

Supplementary Information

**Graphitic Carbon Nitride (g-C₃N₄) as Sustainable Heterogeneous Photocatalyst for
Metal Free and Oxygen-Tolerant Photo Atom Transfer Radical Polymerization
(Photo-ATRP)**

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Experimental section

Materials: Methyl methacrylate (MMA, 99%, Aladdin), benzyl methacrylate (BzMA, 98%, Aladdin), tert-butyl acrylate (tBA, 99%, Aladdin) and 2-(Dimethylamino) ethyl methacrylate (DMAEMA, 99%, Aladdin) were passed through an alumina column to remove the inhibitor. Ethyl α -bromoisobutyrate (EBiB, 98%, Aladdin) and ethyl α -bromophenylacetate (EBP, 95%, Heowns) were used directly. Tetrahydrofuran (THF, 99%), dimethyl sulfoxide (DMSO, $\geq 99.5\%$), N,N-dimethylformamide (DMF, $\geq 99.5\%$), toluene ($\geq 99.5\%$), methanol ($\geq 99.9\%$) and others were purchased from Aladdin (Shanghai, China).

The blue light source (460 nm) used for all experiments was commercial illumination lamps, with 12 W ($\sim 10 \text{ mW cm}^{-2}$) and 5 W ($\sim 4 \text{ mW cm}^{-2}$) bulbs respectively.

Characterization: UV-vis spectra were recorded on a UV1600 which was purchased from Shanghai Jinghua Technology Instrument Co., Ltd. Regarding gel permeation chromatography (GPC), the THF-GPC analysis was performed on an Agilent GPC-1260 liquid chromatography including a PL 1110-6100 mixed gel column (10 μm ; 300 \times 7.5 mm) and a PL 1110-6540 column (5 μm ; 300 \times 7.5 mm). The flow rate was 1.0 mL min⁻¹ (35 °C). The column system was calibrated with standard polymethyl methacrylate (PMMA) for THF-GPC systems. ¹H NMR spectra of products were examined in CDCl₃ at 30 °C and tetramethylsilane was used as the internal standard. The morphologies of sample were characterized on a Hitachi SU-8010 SEM coupled with an energy-dispersive X-ray (EDX) spectrometer. Powder X-ray diffraction (PXRD, Bruker D8, Germany) and X-ray photoelectron spectra (XPS, ULVAC-PHI, Japan) were used for elemental composition and structure characterization. Fourier transform infrared spectroscopy (FT-IR) were measured with an EQUINOX55 spectrometer (Bruker, Germany) using KBr pellets in the range of 500-4000 cm⁻¹. The nitrogen adsorption-desorption analysis was carried out at 77 K on Micromeritics TriStar II 3020 apparatus and the surface areas were calculated using the Brunauer-Emmett-Teller (BET) equation. Room-temperature photoluminescence spectra (PL) were detected on an Edinburgh instruments Ltd. FLSP920 fluorescence spectrometer.

Electrochemical measurements: Cyclic voltammetry (CV) experiments were carried out with a CHI650E electrochemical workstation (Shanghai Chenhua Instrument Plant, China). Glassy carbon disk (diameter 3 mm) was used as the working electrode, a platinum column as the counter electrode, and Ag/AgCl pillar as the reference electrode. Before the electrode is used, firstly polished it with alumina powder (purchased by Shanghai Chenhua) on the Microcloth polishing flannel. 1 mg g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3, g-C₃N₄-4 was dispersed in a mixed solution of 100 μL water, 100 μL ethanol and 20 μL Nafion, respectively. After ultrasonication for 30 minutes, take an appropriate amount and drop it on the working electrode until dry. **The CV scan was performed in a 5 mM K₃[Fe(CN)₆]/0.1M KCl solution (scan rate: 50 mV s⁻¹) and also 0.5M H₂SO₄ solution (scan rate: 100 mV s⁻¹) (Purge the electrolyte with argon for 5 minutes before measurement).**

General procedure for the preparation of g-C₃N₄: Four kinds of g-C₃N₄ were synthesized by thermal treatment of different nitrogen-rich precursors.¹⁻³ The general synthetic procedure is briefly described as follows. The melamine, thiourea and urea as precursors were ground to powder and placed in closed crucible respectively, and then put into a muffle furnace. The temperature was raised to 550 °C for 4 hours at a heating rate of 5 °C min⁻¹ in an air atmosphere. Naturally cooled to room temperature to obtain three product samples, named g-C₃N₄-1, g-C₃N₄-2 and g-C₃N₄-3. Otherwise, urea was used as the precursor and calcined twice in muffle furnace with the same procedure. The yellow g-C₃N₄ powder obtained by the two-step calcination was named g-C₃N₄-4.

General procedure for ATRP using g-C₃N₄: MMA (1.5 g, 14.98 mmol, 200 equiv), EBP (18 mg, 0.075 mmol, 1 equiv), g-C₃N₄ (30 mg), and THF (1.5 g, 20.8 mmol) were added in a magnetically stirred, argon-filled schlenk tube (10 mL) and exposure to blue LEDs. At a specific time in between, a small volume of solution was removed from the flask in an argon atmosphere, and then the *M_n* and PDI of the polymer were analyzed by GPC. After the reaction finished, the polymer solution was diluted with THF, and the polymer was re-precipitated in cold methanol twice for purification. The collected polymer is dried and weighed to calculate the conversion.

General procedure for the synthesis of the macro-initiator (PMMA-Br): MMA (1.5 g, 14.98 mmol, 200 equiv), EBP (18 mg, 0.075 mmol, 1 equiv), g-C₃N₄-4 (30 mg), and THF (1.5 g, 20.8 mmol) were added in a magnetically stirred and argon-filled schlenk tube (10 mL) and reacted according to the above general polymerization procedure for 5 hours. Then, the polymer was dissolved in a small amount of THF and dropped into 30 mL of methanol to remove unreacted monomers and initiator. The product was dried in a vacuum oven to obtain a white powder. GPC was used to analyze the product to determine *M_n* and PDI.

General Procedure of chain extension experiment: In chain-extension polymerization of MMA, MMA (0.25 g, 2.5 mmol, 200 equiv), PMMA-Br (74 mg, 0.012 mmol, 1 equiv), g-C₃N₄-4 (5 mg), and THF (0.25 g, 3.47 mmol) to a schlenk tube. The reaction was irradiated with blue light for 5 hours and then precipitated in methanol to separate the block polymer. In chain-extension polymerization of DMAEMA, DMAEMA (0.25 g, 1.5 mmol, 100 equiv), PMMA-Br (95 mg, 0.015 mmol, 1 equiv), g-C₃N₄-4 (5 mg), and THF (0.25 g, 3.47 mmol) to a schlenk tube. The reaction was irradiated with blue light irradiation for 5 h before the block polymer was purified as mentioned above. In chain-extension polymerization of BzMA, BzMA (0.25 g, 1.4 mmol, 100 equiv), PMMA-Br (85 mg, 0.014 mmol, 1 equiv), g-C₃N₄-4 (5 mg), and THF (0.25 g, 3.47 mmol) to a schlenk tube. The reaction was irradiated with blue light for 9 hours to obtain its block polymer. In chain-extension polymerization of *t*BA, *t*BA (0.25 g, 1.9 mmol, 100 equiv), PMMA-Br (117 mg, 0.019 mmol, 1 equiv), g-C₃N₄-4 (5 mg), and THF (0.25 g, 3.47 mmol) to a schlenk tube. The mixed solution was reacted under blue light for 7 hours. The block polymer is separated according to the general polymerization procedure described above.

General process of the recatalytic cycle: MMA (2.5 g, 24.98 mmol, 200 equiv), EBP (30 mg, 0.123 mmol, 1 equiv), g-C₃N₄ (50 mg), and THF (2.5 g, 34.7 mmol) were added in a

magnetically stirred, argon-filled schlenk tube (10 mL) and exposure to blue LEDs. As g-C₃N₄ is insoluble in the polymerization system, after the reaction finished, it is separated from the final polymer by a high-speed centrifuge (Bioridge, shanghai) for recycling. The resulting mixture was dissolved in THF, then centrifuged at a rate of 8000 r min⁻¹ for 15 min to obtain g-C₃N₄ powders and supernatant. G-C₃N₄ powders were separated and dried. The supernatant was precipitated in methanol and purified to analyze by GPC. The dried g-C₃N₄ and new MMA, EBP and THF were added to the reaction flask, degassed and polymerized under blue LEDs again.

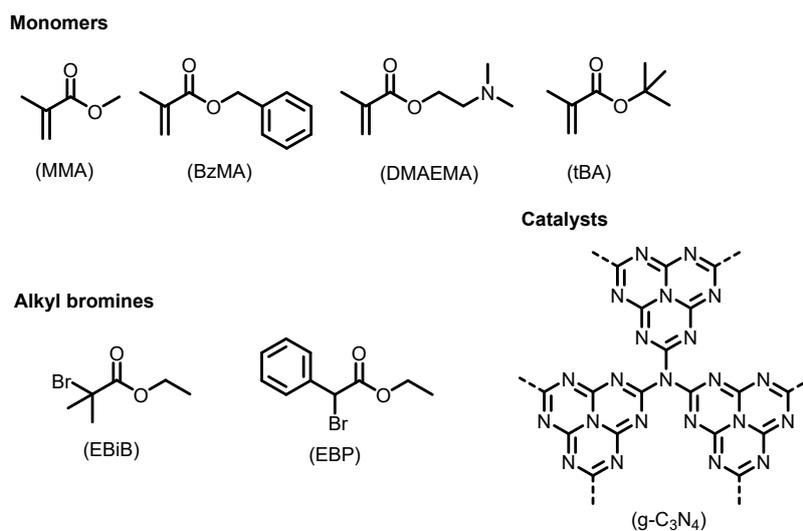


Fig S1. The chemical structures of the monomer, initiators and catalyst used in this work.

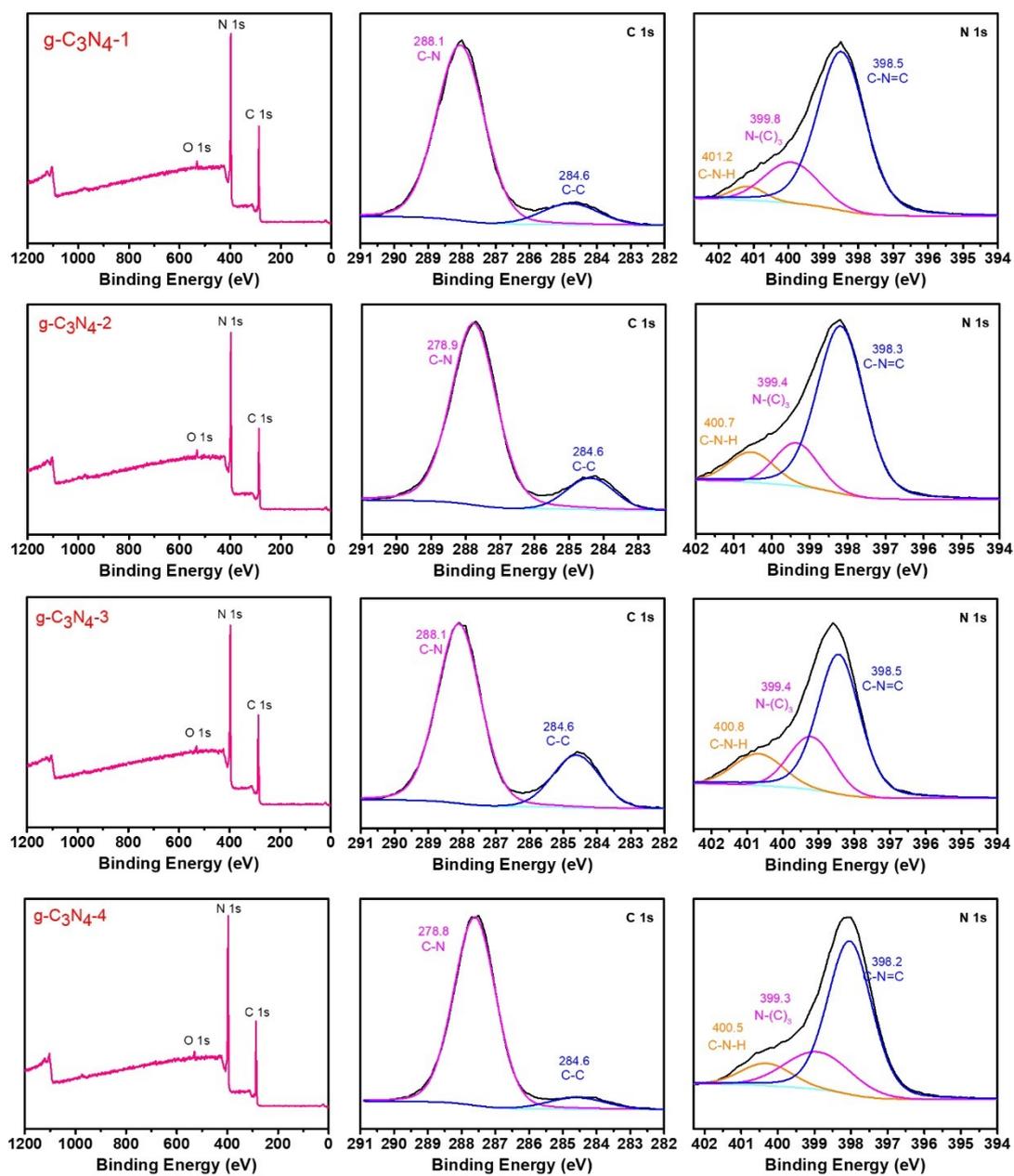


Fig S2. XPS spectra of g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3 and g-C₃N₄-4.

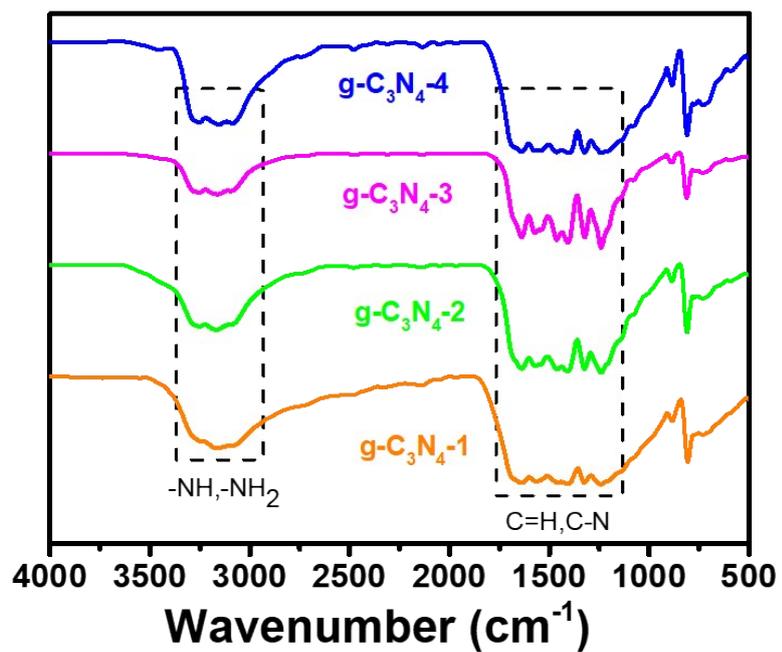
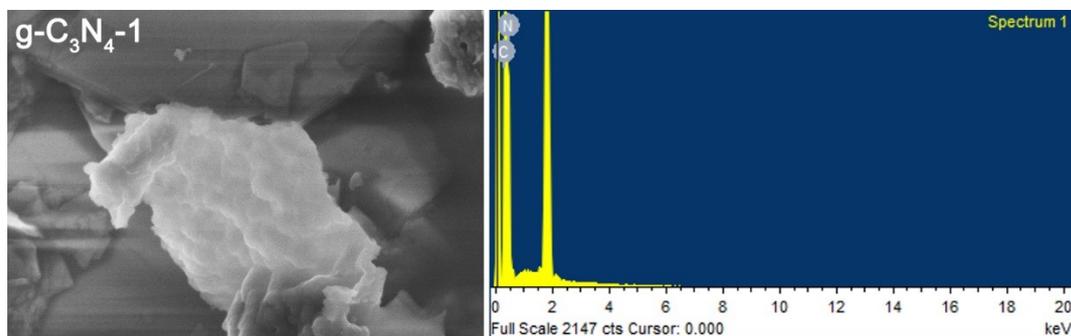
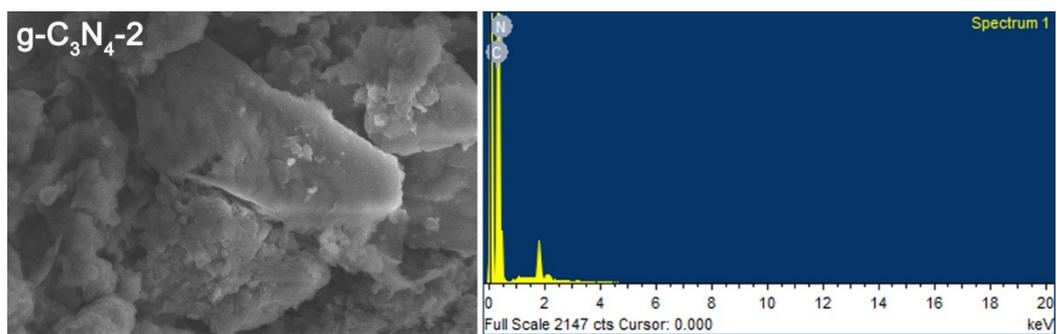


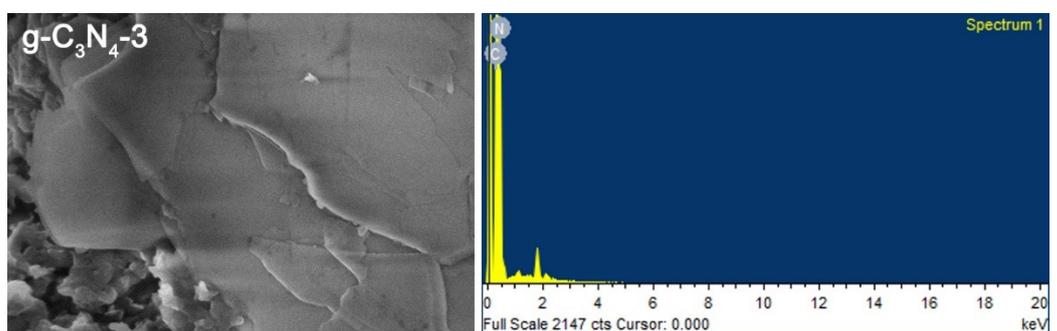
Fig S3. FT-IR spectra of g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3 and g-C₃N₄-4.



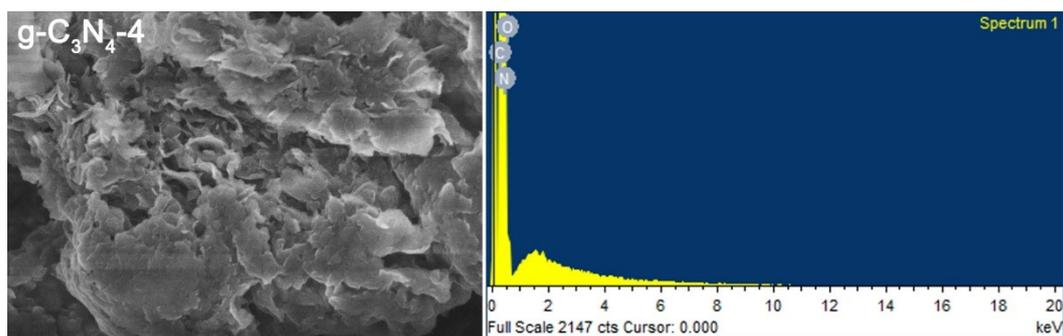
Element	Weight%	Atomic%
C K	27.97	31.17
N K	72.03	68.83



Element	Weight%	Atomic%
C K	53.32	58.44
N K	40.36	37.93
O K	1.86	1.53
Si K	4.46	2.09



Element	Weight%	Atomic%
C K	37.22	41.41
N K	57.22	54.60
O K	3.68	3.07



Element	Weight%	Atomic%
C K	48.97	53.03
N K	47.54	44.14
O K	3.49	2.83

Fig S4. SEM and EDX spectra of g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3 and g-C₃N₄-4.

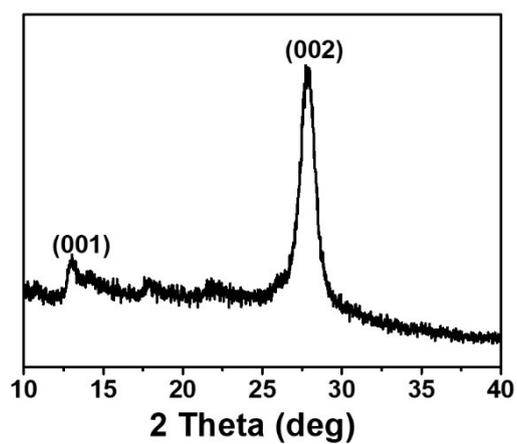


Fig S5. PXRD spectrum of g-C₃N₄-4.

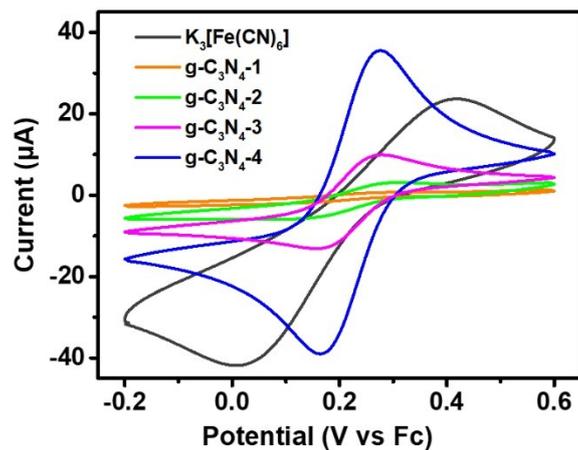


Fig S6. CV curves of K₃[Fe(CN)₆], g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3 and g-C₃N₄-4 in 5mM K₃[Fe(CN)₆]/0.1M KCl solution, scan rate: 50 mV/s⁻¹.

Potential (V vs Fc)

Fig S7. CV curves of g-C₃N₄-1, g-C₃N₄-2, g-C₃N₄-3 and g-C₃N₄-4 in H₂SO₄ solution (0.5 M), scan rate: 100 mV/s⁻¹.

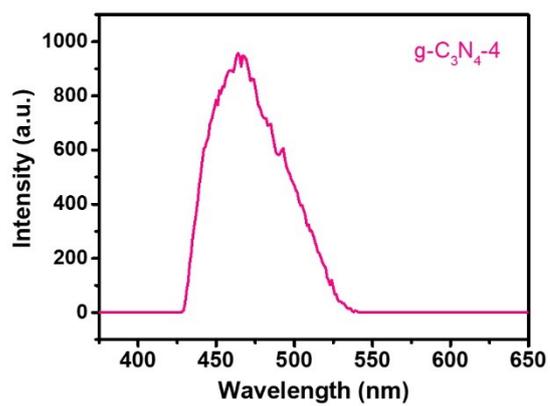


Fig S8. Room-temperature steady-state PL spectrum of g-C₃N₄-4.

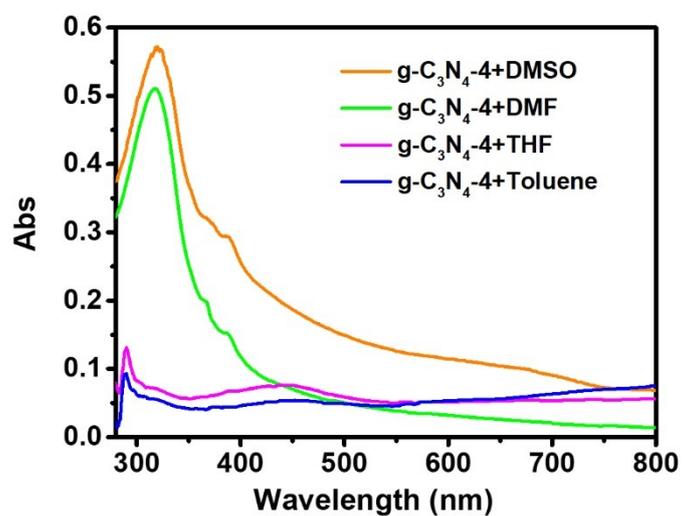


Fig S9. UV-vis spectra of g-C₃N₄-4 in different solvents (0.05 mg mL⁻¹).

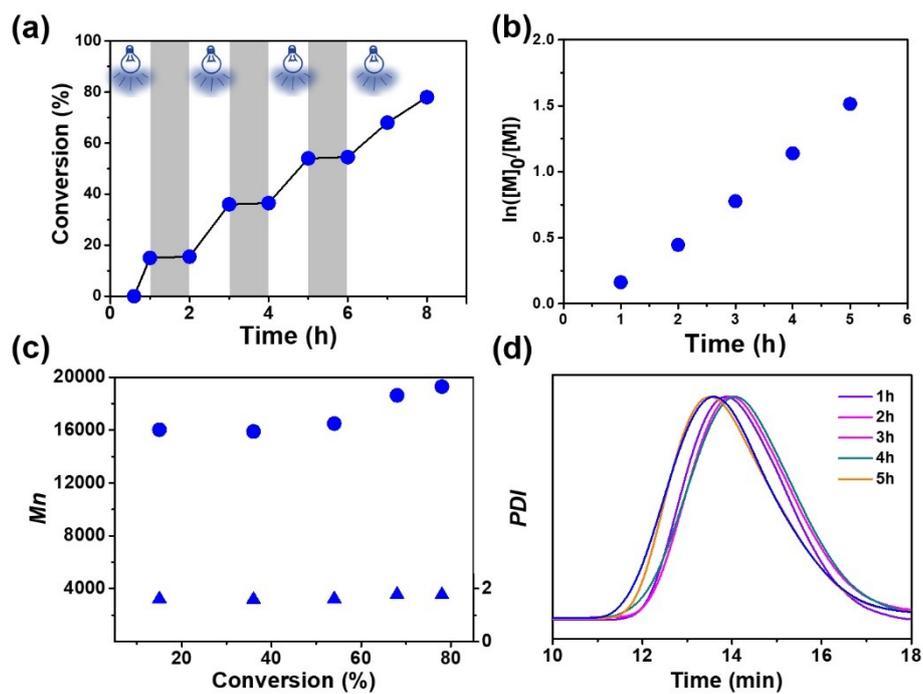


Fig S10. (a) Light on-off experiments and the plot of monomer conversion vs time (entry 7, Table 1). (b) Kinetic plot for the metal-free ATRP. (c) Plot of M_n and PDI vs monomer conversion for the polymerization of MMA under blue LEDs irradiation. (d) GPC traces of PMMA collected at different times.

Chemical shift (ppm)

Fig S11. ^1H NMR spectrum of PMMA-*b*-PMMA.

Chemical shift (ppm)

Fig S12. ^1H NMR spectrum of PDMAEMA-*b*-PMMA. $M_{n,\text{NMR}} = (1.31/2)/(1/3) \times 30 (\text{DP}_{\text{PMMA-Br}}) \times 157.21 \text{ g/mol} + 6000 \text{ g/mol}$ ($M_{n,\text{PMMA-Br}} = 15000 \text{ g/mol}$).

Chemical shift (ppm)

Fig S13. ^1H NMR spectrum of PBzMA-*b*-PMMA. $M_{n,\text{NMR}} = (1.54/2)/(1/3) \times 30 (\text{DP}_{\text{PMMA-Br}}) \times 176.21 \text{ g/mol} + 6000 \text{ g/mol}$ ($M_{n,\text{PMMA-Br}} = 18000 \text{ g/mol}$).

Chemical shift (ppm)

Fig S14. ^1H NMR spectrum of PtBA-*b*-PMMA. $M_{n,\text{NMR}} = (6.80/9)/(1/3) \times 30 (\text{DP}_{\text{PMMA-Br}}) \times 128.17 \text{ g/mol} + 6000 \text{ g/mol}$ ($M_{n,\text{PMMA-Br}} = 15000 \text{ g/mol}$).

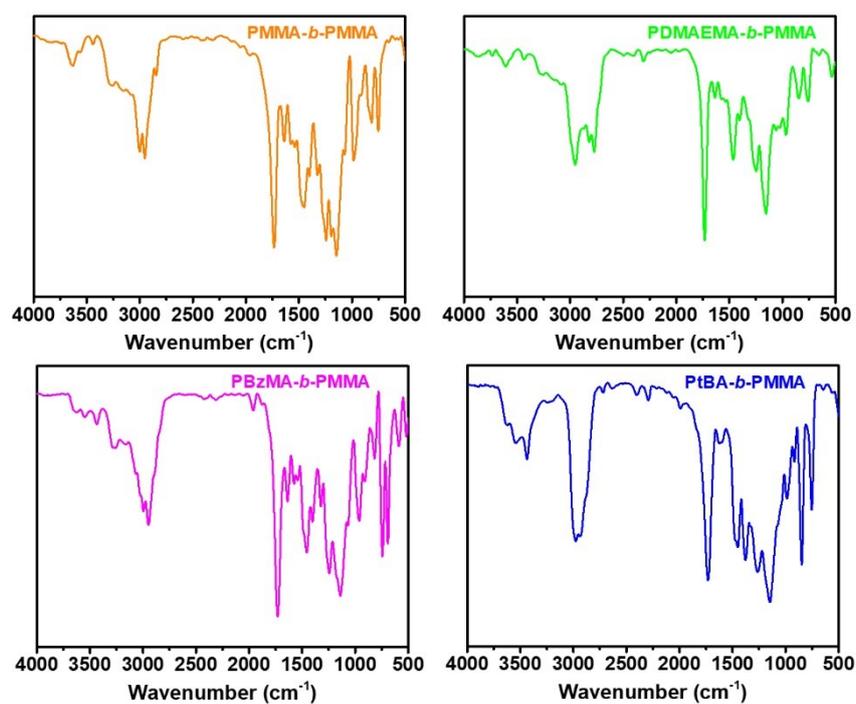


Fig S15. FT-IR spectra of PMMA-*b*-PMMA, PDMAEMA-*b*-PMMA, PBzMA-*b*-PMMA and PtBA-*b*-PMMA.

