Supplementary Information

Long-lived triplet state carbon nitride (urea-CNx) catalyzed metal-free photo-ATRP with oxygen acceleration

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Experimental section

Materials: Methyl methacrylate (MMA, 99%, Aladdin), methyl methacrylate (BzMA, 98%, Aladdin), tert-butyl acrylate (tBA, 99%, Aladdin) and butyl methacrylate (BMA, 99%, Aladdin) were passed through an alumina column to remove the inhibitors. Ethyl α-bromophenylacetate (EBP, 95%, Aladdin) were used directly. Tetrahydrofuran (THF, 99%) and methanol (≥99.9%) were purchased from Aladdin, Shanghai, China.

The blue light source used in all the experiments was procured from Witten LED Lighting.The wattage of the LED light source was 12 W, the wavelength was 460 nm and the intensity of the light source was 10 mw cm^{-2}.

Characterization: UV-VIS-NIR diffuse reflectance spectra were acquired using a Shimadzu UV-3600 PLUS spectrophotometer, employing $BaSO_4$ as the substrate.

For gel permeation chromatography (GPC), the analysis was conducted using an Agilent GPC-1260 liquid chromatography system with a THF phase consisting of a PL 1110-6100 hybrid gel column (10 μm; 300 × 7.5 mm) and a PL 1110-6540 column (5 μm; 300×7.5 mm). The flow rate was set at 1.0 mL min^{-1}, maintaining a temperature of 25 °C. To calibrate the column chromatogram, standard polystyrene (PS) from the THF phase was used, and theconversion to obtain the standard calibration curve for PMMA was performed using the Mark-Houwink Equation.

The samples were dissolved in $CDCl_3$ and the ^{1}H-NMR spectra of the products were acquired using a 400 MHz superconducting NMR instrument, ADVANCE III, manufactured by Bruker in Germany. Tetramethylsilane (TMS) was employed as an internal standard during the detection process.

The morphology of the samples was characterized using a HITACHI S-4800 scanning electron microscope (SEM). For SEM sample preparation, 1 mg of the sample was dispersed in 1 mL of ethanol and sonicated for 0.5 hours. Subsequently, 10 μL of the prepared solution was dropwise added onto a silicon wafer measuring 0.5 mm × 0.5 mm. This process was repeated three times to ensure proper coating. The coated wafers were securely attached to the sample stage using conductive adhesive, and any excess powder was removed by gently blowing with an earwash ball.

Fourier transform infrared spectroscopy (FT-IR) was conducted using an INVENIO spectrometer manufactured by Bruker in Germany. A 1 mg sample was finely ground with 100 mg KBr and compressed to produce a transparent wafer suitable for measurements within the range of 500-4000 cm^{-1}.

Nitrogen adsorption-desorption analysis was conducted using a Micromeritics Tristar II 3020 instrument at a temperature of 77 K, and the specific surface area was determined by applying the Brunauer-Emmett-Teller (BET) equation.

Photoluminescence spectra (PL) were measured using an Edinburgh Instruments Ltd. FLSP 920 fluorescence spectrometer.

Fluorescence lifetime and phosphorescence lifetime were detected on a FLSP920 transient fluorescence spectrometer from Edinburgh Instruments, UK.

X-ray diffraction (XRD) analysis of the sample was conducted on a Bruker D8 Advance X-ray diffractometer.

Detection and analysis of the elemental composition and presence in samples using an ESCALAB Xi$^+$ X-ray photoelectron spectrometer.

General procedure for the preparation of NH₂-CNₓ: Equal amounts of 5 g each of melamine and ammonium sulphate were thoroughly mixed with 30 mL of distilled water, dried in a hot oven at 65 °C, and subsequently finely ground using a mortar. The resulting solid was then transferred to a crucible within a muffle furnace and subjected to calcination at a heating rate of 5 °C min⁻¹ until reaching 550 °C for a duration of 4hours under an air atmosphere. The resultant yellow powder obtained was further refired once under identical conditions before being cooled to room temperature, yielding a light yellow powder sample named NH₂-CNₓ.

General procedure for the preparation of NCN-CNₓ: 2 grams of NH₂-CNₓ were finely ground with 4 grams of dry KSCN in a mortar, and the resulting solid was transferred to a crucible before being placed in a muffle furnace. The sample was calcined under an air atmosphere at a controlled rate of 5 °C min⁻¹ up to 400°C for 1 hour, followed by another controlled rate of 5 °C min⁻¹ up to 500 °C for half an hour. After cooling down to room temperature, residual KSCN was removed through rinsing with deionised water,and the solid was subsequently dried under vacuum at 60°C until it became a dark yellow powder sample named NCN-CNₓ.

General procedure for the preparation of urea-CNₓ: Fifty milliliters of a 1 M aqueous hydrochloric acid solution were added to 1 gram of NCN-CNₓ and stirred for three hours, resulting in the acid hydrolysis reaction of the cyanamide group in NCN-CNₓ to produce urea. The resultant solid was repeatedly washed with deionized water and dried under vacuum at 60°C, yielding a white powder sample named Urea-CNₓ.

General proccess for catalyzing ATRP polymerization using urea-CNₓ: MMA (1 g, 9.99 mmol, 200 equiv), EBP (12 mg, 0.049 mmol, 1 equiv), urea-CNₓ (20 mg), and THF (1 g, 13.9 mmol) were accurately weighed into 5 mL centrifuge tubes. The samples were then sonicated for a duration of 5 minutes before being transferred to larger reaction tubes with a capacity of 25 mL. To ensure an inert atmosphere, the mixture was purged with argon gas for a period of 10 minutes and subsequently exposed to irradiation using two blue LEDs.

During the reaction process at regular intervals, a small aliquot of solution was withdrawn from the reaction vial under an argon atmosphere for subsequent analysis of polymer characteristics such as M_n and PDI by GPC.

Upon completion of the reaction, the polymer solution was diluted with THF and subjected to two additional precipitations in cold methanol to achieve purification. The resulting purified polymer was collected, dried thoroughly, and weighed accurately in order to determine conversion efficiency.

General procedure for the catalytic polymerization of oxygen-tolerant ATRP using urea-CNₓ: MMA (1 g, 9.99 mmol, 200 equiv), EBP (12 mg, 0.049 mmol, 1 equiv), urea-CNₓ (20 mg), and THF (1 g, 13.9 mmol) were accurately weighed into 5 mL centrifuge tubes. The tubes were then subjected to sonication for a duration of 5 minutes before being transferred to pressure-resistant bottles with a capacity of 10 mL. Subsequently, the bottles were sealed tightly and exposed to irradiation from two blue LEDs. At regular intervals during the reaction process,small aliquots of the solution were withdrawn from the reaction vial for analysis of M_n and PDI using GPC techniques.

Upon completion of the reaction, the polymer solution was diluted with THF and subjected to purification by precipitation in cold methanol twice more. The resulting polymer was collected, dried thoroughly, and its weight was determined in order to calculate the conversion rate.

General procedure for the synthesis of macromolecular initiator (PMMA-Br): MMA (1 g, 9.99 mmol, 200 equiv), EBP (12 mg, 0.049 mmol, 1 equiv), urea-CN$_x$ (20 mg), and THF (1 g, 13.9 mmol) were accurately weighed into 5 ml centrifuge tubes and subjected to sonication for a duration of 5 minutes. Subsequently, the contents were transferred to larger reaction tubes with a capacity of 25 mL. The mixture was purged with argon gas for a period of10 minutes followed by irradiation using two blue LEDs for a total time span of five hours. To remove any unreacted monomer and initiator, the resulting polymer was dissolved in a small quantity of THF and subsequently added dropwise into methanol solution measuring approximately30 mL in volume. Finally, the obtained product was dried under vacuumconditions to yield a white powder.The analysis of M_n and PDI values was carried out using GPC technique on the product sample.

General Procedure of chain extension experiment: In the chain extension polymerization of MMA, a mixture of MMA (0.25 g, 100 equiv), PMMA-Br (0.177 g, 1 equiv), and urea-CN$_x$ (0.005 g) was completely dissolved in THF (0.25 g, 50% w/w). The solution was then irradiated under blue light oxygentolerant conditions for 3 hours and subsequently precipitated in methanol to separate the block polymer. As a result, PMMA-*b*-PMMA was obtained.

For the chain extension polymerization of BMA, BMA (0.25 g, 50 equiv), PMMA-Br (0.267 g, 1 equiv), and urea-CN$_x$ (0.005 g) were fully dissolved in THF (0.45 g, 65% w/w). The mixture was subjected to blue light oxygen tolerant conditions for a duration of 7 hours before being precipitated in methanol to isolate the block polymer known as PMMA-*b*-PBMA.

Similarly, during the chain extension polymerization of BzMA, BzMA (0.25 g, 50 equiv), PMMA-Br (0.216 g,1equiv), and urea-CN$_x$(0.005 g) were completely dissolved in THF(0.45 g, 65% w/w).The reaction system was irradiated with blue light under oxygen-resistant conditions for 6 hours and then precipitated in methanol, and the polymerization reaction was successfully completed. The block polymer was precipitated in methanol to obtain PMMA-*b*-PBzMA.

In the chain-expansion polymerisation of tBA, tBA (0.25 g, 100 equiv), PMMA-Br (0.138 g, 1 equiv), and urea-CN$_x$ (0.005 g) were completely dissolved in THF (0.25 g, 50% w/w), irradiated for 8 hours in blue-light oxygen-tolerant conditions, and precipitated in petroleum ether to isolate the block polymers, giving PMMA-*b*-PtBA.

General process of the recatalytic cycle: MMA (1.5 g, 200 equiv, 14.98 mmol), EBP (0.018 g, 1 equiv, 0.074 mmol), urea-CN$_x$ (0.03 g) and THF (1.5 g, 20.8 mmol) were introduced into a schlenk tube (10 mL) and subjected to irradiation for a duration of 7 hours under blue light oxygen tolerant conditions. The resulting product was dissolved in approximately 5 mL of THF and subsequently centrifuged at a speed of 8000 rpm for a period of 20 minutes to obtain urea-CN$_x$ powder and supernatant fractions. The supernatant fraction was decanted while the isolated urea-CN$_x$ powder underwent an additional washing step with another portion of 3 mL THF followed by another round of centrifugation lasting for another duration of 20 minutes. The resultant polymer-containing THF solution was collected and further purified through

precipitation in methanol solvent system. Both the obtained product as well as the urea-CN_x starting material were then dried under vacuum conditions prior to being weighed accurately once again before proceeding with the subsequentpolymerization step involving fresh MMA, EBP, and THF reagents in the reaction vessel.

Superoxide radical anion assay using NBT: 0.5 mg of urea-CN_x, 0.006 g of EBP, 2 mL of a 5×10^{-5} mol/L aqueous NBT solution, and 1 mL of additional deionized water were combined in a 5 mL centrifuge tube and subjected to sonication for a duration of 5 minutes. The resulting solutions were exposed to illumination from two blue lamps with an intensity of 12 W at a wavelength of 460 nm, and samples were collected every 5 minutes for UV-vis spectroscopy analysis.
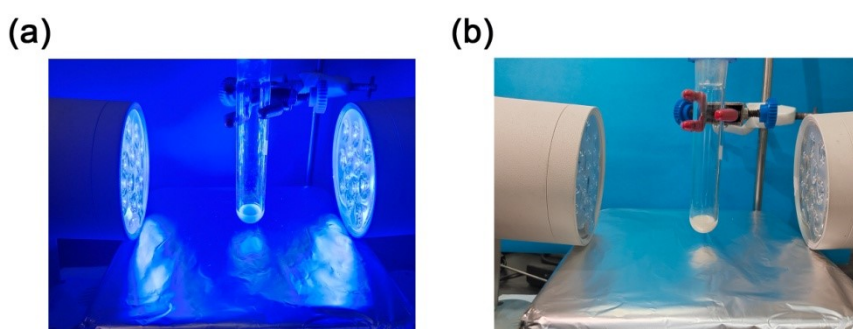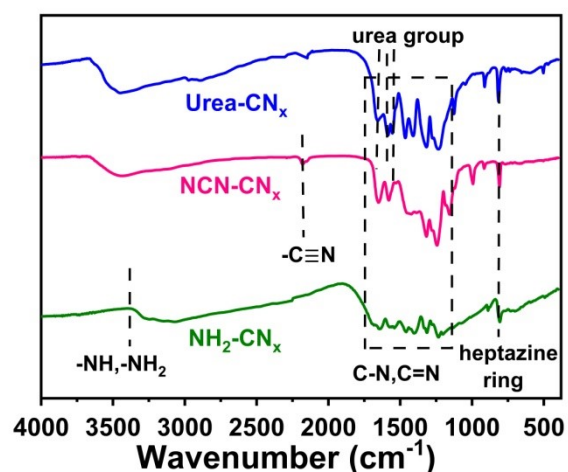

Figure S1. Device for catalyzing photo-ATRP polymerization under blue light (a) light on (b) light off (light intensity: 12 W ($\sim$ 10 mW cm^{-2}) × 2.
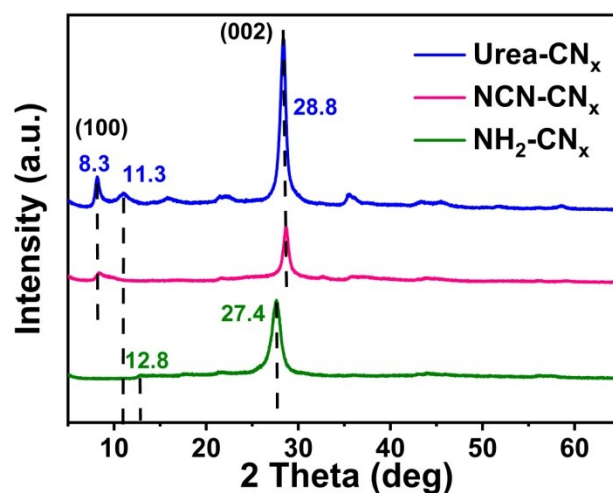
Figure S2. PXRD spectrum of NH_2-CN_x, NCN-$CN_x$and urea-CN_x.
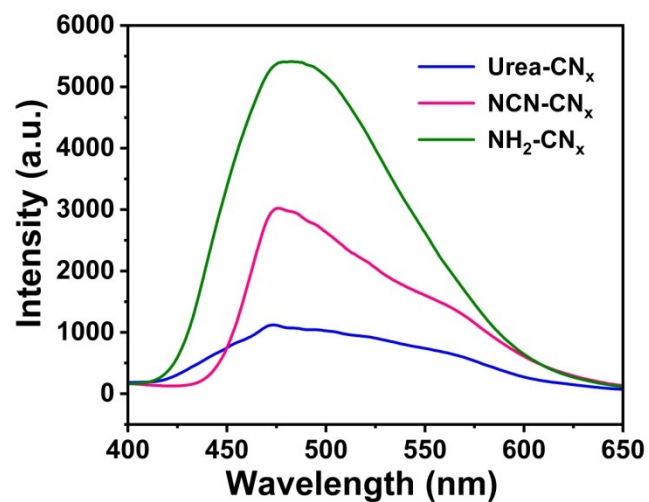
Figure S3. PL spectra of NH_2-CN_x, NCN-CN_x and urea-CN_x.

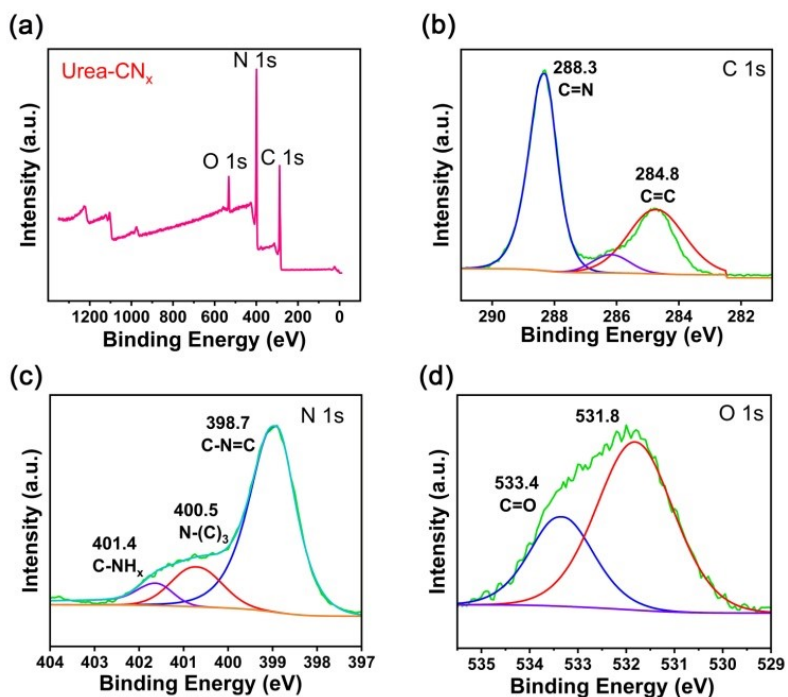**Figure S4.** FT-IR spectra of NH_2-CN_x, NCN-CN_x and urea-CN_x.

Figure S5. XPS spectra of urea-CN$_x$.
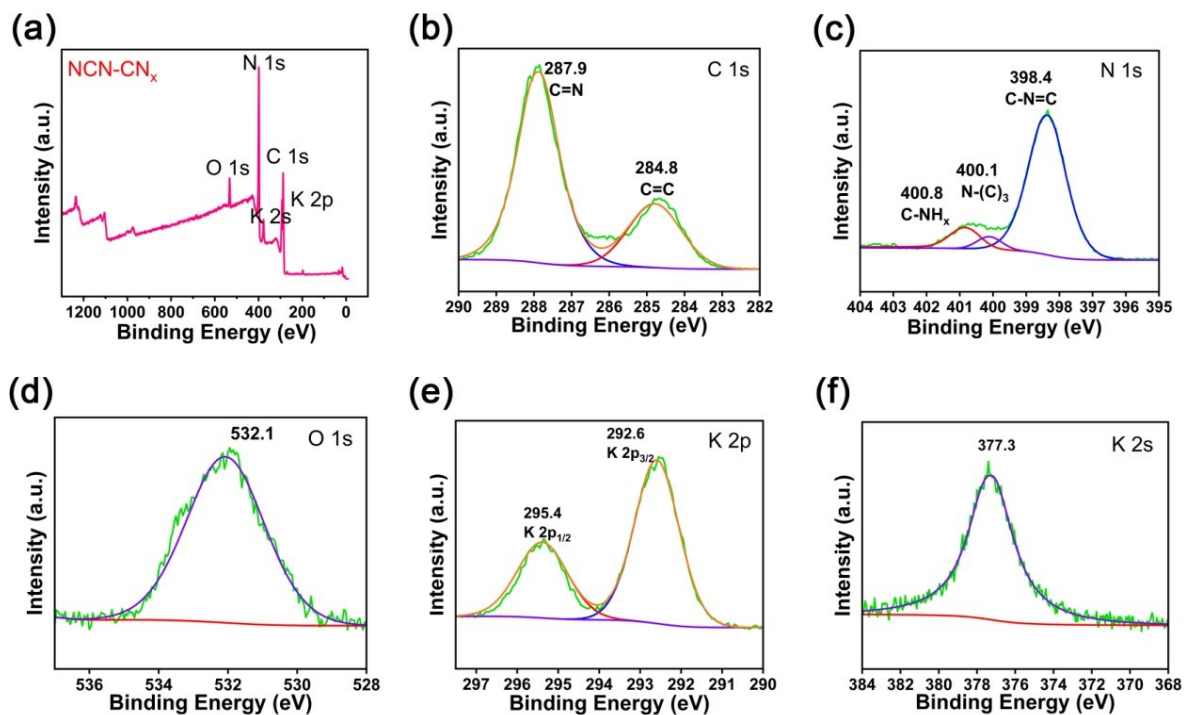
Figure S6. XPS spectra of NCN-CN$_x$.
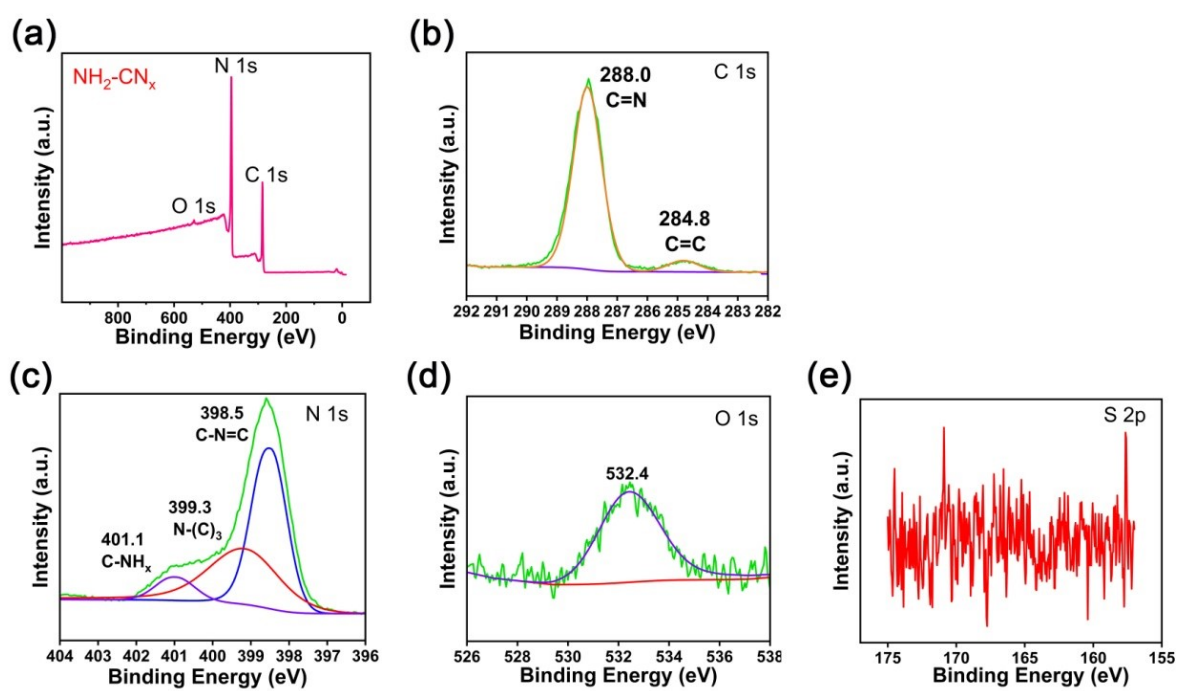
Figure S7. XPS spectra of NH_2-CN_x.

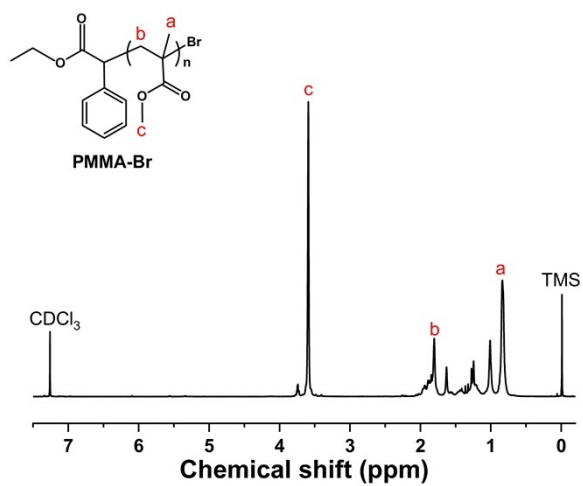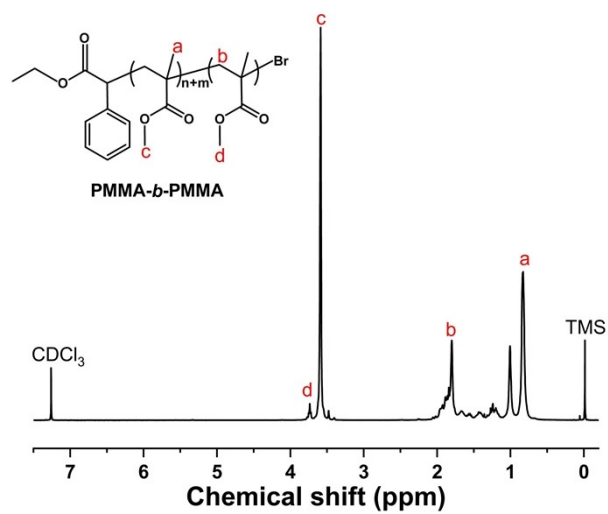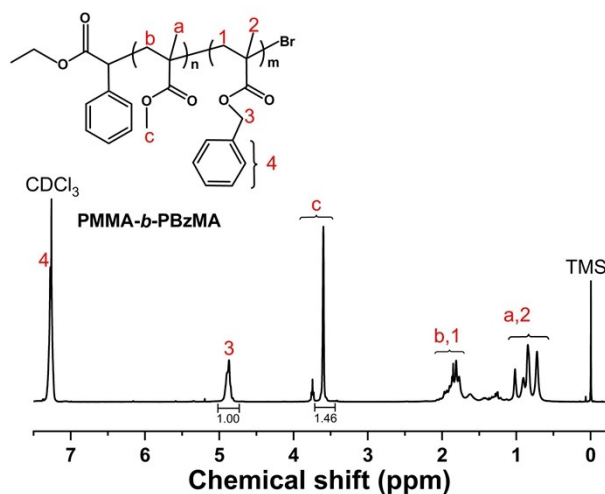**Figure S8.** ^{1}H NMR spectrum of PMMA-Br.

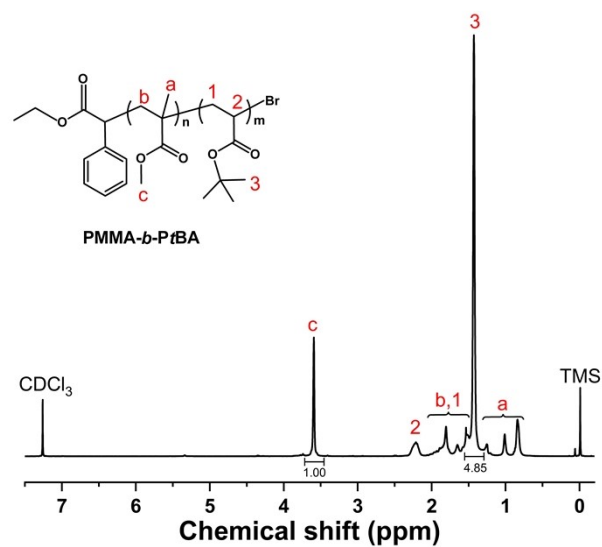**Figure S9.** ^{1}H NMR spectrum of PMMA-*b*-PMMA.

Figure S10. ^{1}H NMR spectrum of PMMA-*b*-PBzMA. $M_{n,NMR}$ = (1/2)/(1.46/3) × 38 (DP$_{PMMA-Br}$) × 176.21 g/mol + 7600 g/mol ($M_{n,PMMA-Br}$) = 14000 g/mol.

Figure S11. ^{1}H NMR spectrum of PMMA-*b*-P*t*BA. $M_{n,NMR}$ = (4.85/9)/(1/3) × 38 (DP$_{PMMA-Br}$) × 128.17 g/mol + 7600 g/mol ($M_{n,PMMA-Br}$) = 15000 g/mol.
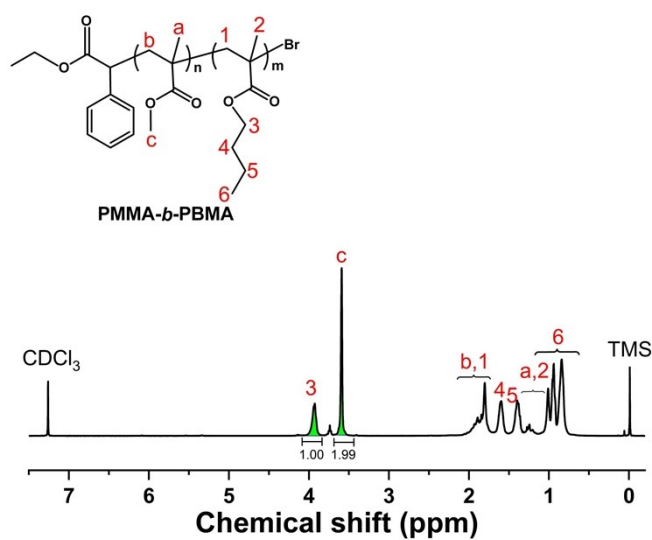
Figure S12. ^{1}H NMR spectrum of PMMA-*b*-PBMA. $M_{n,NMR}$ = (1/2)/(1.99/3) × 38 (DP$_{PMMA-Br}$) × 142.2 g/mol + 7600 g/mol ($M_{n,PMMA-Br}$) = 12000 g/mol.

Table S1. Specific surface area, pore size and pore volume data of urea-CN_x, NCN-CN_x and NH_2-CN_x.

Samples	S_{BET} (m²/g)	Pore width (nm)	V_{BJH} (cm³/g)
NH_2-CN_x	70.49	13.71	0.47
NCN-CN_x	58.86	11.37	0.14
Urea-CN_x	124.18	8.23	0.31

Table S2. Phosphorescence and fluorescence decay lifetime of urea-CN_x.

Urea-CN_x	Decay time		Relative amplitude		Average lifetime
	τ_1	τ_2	A_1	A_2	
Phosphorescent	42.13 µs	503.39µs	564.73	55.04	290.29 µs
Fluorescent	1.47 ns	11.11 ns	699.06	340.07	8.13 ns

$$\langle\tau\rangle=\frac{A_1\tau_1^2 + A_2\tau_2^2}{A_1\tau_1 + A_2\tau_2}$$

Table S3. Results of photo-ATRP with urea-CN_x as photocatalyst under argon gas protection.

Entry	[M]/[EBP]	MMA (g)	Urea-CN_x(g)	Solvent	T (h)	Conv. (%)	$M_{n,GPC}$ ($M_{n,theo}$) (g mol^{-1})	PDI
1	200/1	1	0.02	THF(50%)	4	27	7100(5600)	1.23
2	200/1	1	0.02	THF(50%)	5	38	7600(7800)	1.24
3	200/1	1	0.02	THF(50%)	6	49	10000(10000)	1.34
4	200/1	1	0.02	THF(50%)	7	58	12000(12000)	1.35
5	200/1	1	0.02	THF(50%)	8	65	13000(13000)	1.38

Table S4. ATRP block copolymer with urea-CN$_x$ as photocatalyst.

Entry	Monomer	[M]/[PMMA-Br]	Solvent	T(h)	Conv. (%)	$M_{n,GPC}(M_{n,theo})$ (g mol^{-1})	PDI
1	MMA	100/1	50%THF	3	56	13000(13000)	1.45
2	tBA	100/1	50%THF	8	55	13000(14000)	1.53
3	BzMA	50/1	65%THF	6	68	14000(14000)	1.56
4	BMA	50/1	65%THF	7	57	12000(12000)	1.43

Table S5. Urea-CN$_x$ photocatalyst recovery and GPC results.

Entry	Conv. (%)[a]	Relative Conv. (%)[b]	The Urea-CN$_x$loss (%)[c]	$M_{n,GPC}(M_{n,theo})$	PDI
1	66	100	0	12000(13000)	1.40
2	66	100	3	12000(13000)	1.41
3	64	97	5	12000(13000)	1.41
4	63	95	7	13000(13000)	1.38
5	61	92	10	13000(13000)	1.42
6	60	91	14	13000(13000)	1.40
7	59	89	17	13000(12000)	1.43
8	59	89	20	14000(12000)	1.44
9	57	86	23	14000(11000)	1.45
10	54	82	25	14000(11000)	1.45

[a] Conversions were determined by weighing, [b] relative conversion was calculated by dividing the corresponding conversion by the first conversion, [c] urea-CN$_x$ loss (%) = (urea-CN$_x$ loss g/0.03 g) × 100 %.