

***Supporting Information :***

**The Size Effect of Semiconductor Quantum Dots (QDs) as  
Photocatalysts on PET-RAFT Polymerization**

Yachao Liang,<sup>§</sup> Huanhuan Ma,<sup>§</sup> Wenjie Zhang, Zhe Cui, Peng Fu, Minying Liu, Xiaoguang Qiao\*  
and Xinchang Pang\*

Henan Joint International Research Laboratory of Living Polymerizations and Functional Nanomaterials, Henan Key Laboratory of Advanced Nylon Materials and Application, School of Materials Science and Engineering, Zhengzhou University, Zhengzhou, 450001, China.

\*To whom correspondence should be addressed. <sup>§</sup>These authors contributed equally to this work.

Corresponding Author:

[pangxinchang1980@163.com](mailto:pangxinchang1980@163.com)

[joexiaoguang@hotmail.com](mailto:joexiaoguang@hotmail.com)

## ***Materials.***

Monomers Methyl methacrylate (MMA, 99%, Aladdin), methyl acrylate (MA, 99%, Aladdin), *n*-butyl methacrylate (BA, 99%, Aladdin), *tert*-butyl acrylate (*t*BA, 99%, Aladdin) and styrene (St, 99%, Aladdin) were passed through a column filled with basic alumina oxides to remove inhibitors prior to use. Selenium (Se,  $\geq 99.999\%$ , Aladdin), cadmium oxide (CdO, 99.99%, Aladdin), oleic acid (OA, AR, Aladdin), 1-octadecene (ODE,  $>90.0\%$ , Aladdin), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDTC, 97%, Acme), tri-*n*-octylphosphine (TOP, 90%, J&K), *n*-hexane (AR, Maclin), methanol (AR, Macklin), Triethylamine (TEA, AR, Aladdin) and 4-cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB,  $>97\%$ , Aladdin) were used as received. Tetrahydrofuran (THF, AR, Aladdin), N,N-dimethyl formamide (DMF, 99%, Aladdin), dimethyl sulfoxide (DMSO,  $>99\%$ , Aladdin), Acetonitrile (MeCN, AR, Kai Tong), Anisole (AR, Macklin) and Toluene (PhMa, AR, Kai Tong) were purified to further remove H<sub>2</sub>O.

## ***Characterizations.***

The molecular weights and the distribution of polymers were determined with gel permeation chromatography (GPC) measurement on the equipment (SFD2000) using THF as the eluent. The conversion of polymers were calculated by <sup>1</sup>H NMR (Bruker Avance 400MHz) at 25°C using CDCl<sub>3</sub> as solvent. Power X-ray diffraction (XRD) were obtained on a Pert PRO with a scan step of 2° and the scan range from 20° to 60°. UV-Vis absorption spectra were collected using a Thermo Evolution, and Photoluminescence (PL) spectra were performed on a Thermo Lumina fluorescence

spectrometer with a 465 nm excitation wavelength at room temperature ( $\rho_G=0.28$  mg·mL<sup>-1</sup>,  $\rho_Y=0.36$  mg·mL<sup>-1</sup>, and  $\rho_R= 1.33$  mg·mL<sup>-1</sup>). Dynamic light scattering (DLS) measurements on different CdSe QDs were performed in a Nanotracs wave II (Microtrac Inc) using the software supplied by the manufacturer. Transmission electron microscopy (TEM) measurements were conducted on a JEM-2100.

### ***Preparation of the CdSe QDs***

CdSe QDs with different particle sizes were prepared through hot injection process according to literature<sup>1, 2</sup>. Typically, two different precursor solution were prepared in two separate procedures: (1) Se pellets (0.790 g, 10.0mmol) and TOP (10 ml, 20mmol) were first added to a 50 ml flask and stirred at 100°C under nitrogen atmosphere until the mixture became transparent. (2) CdO (0.318 g, 25.0 mmol), OA (3.45ml, 100 mmol), and 9 ml ODE were mixed and heated to 220 °C under a nitrogen atmosphere until the mixture became transparent.

For the following hot injection process, <sup>1, 3</sup> 50 ml 3-neck flask was degassed by nitrogen for 10 min before the addition of 10 ml of ODE, then the flask was degassed for another 20 min. 12 ml 0.2 M cadmium oleate was introduced to the flask and heated to 270°C . Once the temperature reached the desired temperature, 1.5 ml 1 M TOPSe solution was quickly injected (< 1 s) and the temperature was set to 220°C . The growth process of nucleation was controlled at 10 minutes and quenched by water bath. The QDs were diluted with a certain amount of hexanes, and precipitated in methanol, being collected through centrifugation. The purified QDs was stored in hexane for further use.

### ***CdSe QDs-catalyzed PET-RAFT polymerizations.***

In a typical PET-RAFT polymerization, CdSe QDs (5 mg), MMA (1 ml, 9.43 mmol, 200 equiv), CPADB (13 mg, 0.047 mmol, 1 equiv), TEA (40  $\mu$ l, 0.282 mmol, 6 equiv) and DMF (1 ml) were charged in a 10 mL Schlenk bottle. The system was degassed by three freeze-pump-thaw cycles and backfilled with nitrogen. The reaction was performed under a visible LED light irradiation at room temperature. Samples were taken at predetermined timed intervals for GPC and NMR analysis, respectively.

### ***“on/off” Reactions.***

The light switch experiments were performed in the same fashion. A reaction bottle (10 ml) was charged with CdSe QD (5 mg), MMA (1 ml, 9.43 mmol, 200 equiv), CPADB (13 mg, 0.047 mmol, 1 equiv), TEA (40  $\mu$ l, 0.282 mmol, 6 equiv) and DMF (1 ml) and deaerated by three freeze-pump-thaw cycles, backfilled with nitrogen. The reaction was irradiated under a blue LED light ( $\lambda_{\text{max}}=465$  nm). To verify the temporal control, the light was turned on or off with a certain period of time and switched for several times. Samples were taken at time intervals using a degassed syringe and analysed by GPC and NMR, respectively

### ***General procedure for chain extension experiment.***

In order to study the available of chain end, a similar system was irradiated under blue LED light. The CTA was replaced by a PMMA macroinitiator. The reaction was carried on 24 h, and underwent precipitation and separation. After purified, the product polymer was analyzed by GPC.

**Table S1. Parameters of each size CdSe QDs.**

Sample name	Fluorescence	$D_n$ (nm)	$\lambda_{\max}$ Abs (nm)	$\lambda_{\max}$ PL (nm)
G	Green	3.8	528	508
Y	Yellow	5.1	548	535
R	Red	6.8	578	573

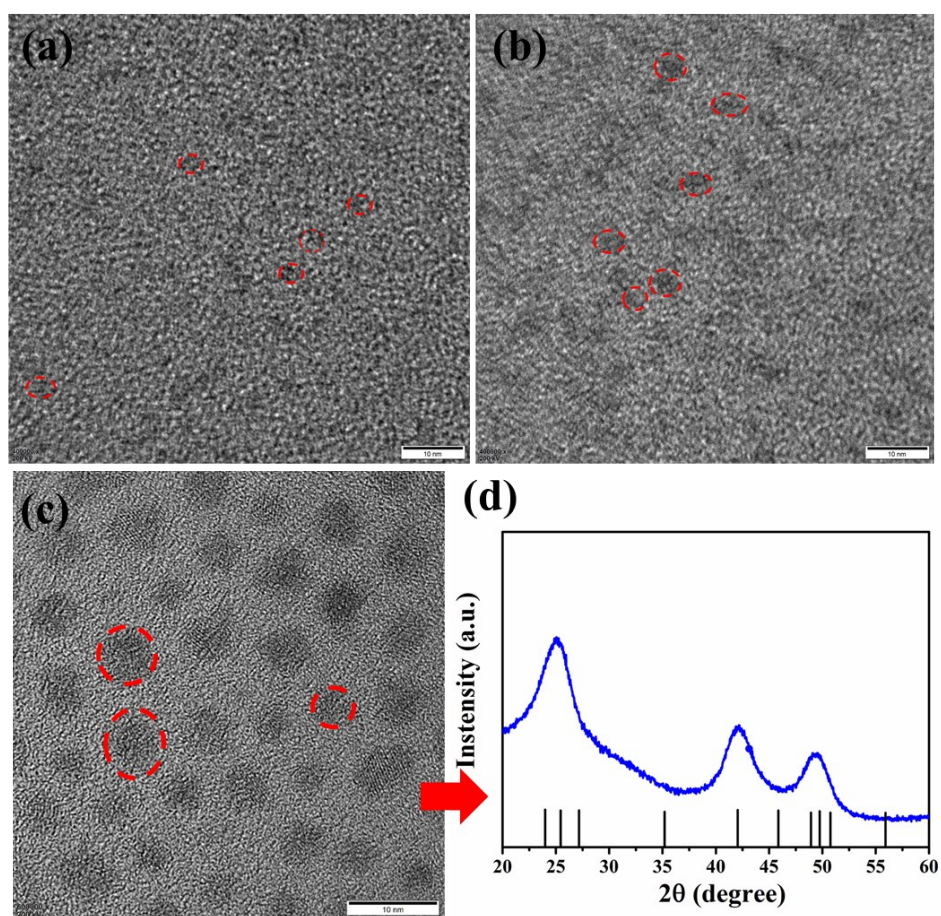


Figure S1. TEM images of CdSe QDs with different sizes: (a)  $D_{n1}=3.8$  nm; (b)  $D_{n2}=5.1$  nm and (c)  $D_{n3}=6.8$  nm. (d) Typical X-ray diffraction pattern of CdSe QDs.

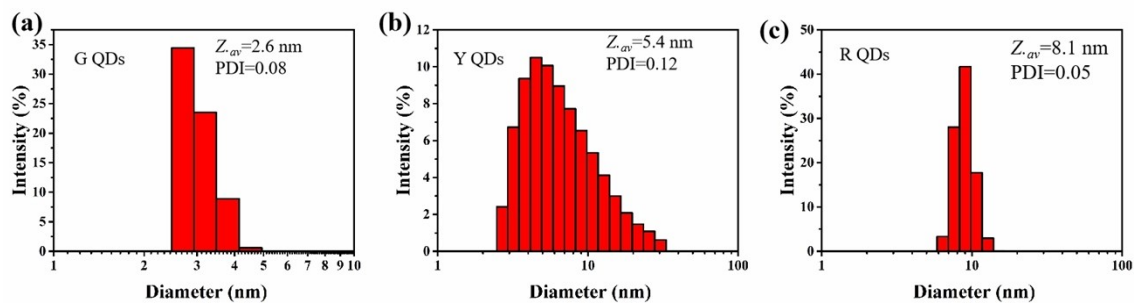


Figure S2. Particle size determination of different CdSe QDs by dynamic light scattering (DLS). (a) G QD, (b) Y QD, and (c) R QD.

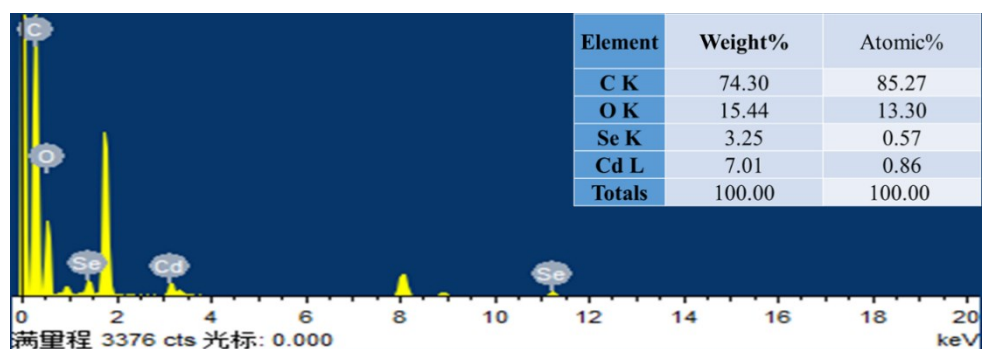


Figure S3. EDS of CdSe quantum dots.

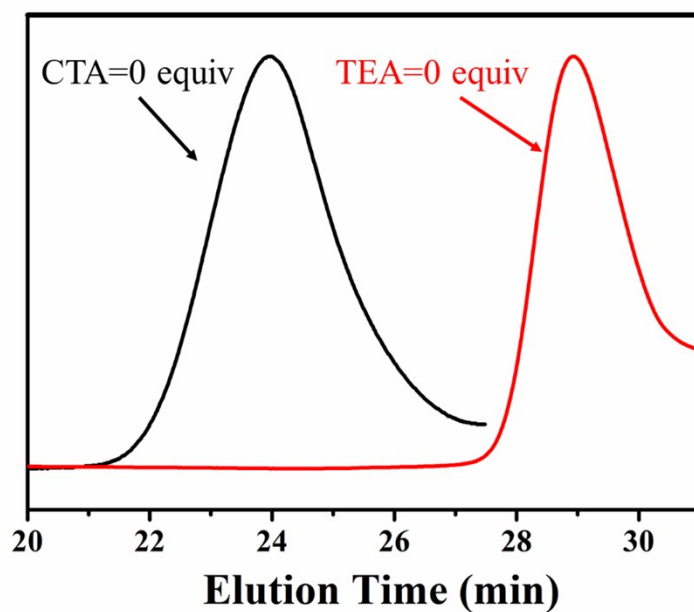


Figure S4. GPC traces of PET-RAFT control polymerization of MMA catalyzed by CdSe QD in Table 1 and S2. (Dark line is without CTA and red line is without TEA).

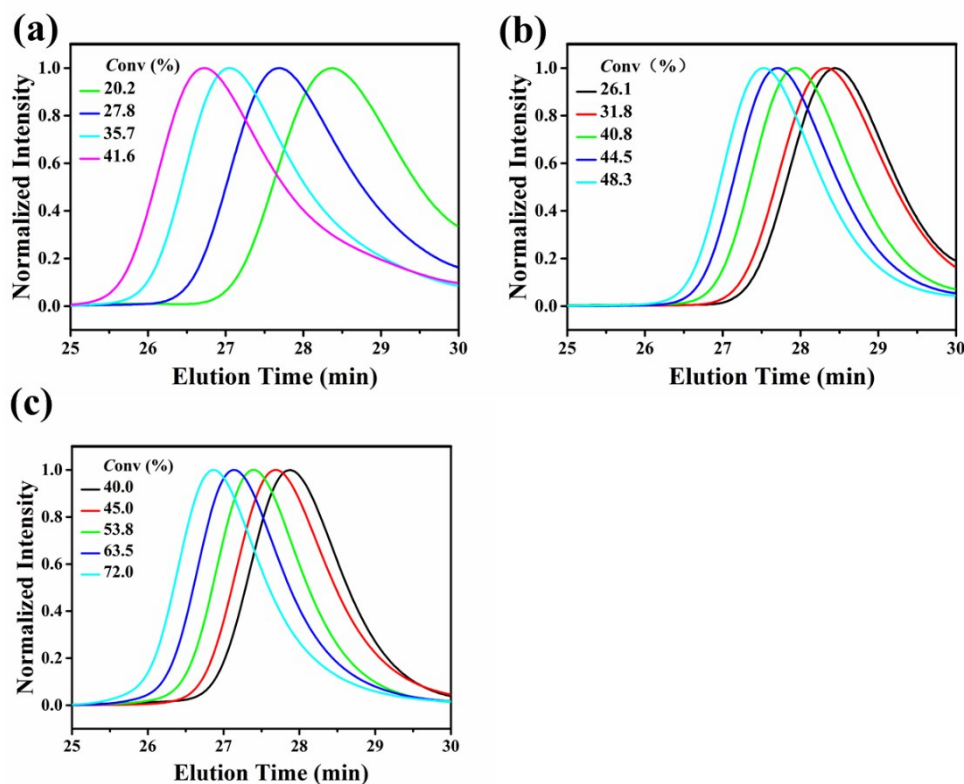


Figure S5. GPC traces of PET-RAFT polymerization of MMA catalyzed by CdSe QD with different size.  $D_n =$  (a) 3.8 nm, (b) 5.1 nm, and (c) 6.8 nm. Room temperature;

Blue light; and [MMA]:[CPADB]:[TEA]= [200]:[1]:[6].

Table S2. R QDs catalyzed PET-RAFT polymerization of MMA with different amount of TEA (blue light,  $\lambda = 465$  nm).

Entry	[MMA]:[CTA]:[TEA] <sup>a</sup>	Solvent	CdSe QDs (mg)	Conv <sup>b</sup> (%)	<i>M</i> <sub>n,th</sub> (kDa)	<i>M</i> <sub>n,GPC</sub> (kDa)	<i>D</i>
C1	[200]:[1]:[0]	DMF	5	22.8	4.6	4.2	1.23
1	[200]:[1]:[3]	DMF	5	53.9	10.9	29.7	1.56
2	[200]:[1]:[4.5]	DMF	5	58.8	11.9	14.1	1.17
3	[200]:[1]:[6]	DMF	5	72.0	14.6	16.4	1.17
4	[200]:[1]:[9]	DMF	5	69.2	14.0	15.1	1.19
5	[200]:[1]:[12]	DMF	5	72.0	14.6	19.6	1.21

<sup>a</sup> All reactions operated for 28 h with CPADB as the CTA. <sup>b</sup> Monomer conversion was calculated based on <sup>1</sup>H-NMR analysis.



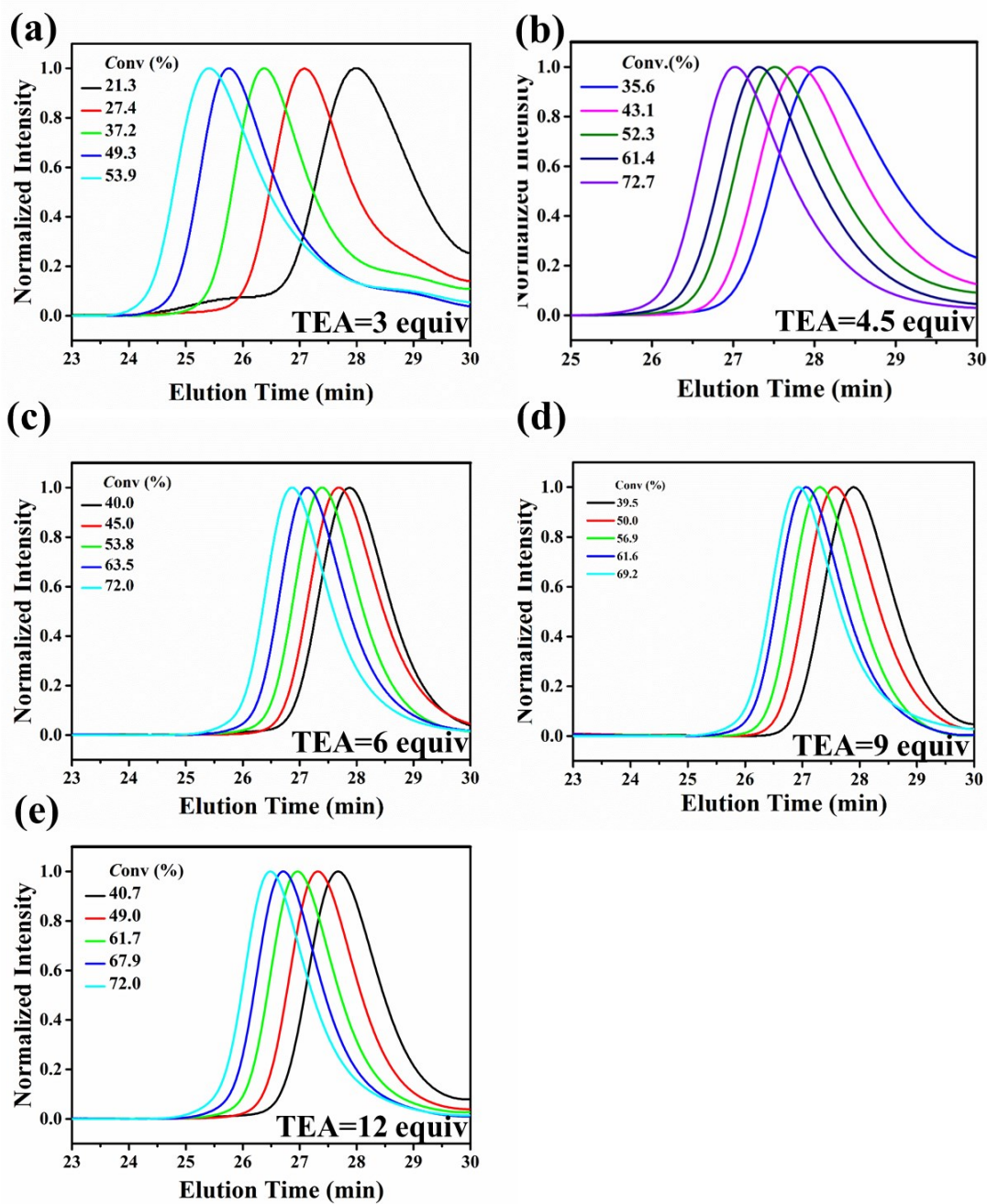


Figure S6. GPC traces of PET-RAFT polymerization of MMA catalyzed by CdSe QD with different equiv TEA. [MMA]:[CPADB]:[TEA]=(a) [200]:[1]:[3], (b) [200]:[1]:[4.5], (c) [200]:[1]:[6], (c) [200]:[1]:[9] and (d) [200]:[1]:[12]. Room temperature; Blue light; and R QDs.

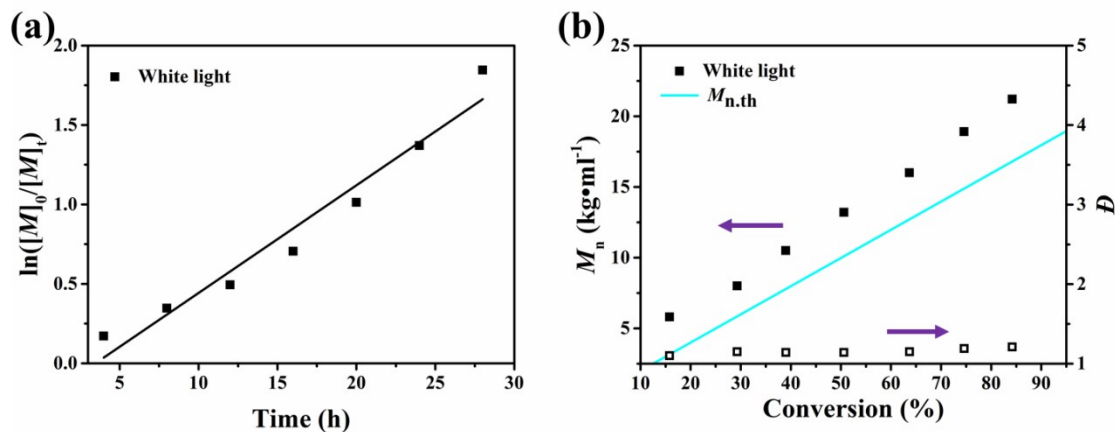


Figure S7. Kinetic plots for PET-RAFT polymerization of MMA catalyzed by CdSe QDs under white light. (a)  $\ln([M]_0/[M]_t)$  vs time and (b)  $M_n$  vs monomer conversion.

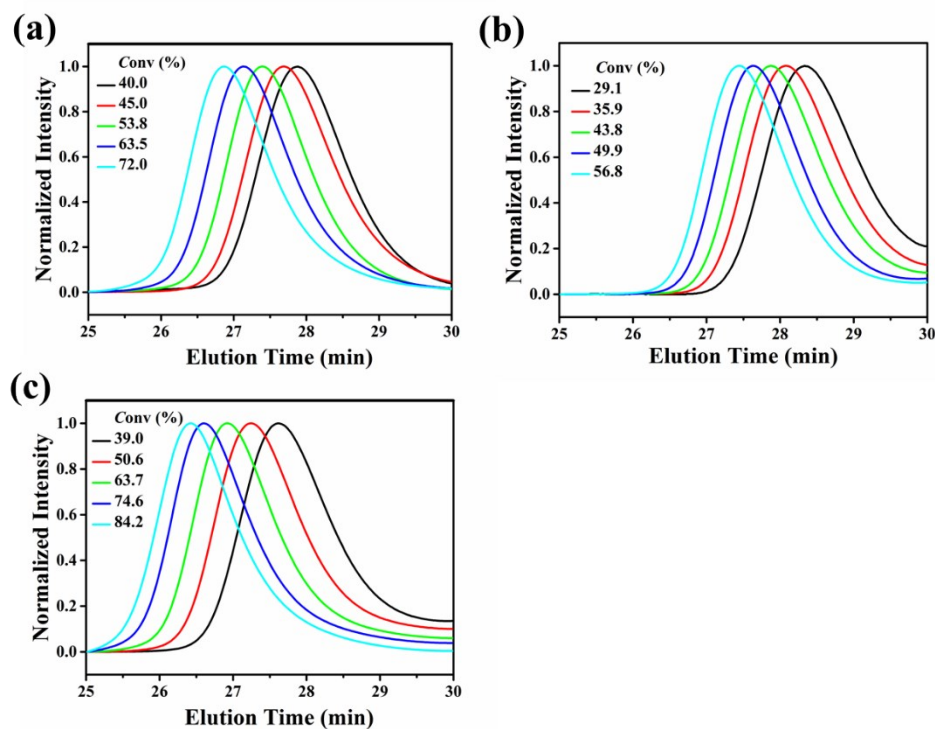


Figure S8. GPC traces of PET-RAFT polymerization of MMA catalyzed by CdSe QD under different wavenumber light. (a) Blue light ( $2.9 \text{ mW/cm}^2$ ), (b) green light ( $1.7 \text{ mW/cm}^2$ ), (c) white light ( $2.6 \text{ mW/cm}^2$ ). Room temperature; R QDs; and  $[\text{MMA}]:[\text{CPADB}]:[\text{TEA}]=[\text{200}]:[\text{1}]:[\text{6}]$ .

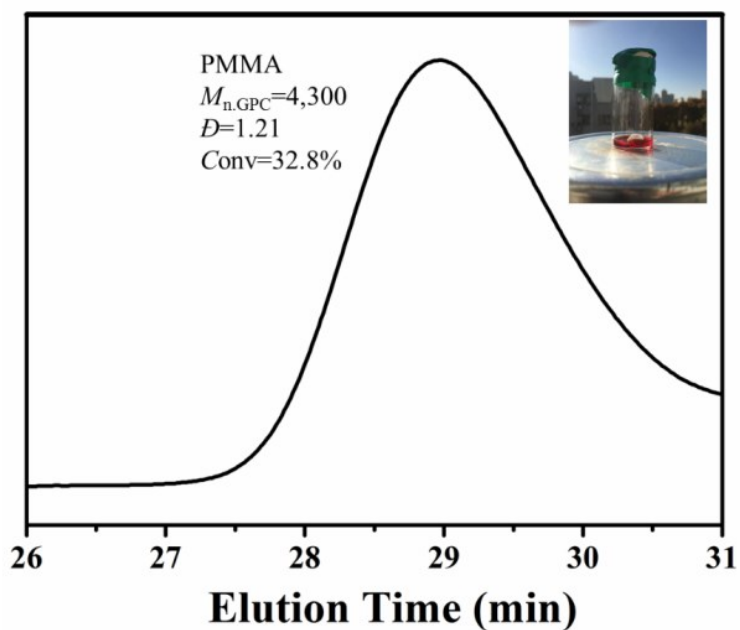


Figure S9. GPC trace of the PET-RAFT of MMA under sunlight. Room temperature; R QDs; and [MMA]:[CPADB]:[TEA]= [200]:[1]:[6]

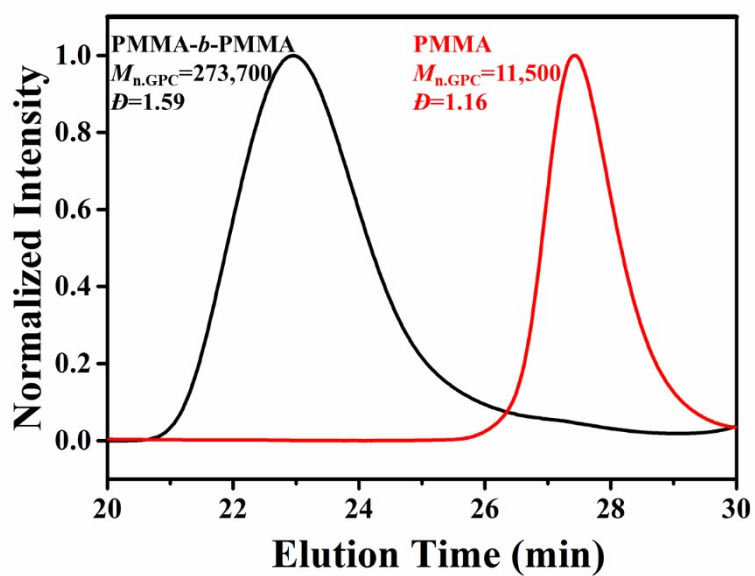


Figure S10. GPC traces of chain extension experiments. Room temperature; Blue light; and R QDs.

**Table S3. CdSe QDs catalyzed PET-RAFT polymerization**

Entry	Monomer	[M]:[CTA]:[TEA] <sup>a</sup>	Solvent	Time(h)	Conv <sup>b</sup> (%)	$M_{n,th}$ (kDa)	$M_{n,GPC}$ (kDa)	$\bar{D}$	$I^*$ <sup>c</sup>
1	MMA	[200]:[1]:[6]	DMSO	28	77.0	15.6	17.7	1.12	0.88
2	MMA	[200]:[1]:[6]	PhMe	28	–	–	–	–	–
3	MMA	[200]:[1]:[6]	THF	28	19.8	4.0	5.9	1.11	0.68
4	MA	[200]:[1]:[6]	DMF	32	29	5.0	13.1	1.18	0.38
5	<i>t</i> BA	[200]:[1]:[6]	DMF	32	94	24.3	22.0	1.19	1.10
6	St	[200]:[1]:[6]	DMF	32	14.6	3.0	3.7	1.19	0.81
7	BA	[200]:[1]:[6]	DMF	32	75.9	21.7	23.0	1.14	0.94
8	MMA	[100]:[1]:[6]	DMF	28	79.5	8.1	11.5	1.16	0.70
9	MMA	[300]:[1]:[6]	DMF	44	86	26.0	32.2	1.18	0.81

<sup>a</sup>CTA for entry C1-C3 and 1-3 was CPADB, and entry 4-7 was CPDTC. <sup>b</sup>Monomer conversion was calculated based on <sup>1</sup>H-NMR analysis.

<sup>c</sup>Initiator efficiency ( $I^*$ ) was determined by  $M_{n,th}/M_{n,GPC}$ .

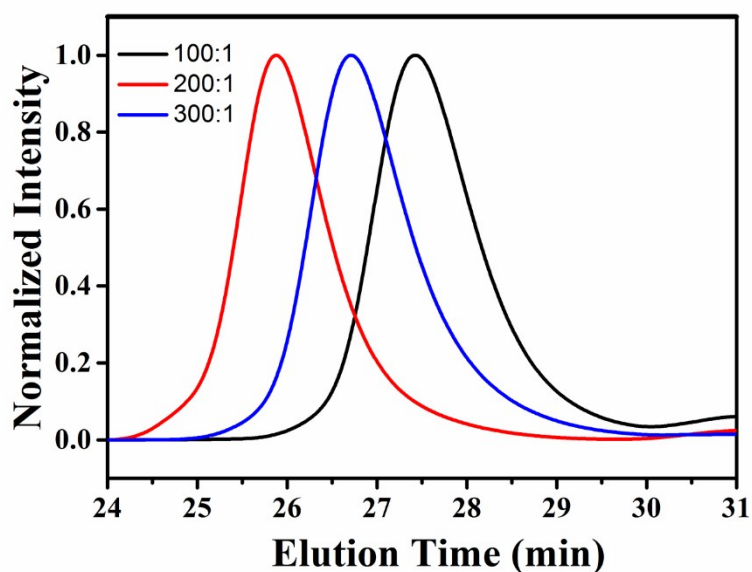


Figure S11. GPC traces of PET-RAFT polymerization of MMA catalyzed by CdSe QD with different DP. Room temperature; Blue light; and R QDs.

## REFERENCES

- (1) Caputo, J. A.; Frenette, L. C.; Zhao, N.; Sowers, K. L.; Krauss, T. D.; Weix, D. J. General and Efficient C-C Bond Forming Photoredox Catalysis with Semiconductor Quantum Dots. *J. Am. Chem. Soc.* **2017**, *139* (12), 4250-4253.
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- (3) Peng, X.; Manna, L.; Yang, W.; Wickham, J.; Scher, E.; Kadavanich, A.; Alivisatos, A. P. Shape control of CdSe nanocrystals. *Nature* **2000**, *404* (6773), 59-61.