Supporting Information

A Photocatalyst Immobilized on Fibrous and Porous Monolithic Cellulose for Heterogeneous Catalysis of Controlled Radical Polymerization

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Experimental Section

Materials

Methyl acrylate (MA, 99%), methyl methacrylate (MMA, 99%) N,N-dimethylacrylamide (DMA, 99%), N-isopropylacrylamide (NIPAAm, 97%), 2-hydroxyethyl acrylate (HEA, 99%) were all purchased from Aldrich. Monomers were deinhibited by percolating over a basic alumina column (Ajax Chemical, AR). Dichloromethane (DCM, Ajax Chemical), tetrahydrofuran (THF, Ajax Chemical), N,N'-dimethylformamide (DMF, 99.8 %, Ajax Chemical), dimethyl sulfoxide (DMSO, Ajax Chemical), methanol (Ajax Chemical) were used as received. 4-hydroxybenzaldehyde (98%), benzaldehyde (98%), pyrrole (98%), propionic acid (99.5%), 2-bromoethanol (95%), succinic anhydride (99%), zinc acetate (99.99%), potassium carbonate (K₂CO₃, 99%) 5,10,15,20-tetraphenyl-21H,23H-porphine zinc 98%), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC), (ZnTPP, and 2-(dodecylthiocarbonothioylthio)propionic acid (DTPA) were purchased from Aldrich and used as received. Premium cotton roll was purchased from Livingstone, 500g per roll. White cellulose sponge was purchased from Kmart, Randwick, Sydney, Australia (2 pieces per pack). Before use, the cotton and sponge were soaked in DMSO for two days, and then DCM for two

days.

Instrumentation

<u>Gel Permeation Chromatography (GPC)</u> was used to characterize synthesized polymer with dimethylacetamide (DMAc) as the eluent. The GPC instrument consists of Shimadzu modular system with an autoinjector, a Phenomenex 5.0 μ M bead sizeguard column (50 x 7.5 mm) followed by four Phenomenex 5.0 μ M bead size columns (105, 104, 103 and 102 Å) for DMAc system, and a differential refractive-index detector and a UV detector (λ = 305 nm). The DMAc system was calibrated based on narrow molecular weight distribution of polystyrene standards with molecular weights of 200 to 106 g mol⁻¹.

<u>Nuclear Magnetic Resonance (NMR)</u> spectroscopy was carried out with Bruker Avance III with SampleXpress operating at 400 MHz for ¹H and 100 MHz for ¹³C NMR using CDCl₃ as solvent. Tetramethylsilane (TMS) was used as a reference. The data obtained was reported as chemical shift (δ) measured in ppm downfield from TMS.

<u>UV-vis Spectroscopy</u> spectra were recorded using a CARY 300 spectrophotometer (Varian) equipped with a temperature controller.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was carried out with 7300 ICP Optical Emission Spectrometer to analyse the trace amount of zinc element in the catalyst@cellulose.

Photopolymerization reaction was carried out in the reaction vessel where the reaction mixtures are irradiated by LED RGB strip light (5050 SMD LED, 2 metres with 120 LEDs, red light, $\lambda_{max} = 635$ nm, 0.2 mW/cm²) rearranged in a glass bath with a diameter of 12 cm showed below. The sample was placed in the centre of the bath. LED strips and remote controller were purchased from RS Components Australia.





Synthesis of TPP-OH. Benzaldehyde (5.47 mL, 54 mmol) and 4-hydroxybenzaldehyde (2.20 g, 18 mmol) were dissolved in propionic acid (180 mL). This solution was charged into a three-necked flask with a reflux condenser and a magnetic stirring bar, and then was heated to 140 °C for several minutes. Pyrrole (5 mL, 72 mmol) was added dropwise to the solution under nitrogen. The reaction mixture was refluxed for 4 h and then cooled to room temperature. Then about half volume of the reaction mixture was removed and methanol (200 mL) was added into the concentrated solution. This dark blue solution was stored overnight in a refrigerator. After filtration, the purple precipitation was collected and washed with cold methanol. Crude product was dried under vacuum and subsequently purified by column chromatography on a silica gel (70-200 micron) with dichloromethane (DCM) as the eluent (Rf = 0.5). ¹H NMR (400 MHz, CDCl₃), δ ppm: 8.86 (m, 8H, β -H), 8.23 (m, 6H, 10, 15, 20-Ar-o-H), 8.09 (m, 2H, 5-Ar-o-H), 7.79 (m, 9H, 10, 15, 20-Ar-m- and p-H), 7.22 (m, 2H, 5-Ar-m-H) (Fig. S1).

Synthesis of TPP-C₂-OH. TPP-OH (0.17 g, 0.27 mmol), 2-bromoethanol (33.7 mg, 0.27 mmol) and potassium carbonate (37.4 mg, 0.27 mmol) were dissolved in 20 mL DMF. The mixture solution was heated for 12 h at 135 °C. After evaporation of the solvent, the purple crude product was purified by column chromatography on a silica gel (40-63 micron) with DCM as the eluent (Rf = 0.2). ¹H NMR (400 MHz, CDCl₃), δ ppm: 8.87 (m, 8H, β -H), 8.24 (m, 6H, 10, 15, 20-Ar-o-H), 8.15 (m, 2H, 5-Ar-o-H), 7.79 (m, 9H, 10, 15, 20-Ar-m- and p-H), 7.31 (m, 2H, 5-Ar-m-H), 4.40 (t, 2H, -O-CH₂-CH₂-), 4.18 (t, 2H, -CH₂-OH) (Fig. S2).

Synthesis of TPP-C₄-COOH. TPP-C₂-OH (47 mg, 0.07 mmol), succinic anhydride (27mg, 0.28 mmol), and DMAP (1.4 mg) were dissolved in 2 mL THF. The mixture was sealed and stirred at room temperature overnight (12h). After evaporation of the solvent, the purple crude product was purified by column chromatography on a silica gel (40-63 micron) with DCM and DCM:MeOH (40:1) as eluent separately. ¹H NMR (400 MHz, CDCl₃), δ ppm: 8.86 (m, 8H, β -H), 8.23 (m, 6H, 10, 15, 20-Ar-o-H), 8.12 (m, 2H, 5-Ar-o-H), 7.78 (m, 9H, 10, 15, 20-Ar-m- and p-H), 7.25 (m, 2H, 5-Ar-m-H), 4.62 (t, 2H, -O-CH₂-CH₂-), 4.38 (t, 2H, -CH₂-OH), 2.81 (s, 4H) (Fig. S3). ¹³C NMR (400 MHz, CDCl₃), δ ppm: 176.28 (1C), δ ppm: 63.29 (1C), δ ppm: 28.93 (1C), δ ppm: 28.73 (1C) (Fig. S4).

Synthesis of TPP-C₄-COOH@cotton and TPP-C₄-COOH@sponge. Commercial cotton and cellulose sponge were cut into small pieces (roughly 20 mg for each piece) and soaked in DMSO for 3 days. Before conjugation, the cotton and sponge were washed with DCM and

then soaked in DCM overnight to exchange the DMSO inside the composites. Typically, TPP-C4-COOH (5 mg), DCC (24 mg), and DMAP (1 mg) were dissolved in DCM (1.5 mL), then 2 pieces of cotton were immersed in the mixture for 3 days. Afterwards, the sienna composites were washed with DMSO for 3 times and then soaked in DMSO overnight.

Synthesis of Zn-TPP-C4-COOH@cotton and Zn-TPP-C4-COOH@sponge. In a typical synthesis, composite TPP-C₄-COOH@cotton and TPP-C₄-COOH@sponge was immersed in DCM/DMF (2/1) solution (1.5 mL) containing zinc acetate (10 mg) for 6 h with stirring. After reaction, the purple composite was washed with DMSO and MeOH for 3 times respectively to remove the reaction solvent and excess of zinc acetate. Afterwards, the purple composite was dried under nitrogen and kept in a sealed vial in dark at room temperature.

General sample preparation procedure for ICP-OES analysis. Sample (ZnTPP@cotton or ZnTPP@sponge, ~20mg) was digested with HNO₃ (200 μ L) for 3 h at 90 °C. After cooling down, H₂O₂ was added and soaked for 30 min to remove the organics. Afterwards, HCl (50 μ L) was added into the mixture to help digest the sample and insoluble particles were removed by filtration. The clear solution was collected and the volume of the solution was adjusted to 10 mL with water, after which zinc amount in the solution was analysed by ICP-OES. The weight percentage of the conjugated catalyst was calculated from the ICP results using the following equation:

$$W_{\text{ZnTPP}}/W_{\text{ZnTPP@cellulose}} = [(W_{\text{zinc-sample}} - W_{\text{zinc-control}})/M_{\text{zinc}})] \times M_{\text{catalyst}}$$

Where $W_{\text{zinc-sample}}$, $W_{\text{zinc-control}}$, M_{zinc} , and M_{catalyst} refer to the zinc amount of the catalyst@material, zinc amount of the blank material, molecular weight of zinc, and molecular weight of the catalyst.

$$W_{\text{ZnTPP}}/W_{\text{ZnTPP}@cotton} = \{ [(5457-7.27) \text{ mg/kg}]/65.38 \text{ g/mol} \} \times 840.26 \text{g/mol} = 70.1 \text{ } \mu\text{g/mg} \}$$
$$W_{\text{ZnTPP}}/W_{\text{ZnTPP}@sponge} = \{ [(5740-11.6) \text{ } \text{mg/kg}]/65.38 \text{ } \text{g/mol} \} \times 840.26 \text{g/mol} = 73.6 \text{ } \mu\text{g/mg} \}$$

Plotting of the UV-vis standard curve of ZnTPP. ZnTPP solution with different concentrations (0 μ g/mL, 0.0625 μ g/mL, 0.125 μ g/mL, 0.25 μ g/mL, 0.5 μ g/mL and 0.97 μ g/mL) were prepared. 1 mL of the solution was aliquoted and analysed by UV-vis spectrometer (Fig. S9A). The standard curve was plotted by the absorbance versus the ZnTPP concentrations (0 μ g/mL, 0.0625 μ g/mL, 0.125 μ g/mL, 0.25 μ g/mL, 0.5 μ g/mL) (Fig. S9B).

General procedure for the kinetic studies of PET-RAFT polymerization of methyl

acrylate (MA) mediated by ZnTPP@cotton and ZnTPP@sponge. Typically, a reaction stock solution consisting of DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.0276 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED strip light ($\lambda_{max} = 635$ nm) at room temperature. Every 6 h, aliquots of the reaction mixtures were withdrawn and analysed by both ¹H NMR and GPC to measure the monomer conversions and numberaverage molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n). After 24 h reaction, the catalyst immobilized composites were separated and washed with DMSO for 3 times and then soaked in DMSO overnight.

Control experiments for the PET-RAFT polymerization in the absence of light or catalyst immobilized composite. Typically, a reaction stock solution consisting of DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.0276 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. For the control experiment in the absence of light, the sealed glass vial was kept in dark for 24 h. For the other control experiment in the absence of catalyst immobilized composite, a reaction stock solution consisting of DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.0276 mmol) and white sponge (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED strip light ($\lambda_{max} = 635$ nm) at room temperature for 24 h. The monomer conversions after 24 h for both reactions were determined by ¹H NMR.

Procedure for the preparation of diblock copolymers by PET-RAFT polymerization mediated by ZnTPP@cotton. In a typical experiment synthesizing the diblock copolymer poly(methyl acrylate)-b-poly(*N*,*N*-dimethylacrylamide) (PMA-b-PDMA), a 5 mL glass vial was equipped with a rubber septum and charged with DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.027 mmol) and ZnTPP@cotton (20 mg). The mixture was sealed and degassed with nitrogen for 20 min. The reaction mixture was irradiated under a red LED strip light at room temperature for 24 h. After reaction, the ZnTPP@cotton was separated, washed with DMSO and then soaked in DMSO overnight. The reaction mixture was precipitated in mixture of methanol/petroleum spirit (1/1, v/v) with stirring. The light-yellow precipitate was collected, re-dissolved in a minimal amount of dichloromethane, and precipitated again from the mixture of methanol/petroleum spirit (1/1, v/v). The final light-

yellow product was collected and submitted for GPC to measure number-average molecular weight and polydispersity, $M_{n,GPC} = 8\ 300\ \text{g/mol}, M_w/M_n = 1.12$.

For the chain extension, a 5 mL glass vial was equipped with a rubber septum and charged with DMSO (0.5 mL), DMA (0.495 g, 5.00 mmol), PMA macro-initiator (84 mg, $M_n = 8\,300$ g/mol, 0.01 mmol) and ZnTPP@cotton (20 mg). The mixture was then irradiated under a red LED strip light at room temperature for 24 h. After separating the ZnTPP@cotton, the final solution was precipitated in methanol with stirring. The light-yellow precipitate was collected, re-dissolved in a minimal amount of dichloromethane, and precipitated a second time from methanol. The final light-yellow precipitate was then collected and dried to give desired products PMA-*b*-PDMA: $M_{n,GPC} = 24\,500$ g/mol, $M_w/M_n = 1.10$.

General procedure for PET-RAFT polymerization of DMA and NIPAAM mediated by ZnTPP@cotton in the presence of CPDTC. Typically, in the polymerization of DMA, a reaction stock solution consisting of DMSO (0.5 mL), DMA (0.481 g, 4.90 mmol), CPDTC (8.39 mg, 0.0245 mmol) and ZnTPP@cotton (20 mg) was prepared in a 4 mL glass vial. In the polymerization of NIPAAm, a reaction stock solution consisting of DMSO (0.5 mL), NIPAAm (0.5 g, 4.42 mmol), CPDTC (7.64 mg, 0.022 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vials were sealed with a rubber septum and the reaction mixtures were degassed with nitrogen for 20 minutes. The glass vials were irradiated under red LED stripe light ($\lambda_{max} = 635$ nm) at room temperature for 24 h. After reaction, aliquots of the reaction mixtures were withdrawn and analysed by both ¹H NMR and GPC to calculate the monomer conversions and to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n).

The procedure for PET-RAFT polymerization of MMA mediated by ZnTPP@cotton in the presence of CPDTC. In the polymerization of MMA, a reaction stock solution consisting of DMSO (0.5 mL), MMA (0.468 g, 4.67 mmol), CPDTC (7.9 mg, 0.023 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED stripe light ($\lambda_{max} = 635$ nm) at room temperature. After 39 h, aliquots of the reaction mixtures were withdrawn and analysed by both ¹H NMR and GPC to calculate the monomer conversions and to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n).

The procedure for PET-RAFT polymerization of HEA mediated by ZnTPP@cotton in the presence of CPDTC. In the polymerization of HEA, a reaction stock solution consisting

of DMSO (1.0 mL), HEA (0.553 g, 4.76 mmol), CPDTC (8.3 mg, 0.024 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED stripe light ($\lambda_{max} = 635$ nm) at room temperature. After 11 h, aliquots of the reaction mixtures were withdrawn and analysed by both ¹H NMR and GPC to calculate the monomer conversions and to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n).

The procedure for PET-RAFT polymerization of MA mediated by ZnTPP@cotton in the presence of DTPA. Typically, a reaction stock solution consisting of DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), DTPA (9.7 mg, 0.0276 mmol) and catalyst immobilized composite (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED stripe light ($\lambda_{max} = 635$ nm) at room temperature for 24 h. After reaction, aliquots of the reaction mixtures were withdrawn and analysed by both ¹H NMR and GPC to calculate the monomer conversions and to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n).

Study for the reusability of the immobilized catalyst in PET-RAFT polymerization of MA using CPDTC as chain transfer agent. In a typical reaction cycle, a 5 mL glass vial was equipped with a rubber septum and charged with DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.0276 mmol) and a newly made catalyst@cotton. The vial was sealed and degassed with nitrogen for 20 min. The reaction system was irradiated under a red LED strip light at room temperature for 24 h. After reaction, aliquots of the reaction mixture were withdrawn and analysed by ¹H NMR, GPC and UV-vis to measure monomer conversion, molecular weight and molecular weight distribution, and the amount of the free catalyst leached from the composite. The catalyst immobilized composite was washed with DMSO for 3 times and then soaked in DMSO before next run.

The procedure for PET-RAFT polymerization of MA mediated by TPP@cotton in the presence of CPDTC and tertiary amine. In the polymerization of MMA, a reaction stock solution consisting of DMSO (0.5 mL), MA (0.475 g, 5.52 mmol), CPDTC (9.5 mg, 0.0276 mmol), TEA (2.79 mg, 0.0276 mmol) and TPP@cotton (20 mg) was prepared in a 4 mL glass vial. The glass vial was sealed with a rubber septum and the reaction mixture was degassed with nitrogen for 20 minutes. The glass vial was irradiated under red LED strip light ($\lambda_{max} = 635$ nm) at room temperature. After 21 h, aliquots of the reaction mixtures were withdrawn

and analysed by both ¹H NMR and GPC to determine the monomer conversions and to measure number-average molecular weights ($M_{n,GPC}$) and molecular weight distributions (M_w/M_n).



Fig. S1: ¹H NMR spectrum of TPP-OH (400 MHz, CDCl₃ as solvent).



Fig. S2: ¹H NMR spectrum of TPP-C₂-OH (400 MHz, CDCl₃ as solvent).



Fig. S3: ¹H NMR spectrum of TPP-C₄-COOH (400 MHz, CDCl₃ as solvent).



Fig. S4: ¹³C NMR spectrum of TPP-C₄-COOH (100 MHz, CDCl₃ as solvent).



Fig. S5: Catalyst leaching test in various solvents. Catalyst immobilized composites (ZnTPP@cotton on the left and ZnTPP@sponge on the right) have been soaked in different solvents for 2 days. There is no obvious purple colour in the solvents, suggesting negligible catalyst (ZnTPP) leaching from the catalyst composites.



Fig. S6: "ON-OFF" study for A) catalyst@cotton and B) catalyst@sponge in PET-RAFT polymerization of MA using CPDTC as chain transfer agent under red light irradiation.



Fig. S7: Molecular weight distributions of diblock copolymers PMA-*b*-PDMA chain extended from PMA macroRAFT agent by PET-RAFT polymerization catalyzed by ZnTPP@cotton in DMSO under red light irradiation.



Fig. S8: Reaction mixtures after 24 h PET-RAFT polymerization of MA using CPDTC as chain transfer agent mediated by A) ZnTPP, B) ZnTPP@cotton, and C) ZnTPP@sponge under red light irradiation. Reaction conditions: MA (0.475 g, 5.52 mmol) and CPDTC (9.5 mg, 0.0276 mmol) were dissolved in DMSO (0.5 mL) in each reaction, and the photoredox catalyst used were ZnTPP (80 ppm), ZnTPP@cotton and ZnTPP@sponge, respectively.



Fig. S9: A) UV-vis absorbance of ZnTPP in different concentrations (0 μ g/mL, 0.0625 μ g/mL, 0.125 μ g/mL, 0.25 μ g/mL, 0.5 μ g/mL and 0.97 μ g/mL); B) UV-vis ZnTPP standard curve was plotted using the absorbance of peak 1.



Fig. S10: (A) Typical examples of the UV-vis absorbance of reaction mixture after polymerization of MA with immobilized catalyst using CPDTC as chain transfer agent under red light irradiation in different reaction cycles. (B) an example of how to calculate the amount of free catalyst in reaction mixture according to the standard curve using the reaction mixture of 5th polymerization cycle mediated by ZnTPP@sponge (refers to the red curve in Fig. S10A). Samples are prepared in 1:10 dilution from the reaction mixture after polymerization.

Amount of the free catalyst is roughly calculated as followed:

$$W_{\text{free catalyst}} = (A_{\text{sample}}/0.6797) \times d_{\text{f}} \times V_{\text{reaction mixture}}$$

Where A_{sample} , d_{f} , and $V_{reaction\ mixture}$ refer to the absorbance of the sample analysed by UV-vis, dilution factor of the sample prepared from the reaction mixture, and the volume of the reaction mixture, respectively. The number of 0.6797 is the slope obtained in Fig. S9B.

However, as showed in Fig. S10B, the trithiocarbonate moiety in polymer chain end in this study also has the absorbance in this area. To eliminate the influence caused by the RAFT agent, we prepared a RAFT solution (DTPA) in same concentration with the reaction mixture and analysed it with UV-vis spectroscopy. Therefore, the actual value of the absorbance of the catalyst in the sample can be calculated as $\alpha = A_1 - A_2$, where A_1 and A_2 refer to absorbance of the sample and the RAFT agent, respectively. The calibrated equation is:

$$W_{\text{free catalyst}} = [(A_1 - A_2)/0.6797] \mu g/mL \times d_f \times V_{\text{reaction mixture }}mL$$

Taking the highest absorbance of the sample showed in Fig. S9A as an example, the amount of free catalyst:

 $W_{\text{free catalyst}} = [(0.1220 - 0.0887)/0.6797] \,\mu\text{g/mL} \times 10 \times 1 \,\text{mL} = 0.49 \,\mu\text{g}$



Fig. S11: Molecular distributions of different polymers synthesized with ZnTPP@cotton under red light irradiation.



Fig. S12: UV-vis absorbance of reaction mixtures after polymerization of different monomers using ZnTPP@cotton under red light irradiation.



Fig. S13: Molecular weight distributions after 24 h polymerization of MA using CPDTC as chain transfer agent mediated by (A) ZnTPP@cotton and (B) ZnTPP@sponge under red light irradiation in different reaction cycles.



Fig. S14: PET-RAFT polymerization of MA using TPP@cotton as catalyst, TEA as cocatalyst, and DTPA as RAFT agent, in DMSO under red light irradiation. (A) Molecular weight, monomer conversion and polydispersity; (B) UV-Vis spectrum for the reaction mixture after polymerization to measure the amount of catalyst leached out from TPP@cotton composite.