Supporting Information:

Facile Synthesis of Size-Tunable Superparamagnetic/Polymeric Core/Shell Nanoparticles by Metal-Free Atom Transfer Radical Polymerization at Ambient Temperature

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Experimental Section

1. Materials.

12-hydroxydodecanoic acid and 2-bromophenylacetyl bromide were purchased from Sigma-Aldrich. Methyl methacrylate (MMA) were purchased from Sigma-Aldrich and distilled over CaH_2 under reduced pressure prior to use. Anhydrous 1-methyl-2-pyrrolidinone (NMP, 99.5%) was purchased from Sigma-Aldrich. Phenothiazine, RuPhos, NaOtBu and RuPhos Precatalyst were purchased from Sigma-Aldrich and used as received. 1-octadecene, trioctylamine and *N, N*-dimethylacetamide (DMA) were purchased from Sigma-Aldrich and used as received. Iron(III) oxide was purchased from Sigma-Aldrich. All other reagents were purified by common purification procedures. LED strips (380 nm) were bought from elemental led (www.elementalled.com). Polymerization reactions by LED irradiation were placed next to the 380 nm lights under vigorous stirring while cooling with compressed air (the light intensity: 0.62 $\mu W/cm^2$).

2. Characterizations.

^1H-NMR and ^{13}C-NMR spectra were recorded with a Bruker DPX-400 (400 MHz), using deuterated trifluoroacetic acid and $CDCl_3$ as solvents, and tetramethyl-silane (TMS) as an internal reference. Morphology of superparamagnetic Fe_3O_4 nanocrystals capped with the metal-free ATRP initiating sites and core/shell superparamagnetic Fe_3O_4/PMMA hybrid nanoparticles were characterized by transmission electron microscope (JEOL 1200EX TEM; operated at 80 kV). The preparation of TEM samples: (1) TEM samples of superparamagnetic Fe_3O_4 nanocrystals capped with the metal-free ATRP initiating sites were prepared by applying a drop of nanocrystals toluene solution (~5 μL at c=1 mg/mL) onto a carbon coated copper TEM grid (300 mesh) and allowing toluene to evaporate at room temperature; (2) TEM samples of core/shell superparamagnetic Fe_3O_4/PMMA hybrid nanoparticles were prepared by applying a drop of nanocrystals toluene (~5 μL at c=1 mg/mL) onto a carbon coated copper TEM grid (300 mesh) and allowing solvent to evaporate at room temperature. In addition, for the TEM characterization of polymers as ligands coating on the surface of Fe_3O_4 nanocrystals, the polymeric ligands (PMMA) were stained with ruthenium tetraoxide (RuO_4) by exposing to the TEM grids to ruthenium tetraoxide (RuO_4) which the PMMA phase as shell was preferentially stained. The crystalline structures of samples were measured by X-ray diffraction (XRD; SCINTAG XDS-2000, Cu Kα radiation). The energy dispersive spectroscopy (EDS) microanalysis of samples was conducted by field emission scanning electron microscopy (FE-SEM; FEI Quanta 250). A superconducting quantum interference device (SQUID) magnetometer (Quantum Design MPMS-5S) was used to determine the magnetic properties of Fe_3O_4 nanocrystals at room temperature. Molecular weight and polydispersity index (PDI) of PMMA grafting chains were measured by GPC, equipped with an Agilent1100 with a G1310A pump, a G1362A refractive detector, and a G1314A variable wavelength detector. THF used as eluent at 35^oC at 1.0 mL/min. One 5 μm LP gel column (500 Å, molecular range: $500\text{-}2 \times 10^4$ g/mol) and two 5 μm LP gel mixed bed columns (molecular range: $200\text{-}3 \times 10^6$ g/mol) were calibrated with PS standard samples. The FT-IR measurement was carried out on a NICOLET 460 spectrometer (KBr pellet) in the range of 4000-400 cm^{-1} with the resolution of $4cm^{-1}$. The concentration of polyamides in KBr pellet(200mg) were about 1%. The weight fraction of the polymer phase in core/shell Fe_3O_4/polymer nanoparticles was determined by thermogravimetric analysis (TGA; TA Instrument TGA Q 50).

3. Synthesis of 10-phenylphenothiazine (PTH) as photocatalyst

10-phenylphenothiazine (PTH) was synthesized by the following procedure.[1] To a flask armed with a magnetic stir bar was added NaOtBu (134 mg), phenothiazine (199 mg), RuPhos Precat (14 mg), and RuPhos (8 mg). The flask was evacuated and backfilled three times with argon before adding dry dioxane (1 mL). Then anhydrous chlorobenzene (143 μL) was added into reaction system. The flask was then placed in an oil bath at 110 °C with stirring for 5 h. After that, the flask was cooled to room temperature and diluted with CH_2Cl_2, washed with DI water, dried with $MgSO_4$, and purified using column chromatography (5 % EtOAc/Hexanes). The product was dried under reduced pressure to yield 0.2236 g of a white solid. ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 7.60 (t, J = 8 Hz, 2H), 7.49 (t, J = 8 Hz, 1H), 7.40 (d, J = 7 Hz, 2H), 7.02 (d, J = 8 Hz, 2H), 6.86-6.79 (m, 4 H), 6.20 (d, J = 8 Hz, 2 H) ppm.

4. Synthesis of bi-functional ligands as the metal-free ATRP initiators[2, 3]

In order to synthesize bi-functional ligands as the metal-free ATRP initiators, the hydroxyl group of 12-hydroxydodecanoic acid was modified by the reaction between the hydroxyl group and 2-bromophenylacetyl bromide (**Scheme S1**). The typical process as follows: Anhydrous 12-hydroxydodecanoic acid (6 mmol) was dissolved in 60 mL anhydrous 1-methyl-2-pyrrolidione (NMP) and cooled to 0°C. 2-Bromophenylacetyl bromide (40mL) was then added dropwise to the β-CD solution with magnetic stirring. The reaction temperature was maintained at 0°C for 2 h and then slowly increased to ambient temperature, after which the reaction was allowed to continue for 24 h. The brown solution obtained was concentrated by vacuum distillation. The resulting product was diluted with 100 mL dichloromethane, and then washed with DI water (3×200 mL). The organic layer obtained was concentrated by vacuum distillation, and then the final bi-functional ligands as the metal-free ATRP initiators was obtained (5.6g, yield =75.5%). ^{1}H-NMR：δ=6.33-7.31 ppm (the protons on phenyl ring), δ=5.55 ppm (Br-C***H***(phenyl)-), δ=4.09 ppm (-O-C***H***$_2$-CH$_2$-), and δ=1.29-2.23ppm (the protons on methene). ^{13}C-NMR：δ=127.2-134.6 ppm (the carbon atoms on phenyl ring), δ=52.3 ppm (Br-***C***H(phenyl)-), δ=173.2 ppm (Br-CH(phenyl)-***C***OO-), δ=64.8 ppm (-O-***C***H$_2$-CH$_2$-), δ=177.6 ppm (-CH$_2$-CH$_2$-***C***OOH) and δ=24.5-36.2 ppm (the carbon atoms on methene). The chemical compositions of bi-functional ligands were confirmed by FTIR: 1735 cm^{-1} ($\nu_{C=O}$), 2933 cm^{-1} ($\nu_{C\text{-}H}$), 1156 cm^{-1} ($\nu_{C\text{-}O\text{-}C}$), 1037 and 1108 cm^{-1} (coupled $\nu_{C\text{-}C}$ and $\nu_{C\text{-}O}$), 2500-3500 cm^{-1} ($\nu_{O\text{-}H}$).

5. Preparation of the iron-carboxylate complex with the metal-free ATRP initiating sites

The iron-carboxylate complex with the metal-free ATRP initiating sites was prepared by reacting iron(III) oxide and bi-functional ligands for the precursors of Fe_3O_4 nanocrystals (**Scheme S2**). In a typical synthesis of iron-carboxylate complex, 10.8 g of iron(III) oxide and 5.0 g of bi-functional ligands was dissolved in a mixture solvent composed of 80 ml ethanol, 60 ml distilled water and 140 ml hexane. The resulting solution was heated to 90 °C and kept at that temperature for 4h. After the reaction was completed, the upper organic layer containing the iron-carboxylate complex was washed three times with 30 ml distilled water. After washing, hexane was evaporated off, resulting in iron-carboxylate complex in a waxy solid form.

6. Fabrication of Fe_3O_4 nanocrystals capped with metal-free ATRP initiating sites with different sizes

The following is a typical synthetic procedure for Fe_3O_4 nanocrystals (~12nm) (**Scheme 1**). 1.8 g of the iron-carboxylate complex synthesized as described above and 0.285 g of bi-functional ligands as described above were dissolved in 10 g of 1-octadecene at room temperature. The reaction mixture was slowly heated to 320 ° under argon, and then kept at that temperature for 30 min. When the reaction temperature of solution system reached to 320 °C, a severe reaction occurred and the initial transparent solution became turbid and brownish black. The resulting solution containing the Fe_3O_4 nanocrystals was then cooled to room temperature, and 30 ml of ethanol was added to the solution to precipitate the Fe_3O_4 nanocrystals. The Fe_3O_4 nanocrystals were separated by centrifugation. When keeping other parameters fixed, the reaction solvent was changed from 1-octadecene to trioctylamine (b.p. 365 ^{o}C), the particle size of the Fe_3O_4 nanocrystals can be tuned from ~12 nm to ~22 nm.

7. Fabrication of core/shell Fe_3O_4/PMMA hybrid nanoparticles by metal-free ATRP

Then MMA monomers were initiated to grow PMMA polymeric chains from the initiating sites on the surface of superparamagnetic Fe_3O_4 nanoparticles by the metal-free ATRP technique for the fabrication of core/shell superparamagnetic Fe_3O_4/PMMA hybrid nanoparticles, composed superparamagnetic Fe_3O_4

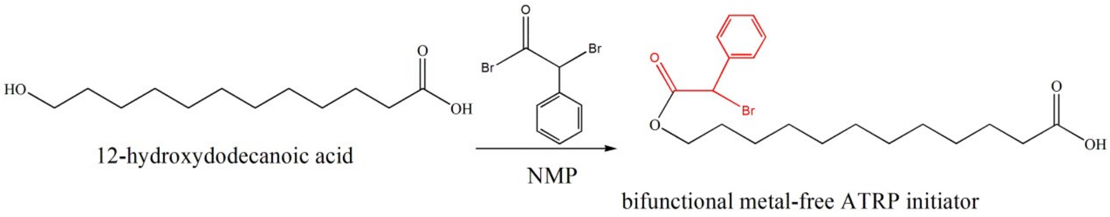
nanoparticles as core and PMMA chains as shell with different sizes, 10-phenylphenothiazine as the catalyst under 380 nm LED irradiation at room temperature. In a typical procedure, an ampule charged with MMA (8mL), PTH as photocatalyst (0.1 mol%), Fe_3O_4 nanoparticle-based initiators (50mg), and 8 mL *N, N*-dimethylacetamide (DMA) was degassed by three freeze-thaw cycles in liquid N_2, then sealed at room temperature. The reaction was vigorously stirred in front of 380 nm LED while cooling with compressed air to maintain ambient temperature. The ampule was taken out from the LED irradiation at different desired times to terminate the polymerization. The solution was then diluted with acetone, and then precipitated in the mixed solvents of methanol/water (v/v = 1/1). After centrifugation, the final product was purified by dissolution/precipitation twice with acetone and methanol/water and dried at 40 ^{o}C in vacuum for 12h.

8. Control experiments by metal-free ATRP

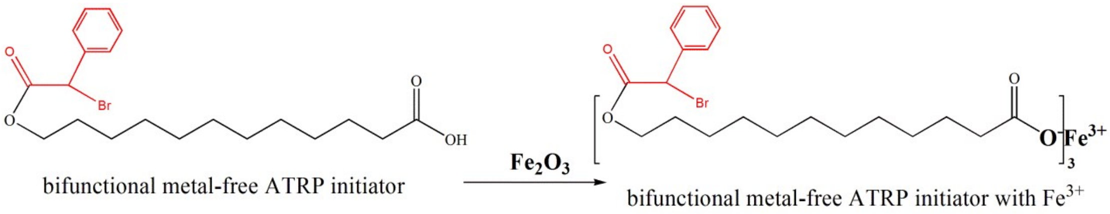
In order to compare with initiating sites on the surface on the surface of Fe_3O_4 nanoparticles, free bi-functional ligands with initiating sites were added in polymerization reaction system to initiate MMA monomers and grow free PMMA polymeric chains by the metal-free ATRP technique, 10-phenylphenothiazine as the catalyst under 380 nm LED irradiation at room temperature. In a typical procedure, an ampule charged with MMA (8mL), PTH as photocatalyst (0.1 mol%), Fe_3O_4 nanoparticle-based initiators (50mg), free bi-functional ligands (10mg), and 8 mL *N, N*-dimethylacetamide (DMA) was degassed by three freeze-thaw cycles in liquid N_2, then sealed at room temperature. The reaction was vigorously stirred in front of 380 nm LED while cooling with compressed air to maintain ambient temperature. The ampule was taken out from the LED irradiation at different desired times to terminate the polymerization. After centrifugation, the Fe_3O_4-based nanoparticles were removed, and then the solution was then diluted with acetone, and then precipitated in the mixed solvents of methanol/water (v/v = 1/1). After filtration, the free PMMA polymers were purified by dissolution/precipitation twice with acetone and methanol/water and dried at 50 ^{o}C in vacuum for 2h.

Detachment of PMMA polymeric chains from the surface of Fe_3O_4 nanoparticles for measuring the molecular weight of PMMA grafting chains

PMMA chains as grafting chains on the surface of Fe_3O_4 nanoparticles were detached from the surface of Fe_3O_4 nanoparticles by dissolving Fe_3O_4 in the acid condition: 0.2g core/shell Fe_3O_4/PMMA hybrid nanoparticles (sample in **Fig. 2**) was dissolved in 50 mL CH_2Cl_2; 10 mL trifluoroacetic acid was then added. The reaction mixture was stirred at room temperature for 24 h. After the reaction, the resulting iron(III) trifluoroacetate was gradually precipitated in CH_2Cl_2. After filtration, the resulting solution was concentrated to dryness, the polymer was dissolved in acetone and precipitated in the mixed solvents of methanol/water (v/v = 1/1). The PMMA polymers were purified by dissolution/precipitation twice with acetone and methanol/water and dried at 50 ^{o}C in vacuum for 2h.



Scheme S1. Synthesis of bi-functional ligands as the metal-free ATRP initiators.



Scheme S2. Synthesis of precursors of Fe_3O_4 nanoparticles by the reaction bi-functional ligands as the metal-free ATRP initiators with iron(III) oxide.

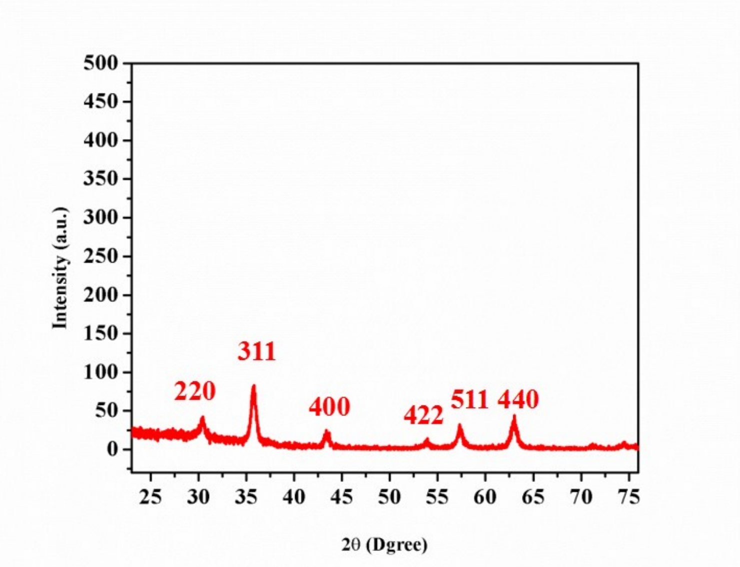
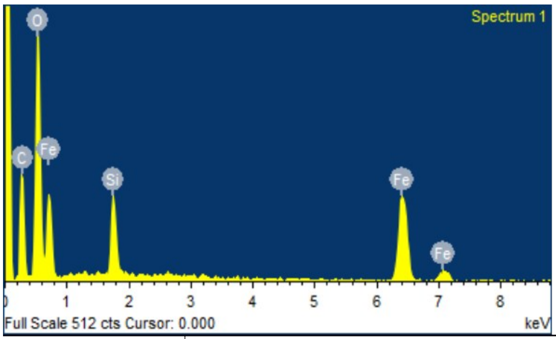


Fig. S1. XRD pattern of Fe_3O_4 nanoparticles capped with metal-free ATRP initiating sites as ligands (~12nm) (JCPDS 76-1849). [4, 5, 6]



Element	Weight%	Atomic%
C K	30.93	46.37
O K	33.71	41.24
Fe K	35.36	12.39
Totals	100.00	

Fig. S2. EDS spectrum of Fe_3O_4 nanoparticles capped with metal-free ATRP initiating sites as ligands (~12nm).

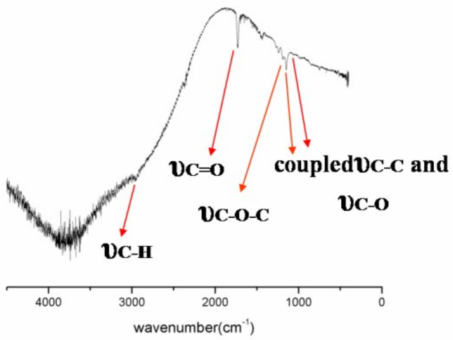


Fig. S3. FT-IR spectrum of Fe_3O_4 nanocrystals capped with metal-free ATRP initiators (sample in **Fig.1**).

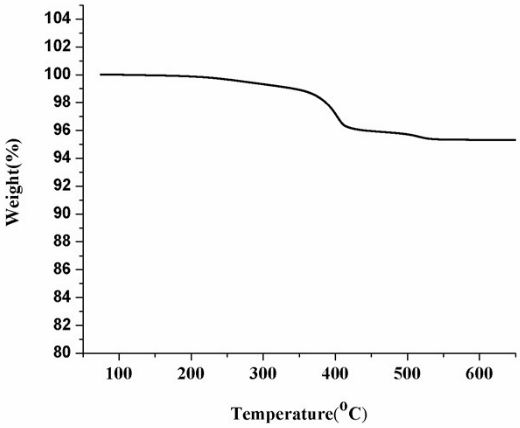


Fig. S4. TGA curve of Fe_3O_4 nanocrystals capped with metal-free ATRP initiators (sample in **Fig.1**).

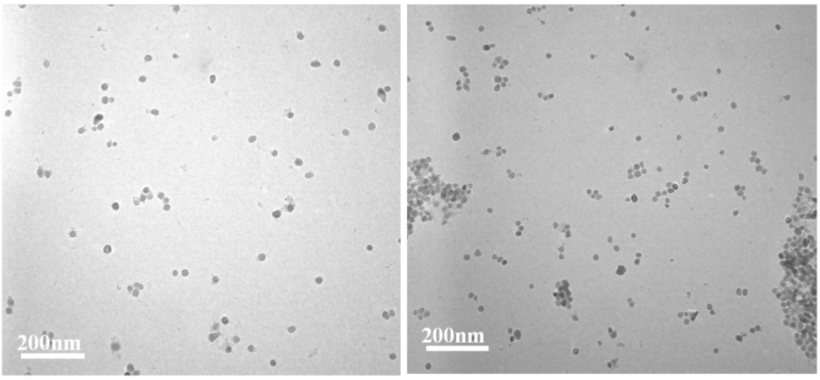


Fig. S5. TEM of Fe_3O_4 nanoparticles capped with metal-free ATRP initiating sites as ligands at different area (~22nm).

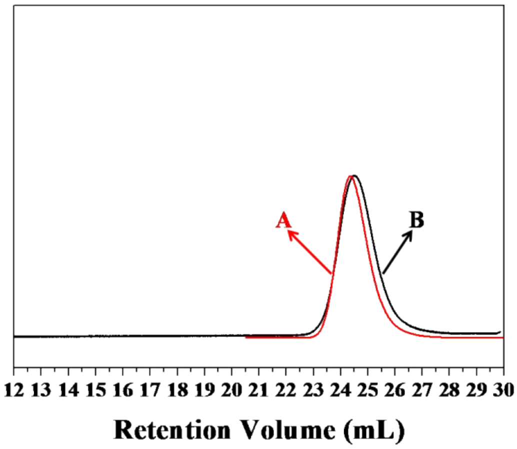


Fig. S6. GPC traces of PMMA polymeric chains obtained from free initiators (A) and detachment (B) from the surface of Fe_3O_4 nanoparticles (sample in Fig.2).

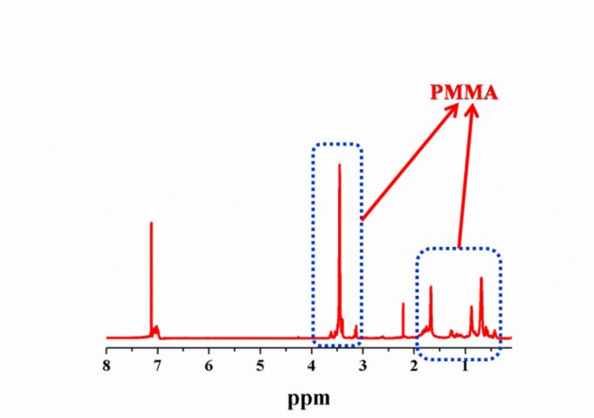


Fig. S7. ^{1}H-NMR spectrum of PMMA polymeric chains obtained from free initiators (sample in Fig.S4(A), $CDCl_3$ as solvents).

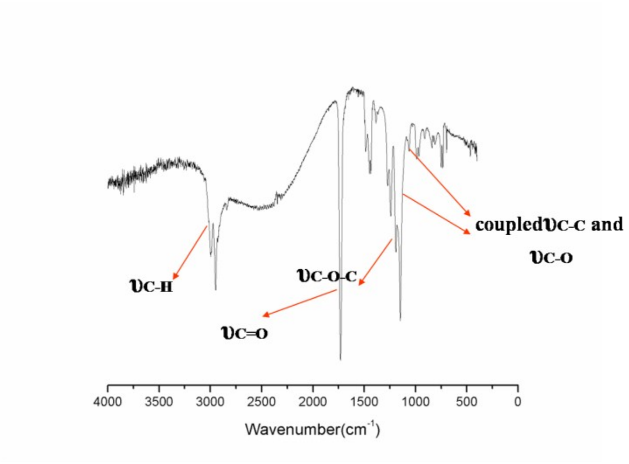


Fig. S8. FT-IR spectrum of core/shell Fe_3O_4/PMMA hybrid nanoparticles (sample in Fig.2).

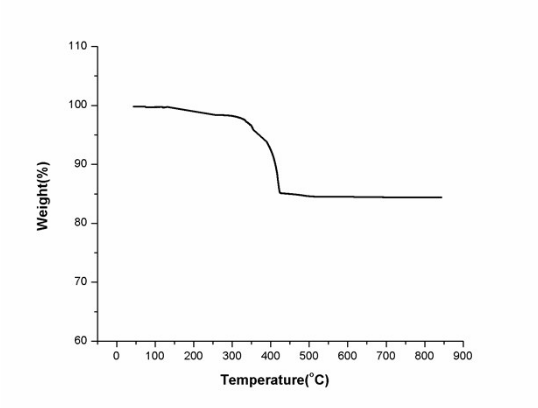


Fig. S9. TGA curve of core/shell Fe_3O_4/PMMA hybrid nanoparticles in N_2 (sample in Fig.2).

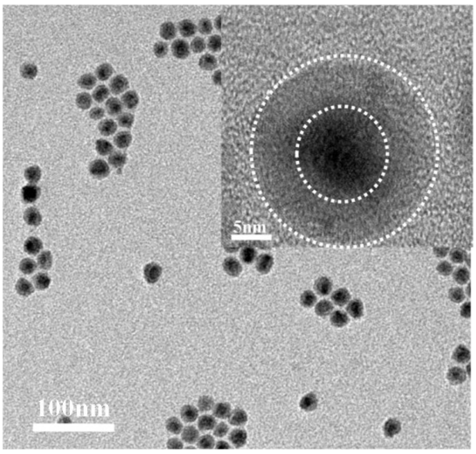


Fig. S10. Representative TEM characterization results of core/shell Fe_3O_4/PMMA hybrid nanoparticles when LED irradiation time is 10 h (thickness of polymeric shell: ~6nm).

Table S1. Summary of core/shell Fe_3O_4/PMMA hybrid nanoparticles

entry[a]	time (h)[b]	thickness (nm)[c]
Sample-1	2	2
Sample-2	5	4
Sample-3	10	6
Sample-4	20	9
Sample-5	40	14

[a] Five samples were prepared by Fe_3O_4 nanocrystals capped with metal-free ATRP initiators as initiators (sample in **Fig.1**). [b]380 nm LED irradiation time at room temperature. [c]Thickness of PMMA shell determined by TEM.

References and notes:

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