

Electronic Supplementary Information

Robust Hollow Nanocomposites with Ruthenium-Bipyridine Complexes for Heterogeneous Catalysis of Logic-Controlled RAFT Polymerization

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Experiment Section

Materials

The following chemicals were purchased from Sigma-Aldrich and used as received unless otherwise indicated: 1,1,1-tris(hydroxymethyl)ethane (TME, 99%), glycidol (GLY, 96%), 2,3-epoxypropyl propargyl ether (EPE, 97%), sodium methoxide (NaOCH₃, 95%), 1,4-dioxane (99.8%), methacryloyl chloride (97%), triethylamine (TEA, ≥99%), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄, 99%), sodium azide (NaN₃, ≥99.5%), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate (Ru(bpy)₃Cl₂, 99.95%), copper(II) acetate (Cu(OAc)₂, 98%), tris[2-(dimethylamino)ethyl]amine (Me₆TREN, 97%), sodium ascorbate (≥99%), [3-(methacryloyloxy)propyl]trimethoxysilane (MPMS, 98%), tetraethyl orthosilicate (TEOS, 98%), ammonium hydroxide solution (28.0~30.0 wt% NH₃ basis), *cis*-dichlorobis(2,2'-bipyridine)ruthenium(II) hydrate (Ru(bpy)₂Cl₂, 97%), hydrofluoric acid (HF, ≥40%), *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). GLY, EPE and 1,4-dioxane were purified by distillation under reduced pressure prior to use. All liquid monomers including methyl acrylate (MA, 99%), *N,N*-dimethylacrylamide (DMA, 99%), *N,N*-diethylacrylamide (DEA, 99%), styrene (St, ≥99%), 2-hydroxyethyl acrylate (HEA, 96%), glycidyl methacrylate (GMA, ≥97%) 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 radical initiator, 2,2'-azobis(2-methylpropionitrile) (AIBN, 97%) was purchased from Kanto Chemical Co. (Tokyo, Japan) and was recrystallized from anhydrous ethanol. 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6'-bromohexyl)fluorene¹

and propargyl 2-(dodecylthiocarbonothioylthio)-2-methylpropionate (PDMAT)² were synthesized following the previously reported method.

Instrumentation

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 spectra were recorded on a Bruker ARX operating at 400 MHz for ¹H using deuterated chloroform (CDCl₃), deuterated dimethyl sulfoxide (DMSO-*d*₆) and deuterated water (D₂O) as the solvents and an internal reference with chemical shifts (δ) reported in ppm. GPC analysis was performed 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(ethylene oxide) (PEO), polystyrene (PSt) or 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.

The absorbance spectra of different samples were measured by UV-vis photospectrometer (Lambda Bio40, PerkinElmer, USA) equipped with a temperature controller. Surface chemistry of the nanoparticles (NPs) was analyzed by X-ray photoelectron spectroscopy (XPS) on a Kratos AXIS Ultra DLD spectrometer sourcing with a monochromatized Al K α X-ray source (1468.71 eV photons). The dynamic laser scattering (DLS) measurements 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. The thermal stability was investigated by thermogravimetric analysis (TGA). The samples were heated from 30 °C to around 800 °C with a heating rate of 10 °C/min under a dry nitrogen atmosphere in a thermal analyzer (TGS-II, PerkinElmer). The morphology of the NPs was observed by transmission electron microscopy (TEM, JEOL-2100, JEOL Ltd., Japan) and field-emission scanning electron microscopy (FESEM, SIGMA, Carl Zeiss AG, Germany).

Synthesis of Methacryloyloxy Functionalized Hyperbranched Poly(glycerol-*co*-glycidyl propargyl ether) (HPGEm) Random Copolymers

The synthesis of hyperbranched poly(glycerol-*co*-glycidyl propargyl ether) (HPGE) random copolymers was accomplished in a straightforward anionic ring-opening multibranching polymerization (AROMP) of GLY and EPE in 1,4-dioxane, using TME as the initiator and NaOCH₃ as the catalyst (Scheme S1).^{3,4} Briefly, TME (I_0 , 181.0 mg, 1.51 mmol) and NaOCH₃ (24.3 mg, 0.45 mmol) were successively dissolved in anhydrous methanol (2 mL) to deprotonate 10% of the hydroxyl groups. The mixture was then stirred at 60 °C for 2 h and subjected to evacuation at 80 °C overnight to afford a white salt of sodium alkoxide. The obtained initiator was dispersed in anhydrous 1,4-dioxane (20 mL) by sonication and deoxygenated by sparging argon for 20 min. The flask was then sealed with a rubber septum and the reaction was allowed to proceed at 95 °C under vigorous stirring. A mixture of freshly distilled, argon-purged GLY (M_1 , 8.00 mL, 120.8 mmol) and EPE (M_2 , 3.13 mL, 30.2 mmol) in an equal volume of anhydrous 1,4-dioxane was slowly syringed to the reaction mixture over a period of 12 h. Afterwards, AROMP was performed for another 6 h for thorough polymerization. The reaction flask was then quenched in an icy water bath and methanol was added to protonate the active

chain ends. Unreacted monomers and solvents were removed by distillation and the crude product was purified by repeated precipitation from DMF into a 10-fold excess of cold diethyl ether and finally dried *in vacuo*, to afford a highly viscous liquid. Yield: 79%. $[M_1]/[M_2]/[I_0] = 80:20:1$; $M_{n,NMR} = 6600$ g/mol. 1H NMR (DMSO- d_6 , δ , ppm, TMS): 4.35-4.84 (H $\times(x+3)$, -OH), 4.10-4.16 (2H $\times y$, -OCH $_2$ C \equiv CH), 3.25-3.79 (H $\times(5x+6y+6)$, -OCH-, -OCH $_2$ -, -OCH $_2$ C \equiv CH), 1.20-1.25 (3H, -CH $_3$), where the notes x and y refer to the degree of polymerization of GLY and EPE monomers in HPGE random copolymers, respectively. GPC (DMF as eluent, PEO standard): $M_{n,GPC} = 5800$ g/mol, $D = 1.22$.

The HPGE polymer ($M_{n,NMR} = 6600$ g/mol, 9.90 g, 1.5 mmol) and TEA (0.84 mL, 6.0 mmol) was dissolved in DMF (50 mL). The flask was immersed in an icy water bath, and methacryloyl chloride (0.58 mL, 6.0 mmol) in DMF (10 mL) were then added dropwise to the reaction mixture. Upon completion of the addition, the reaction mixture was kept in the icy water bath for 1 h and then at room temperature for 24 h. The crude product was precipitated twice from DMF into a 10-fold excess of diethyl ether. The resultant polymers solution was dialyzed against ultrapure water (4 \times 200 mL) with a dialysis membrane (MWCO 1000 Da) at room temperature for 48 h. Finally, HPGE_m was collected via lyophilization and given a highly viscous liquid. Yield: ~95%. $M_{n,NMR} = 6900$ g/mol. 1H NMR (DMSO- d_6 , δ , ppm, TMS): 6.07-6.12 (H $\times z$, -C(CH $_3$)=CH $_2$), 5.68-5.73 (H $\times z$, -C(CH $_3$)=CH $_2$), 4.35-4.84 (H $\times(x-z+3)$, -OH), 4.12-4.19 (2H $\times y$, -OCH $_2$ C \equiv CH), 3.25-3.85 (H $\times(5x+6y+6)$, -OCH-, -OCH $_2$ -, -OCH $_2$ C \equiv CH), 1.88-1.96 (3H $\times z$, -C(CH $_3$)=CH $_2$), 1.21-1.26 (3H, -CH $_3$), where the notes x , y and z refer to the degree of polymerization of GLY and EPE monomers, and the average substitution of

methacryloyloxy groups in HPGEm random copolymers, respectively. GPC (DMF as eluent, PEO standard): $M_{n, \text{GPC}} = 6200 \text{ g/mol}$, $D = 1.19$.

Synthesis of Poly[(9,9-bis(6-azidohexyl)fluorene)-*alt*-(5,5'-(2,2'-bipyridine))] (PFP-N₃)

In a typical procedure, 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(6'-bromohexyl)fluorene (744 mg, 1 mmol), 5,5'-dibromo-2,2'-bipyridine (314 mg, 1 mmol), toluene (4 mL) and K₂CO₃ aqueous solution (1 mL, 276 mg, 2 mmol) were successively added to a Schlenk tube. The reaction mixture was deoxygenated by sparging argon for 20 min. Afterwards, Pd(PPh₃)₄ (20 mg, 0.017 mmol) was added to the above mixture and the polymerization was allowed to proceed at 80 °C for 48 h under vigorous stirring. After that, the polymerization was stopped by immersing the Schlenk tube into an icy water bath, followed by precipitating in a 10-fold excess of methanol to eliminate any unreacted monomers. The purification protocol was repeated thrice. Finally, PFP-Br was dried under vacuum at 60 °C for 24 h and obtained as a yellowish solid. Yield: ~62%. ¹H NMR (CDCl₃, δ , ppm, TMS): 8.30-9.12 (H \times 6*m*, Py-*H*), 7.62-8.25 (H \times 6*m*, Ar-*H*), 3.24-3.38 (H \times 4*m*, -CH₂Br), 0.53-2.22 (H \times 20*m*, -(CH₂)₅CH₂Br), where *m* denotes the degree of polymerization of respective monomers in PFP-Br polymer. GPC (THF as eluent, PSt standard): $M_{n, \text{GPC}} = 14000 \text{ g/mol}$, $D = 1.64$.

PFP-N₃ was prepared by quantitative conversion of the bromohexyl groups in PFP-Br with excessive sodium azide in a postpolymerization substitution reaction. Briefly, PFP-Br (656 mg) and NaN₃ (163 mg, 2.5 mmol) were successively dissolved in DMF (30 mL). The reaction mixture was deoxygenated by sparging argon for 20 min. Then, the reaction flask was sealed with a rubber septum and placed in an oil bath at 70 °C for 48 h. After

that, the reaction was stopped by placing the flask in an icy water bath, followed by precipitating in a large amount of methanol. The crude product was dialyzed against ultrapure water (4×200 mL) with a dialysis membrane (MWCO 1000 Da) at room temperature for 48 h. Finally, PFP-N₃ was collected via lyophilization as a yellowish solid. Yield: ~96%. ¹H NMR (CDCl₃, δ , ppm, TMS): 8.28-9.12 (H \times 6*m*, Py-*H*), 7.58-8.25 (H \times 6*m*, Ar-*H*), 3.06-3.19 (H \times 4*m*, -CH₂N₃), 0.53-2.24 (H \times 20*m*, -(CH₂)₅CH₂N₃), where *m* denotes the degree of polymerization of respective monomers in PFP-N₃ polymer.

Synthesis of Poly[(9,9-bihexylfluorene)-*alt*-(5,5'-(2,2'-bipyridine))]-graft-Poly(*N*-isopropylacrylamide) (PFPPN)

The alkyne-terminated poly(*N*-isopropylacrylamide) (PNIPAM) chains were prepared via photoinduced electron/energy transfer reversible addition-fragmentation chain transfer (PET-RAFT) polymerization of NIPAM using PDMAT as the chain transfer agent (CTA) and Ru(bpy)₃Cl₂ as the photocatalyst.^{2,5-8} In a typical polymerization, NIPAM (M₁, 6.0 g, 53.1 mmol), Ru(bpy)₃Cl₂ (1.99 mg, 50 ppm relative to NIPAM), PDMAT (I₀, 71.6 mg, 1.77 mmol) and DMSO (6 mL) were introduced into a reaction flask. The reaction flask was deoxygenated by sparging argon for 20 min and sealed with a rubber septum. The reaction mixture was then irradiated under blue LED light (4.8 W, $\lambda_{\max} = 465$ nm, 1.0 mW/cm²) at 25 °C. After a certain period (6 h), the polymerization was terminated by ceasing the LED light irradiation and the resultant mixture was quenched by dilution with THF and precipitated into diethyl ether to eliminate any leftover monomers. The dissolution-reprecipitation cycle was repeated twice. The PNIPAM polymer was treated with 1,4-dioxane containing AIBN (20-fold relative to PNIPAM) at 80 °C under argon atmosphere for 6 h. The PNIPAM polymer was collected as a white solid. Yield: ~90%.

$[M_1]/[I_0] = 30:1$; $M_{n,NMR} = 3400$ g/mol. 1H NMR ($CDCl_3$, δ , ppm, TMS): 6.0-6.8 (1H $\times n$, -CONH-), 4.67-4.72 (2H, -COOCH₂-), 3.95-4.05 (1H $\times n$, -CH(CH₃)₂), 2.48-2.51 (1H, -C \equiv CH), 1.26-2.38 (H $\times(3n+6)$, -CH₂CH-, -C(CH₃)₂), 0.92-1.26 (6H $\times n$, -CH(CH₃)₂), where n denotes the degree of polymerization of respective monomers in PNIPAM polymer. GPC (DMF as eluent, PSt standard): $M_{n,GPC} = 3800$ g/mol, $D = 1.08$.

Briefly, PFP-N₃ (568 mg), PNIPAM (1.02 g, 0.3 mmol), sodium ascorbate (118.8 mg, 0.6 mmol), Me₆TREN (80.2 μ L, 0.3 mmol) and Cu(OAc)₂ (54.6 mg, 0.3 mmol) were successively dissolved in THF (30 mL). The reaction mixture was deoxygenated by sparging argon for 20 min. Then, the reaction flask was sealed with a rubber septum and placed in an oil bath at 50 °C for 24 h. After that, the reaction was stopped by placing the flask in an icy water bath, followed by precipitation in a large amount of methanol. The dissolution-reprecipitation cycle was repeated thrice. After being dried in a vacuum oven overnight at room temperature, PFPPN was obtained as a yellowish solid. Yield: ~71%. 1H NMR ($CDCl_3$, δ , ppm, TMS): 8.28-9.12 (H $\times 6m$, Py-H), 7.58-8.25 (H $\times 6m$, Ar-H), 6.0-6.8 (1H $\times np$, -CONH-), 5.56-5.64 (2H $\times p$, -COOCH₂-), 4.42-4.48 (2H $\times p$, -CH₂-triazole), 3.95-4.05 (1H $\times np$, -CH(CH₃)₂), 3.06-3.19 (H $\times(4m-2p)$, -CH₂N₃), 1.93 (6H $\times p$, -C(CH₃)₂), 1.26-2.38 (3H $\times np$, -CH₂CH-), 0.92-1.26 (6H $\times np$, -CH(CH₃)₂), 0.53-2.24 (H $\times 20m$, -(CH₂)₅CH₂-), where m , n and p denote the degree of polymerization of respective monomers and average number of PNIPAM graft chains in PFPPN polymer. GPC (DMF as eluent, PSt standard): $M_{n,GPC} = 29400$ g/mol, $D = 1.58$.

To a degassed round-bottom flask equipped with a reflux condenser and a magnetic stirrer under an argon atmosphere were added PFPPN (116 mg), *cis*-Ru(bpy)₂Cl₂ (150 mg), ethanol (15 mL) and THF (15 mL). The reaction mixture was degassed once again and refluxed for 24 h. After that, the reaction was stopped by placing the flask in an icy water bath, followed by precipitating in a large amount of methanol. The dissolution-reprecipitation cycle was repeated thrice. After being dried in a vacuum oven overnight at room temperature, PFPPNRu was obtained as a red powder. Yield: ~95%. GPC (DMF as eluent, PSt standard): $M_{n, GPC} = 33000$ g/mol, $D = 1.65$.

Synthesis of SiO₂@HPGE Nanoparticles

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. Afterwards, MPMS (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-MPMS NPs were centrifuged and stored in ethanol prior to use.

About 200 mg of SiO₂-MPMS NPs were dispersed into DMF (80 mL) by ultrasonication for 30 min. HPGEm (690 mg) and AIBN (20 mg) were successively added to the reaction flask to initiate the polymerization. The polymerization was conducted at 80 °C for 2 h and stopped by quenching the reaction flask in an icy water bath. The resultant SiO₂@HPGE core-shell NPs were purified by extraction with ultrapure water and ethanol

five times to remove any unreacted monomers and oligomers. The SiO₂@HPGE core-shell NPs were centrifuged and stored in ethanol prior to use.

Synthesis of *h*HPGE-PFPPNRu Nanocomposites via Alkyne-Azide Click Reaction, HF Etching and Metalation Coupling

In a typical procedure, 100 mg of SiO₂@HPGE core-shell NPs were dispersed in DMF (20 mL) by ultrasonication for 20 min. PFPPN (120 mg), sodium ascorbate (39.6 mg, 0.2 mmol), Me₆TREN (26.7 μL, 0.1 mmol) and Cu(OAc)₂ (18.2 mg, 0.1 mmol) were successively added to the mixture under vigorous stirring. The reaction mixture was degassed by purging with argon for 30 min. The reaction was started by immersing the flask in an oil bath at 50 °C for 24 h. The crude products were purified by repeated extraction with THF and water/ethanol mixed solutions five times to eliminate any leftover catalysts and reagents. Furthermore, the SiO₂@HPGE-PFPPN core-shell NPs were dialyzed against ultrapure water (4 × 200 mL) with a dialysis membrane (MWCO 1000 Da) at room temperature for 48 h. Finally, the SiO₂@HPGE-PFPPN NPs were collected by centrifugation and redispersed in 5 mL of ultrapure water prior to use.

About 100 mg of SiO₂@HPGE-PFPPN NPs were added to HF aqueous solution (10 mL, 10 wt%). The etching process was performed at ambient temperature overnight. Afterwards, the crude products were purified by four thorough centrifugation-redispersion cycles in water/ethanol mixed solutions to eliminate the excessive HF and SiF₄. Furthermore, the *h*HPGE-PFPPN nanocomposites were dialyzed against ultrapure water (4 × 200 mL) with a dialysis membrane (MWCO 1000 Da) at room temperature for

24 h. Finally, the *h*HPGE-PFPPN nanocomposites were recovered by centrifugation and redispersed in 10 mL of ultrapure water prior to use.

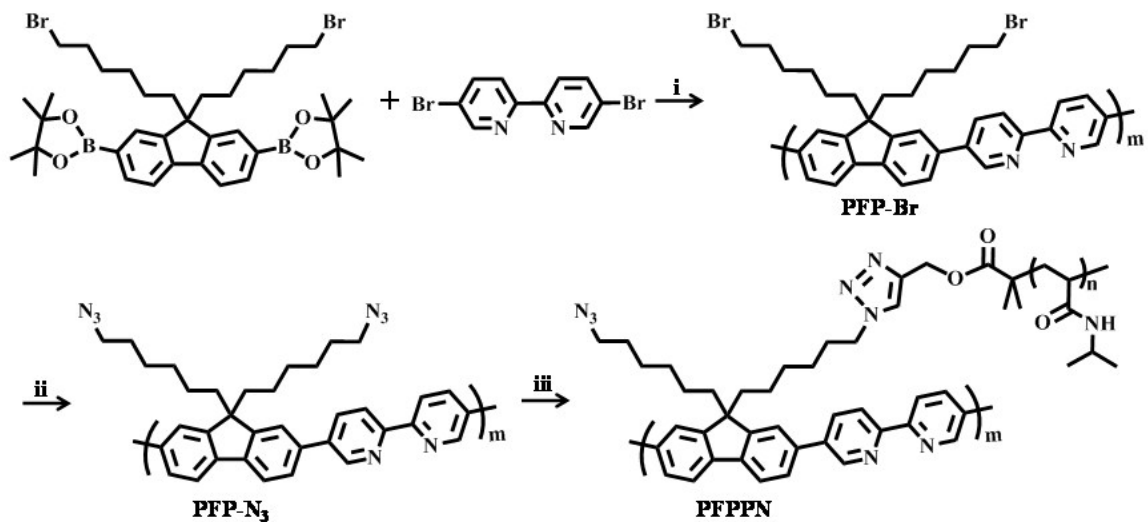
To a degassed round-bottom flask equipped with a reflux condenser and a magnetic stirrer under an argon atmosphere were added *h*HPGE-PFPPN nanocomposites (100 mg), Ru(bpy)₂Cl₂ (150 mg), ethanol (15 mL) and THF (15 mL). The reaction mixture was degassed once again and refluxed for 24 h. Afterwards, the crude products were purified by four thorough centrifugation-redispersion cycles in water/ethanol mixed solutions to remove the impurities. Furthermore, the *h*HPGE-PFPPNRu nanocomposites were dialyzed against ultrapure water (4 × 200 mL) with a dialysis membrane (MWCO 1000 Da) at room temperature for 24 h. Finally, the *h*HPGE-PFPPNRu nanocomposites were recovered by centrifugation and redispersed in 10 mL of ultrapure water prior to use.

General Procedure for the Kinetic Studies of PET-RAFT Polymerization Mediated by *h*HPGE-PFPPNRu Nanocomposites

A typical PET-RAFT polymerization of DMA in aqueous solution was conducted using a molar feed ratio [DMA]:[DDMAT] of 200:1 and predetermined amounts of *h*HPGE-PFPPNRu nanocomposites in ultrapure water (50 vol%). After the reaction mixture was placed in a glass vial with a magnetic stirrer and deoxygenated by sparging argon for 20 min, the vial was sealed with a rubber septum and irradiated to blue LED light (4.8 W, $\lambda_{\text{max}} = 465 \text{ nm}$, 1.0 mW/cm^2) at 25 °C. After a certain period, the polymerization was terminated by ceasing the LED light irradiation, purified by dialysis against ultrapure water and collected by lyophilization. To investigate the polymerization kinetics, aliquots of reaction mixtures were withdrawn periodically by argon-purged syringe and analyzed

by ^1H NMR and GPC measurements. To evaluate the recyclability of the catalysts, the *h*HPGE-PFPPNRu nanocomposites were isolated from the reaction mixture by centrifugation at the end of each run, regenerated by refluxed in ethanol/THF solution containing $\text{Ru}(\text{bpy})_2\text{Cl}_2$ for 24 h, and then dispersed in ultrapure water by ultrasonic agitation and put into another fresh reaction solution.

Following the similar protocol, PET-RAFT polymerization of MA in DMSO was conducted using a molar feed ratio $[\text{MA}]:[\text{DDMAT}]$ of 200:1 and predetermined amounts of *h*HPGE-PFPPNRu nanocomposites in DMSO (50 vol%). After the reaction mixture was placed in a glass vial with a magnetic stirrer and deoxygenated by sparging argon for 20 min, the vial was sealed with a rubber septum and irradiated under blue LED light (4.8 W, $\lambda_{\text{max}} = 465 \text{ nm}$, 1.0 mW/cm^2). After a certain period, the polymerization was terminated by ceasing the LED light irradiation and the resultant mixture was quenched by dilution with DMSO, and precipitated into methanol to eliminate any leftover monomers. To investigate the polymerization kinetics, aliquots of reaction mixtures were withdrawn periodically by argon-purged syringe and analyzed by ^1H NMR and GPC measurements.



Scheme S1. Synthesis of PFPPN graft copolymers. Reagents and conditions: (i) K_2CO_3 , $\text{Pd}(\text{PPh}_3)_4$, toluene, 80 °C, 48 h; (ii) NaN_3 , DMF, 70 °C, 48 h; (iii) PNIPAM, sodium ascorbate, $\text{Cu}(\text{OAc})_2$, Me_6TREN , 50 °C, 24 h.

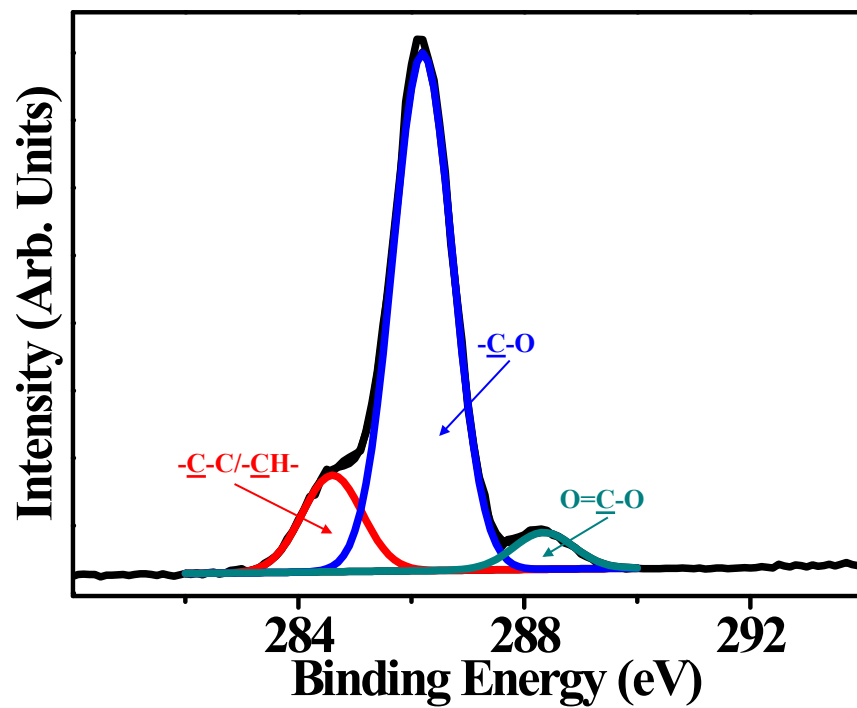


Figure S1. XPS C 1s core-level spectrum of SiO₂@HPGE nanoparticles.

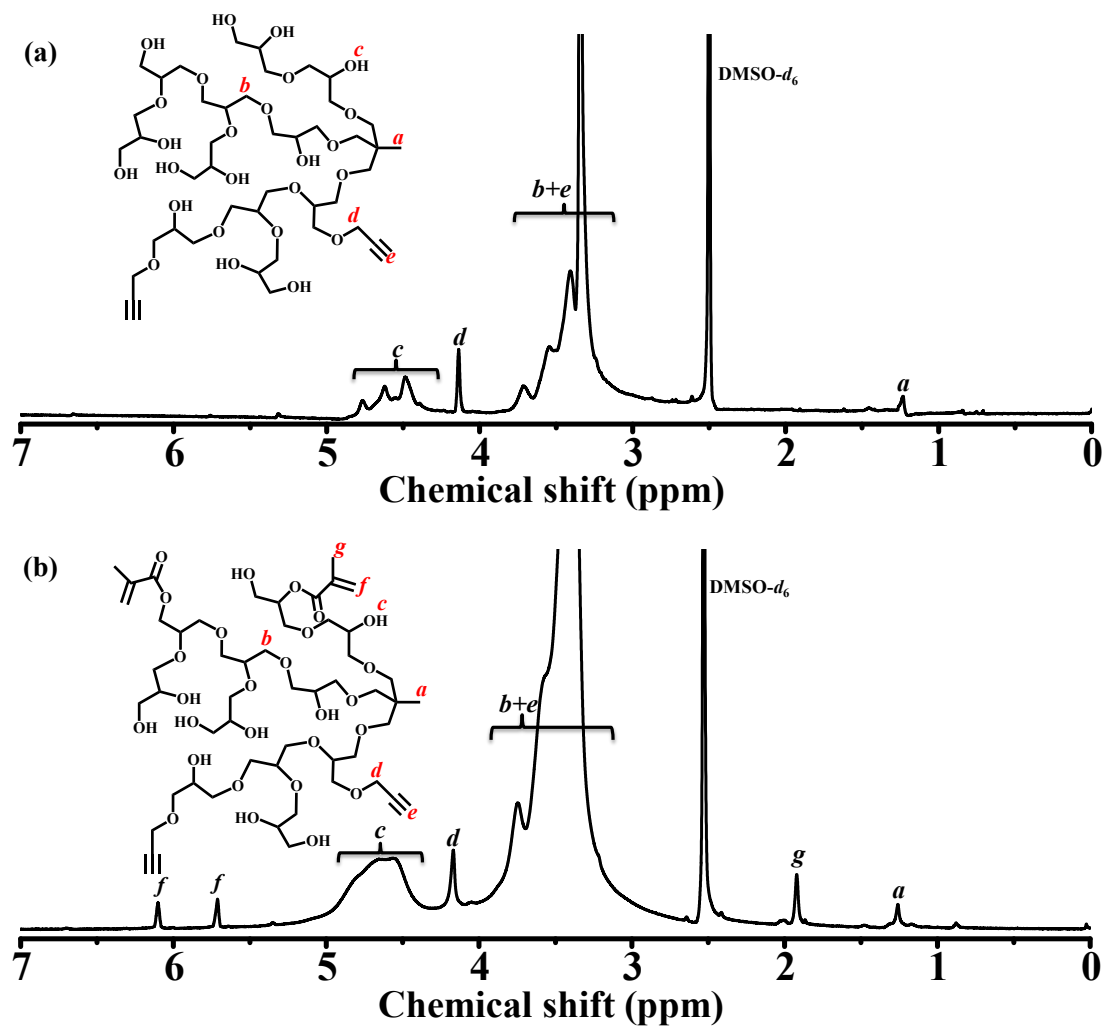
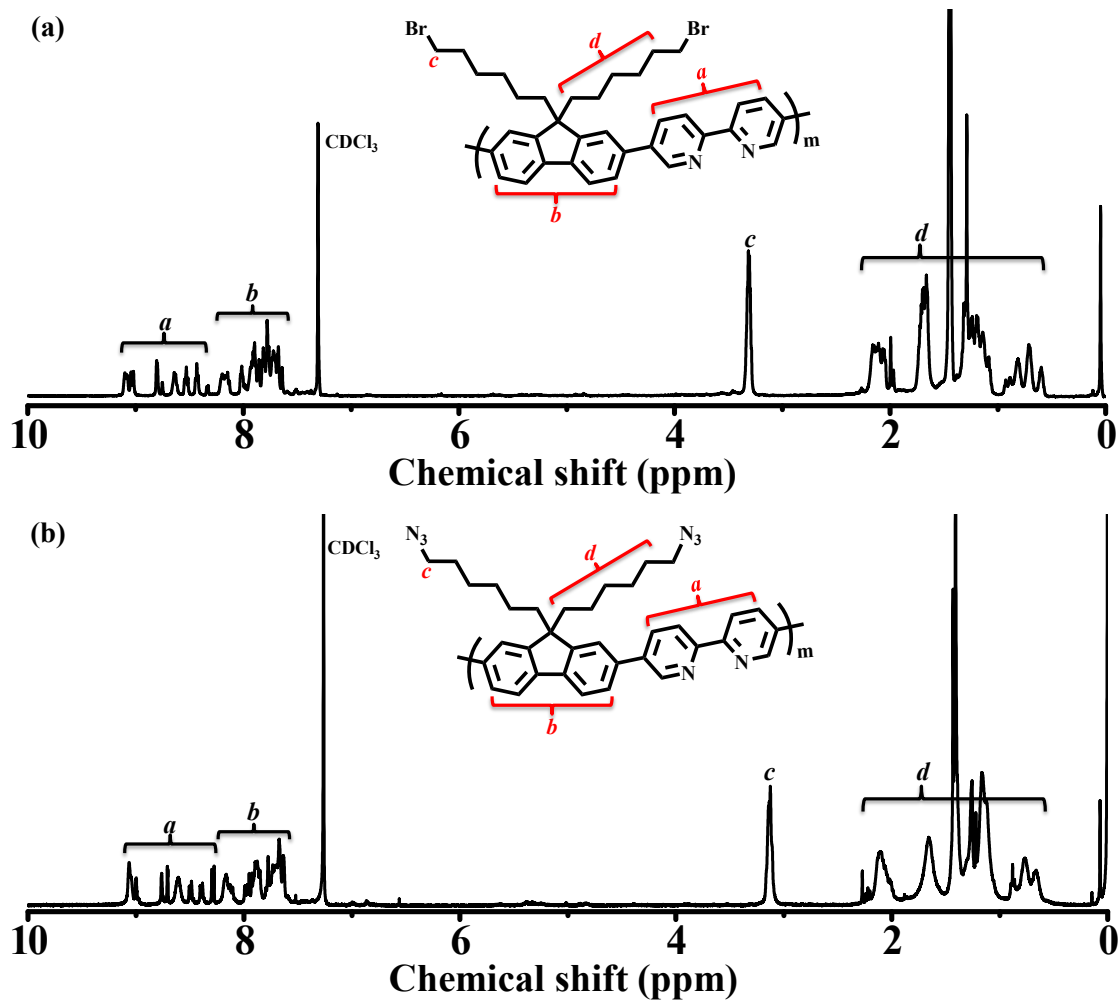


Figure S2. ^1H NMR spectra of (a) HPGE and (b) HPGEm polymers in $\text{DMSO-}d_6$.



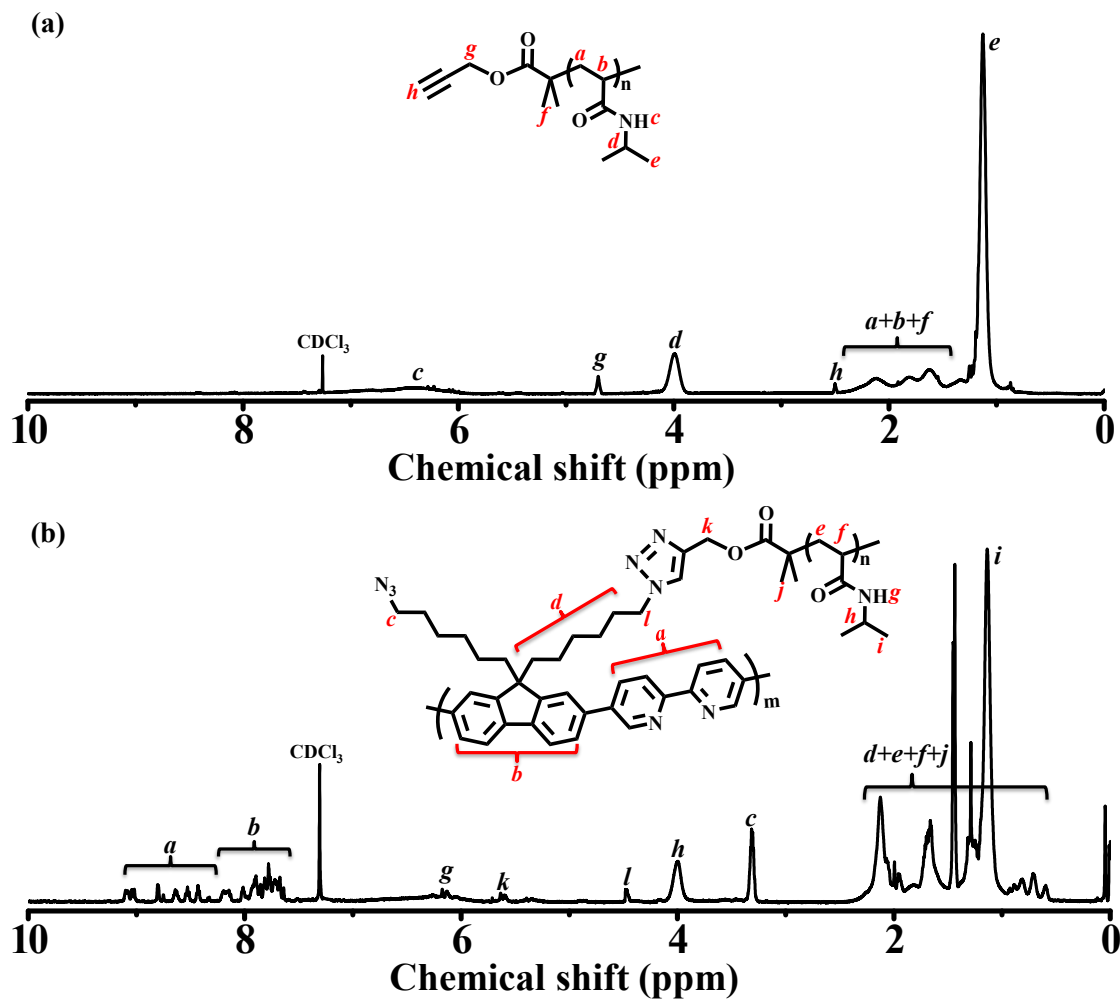


Figure S4. ^1H NMR spectra of (a) PNIPAM and (b) PFPPN polymers in CDCl_3 .

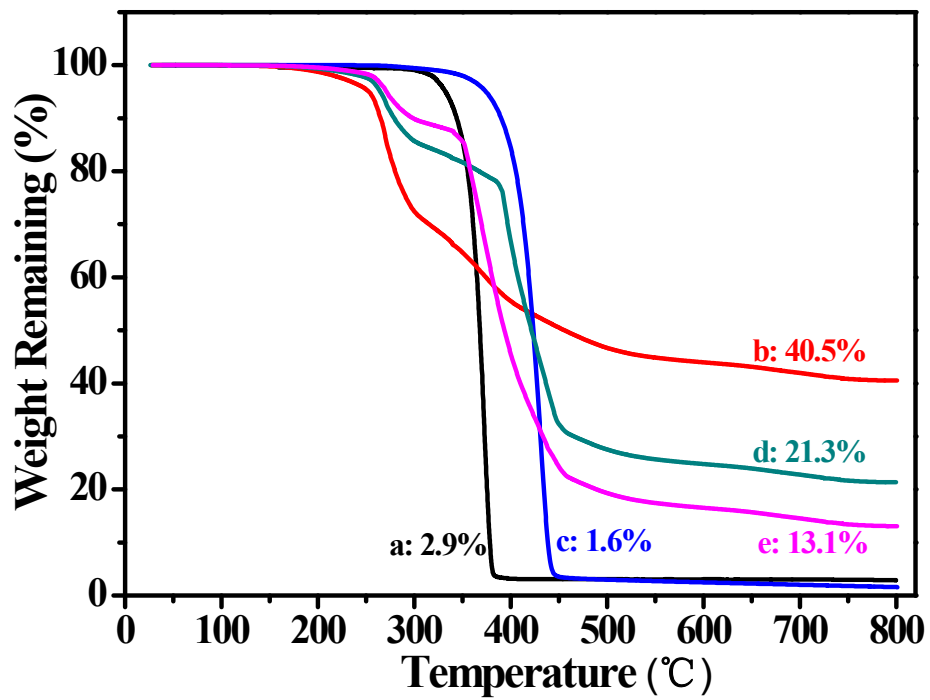


Figure S5. TGA curves of (a) HPGEm, (b) PFP-N₃, (c) PNIPAM, (d) PFPPN polymers and (e) hHPGE-PFPPN nanocomposites.

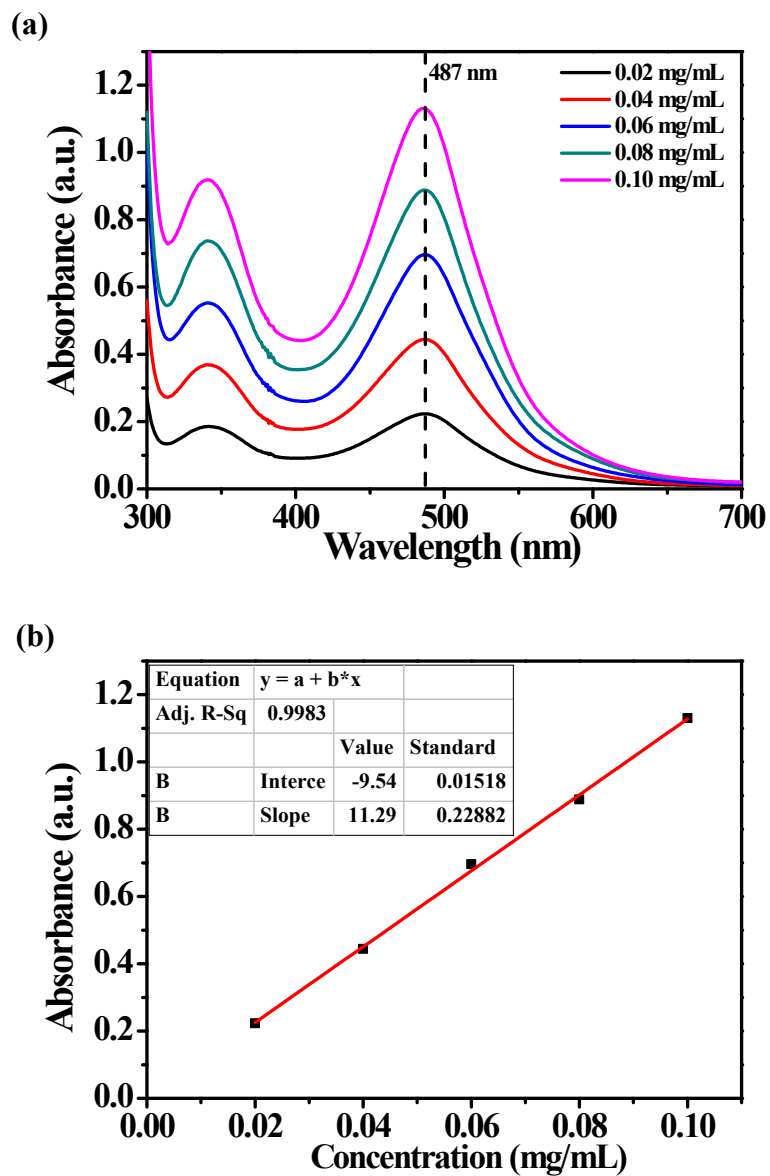


Figure S6. (a) UV-vis absorption spectra of different concentration of PFPPNRu dispersed in water; (b) plot of absorbance at the maximum wavelength ($\lambda_{\text{max}} = 487 \text{ nm}$) as a function of PFPPNRu concentration.

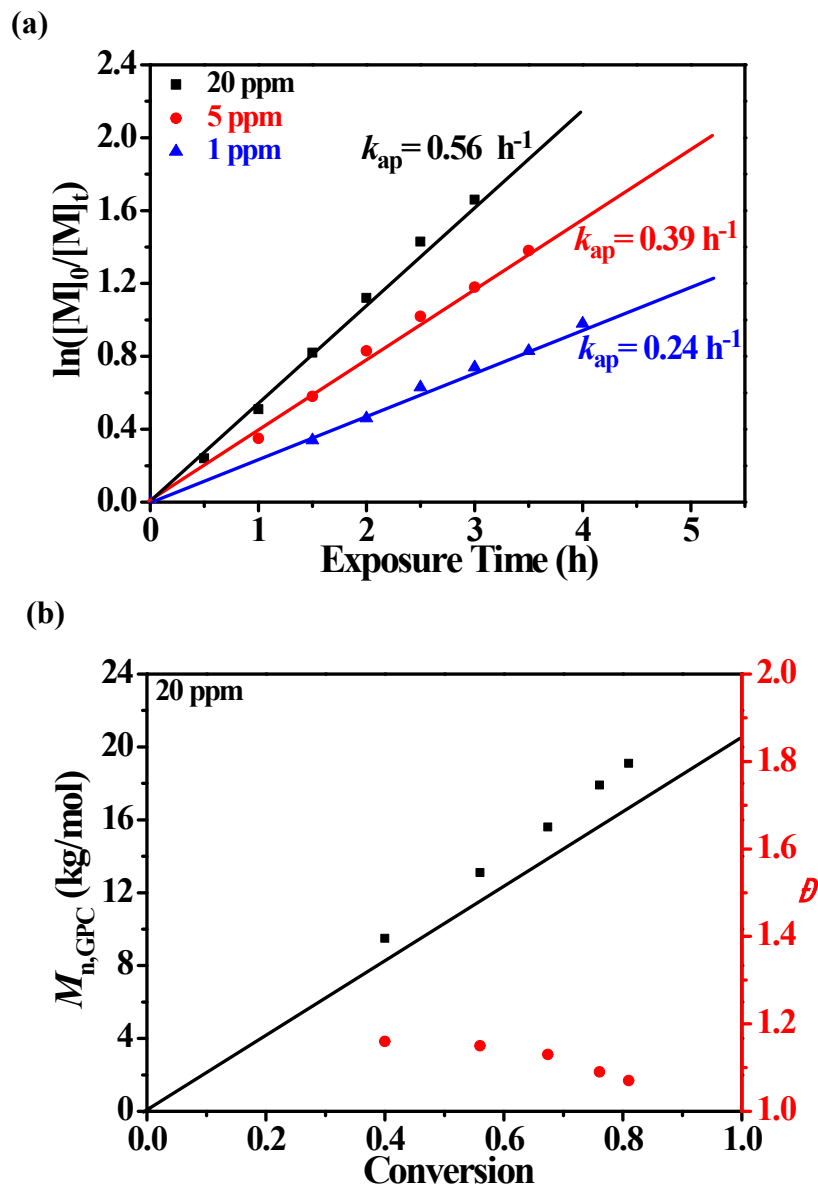


Figure S7. Kinetic analysis of PET-RAFT polymerization of DMA with different concentration of $\text{Ru}(\text{bpy})_3\text{Cl}_2$ in ultrapure water with prior deoxygenation at 25 °C under blue LED light irradiation (4.8 W, $\lambda_{\text{max}} = 465 \text{ nm}$, 1.0 mW/cm^2) with DDMAT as the CTA ($[\text{DMA}]/[\text{DDMAT}] = 200:1$). (a) Plot of $\ln([\text{M}]_0/[\text{M}]_t)$ versus exposure time t at different catalyst concentrations in reference to monomer concentration and (b) $M_{n,\text{NMR}}$, $M_{n,\text{GPC}}$ and D versus monomer conversion.

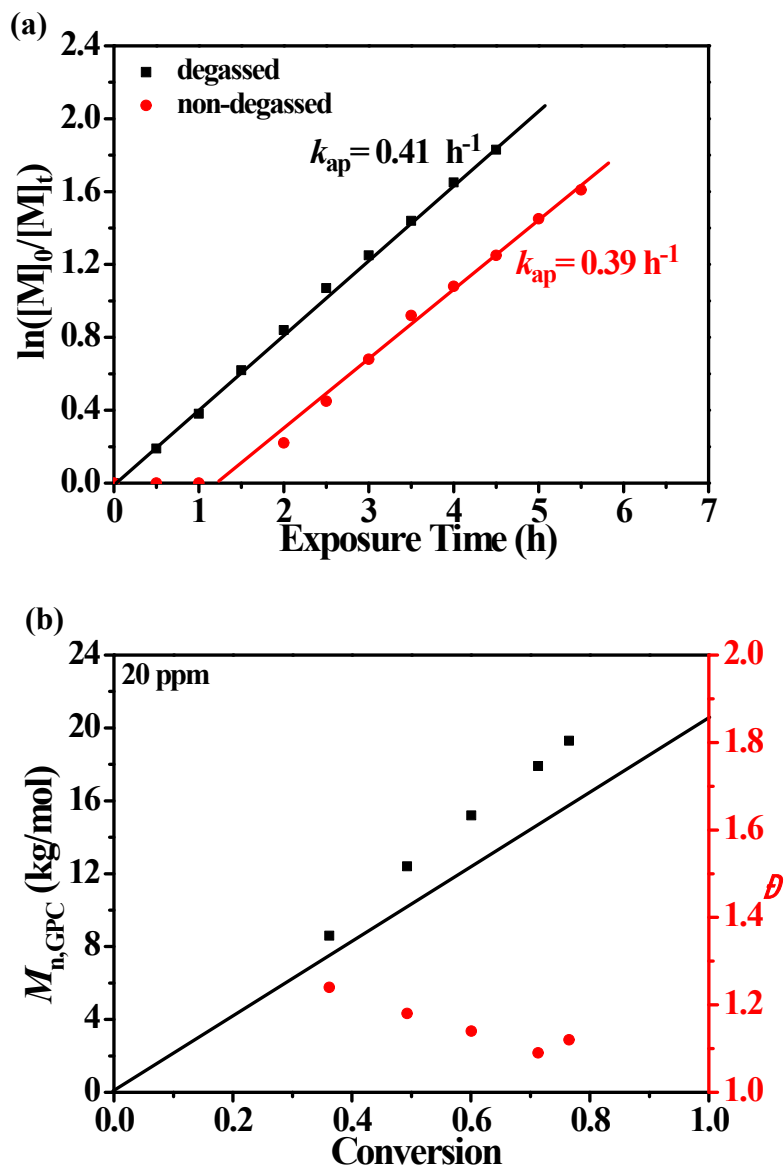


Figure S8. Kinetic analysis of PET-RAFT polymerization of DMA with 20 ppm *h*HPGE-PFPPNRu nanocomposites with and without prior deoxygenation at 25 °C under blue LED light irradiation (4.8 W, $\lambda_{max} = 465 \text{ nm}$, 1.0 mW/cm^2) with DDMAT as the CTA ($[DMA]/[DDMAT] = 200:1$). (a) Plot of $\ln([M]_0/[M]_t)$ versus exposure time t in reference to monomer concentration; and (b) $M_{n, NMR}$, $M_{n, GPC}$ and D versus monomer conversion for the PET-RAFT polymerization of DMA.

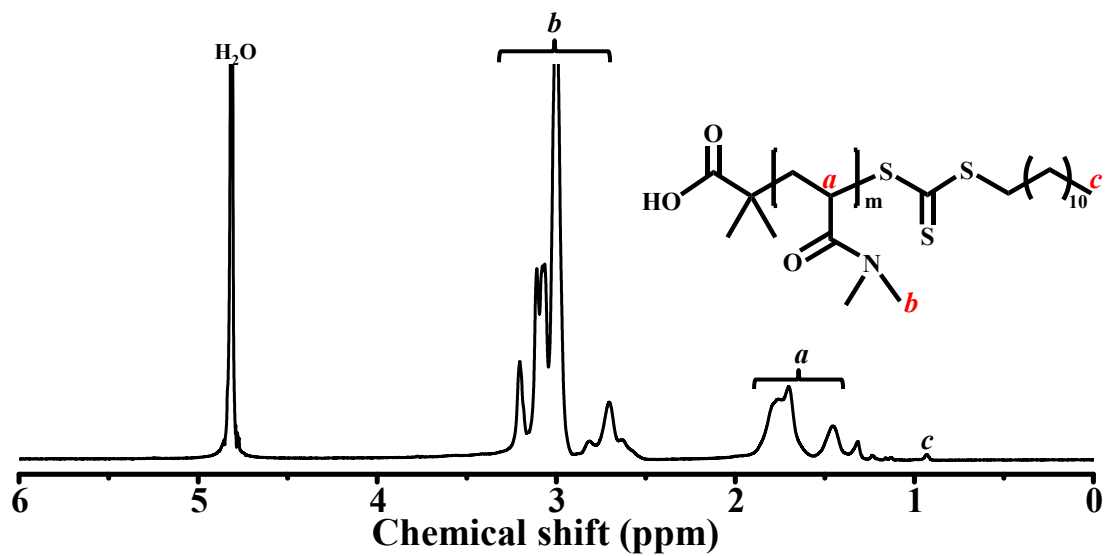


Figure S9. ^1H NMR spectrum of the PDMA-DDMAT macro-CTA in D_2O .

Table S1. PET-RAFT Polymerization of Different Monomers Using *h*HPGE-PFPPNRu Nanocomposites 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)	D^c
1 ^d	<i>h</i> HPGE-PFPPNRu	DMA	DDMAT	DMSO	5	2	91	18.4	21.8	1.06
2	<i>h</i> HPGE-PFPPNRu	DMA	DDMAT	CH ₃ CN	5	2	92	18.6	22.5	1.06
3	<i>h</i> HPGE-PFPPNRu	DMA	DDMAT	CH ₃ OH	5	2	88	17.8	21.4	1.08
4	<i>h</i> HPGE-PFPPNRu	DMA	DDMAT	toluene	20	2	6	-	-	-
5	<i>h</i> HPGE-PFPPNRu	DEA	DDMAT	water	20	4	90	23.2	26.1	1.07
6	<i>h</i> HPGE-PFPPNRu	NIPAM	DDMAT	water	20	2	91	20.9	22.4	1.05
7	<i>h</i> HPGE-PFPPNRu	PEGMA	DDMAT	water	20	24	58	58.4	68.9	1.23
8	<i>h</i> HPGE-PFPPNRu	MA	DDMAT	DMSO	20	2	86	15.1	15.6	1.08
9	<i>h</i> HPGE-PFPPNRu	GMA	DDMAT	DMSO	20	2	92	26.8	29.4	1.06
10	<i>h</i> HPGE-PFPPNRu	HEA	DDMAT	DMSO	20	8	51	12.2	15.8	1.25
11	<i>h</i> HPGE-PFPPNRu	St	DDMAT	DMSO	20	24	21	4.7	5.3	1.14
12	<i>h</i> HPGE-PFPPNRu	DMA	PEG-DDMAT	water	20	4	92	19.3	21.6	1.08
13	<i>h</i> HPGE-PFPPNRu	DMA	PEG-DDMAT	water	1	4	60	13.0	14.5	1.12
14	<i>h</i> HPGE-PFPPNRu	DMA	DDMAT	water	20	6	94	19.0	21.6	1.07
15 ^e	<i>h</i> HPGE-PFPPNRu	DEA	PDMA-DDMAT	water	20	6	88	41.3	48.5	1.14
16 ^e	<i>h</i> HPGE-PFPPNRu	NIPAM	PDMA-DDMAT	water	20	2	90	39.3	44.9	1.09
17 ^e	<i>h</i> HPGE-PFPPNRu	MA	PDMA-DDMAT	DMSO	20	4	88	34.1	38.4	1.14
18 ^e	<i>h</i> HPGE-PFPPNRu	GMA	PDMA-DDMAT	DMSO	20	4	94	45.7	53.2	1.11
19	Ru(bpy) ₃ Cl ₂	MA	DDMAT	DMSO	1	6	92	16.2	16.8	1.05
20	Ru(bpy) ₃ Cl ₂	MA	DDMAT	DMSO	1	1	31	5.7	6.1	1.09
21	SiO ₂ @HPGE-PFPPNRu	MA	DDMAT	DMSO	20	2	88	15.5	16.3	1.09
22	SiO ₂ @HPGE-PFPPNRu	DMA	DDMAT	water	20	6	92	18.6	20.8	1.08

^a The polymerizations were performed under blue LED light irradiation (4.8 W, $\lambda_{max} = 465$ nm, 1.0 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 (\mathcal{D}) = $M_{w,GPC}/M_{n,GPC}$.

^d Abbreviations: Ru(bpy)₃Cl₂, tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate; DMA, *N,N*-dimethylacrylamide; DEA, *N,N*-diethylacrylamide; MA, methyl acrylate; NIPAM, *N*-isopropylacrylamide; St, styrene; HEA, 2-hydroxyethyl acrylate; GMA, glycidyl methacrylate; 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 PDMA-DDMAT in Entry 14 as macro-CTA.

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