

Electronic Supplementary Information

Magnetic Janus Nanocomposites with Iridium(III) Complexes for Heterogenous Catalysis of Logic Controlled RAFT Polymerization with Multiplexed External Switching

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Experiment Section

Materials

The following chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise indicated: iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 95%), 1-octadecene (90%), oleic acid (90%), [3-(2-aminoethylamino)propyl]trimethoxysilane (APMS, 97%), [3-(methacryloyloxy)propyl]trimethoxysilane (MPMS, 98%), tetraethyl orthosilicate (TEOS, 98%), polyoxyethylene (5) nonylphenylether (Igepal CO-520), ammonium hydroxide solution (28.0~30.0 wt% NH_3 basis), 2-phenylpyridine (ppy, 98%), iridium(III) chloride (IrCl_3 , 99.8%), 4-(2-pyridyl)benzaldehyde (pba, 97%), 2-ethoxyethanol (99%), silver trifluoromethanesulfonate (AgOTf , $\geq 99\%$), sodium borohydride (NaBH_4 , $\geq 98\%$), triethylamine (TEA, $\geq 99\%$), methacryloyl chloride (97%), tris[2-phenylpyridinato- C^2,N]iridium(III) (*fac*- $[\text{Ir}(\text{ppy})_3]$, 99%), 4,4',4'',4'''-(porphine-5,10,15,20-tetrayl)tetrakis(benzenesulfonic acid) (TPPS, $\geq 95\%$), tris(2,2'-bipyridyl)dichlororuthenium(II) hexahydrate ($\text{Ru}(\text{bpy})_3\text{Cl}_2$, 99.95%), *S*-dodecyl-*S'*-(α,α' -dimethyl- α'' -acetic acid)trithiocarbonate (DMAT, 98%) and methyl 2-[methyl(4-pyridinyl)carbamoithioylthio]propionate (MMCP, 97%). The monomers including *N*-vinylpyrrolidinone (NVP, $\geq 99\%$), *N*-vinylcaprolactam (NVC, 98%), vinyl acetate (VAc, $\geq 99\%$), dimethyl vinylphosphonate (DVP, $\geq 95\%$), 9-vinylcarbazole (VCz, 98%), methyl acrylate (MA, 99%), *tert*-butyl acrylate (*t*BA, 98%), *N,N*-dimethylacrylamide (DMA, 99%), *N,N*-diethylacrylamide (DEA, 99%), pentafluorophenyl methacrylate (PFMA, 95%) and ethylene glycol dimethacrylate (EGDMA, 98%) 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.

O-Ethyl-*S*-(1-carboxyethyl) dithiocarbonate (ECT) and *O*-ethyl-*S*-(1-ethoxycarbonyl)ethyl dithiocarbonate (EET) were prepared according to procedures described in the literature.¹⁻³

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 acetone (acetone-*d*₆) 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(methyl methacrylate) (PMMA) as the standard 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 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 morphology of the

nanoparticles was observed by transmission electron microscopy (TEM, JEOL-2100, JEOL Ltd., Japan).

Synthesis of [Ir(pma)(ppy)₂]Cl₃ Complexes⁴⁻⁶

To a degassed round-bottom flask, IrCl₃ (1.19 g, 4.0 mmol) and ppy (1.69 mL, 10.0 mmol) were dissolved in a mixed solution of 2-ethoxyethanol (120 mL) and water (40 mL). The reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was diluted with deionized water (80 mL). The yellow precipitate was collected by filtration, washed with deionized water and CH₃OH/water (1:1, v/v) twice. The obtained [Ir(ppy)₂(μ-Cl)]₂Cl₄ yellow powder was used directly without further purification.

[Ir(ppy)₂(μ-Cl)]₂Cl₄ (1.95 g, 1.6 mmol), AgOTf (2.47 g, 9.6 mmol) and *N,N*-dimethylacetamide (DMAC, 80 mL) were introduced into a two-necked round-bottom flask fitted with a condenser. The reaction mixture was degassed with argon for 15 min, heated to 100 °C for 30 min, followed by addition of pba (732.0 mg, 4.0 mmol) through a stream of argon. The reaction was then heated to 130 °C for 6 h. After cooling down to room temperature, the precipitate was filtered and washed with acetonitrile to remove silver salts. The resultant precipitate was redissolved in dichloromethane (DCM), washed with deionized water thrice, dried over anhydrous MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with a gradient starting at DCM/hexane (1:1, v/v) and ending at hexane to give [Ir(pba)(ppy)₂](OTf)₃ as a bright orange powder (yield ~42%). ¹H NMR (DMSO-*d*₆, δ, ppm, TMS): 9.62 (1H, -C(H)=O), 8.31 (1H), 8.15 (2H), 8.00 (1H), 7.88 (1H), 7.71-7.85

(4H), 7.57 (1H), 7.47 (2H), 7.33 (1H), 7.22-7.29 (1H), 7.09-7.21 (3H), 6.77-6.89 (2H), 6.63-6.77 (3H), 6.55 (1H).

A solution of $[\text{Ir}(\text{pba})(\text{ppy})_2](\text{OTf})_3$ (679.2 mg, 0.6 mmol) in anhydrous DCM (30 mL) and ethanol (20 mL) was added dropwise over a period of 10 min to a stirred suspension of NaBH_4 (45.4 mg, 1.2 mmol) in anhydrous ethanol (10 mL) at 0 °C under argon atmosphere. Upon completion of the addition, the reaction mixture was allowed to proceed at room temperature for 12 h. The solvent was removed under reduced pressure and the resultant powder was redissolved in DCM, washed with deionized water thrice, dried over anhydrous MgSO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography on silica gel eluting with DCM to give $[\text{Ir}(\text{pme})(\text{ppy})_2]\text{Cl}_3$ as a bright yellow powder (yield ~92%). ^1H NMR ($\text{DMSO-}d_6$, δ , ppm, TMS): 8.05-8.18 (3H), 8.15 (2H), 7.75 (6H), 7.37-7.51 (3H), 7.02-7.17 (3H), 6.76-6.87 (3H), 6.59-6.73 (5H), 4.85 (1H, $-\text{CH}_2\text{OH}$), 4.16 (2H, $-\text{CH}_2\text{OH}$).

In a typical procedure, $[\text{Ir}(\text{pme})(\text{ppy})_2]\text{Cl}_3$ (396.8 mg, 0.5 mmol), TEA (195 μL , 0.7 mmol) and anhydrous DCM (30 mL) were introduced into a 100 mL single-necked round bottom flask. The flask was immersed in an ice bath and methacryloyl chloride (70 μL , 0.7 mmol) in anhydrous DCM (5 mL) was added dropwise. Upon completion of the addition, the reaction mixture was kept in the ice water bath for 1 h and then at room temperature for 24 h. After solvent removal, the crude product was purified by column chromatography on silica gel eluting with a gradient starting at DCM/hexane (1:1, v/v) and ending at DCM/hexane (3:1, v/v) to give $[\text{Ir}(\text{pma})(\text{ppy})_2]\text{Cl}_3$ as a bright yellow

powder (yield ~94%). ^1H NMR (acetone- d_6 , δ , ppm, TMS): 7.99-8.14 (3H), 7.67-7.78 (6H), 7.56-7.67 (3H), 6.99-7.06 (3H), 6.91 (1H), 6.76-6.88 (5H), 6.65-6.76 (2H), 5.91 (1H, $-\text{CH}_2=\text{C}-\text{CH}_3$), 5.55 (1H, $-\text{CH}_2=\text{C}-\text{CH}_3$), 4.93 (2H, $-\text{C}(=\text{O})\text{OCH}_2-$), 1.83 (3H, $-\text{CH}_3$). ESI-MS (m/z): 753.23, calculated for $[\text{C}_{38}\text{H}_{30}\text{O}_2\text{N}_3\text{Ir}]^+$: 753.20.

Synthesis of $\text{Fe}_3\text{O}_4@ \text{aSiO}_2@ \text{PNMIr}$ Janus Nanocomposites

Monodisperse oleic acid-capped Fe_3O_4 nanoparticles with an average diameter of 12 nm were prepared as described in literature by Part et al.⁷ In a typical procedure, 6 mL of aqueous solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (541 mg, 2 mmol) were dosed to a mixed solution of oleic acid (1.9 mL, 6 mmol), ethanol (8 mL) and hexane (14 mL) under vigorous stirring for 30 min. Afterwards, NaOH (160 mg, 4 mmol) was added to the above solution and the reaction was allowed to proceed at 70 °C for 4 h. After being cooled down to ambient temperature, the organic phase was collected and purified by repeated washing with deionized water. Most of solvents were removed under reduced pressure. The highly viscous iron/oleate complex precursor was redispersed in a mixed solution of oleic acid (0.32 mL, 1 mmol) and 1-octadecene (12.5 mL, 40 mmol), sonicated for 30 min and degassed by bubbling nitrogen for 30 min. The reaction then was allowed to proceed at 320 °C for 30 min under steady and continuous nitrogen flow. After being cooled down to room temperature, the crude product was purified by repeated precipitation from hexane into excessive ethanol. The oleic acid-stabilized Fe_3O_4 nanoparticles were centrifuged and stored in cyclohexane before use.

The heteroepitaxial deposition of silica frameworks on the Fe_3O_4 nanoparticles were conducted using a reverse microemulsion method.⁸⁻¹¹ Typically, the Fe_3O_4 nanoparticles

in cyclohexane (10 mL, 2.5 mg/mL) was dispersed in a mixed solution containing Igepal CO-520 (10.0 g), cyclohexane (240 mL) and ammonium hydroxide solution (4.0 mL, 28~30 wt% NH₃ basis) under ultrasonication treatment. Afterwards, TEOS (0.2 mL) and APMS (0.2 mL) were dropwise dosed to the reaction suspension in 30 min. The rest of TEOS (0.2 mL × 3) and MPMS (0.6 mL × 1) was dosed to the reaction mixture at a time interval of 12 h. Finally, the raw product was collected with a magnet, and purified by three cycles of centrifugation/redispersion/washing in excessive ethanol. The Fe₃O₄@aSiO₂-MPMS Janus nanoparticles were collected by centrifugation and stored in ethanol.

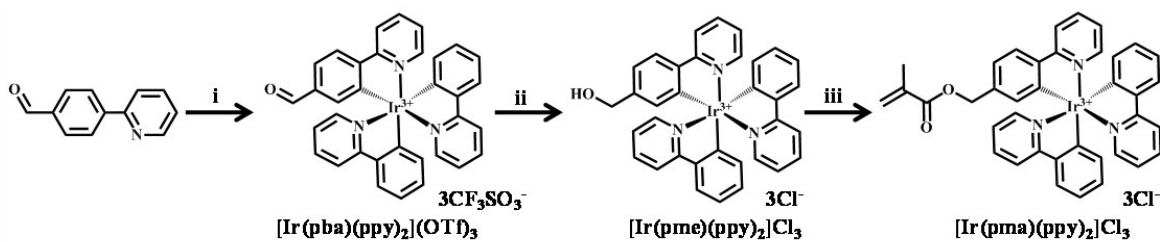
Briefly, about 50 mg of Fe₃O₄@aSiO₂-MPMS Janus nanoparticles were dispersed in DMAC (25 mL) by ultrasonication for 30 min. A mixture of NIPAM (452.0 mg, 4.0 mmol), [Ir(pma)(ppy)₂]Cl₃ (344.6 mg, 0.40 mmol), EGDMA (150.0 μL, 0.80 mmol) and AIBN (20 mg) were then dosed to the reaction flask. The reaction flask was covered with aluminum foil and degassed with argon for 20 min. The polymerization was allowed to proceed at 100 °C for 1 h and stopped by quenching the reaction flask in an ice water bath. The resultant Fe₃O₄@aSiO₂@PNMIr Janus nanocomposites were purified by extraction with acetone and ethanol five times to eliminate any unreacted monomers and oligomers. The Fe₃O₄@aSiO₂@PNMIr Janus nanocomposites were centrifuged and stored in DCM prior to use.

General Procedure for Kinetic Studies of Fe₃O₄@aSiO₂@PNMIr Janus Nanocomposites Catalyzed PET-RAFT Polymerization

A typical PET-RAFT polymerization of NVP in DMSO was performed using a molar feed ratio [NVP]:[ECT] of 200:1 and predetermined amounts of Fe₃O₄@aSiO₂@PNM_{Ir} Janus nanocomposites in DMSO (50 vol%). After the reaction mixture was placed in a glass vial and deoxygenated by sparging argon for 20 min, the reaction vial was sealed with a rubber septum and irradiated to blue LED light (6.4 W, $\lambda_{\text{max}} = 435 \text{ nm}$, 1.6 mW/cm²) at 25 °C. 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 diethyl ether 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. To evaluate the recyclability of the nanocatalysts, the Fe₃O₄@aSiO₂@PNM_{Ir} Janus nanocomposites were separated from the reaction mixture by a strong magnet at the end of each run, regenerated by immersing in DMAC containing [Ir(ppy)₂(μ -Cl)]₂Cl₄ at 130 °C for 6 h, and then redispersed in DMSO by ultrasonic agitation and put into another fresh reaction solution.

Following the similar protocol, PET-RAFT polymerization of NVP in ultrapure water was performed using a molar feed ratio [NVP]:[ECT] of 200:1 and predetermined amounts of Fe₃O₄@aSiO₂@PNM_{Ir} Janus nanocomposites in ultrapure water (50 vol%). After the reaction mixture was placed in a glass vial and deoxygenated by sparging argon for 20 min, the reaction vial was sealed with a rubber septum and irradiated under blue LED light (6.4 W, $\lambda_{\text{max}} = 435 \text{ nm}$, 1.6 mW/cm²). 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.



Scheme S1. Synthesis of $[\text{Ir}(\text{pma})(\text{ppy})_2]\text{Cl}_3$. Reagents and conditions: (i) $[\text{Ir}(\text{ppy})_2(\mu\text{-Cl})_2]\text{Cl}_4$, silver trifluoromethanesulfonate (AgOTf), *N,N*-dimethylacetamide (DMAC), 130 °C, 6 h; (ii) NaBH_4 , $\text{CH}_2\text{Cl}_2/\text{EtOH}$, RT, 12 h; (iii) methacryloyl chloride, triethylamine (TEA), CH_2Cl_2 , RT, 24 h.

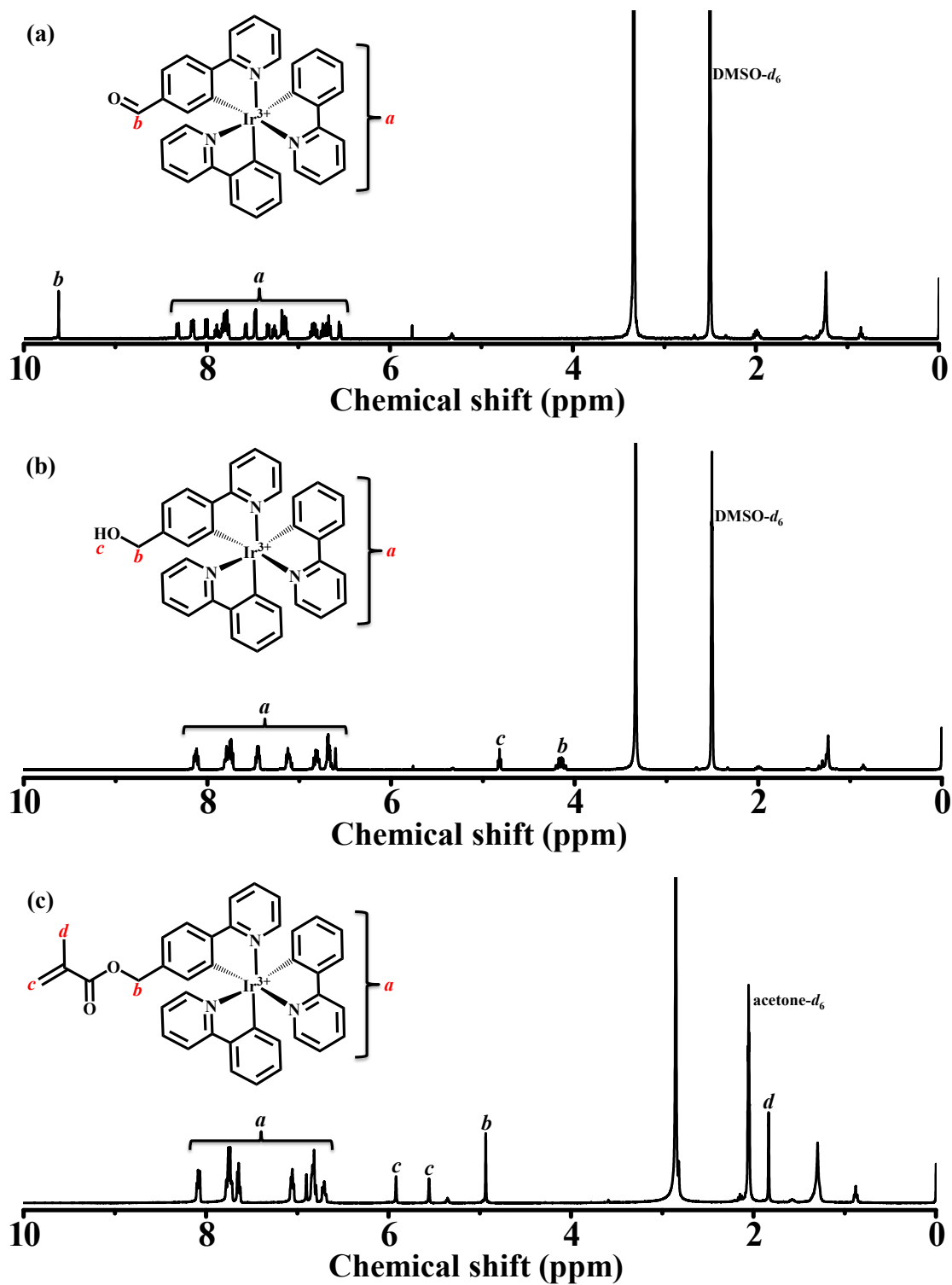


Figure S1. ^1H NMR spectra of (a) $[\text{Ir}(\text{pba})(\text{ppy})_2](\text{OTf})_3$, (b) $[\text{Ir}(\text{pme})(\text{ppy})_2]\text{Cl}_3$ in $\text{DMSO-}d_6$ and (c) $[\text{Ir}(\text{pma})(\text{ppy})_2]\text{Cl}_3$ in $\text{acetone-}d_6$.

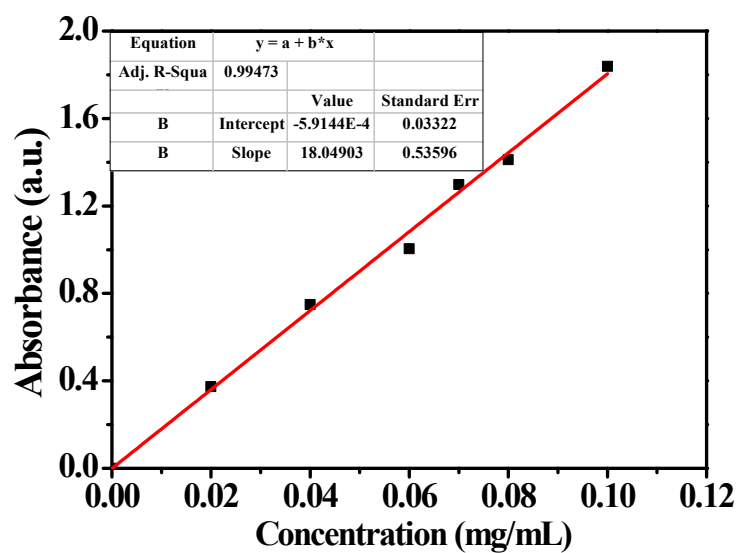
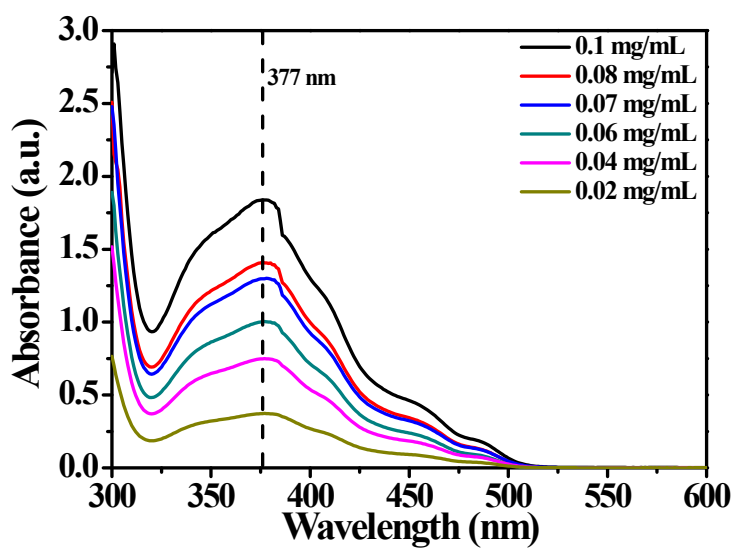


Figure S2. (a) UV-vis absorption spectra of varied concentrations of $[\text{Ir}(\text{pma})(\text{ppy})_2]\text{Cl}_3$ dispersed in DCM; (b) plot of absorbance at the maximum wavelength ($\lambda_{\text{max}} = 377 \text{ nm}$) as a function of $[\text{Ir}(\text{pma})(\text{ppy})_2]\text{Cl}_3$ concentration.

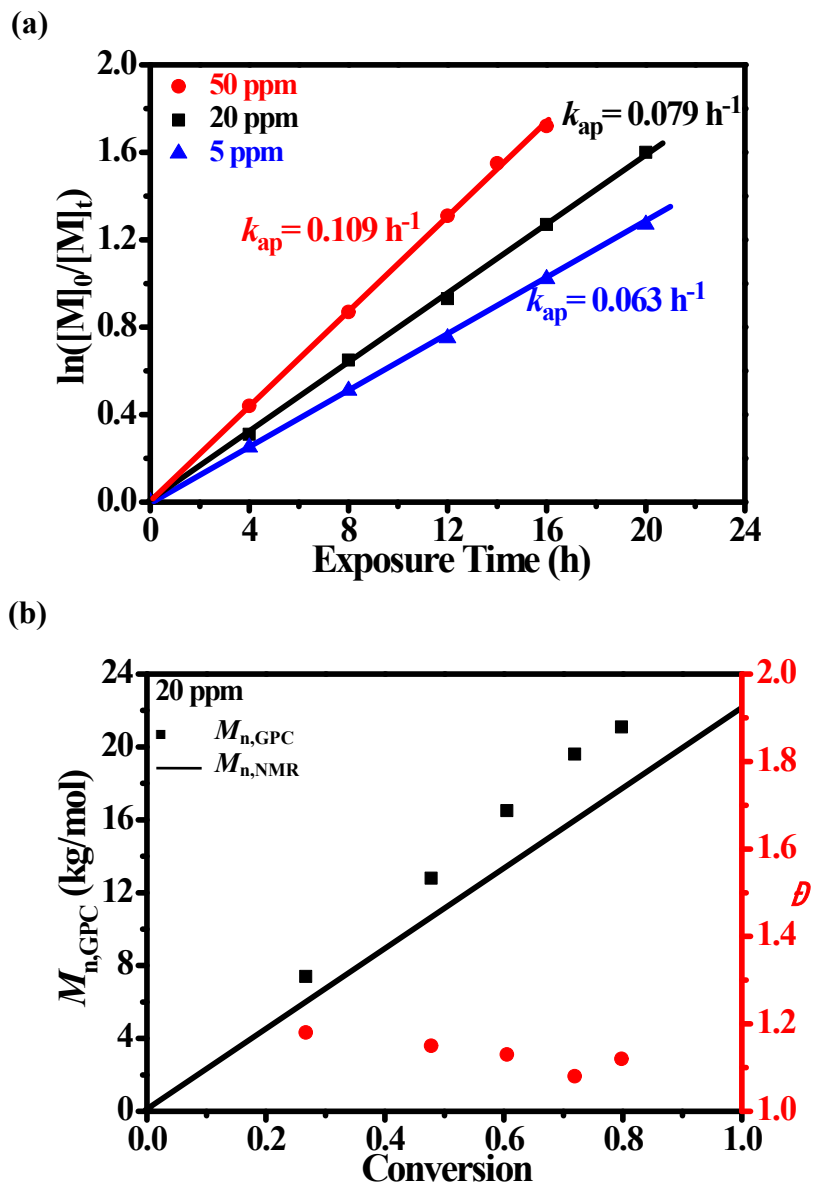


Figure S3. Kinetic analyses of PET-RAFT polymerization of NVP with varied concentrations of *fac*-[Ir(ppy)₃] in DMSO with prior deoxygenation at 25 °C under blue LED light irradiation (6.4 W, $\lambda_{\text{max}} = 435$ nm, 1.6 mW/cm²) with ECT as the CTA ([NVP]/[ECT] = 200:1). (a) Plot of $\ln([M]_0/[M]_t)$ versus exposure time t at different catalyst concentrations in reference to monomer concentration and (b) $M_{n,\text{NMR}}$, $M_{n,\text{GPC}}$ and \bar{D} versus monomer conversion.

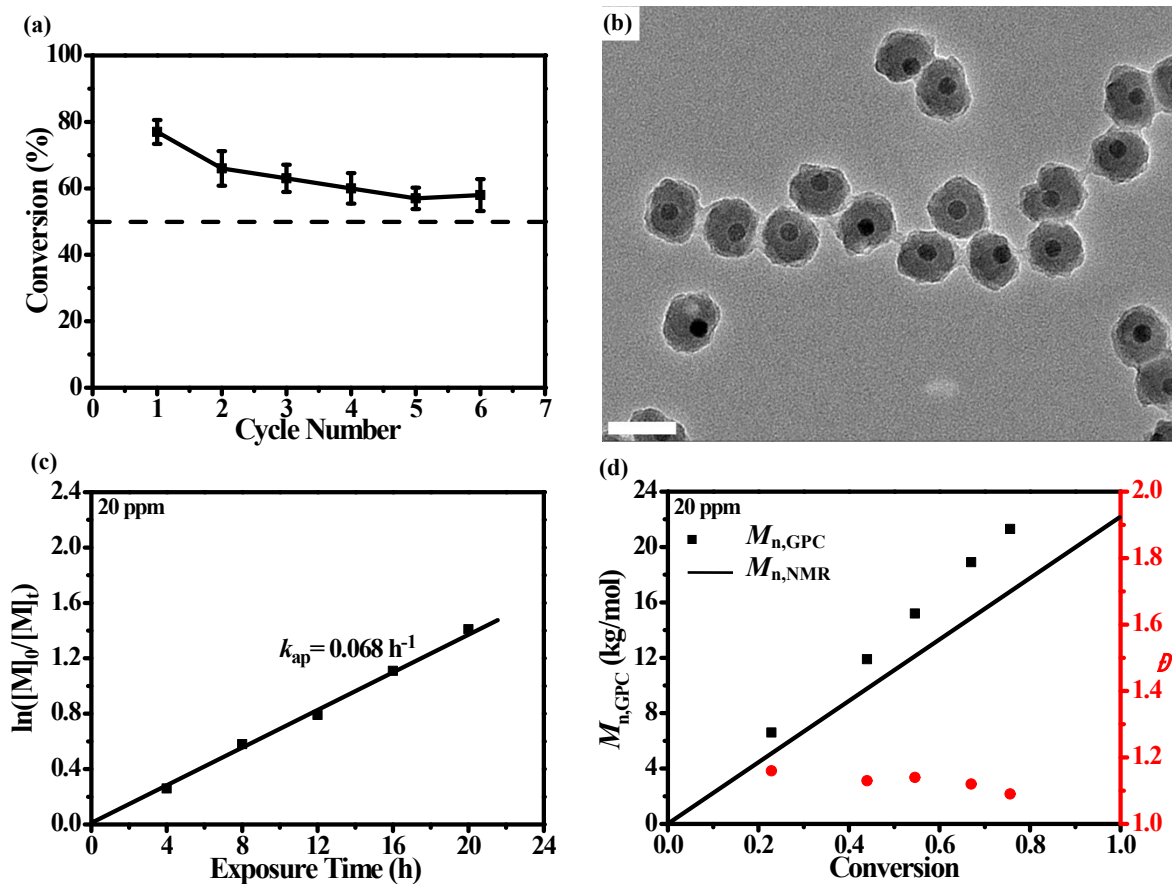


Figure S4. Polymerization of NVP using 20 ppm $\text{Fe}_3\text{O}_4@a\text{SiO}_2@PNMIR$ Janus nanocomposites in DMSO with prior deoxygenation at 25 °C under blue LED light irradiation (6.4 W, $\lambda_{\text{max}} = 435 \text{ nm}$, 1.6 mW/cm^2) with ECT as the CTA ($[\text{NVP}]/[\text{ECT}] = 200:1$). (a) The average monomer conversions after 24 h polymerization of NVP; (b) TEM image of $\text{Fe}_3\text{O}_4@a\text{SiO}_2@PNMIR$ nanocomposites (the scale bar is 100 nm) after six runs of catalytic tests; (c) plot of $\ln([M]_0/[M]_t)$ versus exposure time t and (d) $M_{n,NMR}$, $M_{n,GPC}$ and D versus monomer conversion for PET-RAFT polymerization of NVP after regeneration.

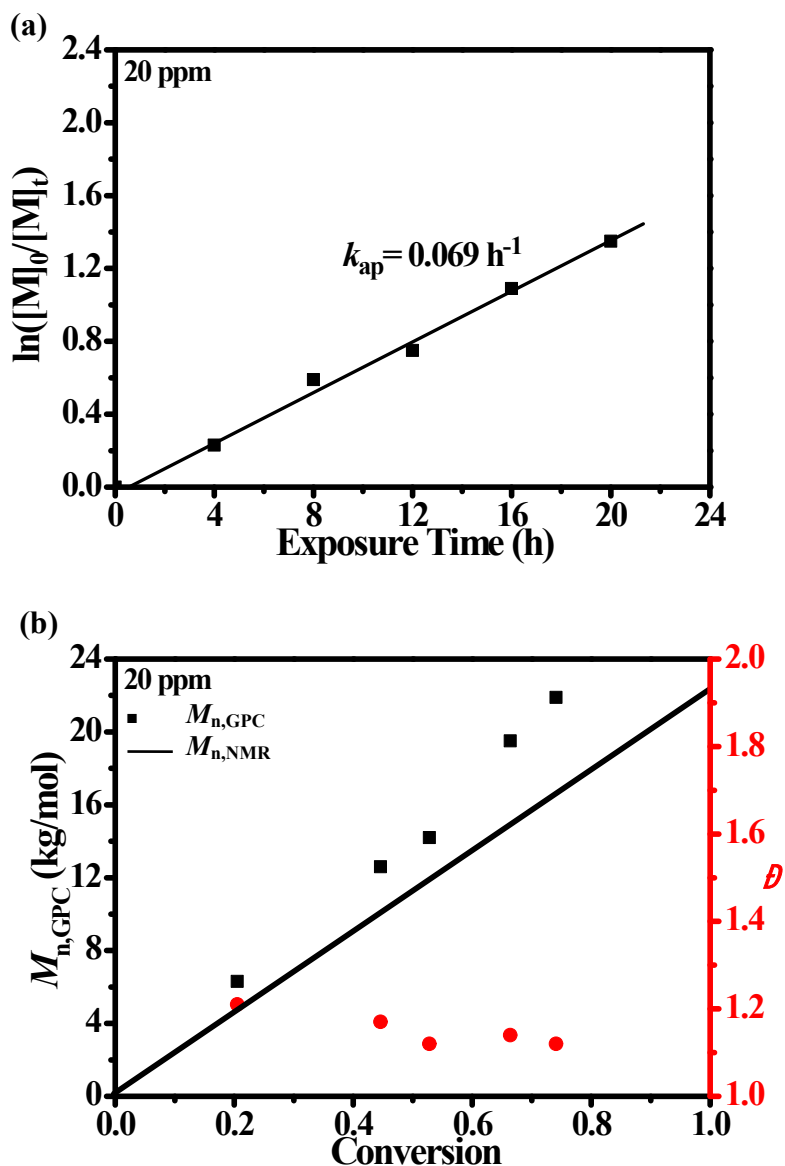


Figure S5. Kinetic analyses of PET-RAFT polymerization of NVP with 20 ppm $\text{Fe}_3\text{O}_4@n\text{SiO}_2@p\text{NMIr}$ Janus nanocomposites in DMSO without prior deoxygenation at 25 °C under blue LED light irradiation (6.4 W, $\lambda_{\text{max}} = 435 \text{ nm}$, 1.6 mW/cm^2) with ECT as the CTA ($[\text{NVP}]/[\text{ECT}] = 200:1$). (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 NVP.

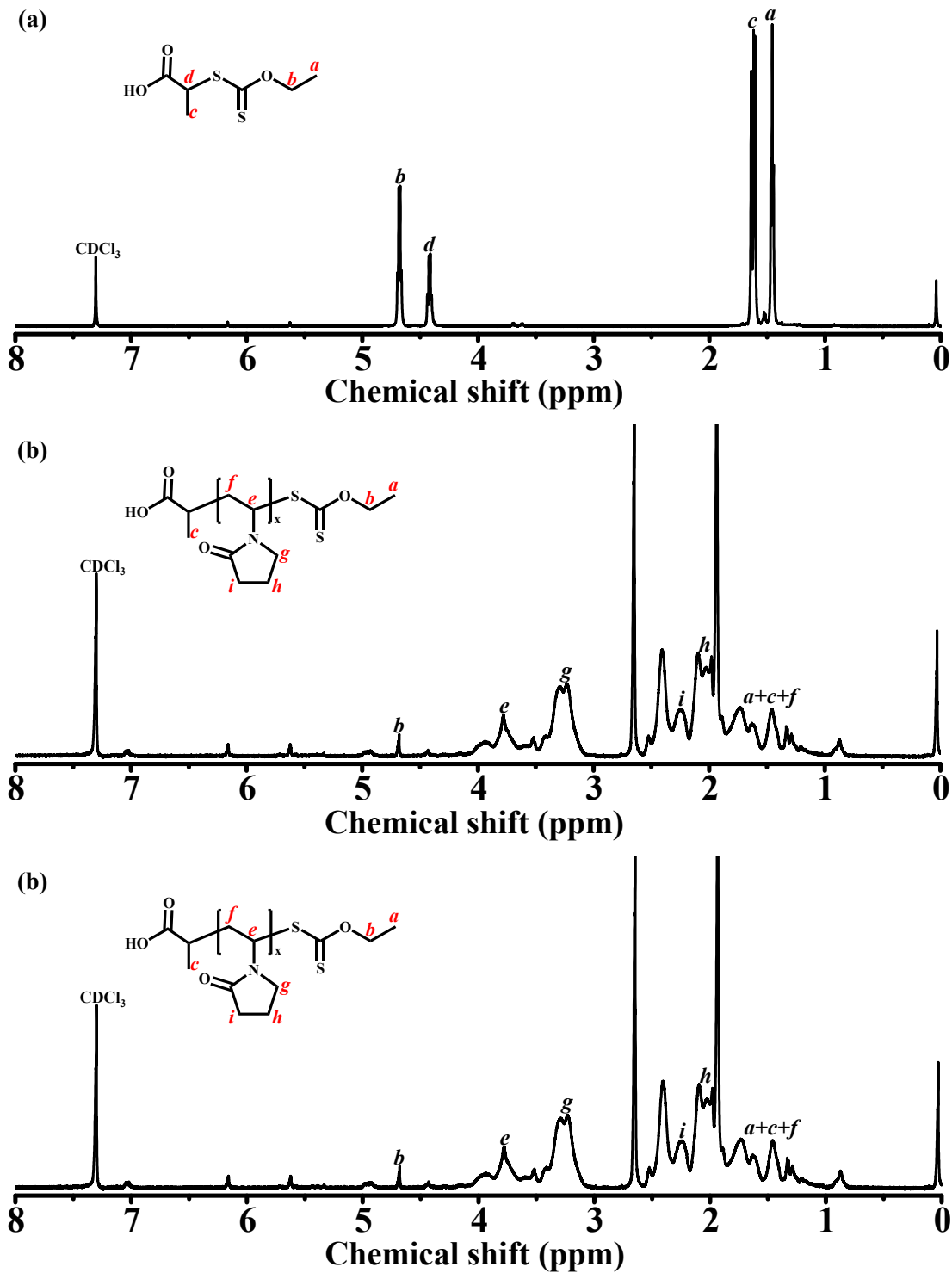


Figure S6. ^1H NMR spectra of (a) ECT, (b) PNVP-ECT and (c) PNVP-*b*-PNVC-ECT in CDCl_3 .



Figure S7. Experimental setup for photo-polymerization using blue LED light.

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