

Supporting information for:

## Phosphorus and nitrogen codoped carbon dots (PN-CDs) catalyzed Vis-NIR light induced photoATRP

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## **Experimental Section**

## Materials

Acetonitrile (MeCN, AR, KaiTong), Copper(II) bromide ( $\text{CuBr}_2$ , 99%, Aladdin), Diammonium hydrogen phosphate (98.5%, Aladdin), Dimethyl sulfoxide (DMSO, >99%, Aladdin), Ethyl  $\alpha$ -bromophenylacetate (EBPA, 98%, Macklin), Methyl methacrylate (MMA, 99%), Methyl acrylate (MA, 99%) were purchased from Aladdin and used after removing the inhibitor. N,N-dimethyl formamide (DMF, 99%, Aladdin), N,N,N',N'',N'''-Pentamethyldiethylenetriamine (PMDETA, 99%, Aladdin), Poly(ethylene glycol) diacrylate (PEGDA), Sodium citrate (98%, Aladdin).

## Characterizations

Ultraviolet-visible Spectrophotometer (UV-Vis) characterization was performed on a Thermo Fisher Scientific Evolution 300 UV-Vis spectrophotometer. Photoluminescence (PL) spectra were performed on a Thermo Lumina fluorescence spectrometer 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  $\text{Al K}\alpha$  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. NIR-ATRP photopolymerization was performed in a 10ml scintillation bottle, and the reaction mixture was irradiated with an 808 nm near-infrared laser ( $4.0 \text{ mW cm}^{-2}$ ) in a darkroom. The distance between the reaction vessel and the light source is maintained at 5 cm, and a fan is used to reduce

the temperature increase during the polymerization process caused by near-infrared laser irradiation. The polymer number average molecular weights ( $M_n$ ) and dispersities ( $M_w/M_n$ ) were determined by Size Exclusion Chromatography (SEC) (SFD2000). Butylene oxide (THF) was used as eluent at a flow rate of 1 mL min<sup>-1</sup>. The conversion of polymers was calculated by <sup>1</sup>H NMR (Bruker Avance 400 MHz) at 25 °C using CDCl<sub>3</sub> as solvent.

Valence band maximum (VBM) was determined by Valence Band X-ray Photoelectron Spectroscopy (VB-XPS) analysis, the bandgap energy ( $E_g$ ) was estimated by Tauc plots based on UV-Vis Diffuse Reflectance Spectroscopy (DRS) and conduction band minimum (CBM) was estimated by subtracting the bandgap energy from VBM.<sup>1, 2</sup> Firstly, determine VBM. VBM is defined as the energy at which the DOS goes to zero. It was obtained by extrapolating the falling edge of the valence band to the zero energy axes. Taking PN-CDs as an example, the intersection point in Fig. S5 (a) was estimated to be 3.53 eV. Next, instrument work function correction was needed. The value of instrument work function depends on the specific XPS instrument used for measurement, which was 4.20 eV in this case and needs to be subtracted from the intersection position. That is, VBM of PN-CDs was estimated to be 3.53 eV - 4.20 eV = -0.67 eV, relative to vacuum level. To change into NHE potentialis - 4.5 eV - (- 0.67 eV) = -3.83 eV. Secondly, determine the bandgap energy. The  $E_g$  was estimated according to Tauc method, based on the following equation:  $(\alpha h\nu)^{1/\gamma} = B (h\nu - E_g)$ , where  $\alpha$  is the energy-dependent absorption coefficient,  $h$  is the Plank constant,  $\nu$  is the photon's frequency,  $\gamma$  factor equals to 1/2 or 2 for the direct or

indirect transition band gaps, respectively, and B is a constant. The x-axis intersection point in Fig.S5 (b) of the linear fit of the Tauc plot gives an estimation of  $E_g = 2.30$  eV. Thirdly, determine CVM. As the  $E_g$  of a semiconductor refers to the energy needed to excite an electron from the valence band to the conduction band. That is, to give any two of the three parameters -VBM,  $E_g$  and CBM-the third can be calculated. In this case,  $CBM = VBM - E_g = 3.53\text{eV} - 2.30\text{eV} = 0.93\text{eV}$ , relative to NHE.

### **Synthesis of N-CDs and PN-CDs**

Citric acid (1.05g) and L-tryptophan (1.02g) were dissolved in deionized water (10mL), and then the aqueous solution was added to reaction kettle and heated at 180°C for 5h. After the reaction, the sample was cooled naturally to room temperature, filtered with a 220  $\mu\text{m}$  filter, and the mother liquor was dialyzed into a dialysis bag with a trapped amount of 1000Da for 24 hours, and it was dried to obtain the carbon dots sample. The samples were named as N-CDs.<sup>3</sup>Add diammonium hydrogen phosphate (2.311 g) to the precursor and repeat the above steps to obtain a carbon dots sample, named PN-CDs.<sup>4</sup>

### **General procedure of PN-CDs catalyzed photoATRP**

For a typical PN-CDs catalyzed photoATRP, MMA (2 mL, 18.7 mmol), EBPA (13.7  $\mu\text{L}$ , 0.093 mmol),  $\text{CuBr}_2$  (2.08 mg, 0.0093 mmol) and PMDETA (9.76  $\mu\text{L}$ , 0.047 mmol) 200/1/0.1/0.5 ratio solution was added to 10mL flask, then 2 mL DMSO/DMF/MeCN and 10 mg PN-CDs ( $2.5 \text{ mg ml}^{-1}$ ) were added. The flask was sealed, and the oxygen was removed via six freeze-pump-thaw cycles. The visible light induced photoATRP were performed with different LED irradiation: blue ( $\lambda_{\text{max}} =$

460 nm, 2.0 mW cm<sup>-2</sup>), green ( $\lambda_{\text{max}} = 520$  nm, 2.0 mW cm<sup>-2</sup>) and red ( $\lambda_{\text{max}} = 620$  nm, 2.0 mW cm<sup>-2</sup>). NIR-ATRP was performed with 808 nm and 980 nm laser sources (4.0 mW cm<sup>-2</sup>). Samples were extracted periodically with degassing syringe, the monomer conversions were calculated by <sup>1</sup>H NMR, and the molar mass and distributions were characterized by GPC.

### **“ON and OFF” and chain extension experiment**

The "on and off" reaction was established according to the general procedure of PN-CDs catalyzed NIR-ATRP of MMA, with 808 nm laser source. The cycle time of switching light "on and off" was 1 h. Samples were taken followed the cycle time and analyzed through <sup>1</sup>H NMR analysis and GPC.

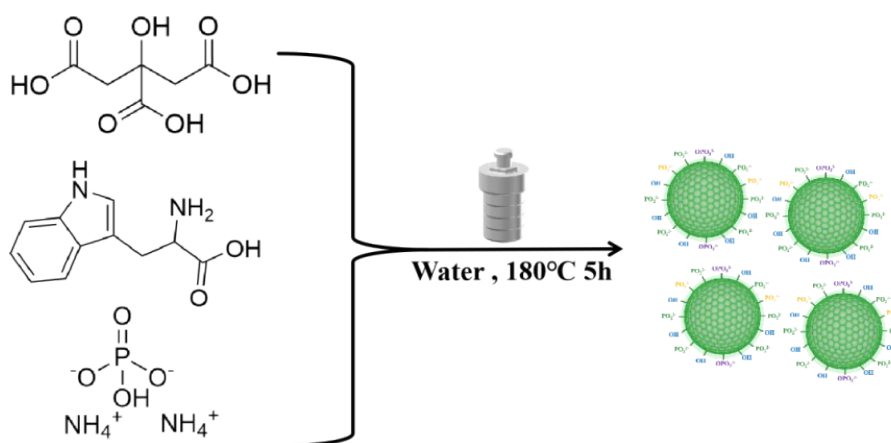
The chain extension was performed with PMMA macroinitiator ( $M_{n,\text{GPC}} = 7500$  g mol<sup>-1</sup>,  $M_w/M_n = 1.24$ ). Typically, MA (0.004 mmol), PMMA macro initiator (160 mg, 0.020 mmol), CuBr<sub>2</sub>/PMDETA (0.002 mmol CuBr<sub>2</sub>, 0.00098 mmol PMDETA) stock solution and DMSO were added in a 10 mL flask. The flask was sealed, and the oxygen was removed via six freeze-pump-thaw cycles and then irradiated with 808 nm laser source for 3 h. After polymerization, samples were extracted for <sup>1</sup>H NMR analysis and GPC analysis.

### **Penetration NIR-ATRP and gel formation**

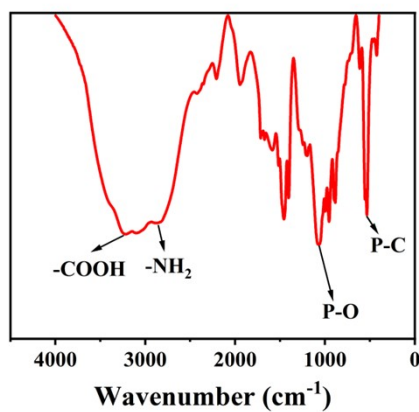
With the same formula of PN-CDs catalyzed photoATRP as listed in the general procedure, penetration NIR-ATRP was performed with a pig skin (2.5 mm) as the barrier. The pig skin was achieved from the DENNIS supermarket and was taken from edible pork. The pig skin packed flask was irradiated with an 808 nm laser for 4

h. The gel formation formula was: 10 mg PN-CDs, MA (1 mL, 3.5mmol), EBPA (4.88  $\mu$ L, 0.028 mmol), CuBr<sub>2</sub> (0.62 mg, 0.003mmol), PMDETA (2.91  $\mu$ L, 0.014 mmol) and PEGDA<sub>600</sub> (0.15 ml, 0.28mmol). The gel formation was performed in a 10 ml vial under the irradiation of 808 nm laser source for 30 min.

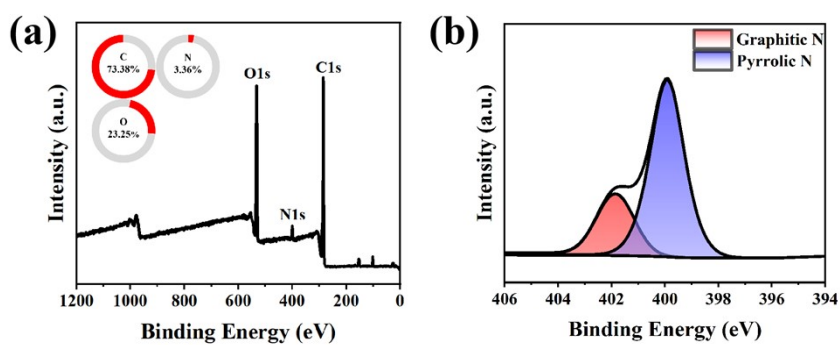
### Supporting Figures



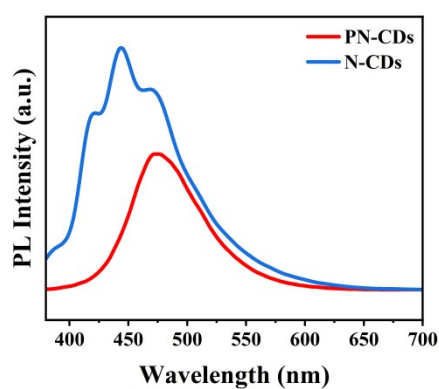
**Figure S1.** The synthetic method of PN-CDs.



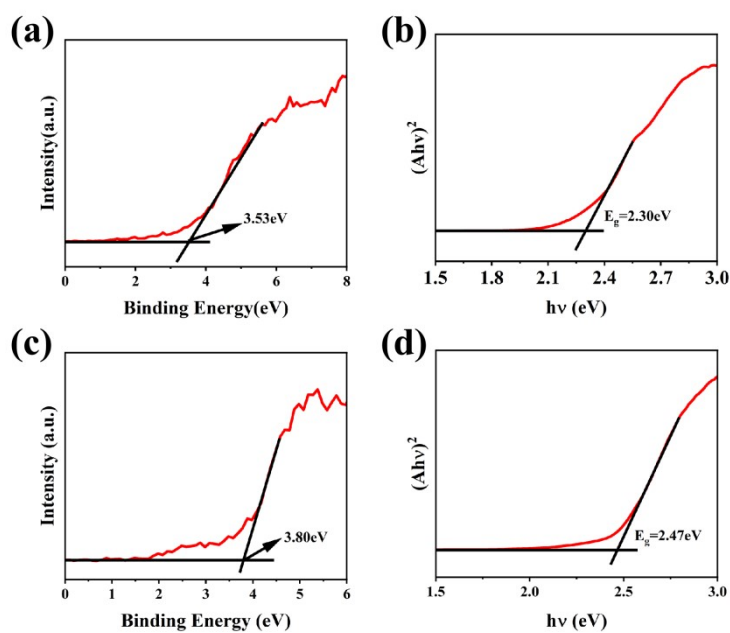
**Figure S2.** FTIR spectrum of PN-CDs.



**Figure S3.** (a) XPS survey spectra of the N-CDs. (b) XPS analysis of N elements.

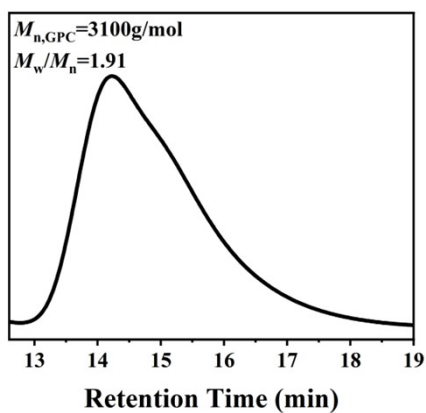


**Figure S4** Fluorescence plot of PN-CDs and N-CDs in DMSO solution under excitation at 365 nm.

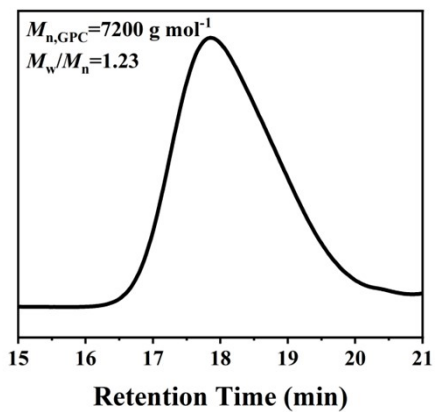


**Figure S5.** (a) VB-XPS spectrum of PN-CDs. (b) Tauc plot of PN-CDs. (c) VB-XPS spectrum of N-CDs. (d) Tauc plot of N-CDs.

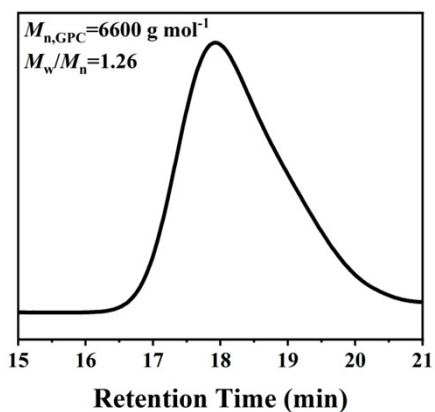




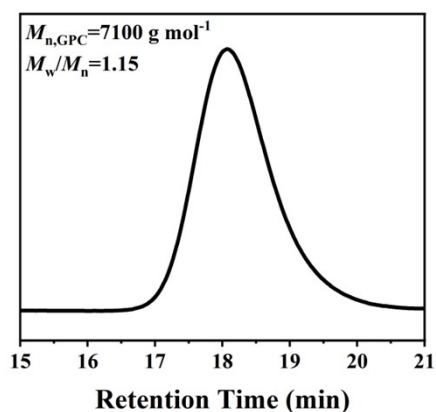
**Figure S6.** GPC traces of the polymerized MMA of the N-CDs at 460 nm.



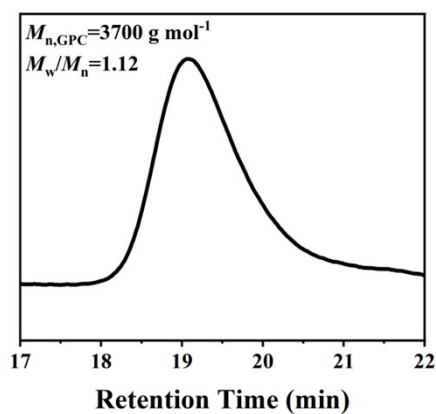
**Figure S7.** GPC traces of the polymerized MMA of the P-CDs at 520 nm.



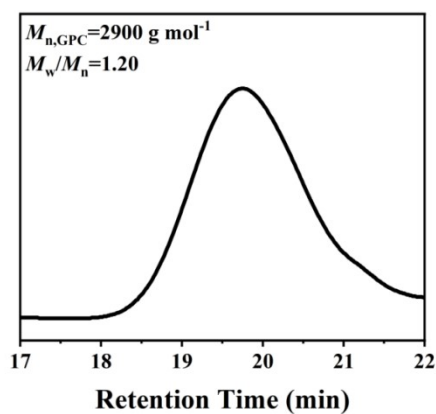
**Figure 8.** GPC traces of the polymerized MMA of the P-CDs at 620 nm.



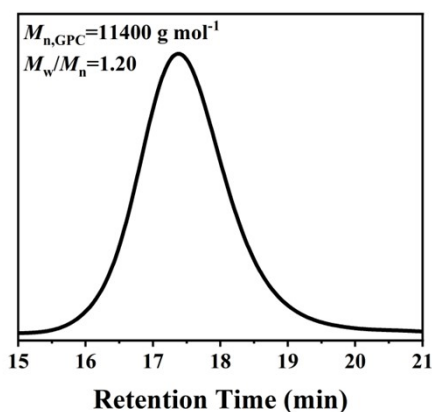
**Figure S9.** GPC traces of the polymerized MMA of the P-CDs at 980 nm.



**Figure S10.** GPC traces of P-CDs polymerized MMA at 808 nm with DMF solution.



**Figure S11.** GPC traces of P-CDs polymerized MMA at 808 nm with MeCN solution.



**Figure S12.** GPC traces of the polymerized MA of the P-CDs at 808 nm.

**Table S1** Results of P-CDs mediating the ATRP response under different light irradiation.<sup>a</sup>

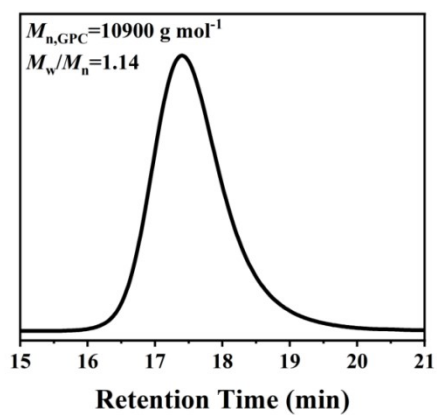
Entry	monomer	CDs <sup>b</sup>	$E_{m \lambda_{max}}$ <sup>c</sup>	solvent	$M_{n,th}$ <sup>d</sup> (Da)	$M_{n,GPC}$ <sup>e</sup> (Da)	$M_w/M_n$	Conv. <sup>f</sup> (%)
1	MMA	P-CDs	520	DMSO	9253	10900	1.14	45%
2	MMA	P-CDs	620	DMSO	8853	10000	1.18	43%
3	MMA	P-CDs	980	DMSO	8052	9400	1.20	39%
4	MMA	P-CDs	808	DMF	4047	5900	1.14	19%
5	MMA	P-CDs	808	MeCN	2645	4600	1.15	12%

<sup>a</sup>Reaction conditions:  $[MMA]_0/[EBPA]_0/[CuBr_2]_0/[PMDETA]_0 = 200/1/0.1/0.5$ . at room temperature for 6 h. <sup>b</sup>The dosage of P-CDs or N-CDs was 2.5 mg ml<sup>-1</sup> for all the polymerization.

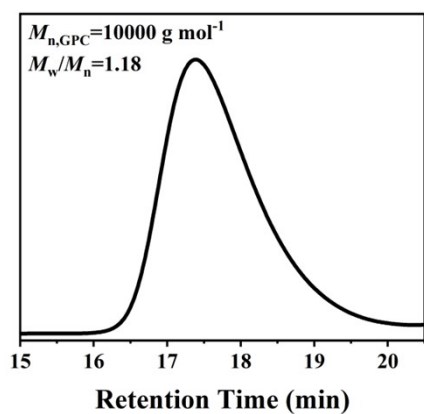
<sup>c</sup>Reactions were performed in light reactors with light intensity 2.0 mW cm<sup>-2</sup> or 4.0 mW cm<sup>-2</sup>, different wavelengths.

<sup>d</sup>Calculated on the basis of conversion (i.e.,  $M_{n,th} = M_{EBPA} + 200 \times \text{conversion} \times M_{monomer}$ ).

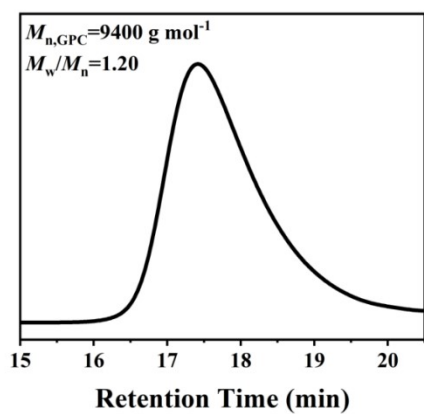
<sup>e</sup>Determined by GPC in THF, based on linear PMMA as the calibration standard. <sup>f</sup>Monomer conversions were determined by <sup>1</sup>H NMR spectroscopy.



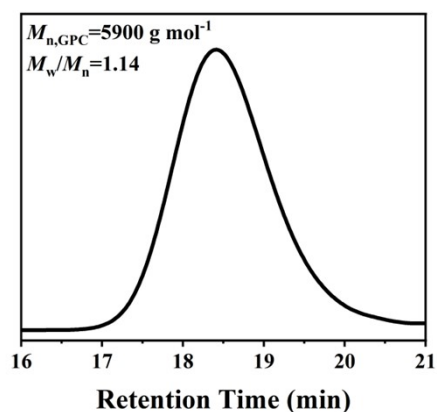
**Figure S13.** GPC traces of polymerized MMA extended to 6 h at 520 nm.



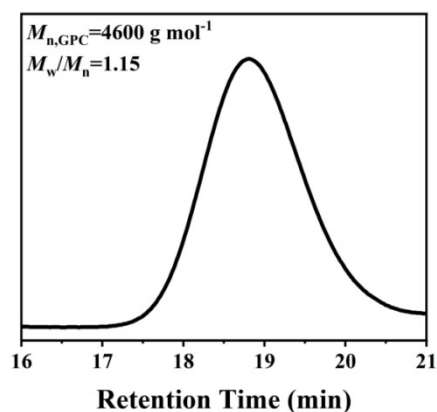
**Figure S14.** GPC traces of polymerized MMA extended to 6 h at 620 nm.



**Figure S15.** GPC traces of polymerized MMA extended to 15 h at 980 nm.



**Figure S16.** GPC traces of polymerized MMA extended to 6 h at 808 nm with DMF solution.



**Figure S17.** GPC traces of polymerized MMA extended to 6 h at 808 nm with MeCN solution.

## References

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