

***Supporting Information for:***

**Effect of Nitrogen type on Carbon Dot Photocatalysts for Visible-  
Light-Induced Atom Transfer Radical Polymerization**

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## Materials

Methyl methacrylate (MMA, 99%), methyl acrylate (MA, 99%) and *tert*-butyl acrylate (*t*BA, 99%) were purchased from Aladdin and used after removing the inhibitor. *o*-phenylenediamine (98%, Macklin), citric acid monohydrate (99.5%, Aladdin), ethylenediamine (99%, Aladdin), L-tryptophan (99%, Aladdin), ethyl  $\alpha$ -bromoisobutyrate (EBiB, 98%, Macklin), N,N,N',N'',N'''-Pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin), copper(II) bromide (CuBr<sub>2</sub>, 99%, Aladdin) were used as received; N,N-dimethyl formamide (DMF, 99%, Aladdin), dimethyl sulfoxide (DMSO, >99%, Aladdin), Acetonitrile (MeCN, AR, Kai Tong) were purified to remove H<sub>2</sub>O before using.

## Characterizations

The molecular weight and molecular weight distribution of polymers were determined with gel permeation chromatography (GPC) measurement on the equipment (SFD2000) using THF as the eluent and polymethyl methacrylate (PMMA) as the calibration standard. The conversion of polymers was calculated by <sup>1</sup>H-NMR (Bruker Avance 400MHz) at 25°C using CDCl<sub>3</sub> as solvent. UV-vis absorption spectra were collected using a Thermo Evolution, and Photoluminescence (PL) spectra were performed on a Thermo Lumina fluorescence spectrometer with a 380 nm excitation wavelength at room temperature. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100. The X-ray Photoelectron Spectroscopy (XPS) instrument used in this experiment was the Axis Supra from Kratos, UK using Al K $\alpha$  1486.6 eV X-ray as the excitation source, with a voltage of 15 kV, and a C 1s

peak binding energy of 284.8 eV for charge correction. Fourier transform infrared spectroscopy spectra (FT-IR) were obtained using a Thermo Nicoletis5 transform infrared spectrometer. The LED lamp sources were prepared by mounting 5 m long LED strips (blue:  $\lambda_{\max}$  =465 nm, 2 mW cm<sup>-2</sup>, green:  $\lambda_{\max}$  =535 nm, 1.5 mW cm<sup>-2</sup>, red:  $\lambda_{\max}$  =630 nm, 1 mW cm<sup>-2</sup>, white: 2 mW cm<sup>-2</sup>) inside a glass jar with a depth of 30 cm and a diameter of 20 cm and the LED strips were purchased from RISHANG photoelectric corporation.

### **Hydrothermal synthesis of carbon dots (CDs)**

Six kinds of CDs with different nitrogen sources were synthesized by the previously reported hydrothermal methods.<sup>1-5</sup> The general synthetic procedures were brief described as follows. Firstly, different precursors were dissolved in deionized water and the solution was sealed in a 50 mL Teflon-lined autoclave. After hydrothermal treatment at a pre-determined temperature, the reaction solution was allowed to cool naturally, and then filtered with a 220  $\mu$ m filter. The mother liquor was taken and dialyzed based on dialysis bag with a cut-off volume of 1000 Da. The carbon dots were obtained by rotary evaporation to remove deionized water and then dried by a freeze dryer, which were named CD<sub>1</sub>, CD<sub>2</sub>, CD<sub>2a</sub>, CD<sub>2b</sub>, CD<sub>3</sub>, and CD<sub>4</sub>. The following are the reagents used to prepare CDs and the corresponding hydrothermal conditions: (1) CD<sub>1</sub>, 0.1 g *o*-phenylenediamine was dissolved in 10 mL deionized water, and performed hydrothermal reaction at 200°C for 8 h. (2) CD<sub>2-series</sub>, different ratios of citric acid monohydrate and ethylenediamine were dissolved in 10 mL deionized water, and performed hydrothermal reaction at 180°C for 5 h (CD<sub>2</sub>: 1.05 g citric acid monohydrate

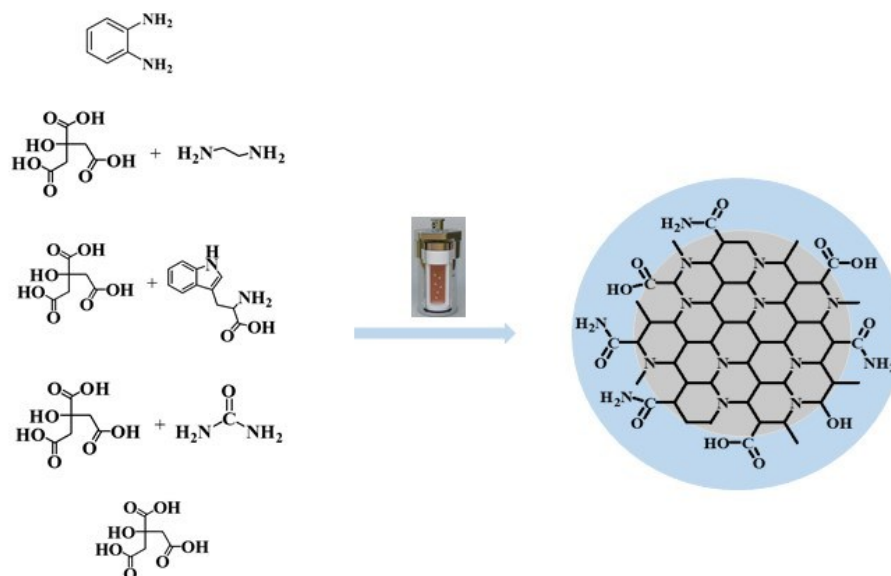
and 335  $\mu\text{L}$  ethylenediamine (1:1). CD<sub>2a</sub>: 0.52 g citric acid monohydrate and 335  $\mu\text{L}$  ethylenediamine (1:2) and CD<sub>2b</sub>: 0.26 g citric acid monohydrate and 335  $\mu\text{L}$  ethylenediamine (1:4). (3) CD<sub>3</sub>: 1.05 g citric acid monohydrate and 1.02 g L-tryptophan were dissolved in 10 mL deionized water and reacted hydrothermally at 180°C for 5 h. (4) CD<sub>4</sub>: 1.05 g citric acid monohydrate was dissolved in 10 mL deionized water, and performed hydrothermal reaction at 180°C for 5 h.

### **General procedure of CDs-catalyzed ATRP**

A mixture of MMA (2 mL, 18.6 mmol), EBiB (13  $\mu\text{L}$ , 0.093 mmol), PMDETA (10  $\mu\text{L}$ , 0.046 mmol) and CuBr<sub>2</sub> (2.7 mg, 0.0093 mmol) with a ratio of 200/1/0.5/0.1 was put into a 10 mL Schlenk tube with 2 mL DMF and 10 mg CDs. The reaction mixture was degassed with three freeze-pump-thaw cycles and finally filled with nitrogen. The reaction system was irradiated with visible light at room temperature. Samples were characterized by GPC and <sup>1</sup>H-NMR.

### **“ON/OFF” polymerization.**

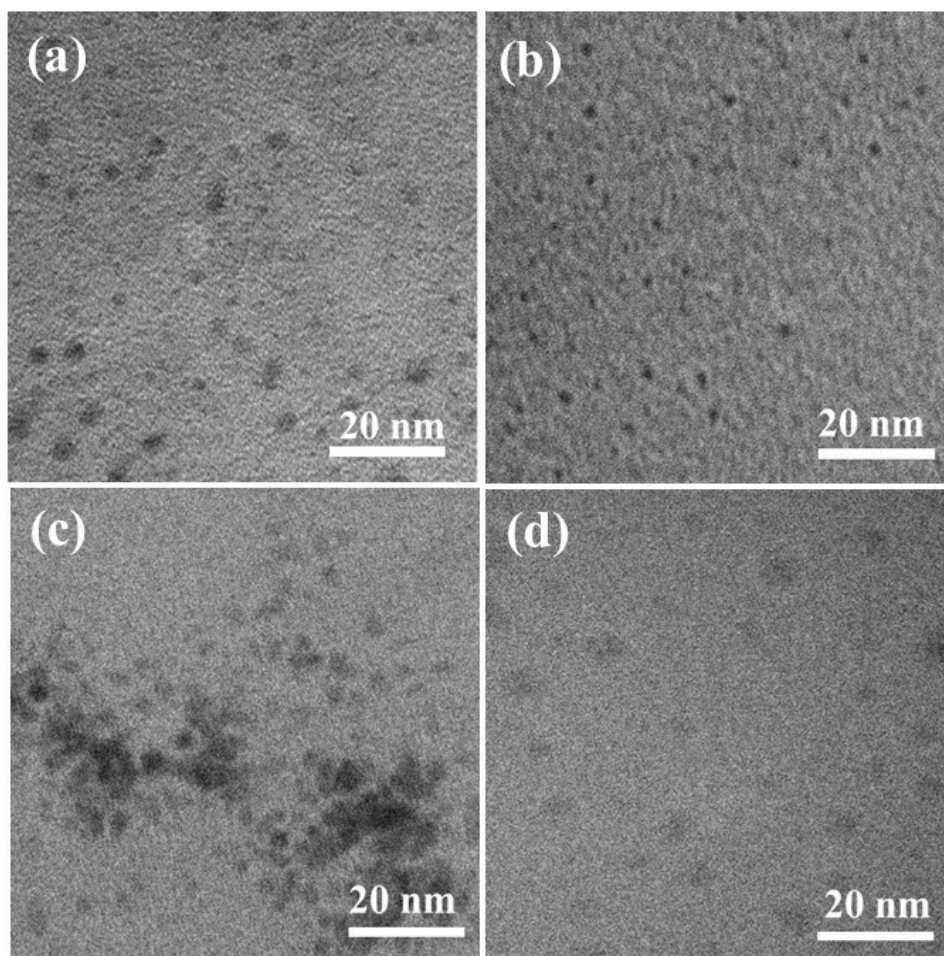
The light switch experiments were performed at the same ratio. A mixture of MMA (2 mL, 18.6 mmol), EBiB (13  $\mu\text{L}$ , 0.093 mmol), PMDETA (10  $\mu\text{L}$ , 0.046 mmol) and CuBr<sub>2</sub> (2.7 mg, 0.0093 mmol) with a ratio of 200/1/0.5/0.1 was put into a 10 mL Schlenk tube with 2 mL DMF and 10 mg CDs. The reaction mixture was degassed with three freeze-pump-thaw cycles and finally filled with nitrogen. To study the temporal control of the reaction, the light was turned on and off within a certain period of time for several times. Samples were analyzed by GPC and <sup>1</sup>H-NMR, respectively.



**Figure S1.** Synthetic route of CDs from different nitrogen sources.

**Table S1.** Hydrothermal synthesis of CDs.

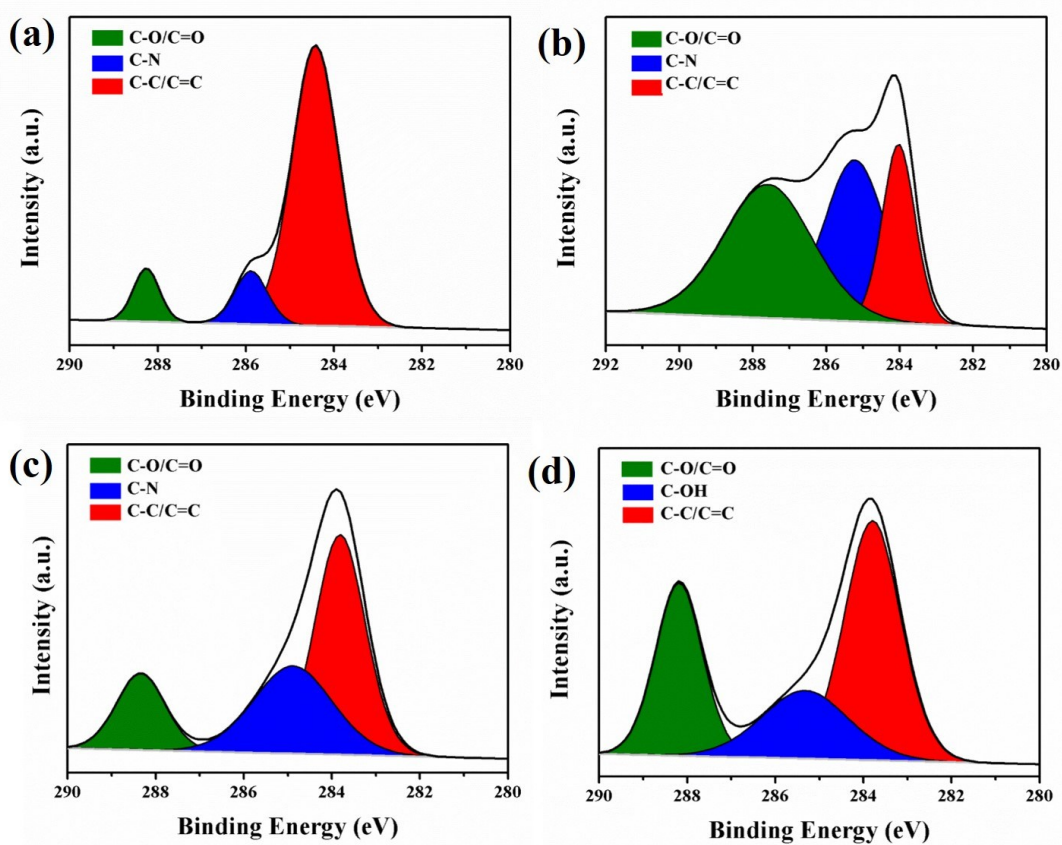
CDs	Precursor 1	Precursor 2	At% (pyridinic N)	Precursor 1: Precursor 2
CD <sub>1</sub>	<i>O</i> -phenylenediamine	/	100%	1:0
CD <sub>2</sub>	Citric acid monohydrate	Ethylenediamine	55%	1:1
CD <sub>2a</sub>	Citric acid monohydrate	Ethylenediamine	45%	1:2
CD <sub>2b</sub>	Citric acid monohydrate	Ethylenediamine	35%	1:4
CD <sub>3</sub>	Citric acid monohydrate	L-tryptophan	0	1:1
CD <sub>4</sub>	Citric acid monohydrate	/	0	1:0



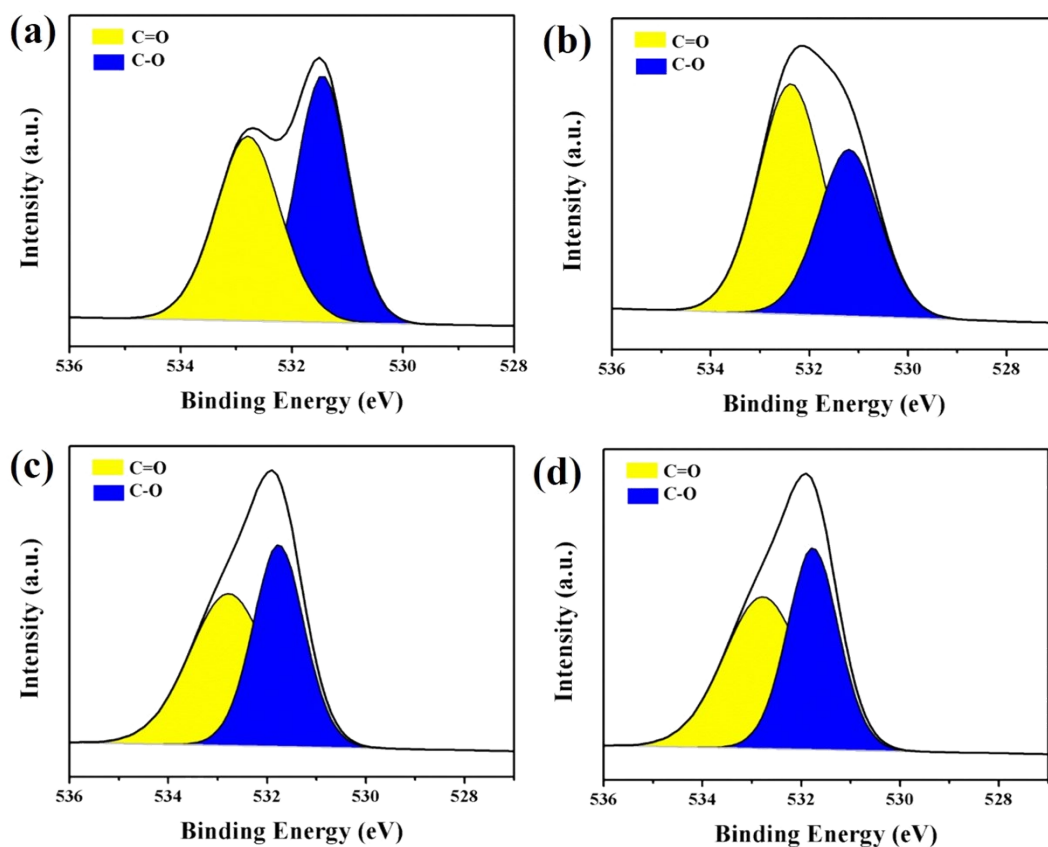
**Figure S2.** TEM of CDs synthesized from different nitrogen sources. (a) CD<sub>1</sub>. (b) CD<sub>2</sub>. (c) CD<sub>3</sub>. (d) CD<sub>4</sub>.

**Table S2.** Fluorescent properties of CDs in DMF.

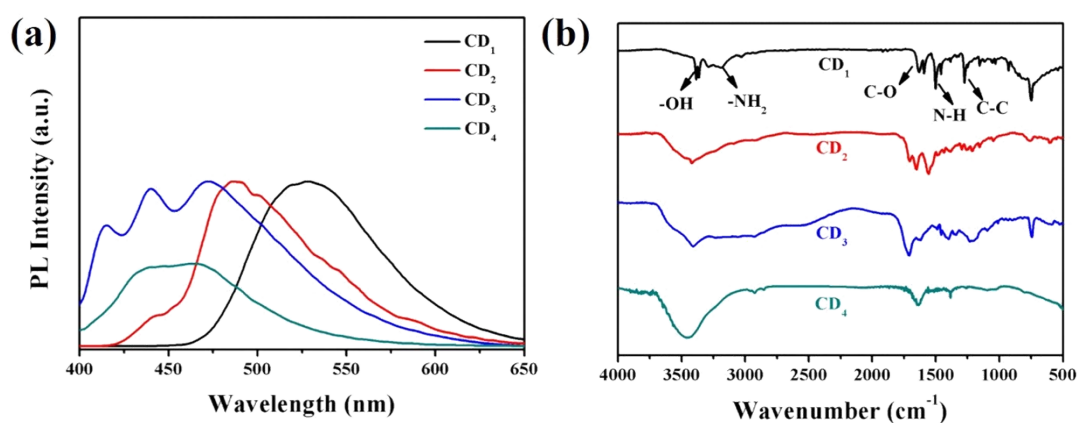
CDs	1	2	3	4
D <sub>n</sub> (nm)	3	2	3	5
λ <sub>max</sub> Abs (nm)	435	360	370	350
λ <sub>max</sub> PL (nm)	520	495	475	430
At% (N)	3.76	11.77	5.26	0



**Figure S3.** High-resolution C 1s and peak fitted XPS spectra of CDs synthesized from different nitrogen sources. (a) CD<sub>1</sub>. (b) CD<sub>2</sub>. (c) CD<sub>3</sub>. (d) CD<sub>4</sub>.

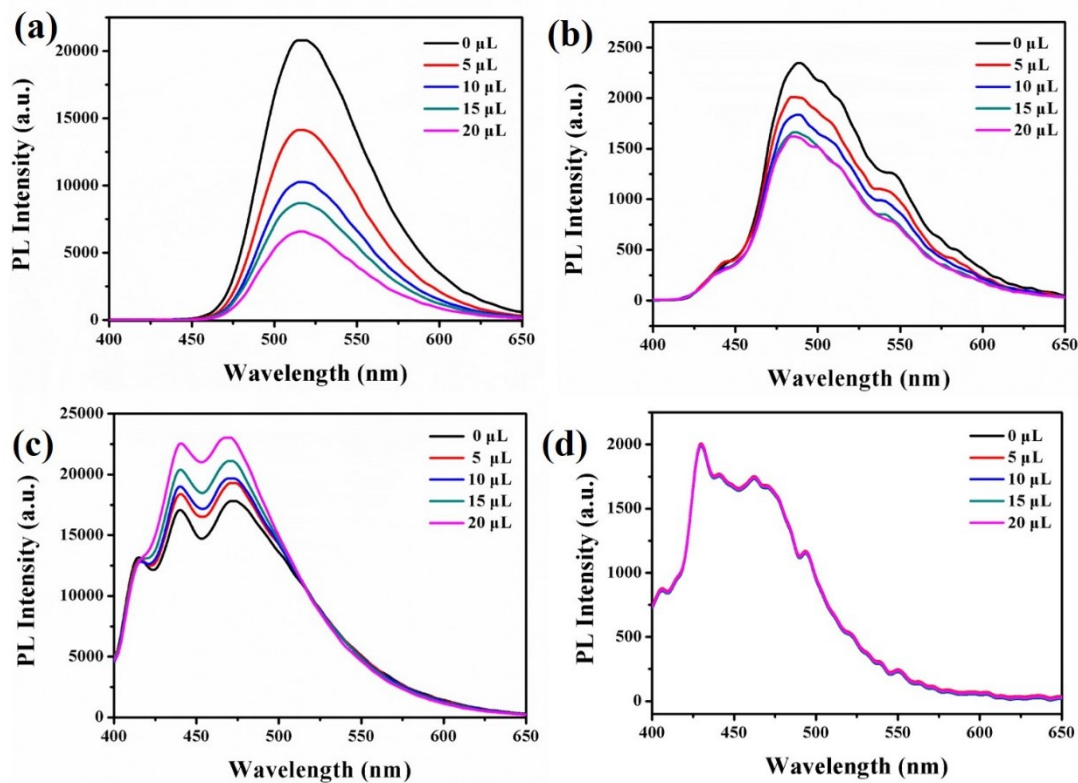


**Figure S4.** High-resolution O 1s and peak fitted XPS spectra of CDs synthesized from different nitrogen sources. (a) CD<sub>1</sub>. (b) CD<sub>2</sub>. (c) CD<sub>3</sub>. (d) CD<sub>4</sub>.

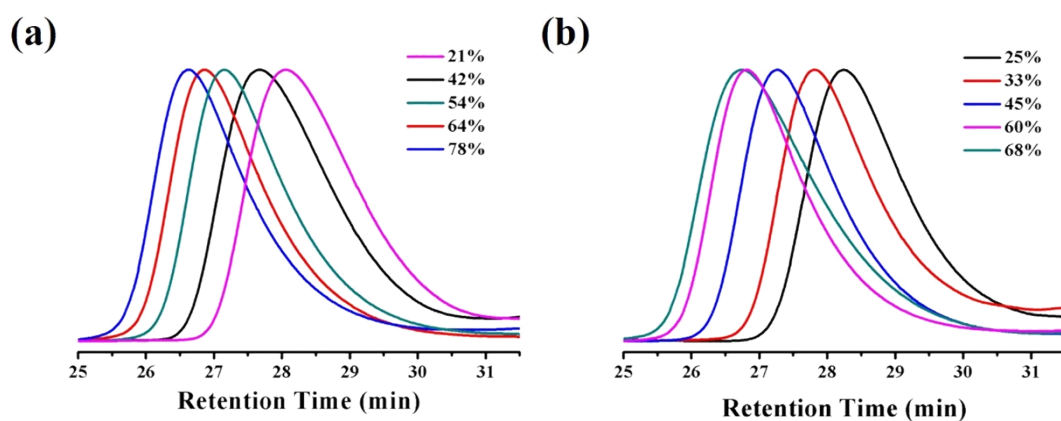


**Figure S5.** (a) The photoluminescence (PL) spectra of CDs synthesized from different nitrogen sources. (b) FT-IR spectra of CDs synthesized from different nitrogen sources.

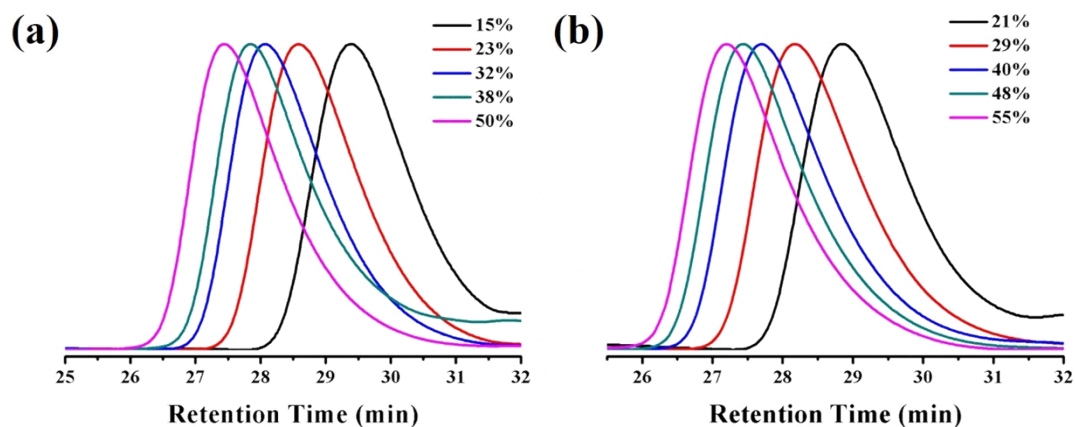




**Figure S6.** Fluorescence quenching study of CDs ( $1 \text{ mg mL}^{-1}$ ) in 2 mL DMF with varying amount of  $0.04 \text{ mol/mL}$  Cu(II)/PMDETA complex. (a) CD<sub>1</sub>. (b) CD<sub>2</sub>. (c) CD<sub>3</sub>. (d) CD<sub>4</sub>.



**Figure S7.** CDs mediated photoinduced ATRP of MMA under blue light irradiation ( $\lambda_{\text{max}} = 465 \text{ nm}$ ,  $2 \text{ mW cm}^{-2}$ ). (a) GPC traces of PMMA catalyzed by CD<sub>1</sub> after different reaction time. (b) GPC traces of PMMA catalyzed by CD<sub>2</sub> after different reaction time.



**Figure S8.** (a) GPC traces of PMMA catalyzed by CD<sub>1</sub> after different reaction times under green light irradiation. ( $\lambda_{\text{max}}=535$  nm,  $1.5$  mW cm<sup>-2</sup>) (b) GPC traces of PMMA catalyzed by CD<sub>1</sub> after different reaction time under red light irradiation ( $\lambda_{\text{max}}=630$  nm,  $1$  mW cm<sup>-2</sup>).

**Table S3.** Different ligands mediated ATRP reactions under green and red-light irradiation.

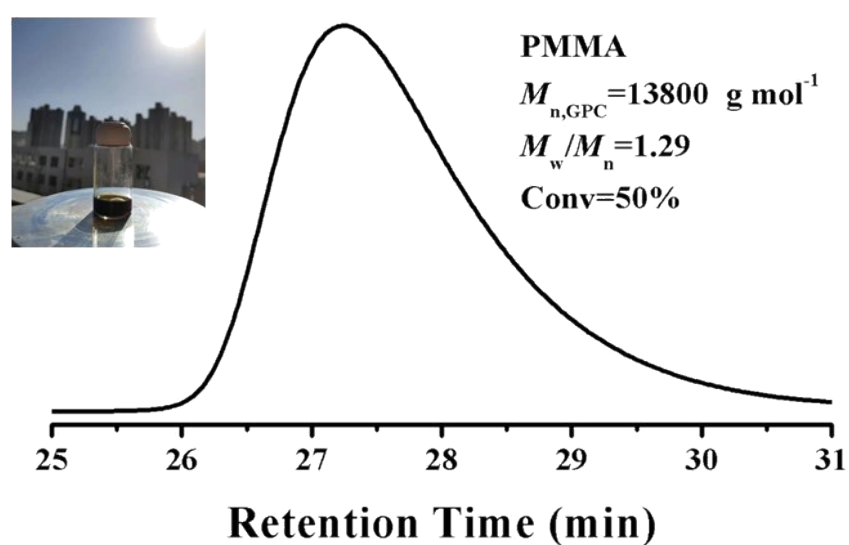
Entry	Light	CDs	Ligand	$M_{n, \text{GPC}}$ (Da)	$M_{n, \text{th}}$ (Da)	Conv. (%)	$\bar{D}$
1	Green	CD <sub>1</sub>	PMDETA	10500	9300	46	1.25
2	Red	CD <sub>1</sub>	PMDETA	10000	9100	45	1.25
3	Green	/	TPMA	/	/	/	/
4	Red	/	TPMA	/	/	/	/

**Table S4.** The results of CDs mediated ATRP reactions under blue light irradiation with different monomer.

Entry	CDs	M	$M_{n, GPC}$ (Da)	$M_{n, th}$ (Da)	Conv. (%)	$\bar{D}$
1	CD <sub>1</sub>	MMA	13300	12100	60	1.28
2	CD <sub>2</sub>	MMA	11600	10500	52	1.27
3	CD <sub>3</sub>	MMA	46200	4500	22	1.52
4	CD <sub>1</sub>	MA	5400	6100	30	1.28
5	CD <sub>2</sub>	MA	3200	4300	21	1.31
6	CD <sub>3</sub>	MA	18200	3700	18	1.85
7	CD <sub>1</sub>	<i>t</i> BA	6000	5300	26	1.35
8	CD <sub>2</sub>	<i>t</i> BA	4300	3700	18	1.32
9	CD <sub>3</sub>	<i>t</i> BA	21800	8100	40	2.01

**Table S5.** The results of CDs mediated ATRP reactions under blue light irradiation with different solvents.

Entry	CDs	Solvent	$M_{n, GPC}$ (Da)	$M_{n, th}$ (Da)	Conv. (%)	$\mathcal{D}$
1	CD <sub>1</sub>	DMF	13300	12100	60	1.28
2	CD <sub>2</sub>	DMF	11600	10500	52	1.27
3	CD <sub>3</sub>	DMF	46200	4500	22	1.52
4	CD <sub>1</sub>	DMSO	15200	14100	70	1.45
5	CD <sub>2</sub>	DMSO	13100	12300	61	1.48
6	CD <sub>3</sub>	DMSO	53200	6100	30	2.01
7	CD <sub>1</sub>	MeCN	7300	5600	27	1.21
8	CD <sub>2</sub>	MeCN	5600	3700	18	1.16
9	CD <sub>3</sub>	MeCN	17900	3100	15	1.52



**Figure S9.** GPC profile of ATRP of MMA with CD<sub>1</sub> under sunlight for 20 h.

$[\text{monomer}]_0/[\text{EBiB}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 200/1/0.1/0.5$ .

## References

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