i>h</i> PGM-ZnTPP	DEA	DDMAT	water (pH 7.0)	10	12	95	24.5	30.8	1.16
8	<i>h</i> PGM-ZnTPP	PEGMA	DDMAT	water (pH 7.0)	10	24	48	48.4	58.9	1.17
9	<i>h</i> PGM-ZnTPP	DMA	DDMAT	water (pH 7.0)	10	12	90	18.2	21.8	1.09
10	<i>h</i> PGM-ZnTPP	DMA	PEG-DDMAT	water (pH 7.0)	10	12	91	19.3	23.4	1.07
11	<i>h</i> PGM-ZnTPP	DMA	PEG-DDMAT	water (pH 7.0)	50	12	95	19.7	25.1	1.05
12 ^e	<i>h</i> PGM-ZnTPP	MA	DDMAT	DMF	10	2	35	6.5	7.2	1.12
13 ^e	<i>h</i> PGM-ZnTPP	MA	DDMAT	DMF	10	24	94	16.5	17.9	1.16
14 ^f	<i>h</i> PGM-ZnTPP	<i>n</i> BA	PMA-DDMAT	DMSO	10	12	88	38.7	43.2	1.08
15 ^f	<i>h</i> PGM-ZnTPP	DMA	PMA-DDMAT	DMSO	10	12	91	34.2	41.6	1.13
16	<i>h</i> PGM-ZnTPP	MA	PDMA-DDMAT	DMSO	10	6	95	34.5	42.8	1.08
17	<i>h</i> PGM-ZnTPP	DEA	PDMA-DDMAT	water (pH 7.0)	10	12	92	41.6	49.5	1.11
18	SiO ₂ @PGM-ZnTPP	MA	DDMAT	DMSO	10	6	93	16.3	17.2	1.05
19	SiO ₂ @PGM-ZnTPP	MA	DDMAT	DMSO	50	6	95	16.5	17.5	1.07
20	ZnTPP-Pra	MA	DDMAT	DMSO	10	12	97	17.1	18.2	1.04
21	ZnTPP-Pra	MA	DDMAT	DMSO	50	2	96	16.9	18.4	1.06

^a The polymerizations were performed under green LED light irradiation (5 W, $\lambda_{max} = 520$ nm, 1.2 mW/cm²) with prior deoxygenation at 25 °C ([M]₀/[CTA] = 200:1).

^b The molecular weight was calculated using the following equation: $M_{n,NMR} = [M]_0/[CTA] \times MW^M \times \alpha + MW^{CTA}$, where [M]₀, [CTA], MW^M, α and MW^{CTA} correspond to initial monomer concentration, initial CTA concentration, molar mass of monomer, monomer conversion derived from ¹H NMR spectroscopy, and molar mass of CTA.

^c Derived from GPC profiles (calibration with PMMA molecular weight standards), polydispersity index (\bar{D}) = $M_{w,GPC}/M_{n,GPC}$.

^d Abbreviations: PC, photocatalyst; ZnTPP-Pra, 5-(4'-propargyloxyphenyl)-10,15,20-triphenyl-21*H*,23*H*-porphine zinc; MA, methyl acrylate; DMA, *N,N*-dimethylacrylamide; *n*BA, *n*-butyl acrylate; HEMA, 2-hydroxyethyl methacrylate; NIPAM, *N*-isopropylacrylamide; HPMA, *N*-(2-hydroxypropyl) methacrylamide; St, styrene; DEA, *N,N*-diethylacrylamide; PEGMA, poly(ethylene glycol) methyl ether methacrylate ($M_n = 500$ g/mol); CTA, chain transfer agent; DDMAT, *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate; PEG-DDMAT, methoxy poly(ethylene glycol) *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetate)trithiocarbonate ($M_n = 1100$ g/mol).

^e The block copolymers were prepared using PMA-DDMAT in Entry 6 as macroinitiators.

^f The block copolymers were prepared using PDMA-DDMAT in Entry 9 as macroinitiators.

References

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