Supplementary Information

PET-RAFT polymerization catalyzed by cadmium selenide quantum dots (QDs): *Grafting-from* QDs photocatalysts to make polymer nanocomposites

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Materials

All the chemicals used in this study including methyl methacrylate (MMA), butyl methacrylate (BMA), benzyl methacrylate (BzMA), 2,2,2-Trifluoroethyl methacrylate (TFEMA), oligo-(ethylene glycol) methyl ether methacrylate (OEMA, average M_n= 500 g/mol), butyl acrylate (BA), methyl acrylate (MA), 4-Cyano-4-(phenylcarbonothioylthio) pentanoic acid (CPADB), 2-Cyano-2-propyl dodecyl trithiocarbonate (CPDT), cadmium oxide, selenium, 1-octadecene (ODE), oleic acid, tri-n-octylphosphine and *N, N*-Diisopropylethyamine (DIPEA, purified by distillation, 99.5%) were purchased from Sigma Aldrich and used as received unless otherwise specified. All monomers were used after disinhibition by percolating over a column of the mixture of neutral alumina and silica gel (particle size 0.063nm-0.200nm). Solvents used for reactions including dimethyl sulfoxide (DMSO), *N,N'*-dimethylacetamide (DMA), N,N'-dimethylformamide (DMF), acetonitrile (MeCN) and toluene were dried with molecular sieves before using. 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid, 2-Cyano-2-propyl dodecyl trithiocarbonate and Cadmium selenide (CdSe) were stored in a glove box and covered with aluminum foil.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectra were obtained on a NMR Bruker 500 MHZ operated at room temperature. Wilmad low pressure/vacuum NMR tube (Sigma-Aldrich, catalog number Z568139) was used for kinetic studies. Absorption and photoluminescence spectra were measured with Agilent Cary-60 UV-Vis spectrometer and Cary Eclipse fluorometer, respectively. Gel permeation chromatography (GPC) was carried out on an Agilent 1260 Infinity LC system and calibrated with polystyrene standards in THF. Fourier transform infrared spectroscopy (FTIR) spectra was recorded using a Nicolet FTIR Infrared Microscope in the ATR mode. Dynamic light scattering (DLS) was spectrum recorded using NanoPlus-3 particle analyzer. Transmission electron microscopy (TEM) was executed using a JEOL Field Emission Gun Transmission Electron Microscope at an accelerating voltage of 160 kV and JEOL 2010 Transmission Electron Microscope (TEM) with Cryo at an accelerating voltage of 80 KV. Commercially available High Led Spot Lamps with switchable light wavelength were used for photopolymerization and light intensity was measured by photometer.

Preparation of the CdSe quantum dots (QDs).

In a glovebox, selenium pellets (0.790 g, 10.0 mmol) were combined with 10 mL of tri-*n*-octylphosphine (20 mmol) and was stirred and heated to 100°C until the pellets were fully dissolved. In a separate procedure, precursor solution (0.2 M) was prepared according to a previous report.[1] A mixture of cadmium oxide (0.318 g, 25.0 mmol), oleic acid (3.45 mL, 100 mmol), and 9 mL ODE was heated to 220°C under a nitrogen atmosphere until the solution turned clear and colorless, in approximately one hour. The product was a white solid at room temperature and needed to be heated to 60°C before use.

CdSe QDs were synthesized using an adapted hot injection method as previously reported.[1,2] In a 100 mL 3-neck flask, 10 mL of ODE was degassed for 30 minutes by evacuating the flask to below 20 mTorr. Then, 15 mL 0.2 M cadmium oleate was added under nitrogen and the mixture was heated to 270°C. Once the solution reached the set temperature, 1.5 mL 1 M TOPSe solution was injected and the temperature was set to 220°C. The reaction was allowed to grow for six minutes and quenched by cooling the flask, first with cool air followed by a water bath. The QD was washed with methanol and hexanes, and the resulting QD product in hexanes was stored in a glove box.

General procedure for monophase ligand exchange to graft chain transfer agent (CTA)

To 0.05 mL CdSe QDs stock solution, 3.2 mg 4-Cyano-4-(phenylcarbonothioylthio)pentanoic acid (CPADB) and 0.25 mL methyl methacrylate (MMA) were added. ([monomer]: [CTA]= 200:1) The mixture was covered with aluminum foil and stirred, until the solution became clear (around 5 mins in MMA). The chain transfer agent grafted QDs were used directly in the polymerization step without any further purification.

General Procedure for characterizing grafting of the RAFT agent to the CdSe QDs

To characterize the grafting of the RAFT agent to the quantum dot, Fourier transform infrared spectroscopy (FTIR) using a Nicolet FTIR Infrared Microscope in the ATR mode and NMR spectroscopy was utilized. The mixture from the grafting procedure was precipitated with methanol and centrifuged to obtain QDs precipitate, re-dissolved in small amount chloroform and repeat this procedure for 3 times to wash out free CTA. The precipitate was re-dissolved in chloroform for FTIR detection and dissolved in deuterated chloroform to obtain ^{1}H NMR.

General procedure for photocatalyzed RAFT polymerization of MMA

0.25 mL of DMF and 20 μL of DIPEA were added to the 0.25 ml solution of QDs grafted with CPADB in MMA in a 7 mL vial equipped with a rubber septum. The mixture was deaerated by three freeze-pump-thaw cycles, backfilled with argon, and constantly stirred at ambient temperature under irradiation of a 10 W household 480 nm blue LED lamp for 24 hours. The reaction vial was placed approx. 15 cm from the lamp, where the light intensity was 10 mW/cm^2, unless otherwise specified. The whole setup was covered with aluminum foil to block exposure any other light sources. In control experiments when the reaction was conducted in the presence of oxygen, mixture simple was left as prepared without any degassed procedure and closed with a vial cap. The solution is around 0.5 mL and the vial headspace with air is around 6.5 ml. When the reaction was conducted in the dark, the reaction vial was completely wrapped with aluminum foil to block exposure to any light source from entering the vial.

To determine the monomer conversion by ^{1}H NMR, 2-3 drops of the polymerization mixture was dissolved in 0.5 mL deuterated chloroform and used as such for ^{1}H NMR analysis. Monomer conversion of MMA polymerization was calculated by the following equation using ^{1}H NMR spectroscopy : Conversion = $(1- (I^{5.5} + I^{6.0})/2/I^{(3.5 \sim 3.7)}/3)X\ 100\%$. $I^{5.5}$ and $I^{6.0}$ are the integration of the peak located at 5.5 and 6.0 ppm. These peaks represent two protons on the carbon-carbon double bond from the methyl methacrylate monomers. $I^{(3.5 \sim 3.7)}$ is the integration of the peaks ranging from 3.5-3.7 ppm, which represents the three protons of methoxy from both monomers and polymers. A couple milligrams of polymer was dissolved in THF, then filtered with PTFE (pore size 0.2 μm) filters, and then analyzed on the GPC. The resulting solution was precipitated in 50 mL methanol under stirring for overnight. The polymer product was then collected by filtration.

General procedure for photocatalyzed RAFT polymerization of BA

To 0.05 mL CdSe QDs stock solution, around 3.9 μL CPDT and 0.33 mL BA was added. The mixture was stirred for 3 minutes covered with aluminum foil to block exposure any other light sources. Then 0.25 mL of DMF and 20 μL of DIPEA was added and mixture was degassed by three freeze-pump-thaw cycles followed with backfilling with argon. The reaction vial was placed under irradiation of a 10 W household 480 nm blue LED lamp. After 24 hours, the resulting solution was precipitated in the mixture of 25 mL methanol and 25 mL ethanol under stirring for overnight. The polymer product was then collected by filtration.

General procedure for first order kinetics study

To study the reaction kinetics, polymerization was carried out in a sealable NMR tubes. First, 0.5 ml CTA grafted QDs - MMA solution was mixed with 0.5 ml deuterated DMSO and 40 μL DIPEA. The stock solution was divided in halves and either half (0.5 mL) was transferred to a sealable NMR tube (diameter 5 nm) and placed under 480 nm blue LED without degassing procedure. The other half was degassed with three freeze-pump-thaw cycles and transferred into another NMR tubes in the glovebox. The tubes were then sent for irradiation at 480 nm blue LED. At specific time points, the tubes were removed from the light, sent for NMR for monomer conversion analysis and returned thereafter.

General Procedure for "ON/OFF" light switch reactions

To study the temporal control of the reaction, an "on" and "off" light experiment was executed where the reaction was put under regular internals of light and dark. After several light and dark cycles, the reaction was put in the dark overnight. The whole reaction process was characterized throughout via NMR spectroscopy.

In situ chain extension of poly(methyl methacrylate), PMMA and poly(butyl acrylate), PBA

The first block was polymerized with the ratio of monomer: CTA=100:1. MMA (0.25 mL) and BA (0.33 mL) was polymerized following the general polymerization procedure mentioned above. Polymerization was allowed to run for 36 hours until an almost full monomer conversion was achieved (over 95%). An aliquot of the reaction mixture was withdrawn for ^{1}H NMR and GPC analysis. The remaining small amount monomer was vacuumed out and reaction vial was then backfilled with argon. For the iterative chain extensions, 0.10 mL degassed monomer and 10 μL DIPEA mixed solution were added into the rest of solution via a nitrogen-purged syringe. The resulting solution was then irradiated for 12 hours with the same light source.

General Procedure for characterizing QD-polymer nanocomposites

TEM was used to characterize the polymer-QD nanocomposite, samples were prepared by drop-casting reaction mixture on lacy carbon grids. Samples were viewed under 200,000x magnification and the size of the polymer shell was characterized using the corresponding TEM image capturing software. Figure S12a,c and d were obtained by JEOL Field Emission Gun Transmission Electron Microscope and Figure 3 and Figure S12b was obtained on JEOL 2010 Transmission Electron Microscope (TEM) with Cryo

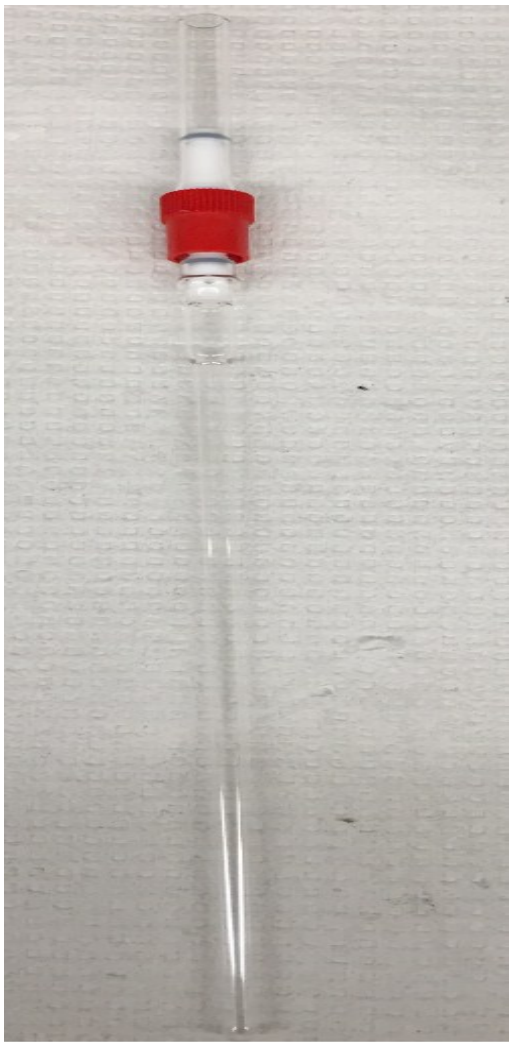


Figure S1. Picture of sealable NMR tube used in kinetic study.

Figure S2. Pictures of OA capped QDs in the mixture of MMA and DMF (right) and and CPADB capped QDs in the mixture of MMA and DMF (left). MMA and DMF volume ratio = 1:1.

Note: As we can see above, after mixing CPADB and CdSe QDs in MMA, QDs exhibited excellent solubility in DMF, even under irradiation of blue LED for a long time. In contrast, OA capped QDs solution was turbid. QDs aggregated in DMF and some of them precipitated out. This suggests that CPADB is successfully exchanged onto CdSe QDs.

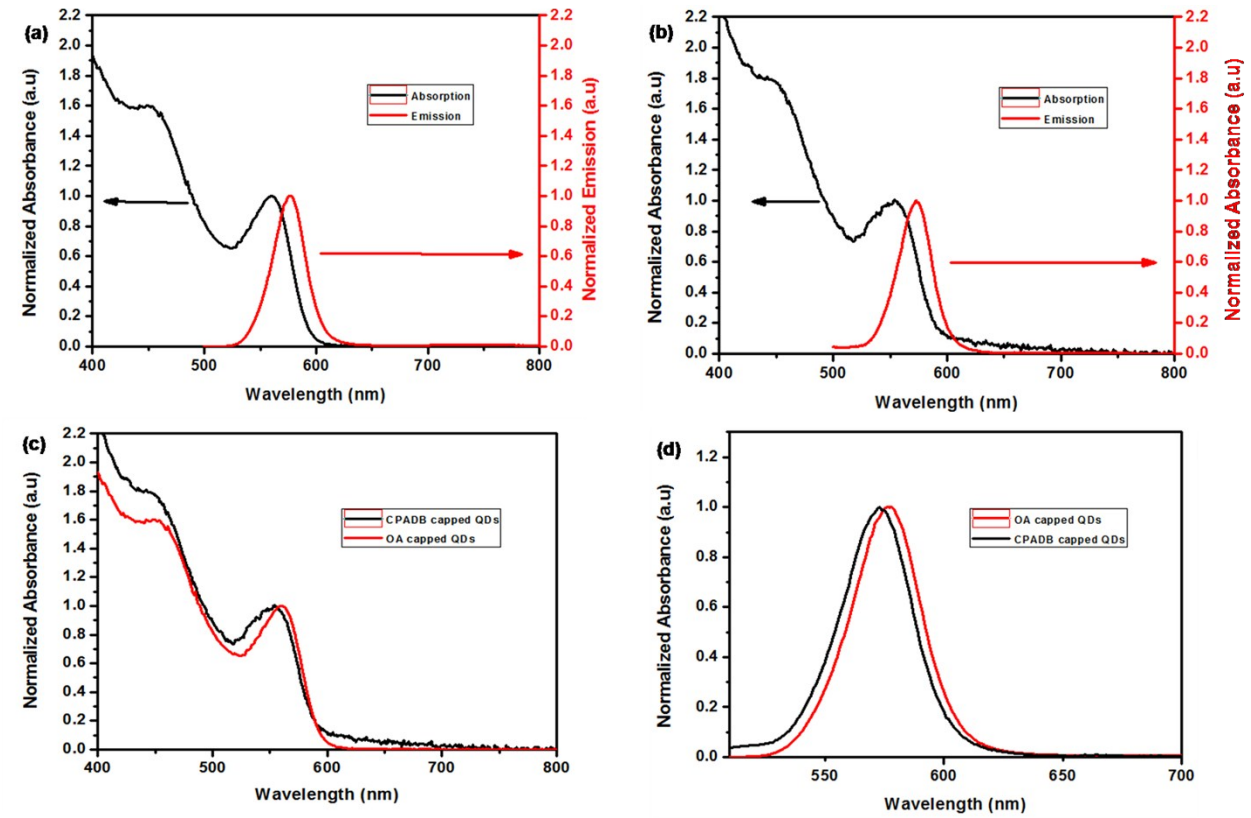


Figure S3. (a) Normalized absorption (black) and fluorescence emission (red) spectra of OA capped CdSe QDs photocatalyst in chloroform (b) Normalized absorption (black) and fluorescence emission (red) spectra of CPADB capped CdSe QDs photocatalyst in chloroform (c) Normalized absorption of both CPADB and OA capped QDs (d) Normalized fluorescence emission of both CPADB and OA capped QDs.

Note: As seen above, both absorption and emission have around 4 to 6 nm blue shift, which may be due to the change of CdSe QDs surface ligand.

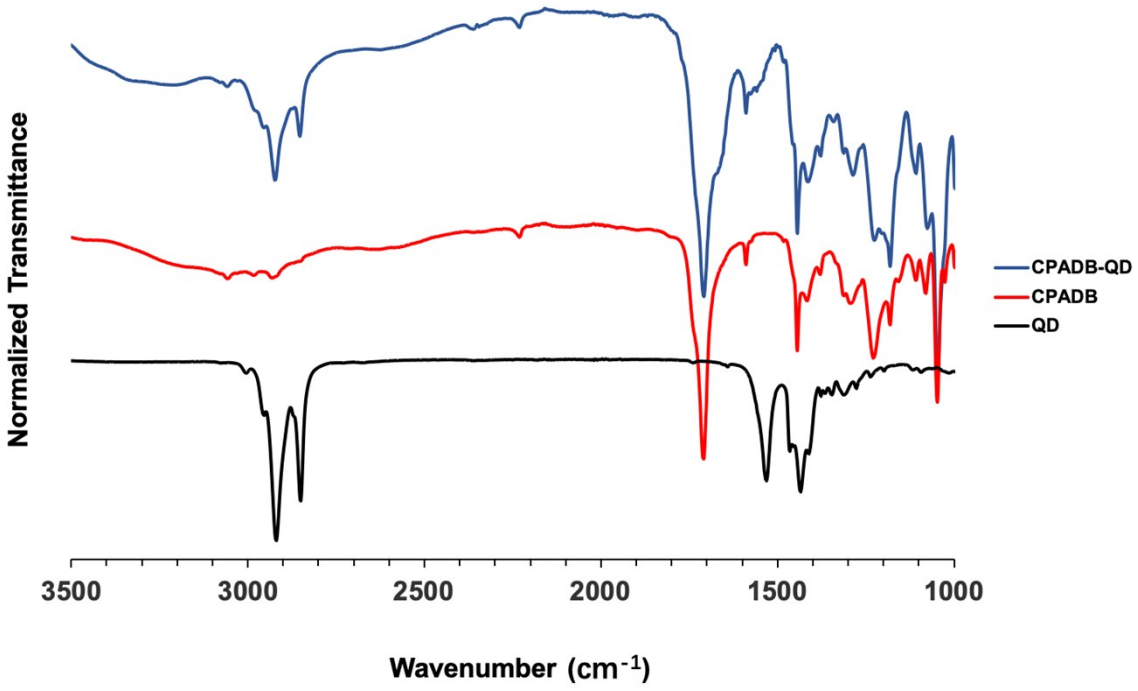


Figure S4. FTIR spectrum of CPADB grafted QDs, CPADB and original OA capped QDs

Note: The peak observed around 3500 cm^{-1} can be attributed to solvated water molecules, showing QDs are hydrophilic after ligand exchange. 2923 cm^{-1}(C-H) may belong to OA and peak at 1706 cm^{-1}may belong to C=O of CPADB.

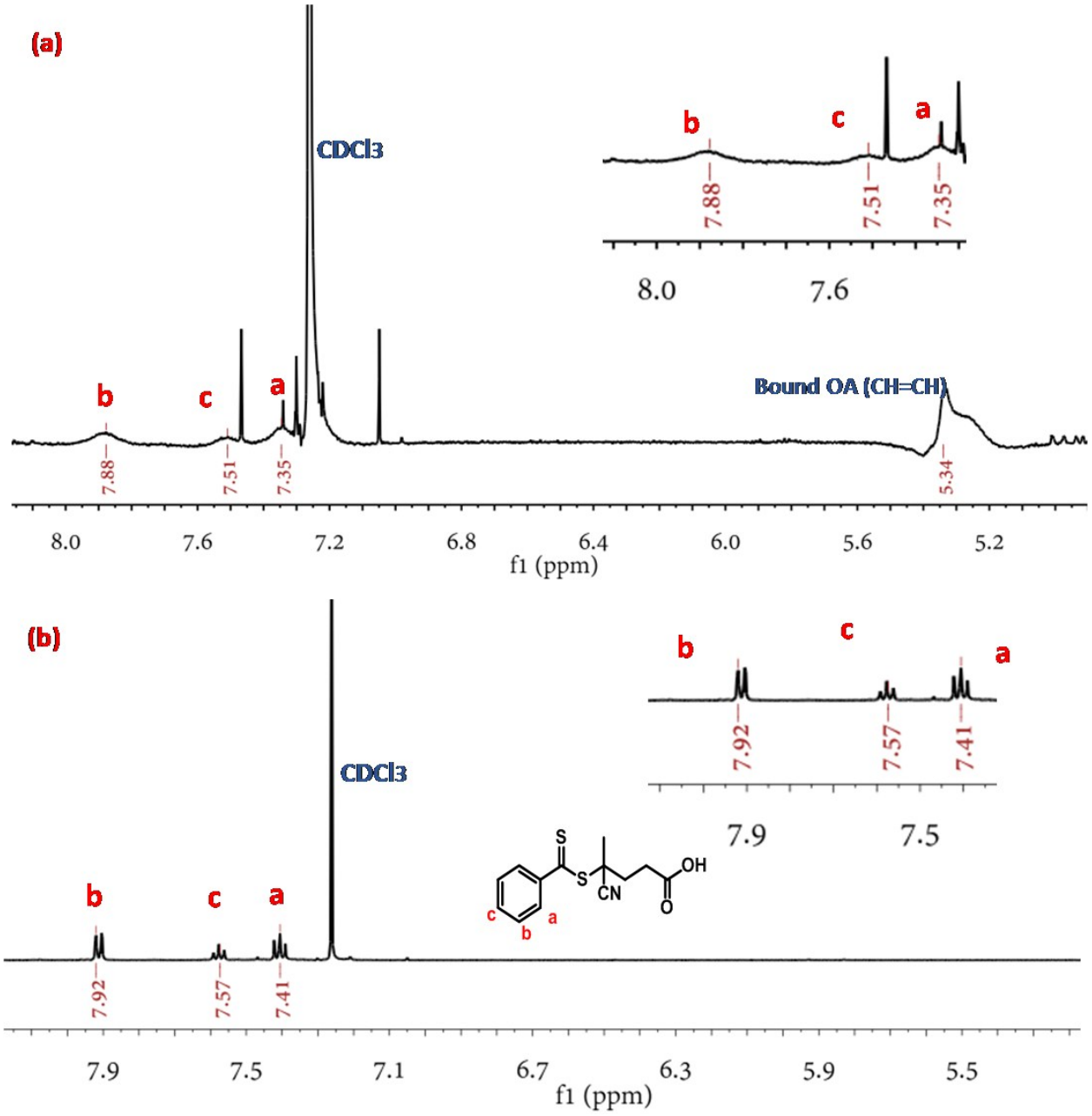


Figure S5 (a).[1]H-NMR spectrum of CPADB grafted CdSe QDs (b). [1]H-NMR of CPADB in phenyl group region

Note: As can be seen in [1]H-NMR spectrum Figure S5(a), the broad peaks at δ = 7.35, 7.51, and 7.88 ppm can be attributed to phenyl group of CPADB. One evidence of successfully grafting CPADB onto CdSe is that the phenyl peaks' signal of grafted CPADB had a slight right shift to lower ppm compared to the free CPADB. Besides, the broadened peaks at phenyl region also

demonstrates that CPADB grafting is successful. The peak at around 5.4 ppm corresponds to bound OA (C**H**=CH), indicates there is still remaining OA, which may help stabilizing QDs.

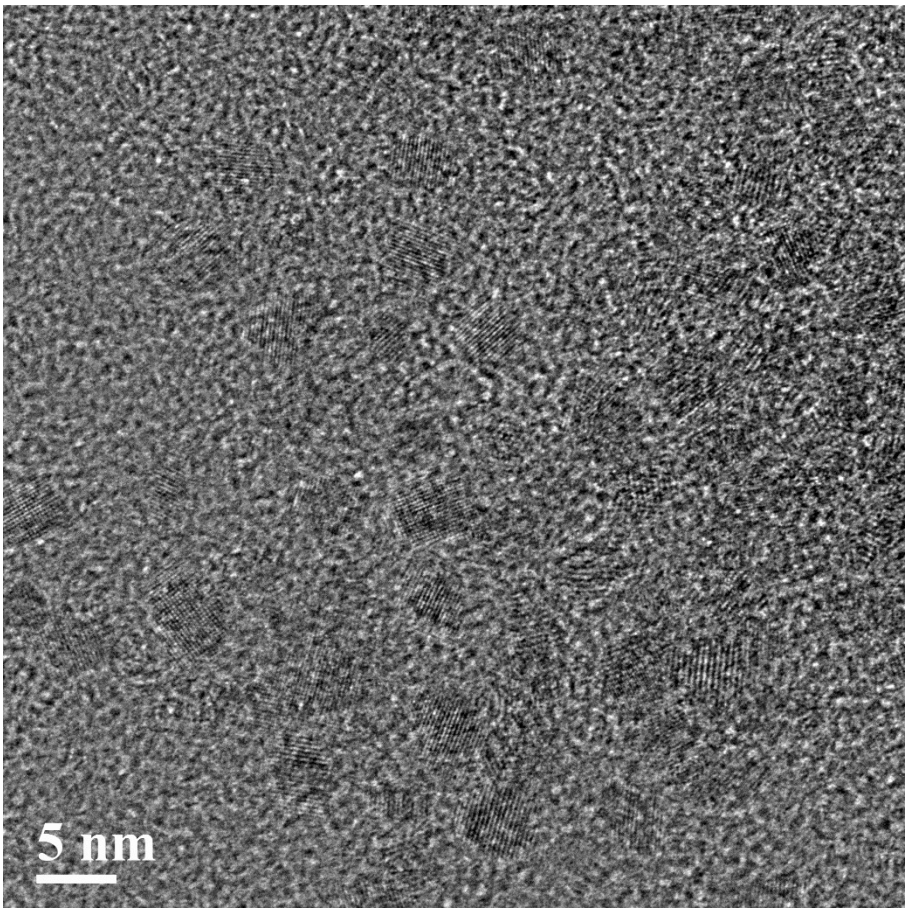


Figure S6. TEM images of CPADB capped QDs.

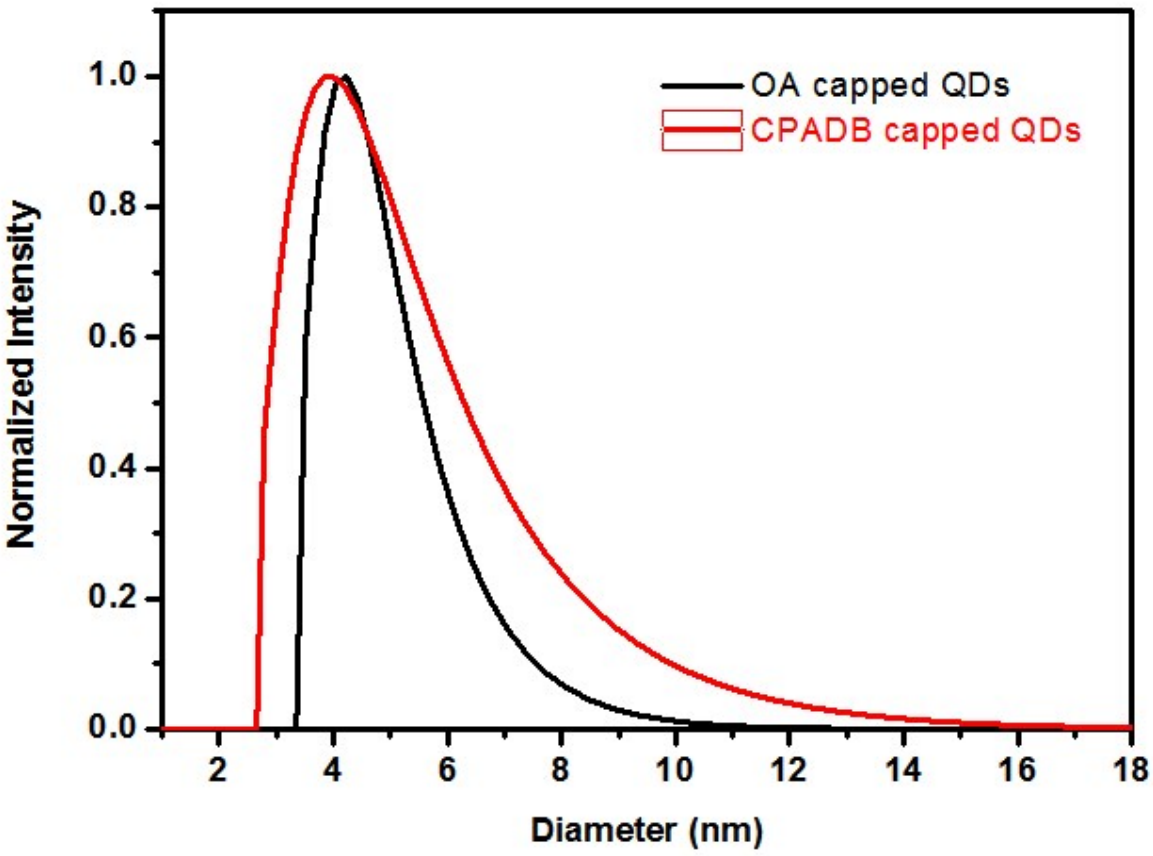


Figure S7. Dynamic light scattering spectrum of OA capped QDs (before ligand exchange, black line) and CPADB capped QDs (after ligand exchange, red line) in chloroform (concentration of QDs is $2*10^{-2}$ M). The mean size of OA capped CdSe QDs is 4.2 nm and the mean size of CPADB capped QDs is 3.8 nm.

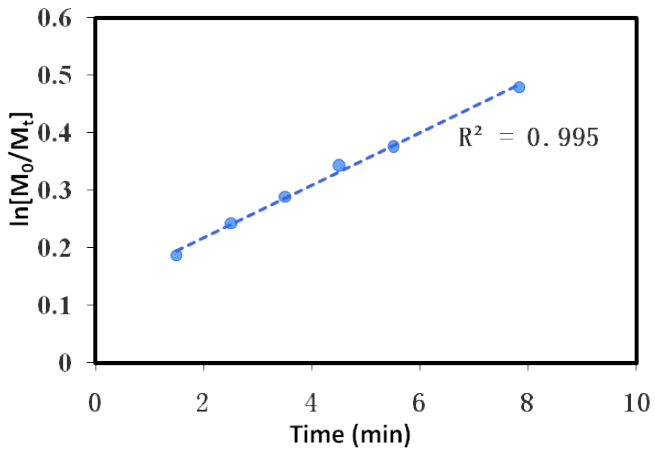


Figure S8. First order kinetic study of CdSe QDs catalyzed PET-RAFT polymerization in the presence of air

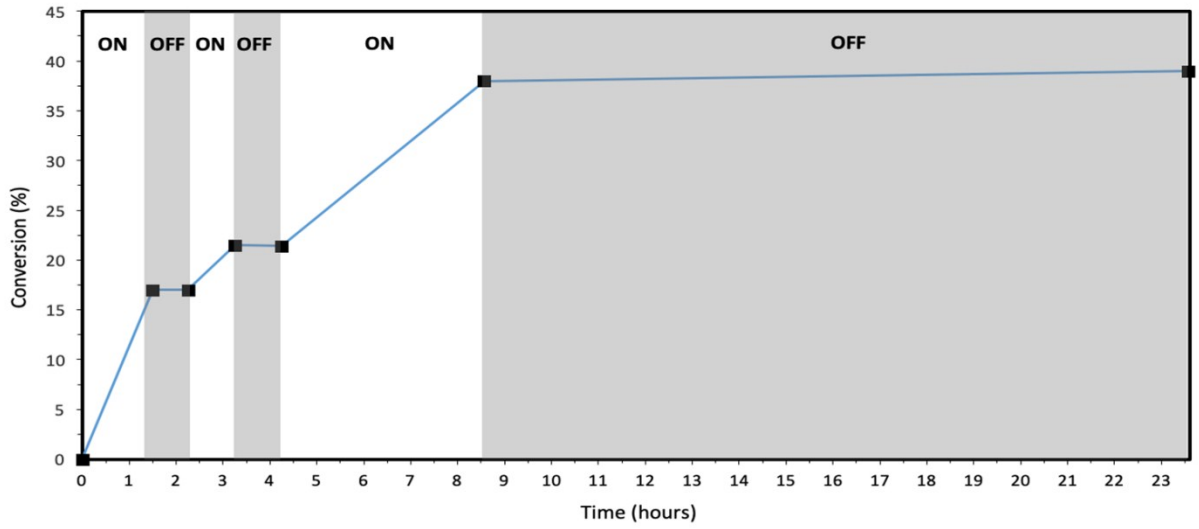
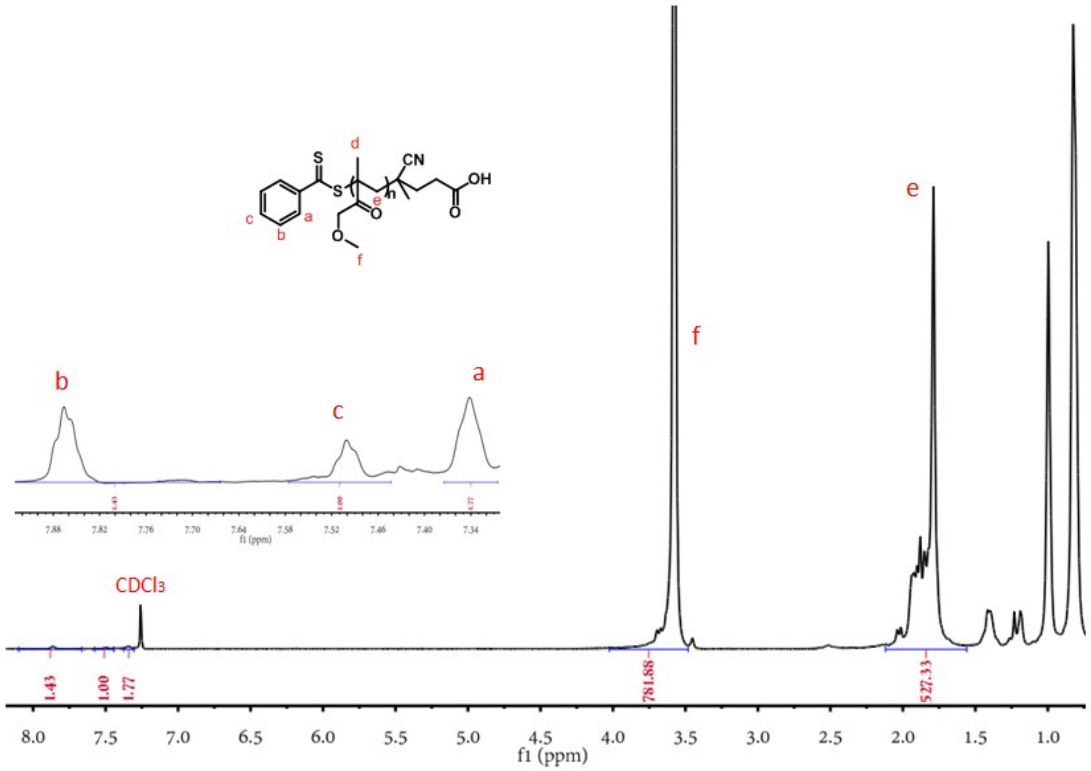


Figure S9. Switch light "on-off" study of CdSe QDs catalyzed PET-RAFT polymerization in the presence of air



Chemical shifts (ppm)

Figure S10. ^{1}H-NMR spectrum of PMMA prepared by CdSe QDs catalyzed PET-RAFT polymerization.

Note: Reaction condition: molar ratio [MMA]:[CPADB]:[DIPEA] = 200:1:5, QDs loading in DMSO at room temperature for 10 hours. PMMA was precipitated in MeOH, filtered, redissolved in THF and precipitated in MeOH again. This process was repeated for three times. Purified polymer was then analyzed via GPC: M_n= 20.4KDa, M_w=21.6 KDa, $Đ$=1.05

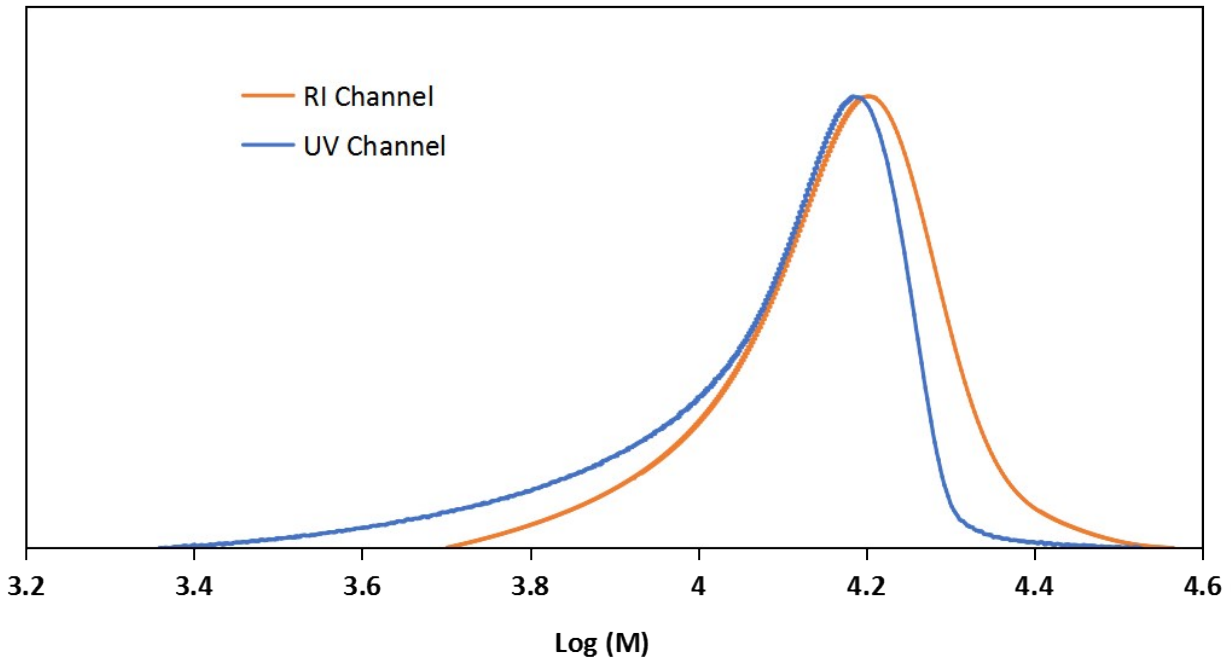


Figure S11. Comparison of molecular weight distributions recorded using a RI and UV (λ = 305 nm) detector for purified PMMA via CdSe QDs catalyzed PET-RAFT polymerization.

Note: M_n from RI detector = 13.1 KDa, = 1.12; M_n from UV detector =15.0 KDa, = 1.13;This result confirmed that obtained polymer from CdSe QDs catalyzed PET-RAFT polymerization were functionalized by a dithioester end group.

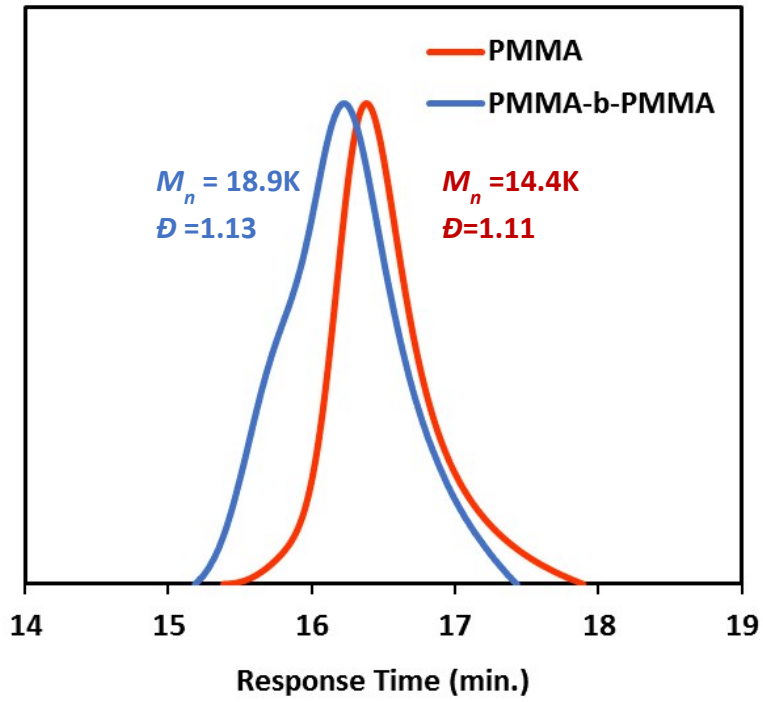


Figure S12. GPC traces of PMMA macro-initiator and PMMA-b-PMMA block copolymers synthesized by CdSe QDs catalyzed PET-RAFT polymerization.

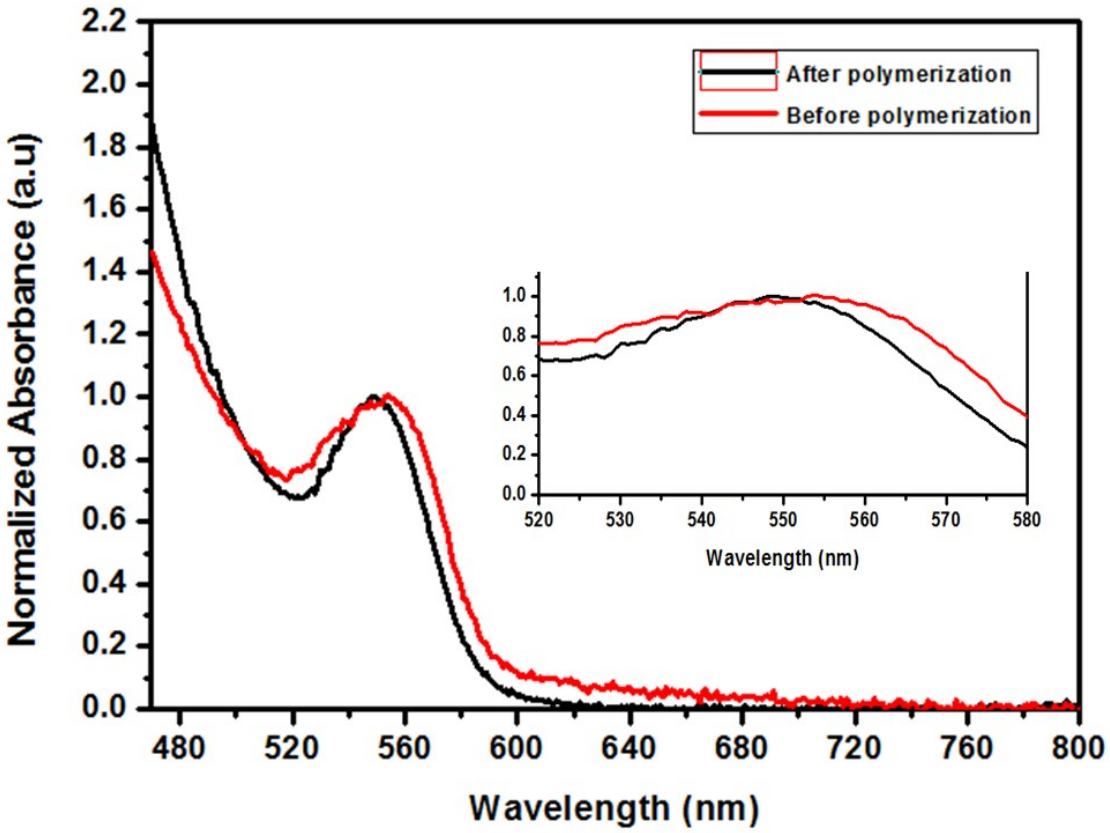


Figure S13. Normalized absorption spectra of CPADB capped CdSe QDs photocatalyst before (red) and after (black) reaction in chloroform

Note: There is only a slight blue shift (around 4 nm) of the first excitonic peak before and after reactions. First excitonic peak before polymerization (CPADB capped QDs) located at around 553 nm) and after reactions located at around 549 nm. Besides, the shape of the first excitonic peak remained after reaction. Hence, the blue shift is more likely due to the grafting of polymer shell on QDs rather than surface etch.

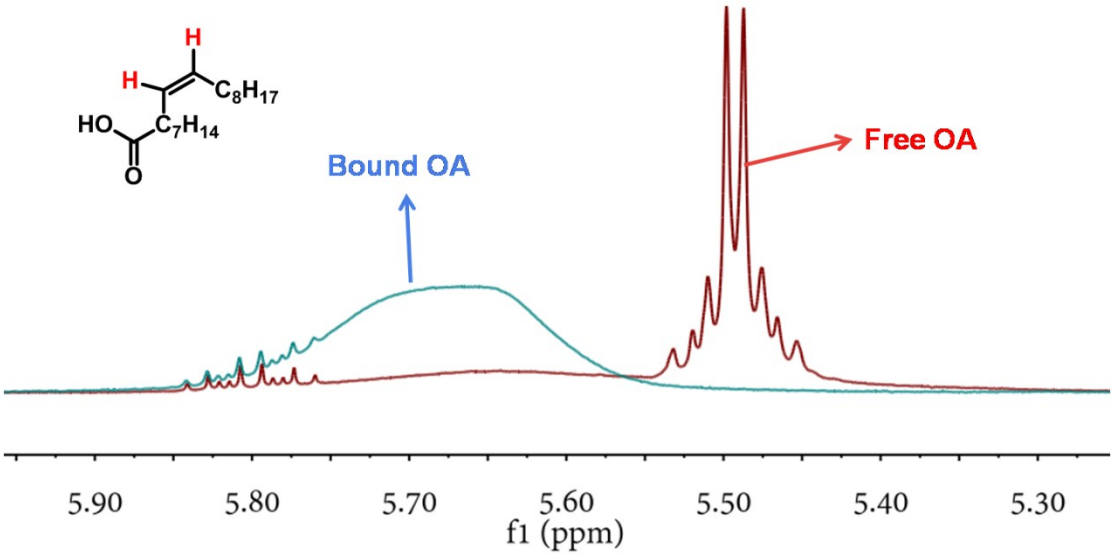


Figure S14. ^{1}H NMR of vinyl regions of OA (the protons marked in red on OA) capped CdSe QDs (blue) and CdSe QDs treated with 330 eq CPADB (red) in C_6D_6.

Note: We calculated the number of CPADB capped on per QDs and grafting density using ^{1}HNMR according to the previous report.[3]To quantify the bound OA in the OA capped CdSe QDs sample, we used a portion of the NMR spectra ranging from 5.4 to 5.9 ppm, which represents the vinyl region of oleic acid (Figure S13). The bound signal centered at ~5.65 ppm corresponds to the bound oleic acid and the sharp peaks at ~5.50 ppm correspond to free oleic acid. The NMR in blue represents the OA capped QDs and the NMR in red represents CdSe QDs after ligand exchange with 330 eq CPADB (typical amount of CPADB used in the reaction). To obtain the bound OA in the OA capped CdSe sample, the following equation was used:

$$\varepsilon(OA) = 5\frac{I\,(tot) * M\,(int)}{I\,(int) * M\,(QD)}$$

$\varepsilon(OA)$ stands for the total bound OA per QD; M(int) is the concentration of the internal standard (ferrocene); I(int) is the integrated value of the internal standard from NMR; M(QD) is the concentration of the QDs. I(tot) is the integrated value of the bound OA from NMR.

To get the Bound OA: Free OA ratio after ligand exchange, we integrated the right half of the bound peak to avoid interaction of impurity peaks centered at 5.80 ppm. The bound OA: free OA is around 0.42: 1; According to the previous report, one dithio group could displace on average two bound oleates;[3] Therefore, bound CPADB per QDs = displaced OA per QDs/2.

On average, 61 CPADB molecules capped on per QDs (diameter 3.2 nm). The surface area of 3.2 nm QDs are were obtained according to previous report,[4] which is 32.28 nm^2. Thus, grafting density is around 1.89 ligands/nm^2,

All the calculated results are provided in Table S2

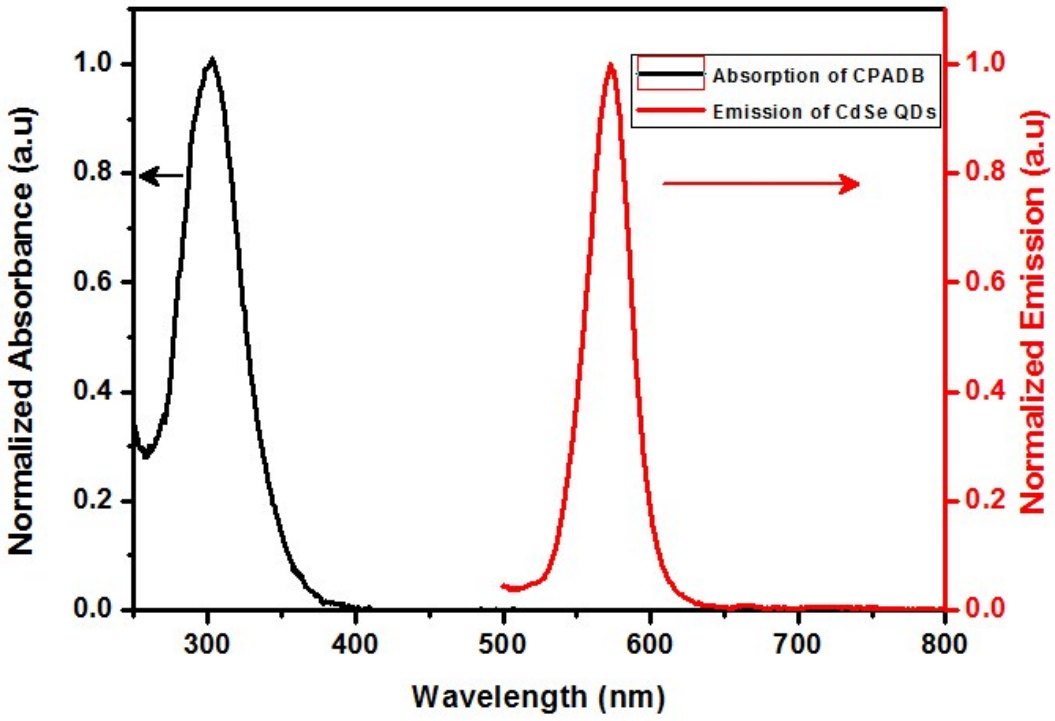
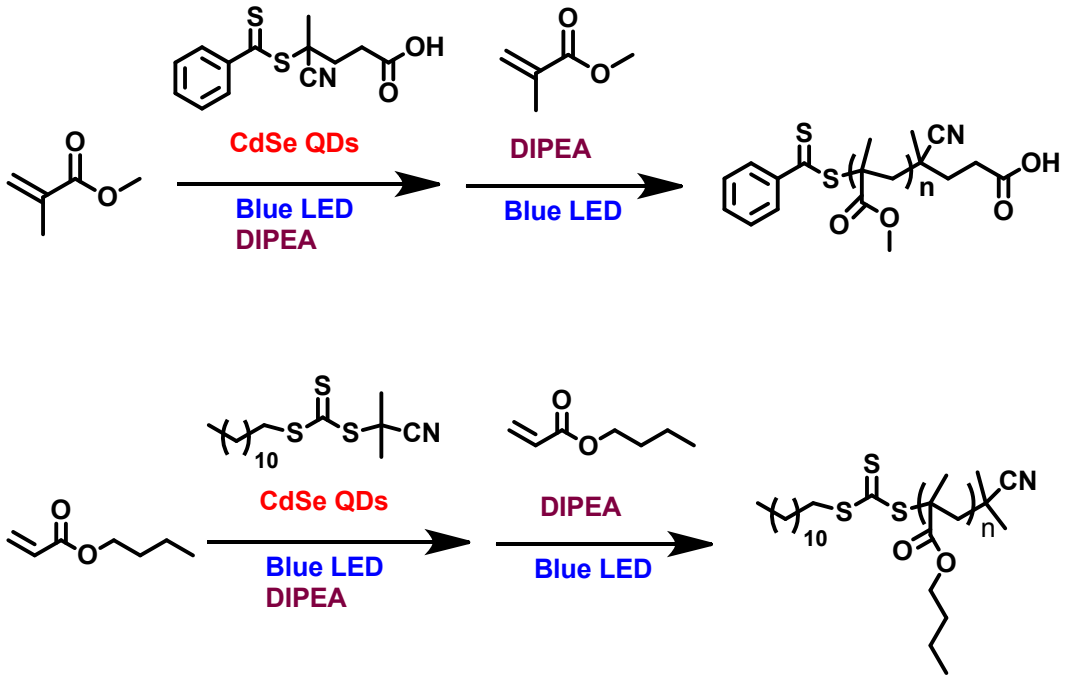


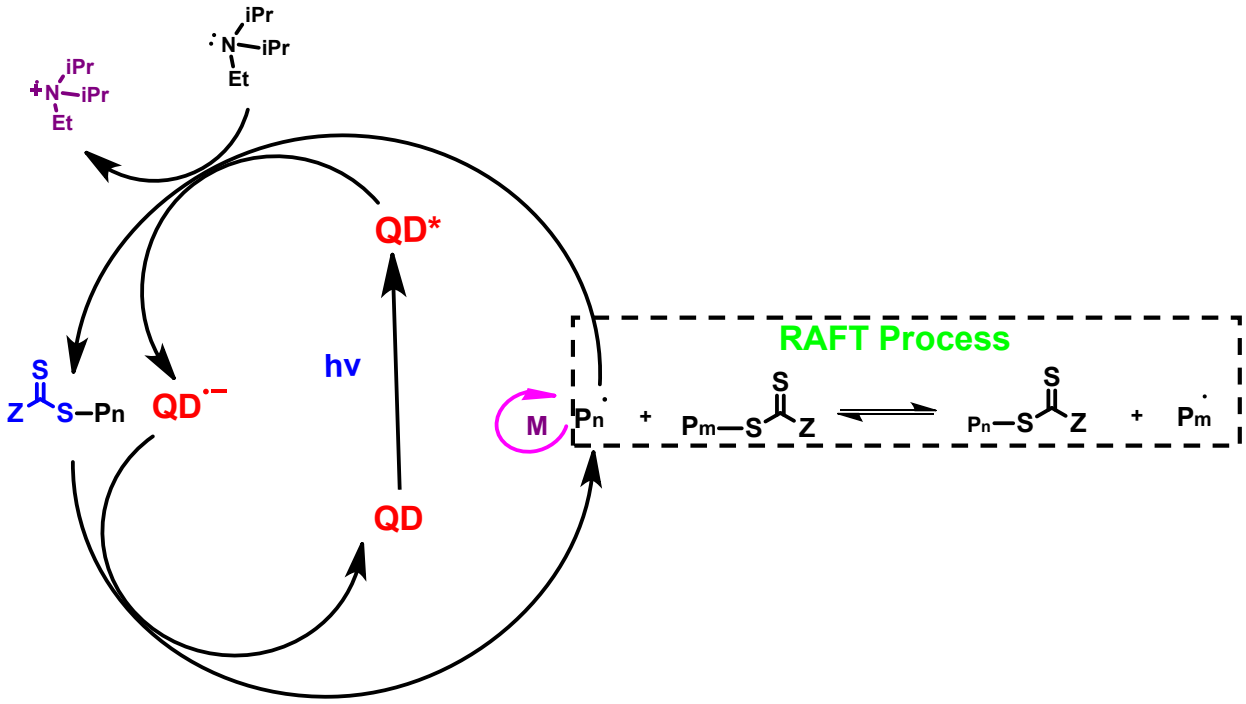
Figure S15. The fluorescence spectrum of the CdSe QDs in chloroform (red line) and the absorbance spectrum of CPADB in chloroform (black line).

Note: It would be also important to know if there is any Förster resonance energy transfe (FRET) happening between CdSe QDs and CPADB. Although we can't rule out the energy transfer mechanism between QDs and RAFT agents, we think FRET is unlikely to happen. For FRET to happen, the fluorescence spectra of the donor (CdSe QDs) should have overlap with the acceptors (CPADB) absorbance. The acceptors (CPADB) absorbance should center at a longer wavelength compared to the fluorescence spectra of the donor. However, the fluorescence of the QDs has no overlap with the CPADB absorbance (Figure S15) and absorbance of CPADB is centered at lower wavelength (300 nm) compared to fluorescence of QDs (560 nm). Thus, FRET is unlikely to happen.

Scheme S1. Schematic illustration of in-situ synthesizing diblock copolymers



Scheme S2. Proposed mechanism for CdSe QDs catalyzed PET-RAFT polymerization



Note:

We proposed herein a similar mechanism to the one in paper (Figure 1B), but the reduction of oxidized polymer radical is different. Under light irradiation, photoexcited CdSe QDs react with RAFT agent via PET process while holes in valence band can be scavenged by the sacrificial donor DIPEA. Radicals generated by the reduced RAFT agent can initiate the polymerizations, participate in RAFT process. The difference is instead of giving an electron to DIPEA radical cation, the polymer radical may transfer an electron back to excited states CdSe QDs and form the dormant state. DIPEA cannot be recycled in this mechanism but be considered as a sacrificial reagent.

Table S1. CdSe QDs catalyzed PET-RAFT polymerizations with different monomers under blue LED (λ_{max}=465 nm) irradiation unless otherwise specified.

Entry	Monomer	[M]:[CTA]:[DIPEA] [a]	solvent	Conversion (%)[b]	Mn (kDa)[c]	$Đ^{c}$	$M_{n,theo}$ (kDa)[d]
1	MMA	200:1:5	DMA	49.4	16.7	1.12	10.0
2	MMA	200:1:5	DMSO	77.3	30.3	1.13	15.7
3	MMA	200:1:5	MECN	30.1	29.0	1.30	6.3
4	MMA	200:1:5	Toluene	2.2	/	/	/
5	MMA	200:1:1.25	DMF	36.6	17.8	1.34	7.5
6	MMA	200:1:0.625	DMF	38.9	19.0	1.31	8.1
7	MMA	100:1:5	DMF	68.0	12.0	1.13	7.1
8	MMA	400:1:5	DMF	39.3	20.3	1.23	16.0
9	BMA	200:1:5	DMF	41.0	13.2	1.29	11.9
10	TFEMA	200:1:5	DMF	46.2	19.3	1.25	15.8
11[e]	MA	200:1:5	DMF	30.2	7.0	1.06	5.4
12[e]	BA	200:1:5	DMF	13.0	12.0	1.05	3.7
13	MMA	200:0:5	DMF	37.1	80.0	2.0	/
14[f]	MMA	200:1:5	DMF	27.2	5.9	1.23	5.7

a.[QD]= 15 ppm, CTAs for entry 1 to 7 and 13 to 14 are CPADB and entry 8 to 9 is CPDT; reaction time is 24 hours b. Conversion measured by ^{1}HNMR.c. Mn measured by GPC in THF, based on linear polystyrene as calibration standard. d.Mn,theo = [monomer]/[initiator] * conversion* MW(monomer)+ MW（initiator）e. polymerization was conducted in the absence of CdSe QDs f. Polymerization was performed under green LED (λmax =535 nm).

Table S2. The number of Bound CPADB Ligands per QD determined from ^{1}H NMR.

	Total bound OA per QD $\varepsilon(OA)$	Displaced OA per QDs	Bound CPADB per QDs
OA -CdSe	210	-	-
CPADB -CdSe	210	122	61

References:

(1) Yu, W. W.; Peng, X. Formation of High-Quality CdS and Other II-VI Semiconductor Nanocrystals in Noncoordinating Solvents: Tunable Reactivity of Monomers. *Angew. Chemie - Int. Ed.* **2002**, *41* (13), 2368–2371.

(2) 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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(4) Morris-Cohen, A. J.; Malicki, M.; Peterson, M. D.; Slavin, J. W. J.; Weiss, E. A. Chemical, Structural, and Quantitative Analysis of the Ligand Shells of Colloidal Quantum Dots. *Chemistry of Materials*. April 23, 2013, pp 1155–1165.