Thiol ligand capped quantum dot as an efficient and oxygen tolerance photoinitiator for aqueous phase radical polymerization and 3D printing under visible light

Supporting Information

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Materials and methods

Materials and instruments.

All commercially available chemicals were purchased from Sigma-Aldrich and were used as received unless otherwise specified. Single wall carbon nanotubes (P3-SWNT) are purchased from Carbon Solutions, Inc. All reagents used in CdSe QDs preparation were degassed and stored in a glovebox prior to use. Trioctylphosphine selenide (TOPSe) and cadmium oleate precursor stock solutions were prepared according to reported procedures.[1] Commercially available monomers were purified (if needed) by filtering through silica and neutral alumina plugs immediately prior to polymerization. Nuclear magnetic resonance (NMR) spectra were obtained on an NMR Bruker 500 MHZ operated at room temperature. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on a Nicolet FTIR Infrared Microscope. Gel permeation chromatography (GPC) was carried out on an Agilent 1260 Infinity LC system and calibrated with polystyrene standards in THF. Absorption and photoluminescence spectra were measured with Agilent Cary-60 UV-Vis spectrometer and Cary Eclipse fluorometer, respectively. Dynamic light scattering (DLS) was spectrum recorded using NanoPlus-3 particle analyzer. X-ray photoelectron spectroscopy (XPS) was performed on a PHI Quantera XPS, which uses a focused monochromatic Al Kα X-ray (1486.7 eV) source for excitation. The 50 W, 15 kV and 200 μm diameter X-rays were shoot on the sample. High resolution scan spectra were recorded in 0.1 eV steps with a pass energy of 26 eV. Low energy electrons and Ar+ ions were conducted for specimen neutralization in each measurement. The Envision TEC Perfactory 3DSP 3D printer using digital light

processing technology was used for photo 3D printing. Scanning electron microscopy (SEM) was performed on an FEI Quanta 400 FESEM operating at 30.00 kV.

Preparation of the CdSe quantum dots (QD) with nonpolar ligand oleic acid.

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 previous reports.[1] A mixture of cadmium oxide (0.318 g, 25 mmol), oleic acid (3.45 mL, 100 mmol), and 9 mL 1-octadecene 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 needs 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 QDs were washed with methanol and hexanes, and the resulting QD product in hexanes was stored in a glove box.

General procedure for biphase ligand exchange to transfer CdSe QDs into water

To 0.01 mL QD stock solution, hexanes and a solution of thiol ligand in water (0.15 M) was added. The mixture was stirred for 30 minutes or until a colorless hexane layer was observed. The aqueous phase becomes red. The hexane layer was removed and then the

remaining solution of QD in water was put under vacuum. The new QD stock solution was used directly in the polymerization step without any further purification.

General procedure for Ethylenediamine-Assisted ligand exchange to obtain 3-Mercaptopropionic acid (MPA) capped CdSe QDs

Ligand exchange was operated following reported procedure.[3] To a 0.5 ml CdSe QDs $CHCl_3$ solution, 0.3 mL portion of ethylenediamine (EDA) was added under vigorous stirring. After 30 min, 0.5 mL MPA water solution (0.15M) was added to the mixture. One hour later, the aqueous phase becomes red and colorless organic phase becomes colorless. The colored layer was taken out and excess methanol were added. The QDs were then centrifuged, so extra MPA were washed away and a QDs pellet were obtained. The pellet then was dispersed into water.

General procedure for photocatalyzed polymerization

Generally, to a mixture of 1.16 mmol monomer and 2 ml water, stocked QDs from the ligand exchange (3 ppm) and 6 mol% MPA was added. The mixture was stirred at ambient temperature under the irradiation of a household blue LED lamp (the maximum wavelength-(λ_{max}) is 460 nm and the intensity of the light source is 10 mW/cm^2). If the reaction was operated in the absence of oxygen, the mixture deaerated by three freeze-pump-thaw cycles and backfilled with argon. 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 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 were dissolved in 0.7 mL D_2O and used as such for ^{1}H NMR analysis. A couple milligrams of polymer was dissolved in THF, then filtered, and then analyzed on the GPC.

General procedure for monitoring the MPA-CdSe QDs photocatalyzed polymerization of PEGDA using FTIR

The polymerization kinetics of PEGDA with water-soluble CdSe QDs were investigated by Nicolet FTIR Infrared Microscope, using a revised procedure according to the previous report.[4] Briefly, 0.25 ml PEGDA monomers were mixed with as-prepared CdSe QDs in water (14 ppm), 0.25 ml water, and 6 μL MPA. For each measurement, approximately 15 μL of mixture solution was dropped on the top of the diamond and covered with a piece of transparent polyethylene terephthalate film. The solution was irradiated using the blue LED@460 nm. The light intensity was adjusted to 20 mW/cm^2. IR absorbance spectrums were recorded by different irradiation time. The conversion of the C=C group was measured by calculating the decreasing spectrum area of the C=C peak (1600 cm^{-1} to 1650 cm^{-1}).[4] The background of only water was subtracted from the curves, leaving only the feature of the PEGDA monomers. The calculation was followed using the following equation, where I is the integration of initial C=C peak area and I' is the integration of the area at the specific irradiation time:

$$\text{Conversion (\%)} = \frac{\mathrm{I} - \mathrm{I}'}{\mathrm{I}} * 100$$

General procedure for thiol-ene click reaction of norbornene and MPA

In a typical experiment, 2-norbornene (43.0 mg, 0.46 mmol), MPA (48.72 mg, 0.46 mmol), dimethylaniline (2.5 mg, 0.024 mmol), CdSe QDs stock solution (0.05 ml, 0.67 × 10^{-6} mmol),

and MeCN (1.2 mL) were mixed in a 4 mL glass vial without degassing. The reaction mixture was then irradiated by blue LED light (10 mW/cm^2). After an hour, the reaction was stopped and the solvent MeCN was removed under reduced pressure. The crude product was analyzed by ^{1}H NMR.

General procedure for thiol-ene polycondensation

A 4 mL glass vial was charged with N-methyl-2-pyrrolidone (0.3 mL), 1,5-hexadiene (HD, 0.16 ml, 1.34 mmol 1 equiv.), 2,2′- (ethylenedioxy)diethanethiol (EDDT, 0.21 ml, 1.34 mmol, 1 equiv), CdSe QDs water solution (0.1 ml, 1.34 × 10^{-4} mmol/ml, 10 ppm) and p-toluidine (7.1 mg, 0.07 mmol, 0.05 equiv.). The mixture was then irradiated under blue LED light (10 mW/cm^2). After one hour, 2-3 drops of the polymerization mixture were dissolved in CDCl3 to determine the HD conversion by ^{1}H NMR. The reaction mixture was then precipitated in MeOH/petroleum spirit (1/1, v/v). The oily precipitate was filtered, washed with MeOH/petroleum spirit (1/1, v/v) and dried under vacuum, then subjected for ^{1}H NMR ($CDCl_3$) and GPC (THF) analysis. The yielding poly-ethylenedioxy thioether has M_n = 4.0 kDa, and $Đ$ = 1.50.

General procedure for 3D printing of Rice Tag without the addition of P3-SWNT

The 3D model was built with the computer-aided design and saved as a STL file. The resin samples contained 6 mL poly(ethylene glycol) diacrylate (PEGDA) and 20 uL MPA, along with the CdSe QDs. The projector brightness was set to 2 mW/cm^2 and a wavelength centered at 410 nm and there were switches between the 75 mm and 85 mm lens. The amount of quantum dots, was changed as well as the exposure time for each layer was changed in order to get the optimal results, while the amount of water used is kept as 2.8 ml. Layer thickness

for the tag shown in the Figure 1 is 15 um and light exposure time is 24 s.

General procedure for 3D printing of objects in Figure 1 c-g with the addition of 0.22wt% P3-SWNT

The resin samples contained 3 mL Poly(ethylene glycol) diacrylate, 0.22 wt % P3-SWNT and 10 uL MPA, along with the 14 ppm CdSe QDs. Details of the 3D printer parameter: light intensity: 2 mW/cm^2 ; Wavelength centered at 410 nm**;** Lens focal length: 85 mm; Average voxel depth: 15 um**;** Exposure time for burn-in range: 35000 ms**;** Thickness of burn-in range: 200 um**;** Exposure time for standard range: 24000 ms. Object size: **Figure 1c** (Rice Owl) 32 mm x 27 mm x 2 mm; **Figure 1d** (butterfly) 40 mm x 30 mm x 2 mm; **Figure 1e** (wheel) 17 mm x 17 mm x 2 mm; **Figure 1f** (spatula) 45 mm x 8.5 mm x 2 mm; **Figure 1g (**spanner) 29 mm x 7.4 mm x 2 mm;

Supporting Data

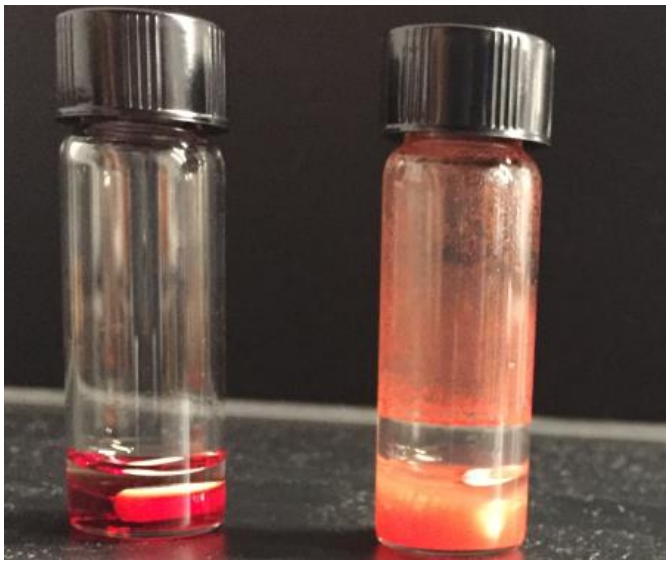

Figure S1. Pictures of CdSe QDs after ligand exchange.

Note: The left one is the photo of QDs after ligand exchange using Method A and AET. The top layer is hexane, and the bottom layer is water; the right one is the photo of QDs after ligand exchange using Method A with MPA. The top layer is hexane, and the bottom layer is water. As we can see here, ligand exchange with AET is good, and QDs were well dispersed. For the ligand exchange with MPA, QDs can be transferred to the water phase, but aggregation was observed. This is similar to the previous report.[3]

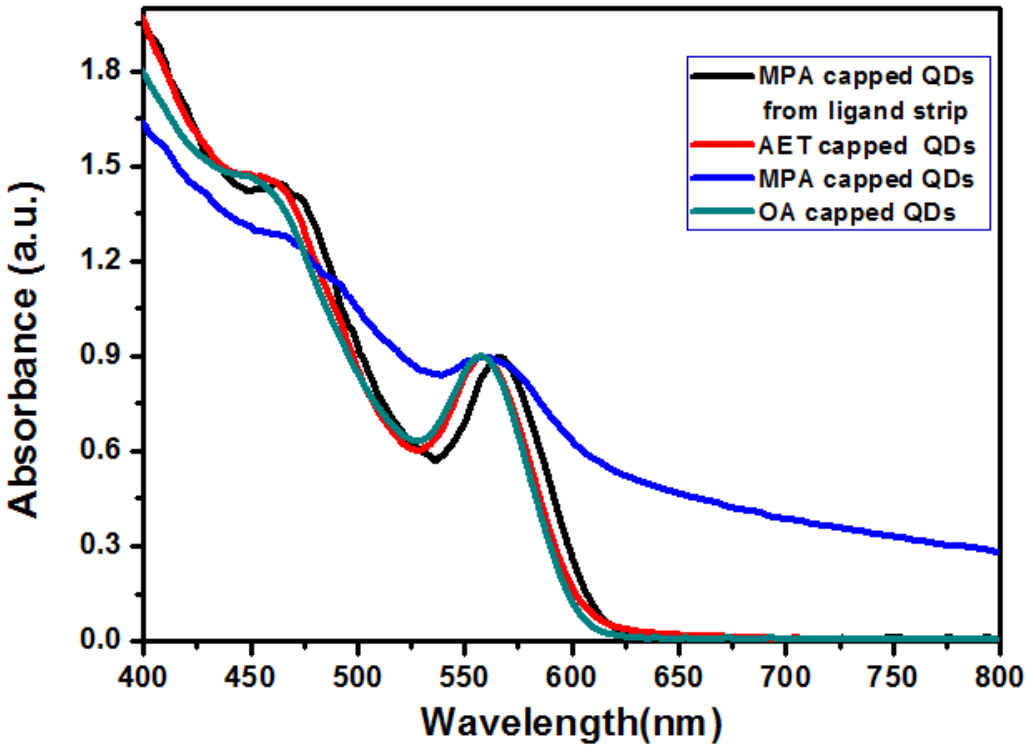

Figure S2. Normalized UV absorption of quantum dots with different ligand shells and ligand exchange method

Note: First, the biphasic ligand exchange method[5] was used to cap CdSe QDs with ligand aminoethanethiol hydrochloride (AET) (**Scheme 1a**). To conduct a ligand exchange, a solution of AET (0.15 M) in water was added to oleic acid capped CdSe QDs in hexane and stirred for 5 hours. The hexane phase turned colorless, while the aqueous solution turned to a red color, indicating that CdSe QDs were transferred to the aqueous layer. While this method resulted in a well-dissolved AET-capped QDs in aqueous solution (**Figure S1**), excess of AET ligands were required to maintain the stability of CdSe QDs. Attempts to wash out the extra thiol ligand led to the aggregation of QDs. The UV-vis absorption spectrum of CdSe capped with AET using Method A shows a flat baseline and a narrow first excitonic peak (**Figure S2**) similar to that of CdSe spectra before the ligand exchange, indicative of good solubility in

water without compromising the optical properties of CdSe. In contrast, attempts to expand the same approach to MPA ligand led to a dispersion of QDs in water instead of a homogeneous solution (**Figure S1**). Absorption spectra of yielding MPA capped CdSe QDs showed a strong scattering and a tail at 600-800 nm, suggesting that the QDs are not well-dispersed in water (**Figure S2**).

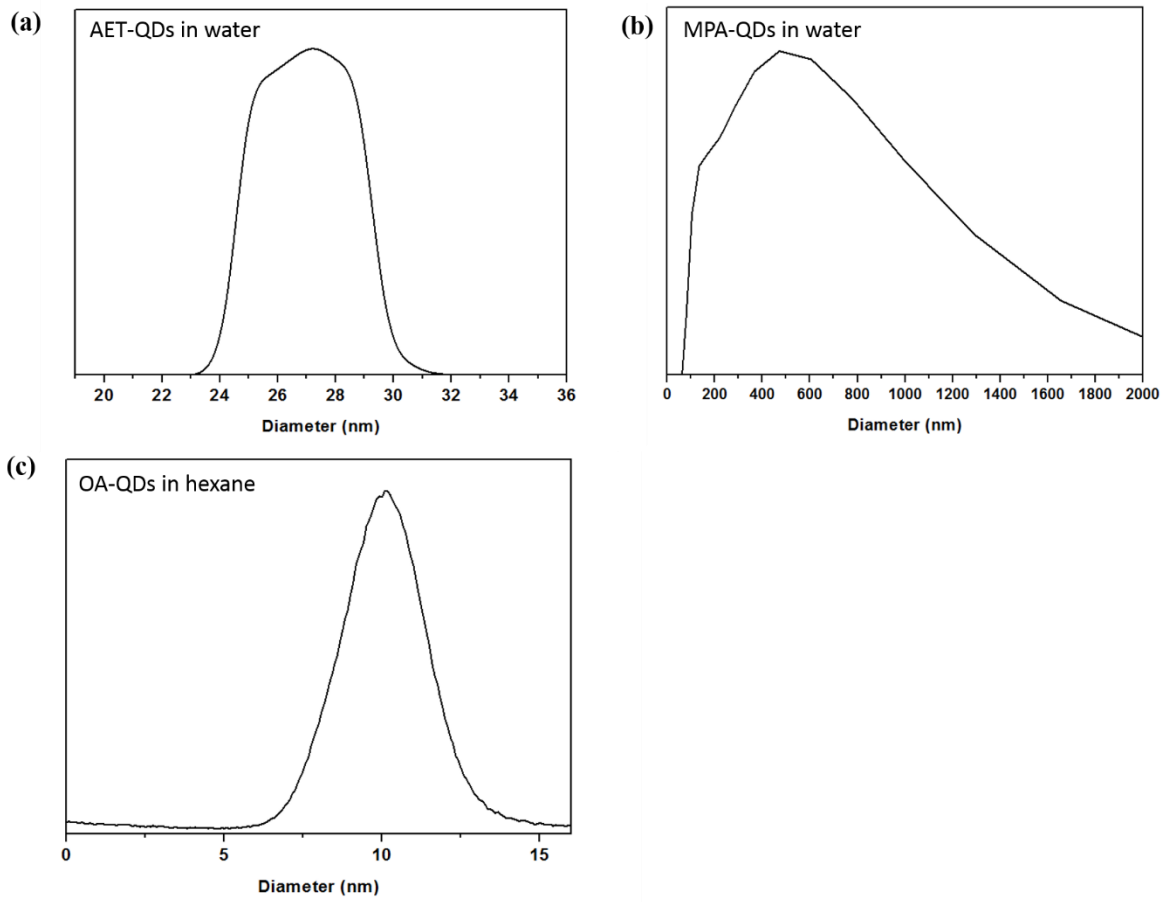

Figure S3. Size distribution of (a). AET capped QDs in water using ligand exchange method A (b). MPA capped QDs in water using ligand exchange method A (c). OA capped QDs before ligand exchange in hexane. The profile for the distribution of QDs was obtained by dynamic light scattering.

Note: The large size of AET capped QDs might be because positively charged AET-QDs and negatively charged ion in water may form an ionic combination and increase the hydrodynamic size.[6]

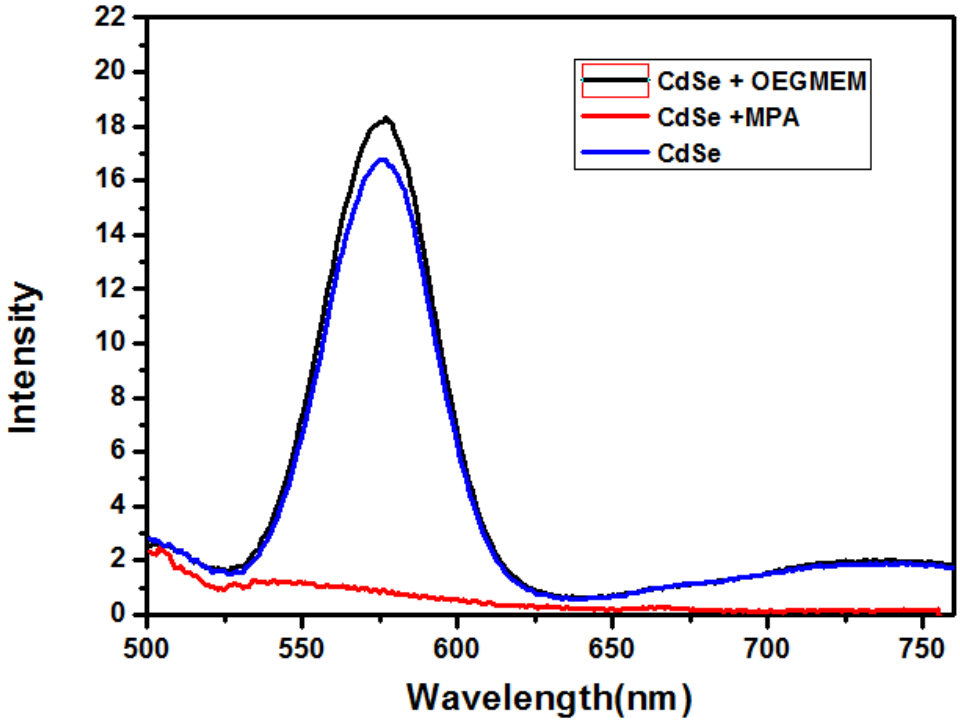

Figure S4. Fluorescence quenching of CdSe QDs at an excitation wavelength of 460 nm(0.01 mmol MPA and 0.01 mmol OEGMEM monomer were respectively added into 1ml $3.0*10^{-7}$ M MPA capped CdSe QDs water solution from Method B)

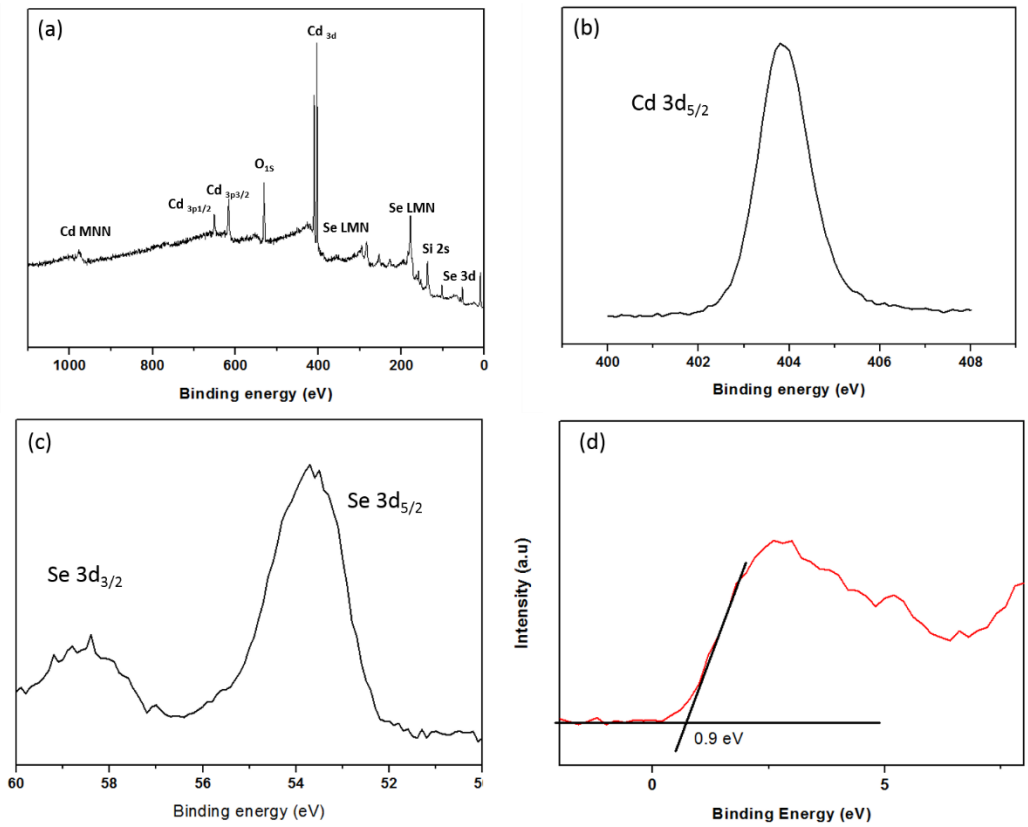

Figure S5. (a). XPS survey scans of MPA-capped QDs using Method B. The spectra match well with the previous report.[7] Note: Si was chosen as the background to load the simple. Thus, we can observe the peak of Si 2s around 155 eV. (b). Elemental scan of Cd. (c). Elemental scan of Se. (d) Valence band spectra of MPA-capped QDs using Method B. All the spectra were calibrated using carbon peak located at 284.5eV.

Note: The valence band maximum (VBM) of MPA-capped QDs using Method B was obtained as follows.[8] First, we got the value (0.9 eV) of the intersection of the horizontal line and the tangent line of the curve around 0 eV (**Figure S5d**). The work function of the XPS is 4.3 eV, so the VBM was calculated to be -5.2 eV vs vacuum, which is around 0.456 V vs SCE.

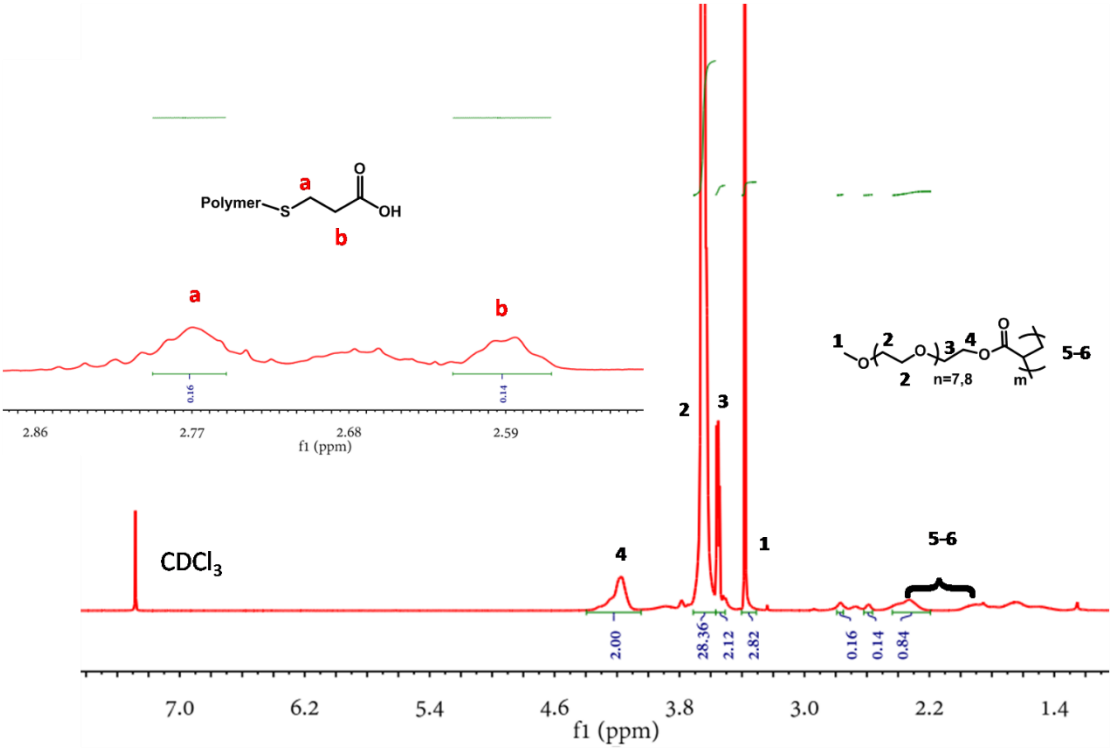

Figure S6. ^{1}H NMR spectrum of poly-(ethylene glycol) methyl ether acrylate ($M_{n,GPC}$= 7.1 kDa, ***Đ*** =1.39). Broad peaks centered at 2.77 ppm and 2.59 ppm could be attributed to the MPA chain-end, as the chemical shift is close to the MPA small molecular.

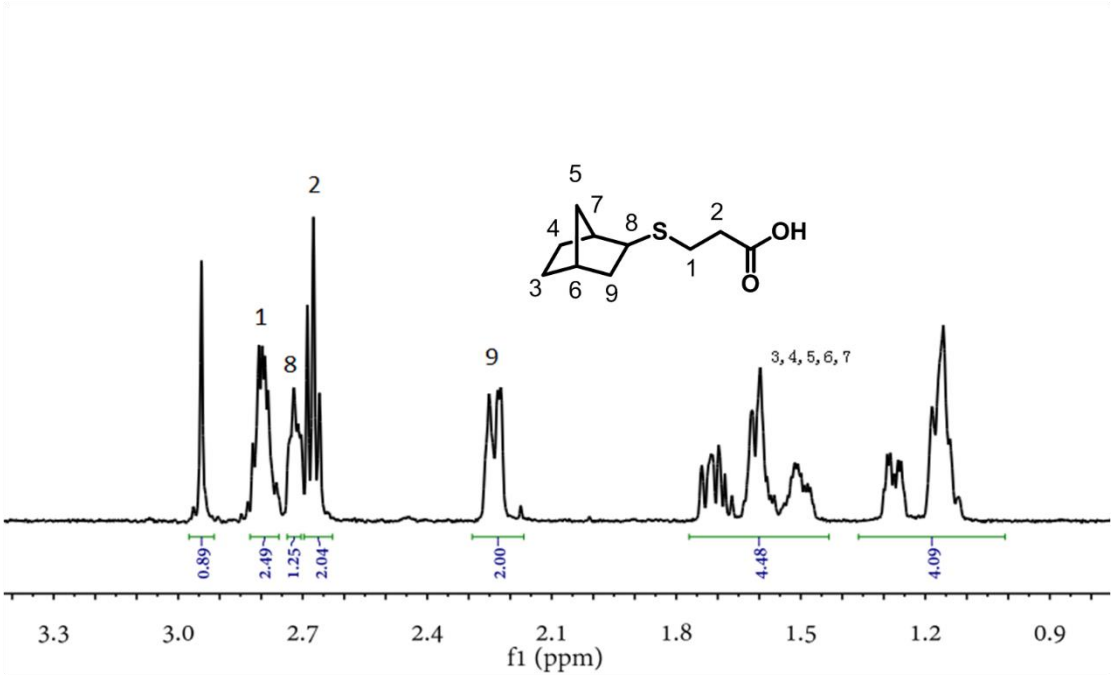

Figure S7. ^{1}H NMR spectrum (in $CDCl_3$) for crude product of thiol-ene reaction between norbornene and MPA

Note: The peak at 2.95 ppm is corresponding to the proton from methyl groups of dimethylaniline.

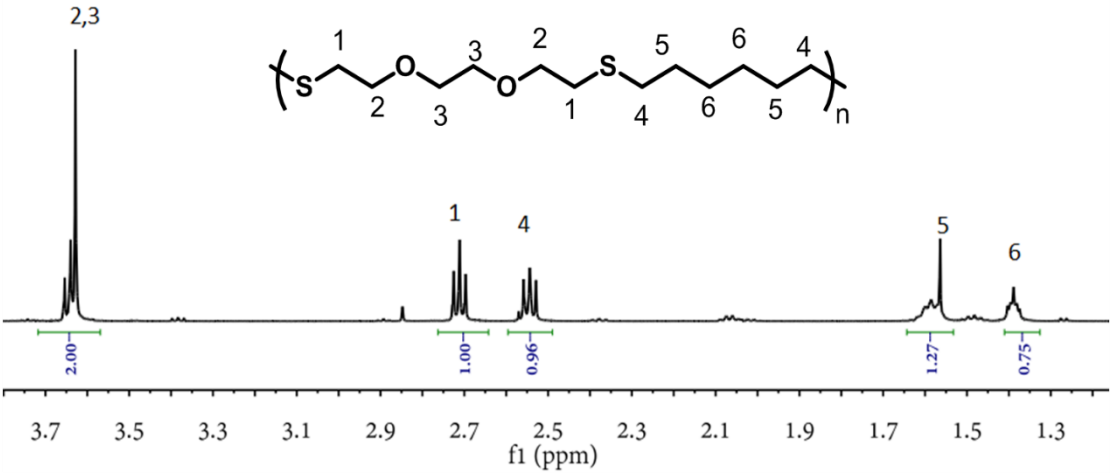

Figure S8. ^{1}H NMR spectrum for purified product by thiol–ene polycondensation.

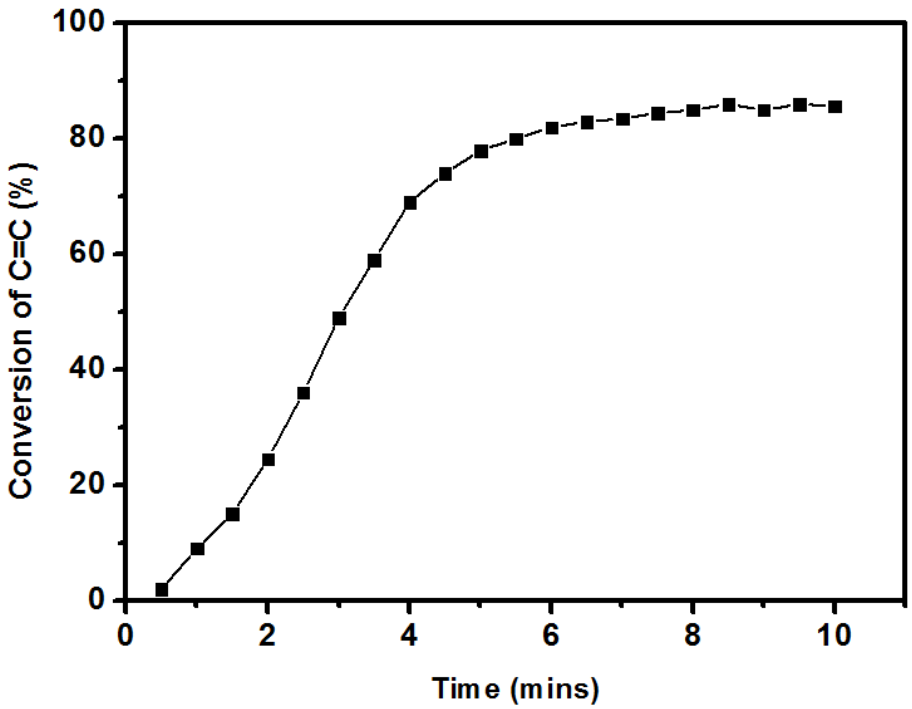

Figure S9. Photopolymerization profiles (double bond conversions vs time) of PEGDA

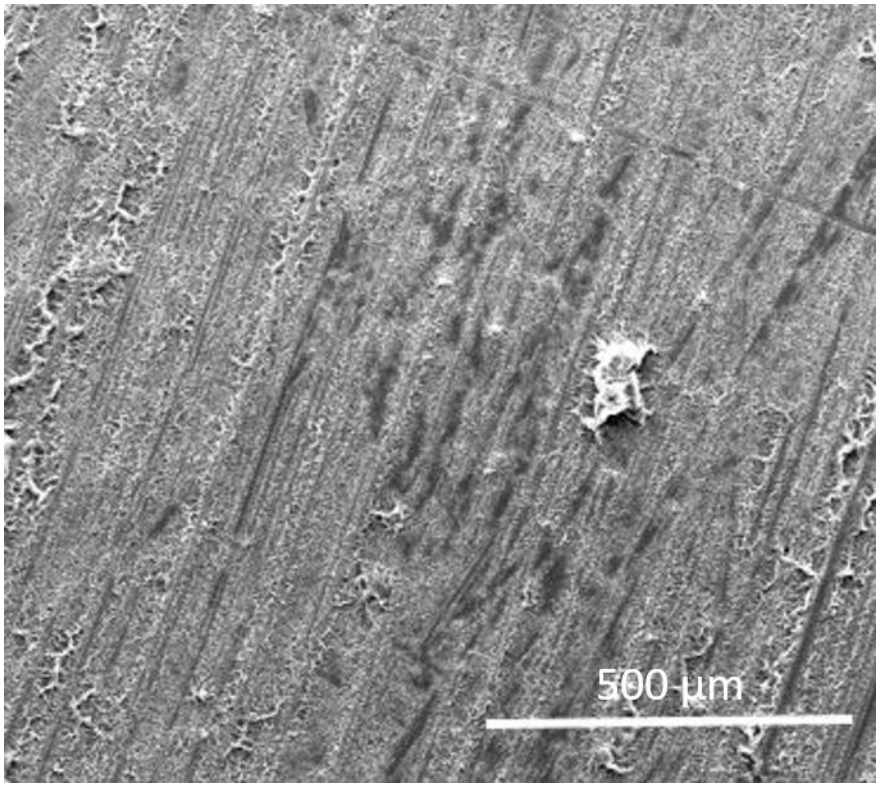

Figure S10. SEM image of printed polymer-nanocomposites (a part peeled from the object in Figure 1c).

Table S1. Results of photoinduced free radical polymerization initiated by CdSe QDs in water[a]

Entry	[QD]:[M] (ppm)	Time (hour)	Ligand exchange method	Conv (%)[b]	M_n (kDa)[c]	Đ	Note
1	12	3	Method A	98.0	26.9	1.59	
2	12	3	Method A	Gel	Gel	Gel	AET-capped QDs
3	3	1	Method B	/	/	/	With 0.1 mmol TEMPO
4	3	5	Method B	/	/	/	With 0.1 mmol TEMPO

a.Reaction condition: 0.54 ml OEGMEM, 2 ml water, with MPA-capped QDs water solution and 6 mol% MPA with 3 hours irradiation under blue LED light (10 mW/cm^2) unless other noted b. Conversion determined by ^{1}H NMR.c. Determined by GPC in THF, based on linear polystyrene as calibration standard

Table S2. Thiol-ene step-growth polymerization catalyzed by CdSe QDs under blue LED[a]

Entry	[QD]:[M][b] (ppm)	Ligand exchange method	Time (hour)	Conv (%)[c]	M_n (kDa)[d]	*Đ*
1	10	Method B	1	100	4.0	1.50
2[e]	10	Method B	1	trace	/	/
3	0	Method B	1	0	/	/

a. Reaction condition: A 4 mL glass vial was charged with N-methyl-2-pyrrolidone (0.3 mL), 1,5-hexadiene (HD, 0.16 ml, 1.34 mmol 1 equiv.), 2,2′- (ethylenedioxy)diethanethiol (EDDT, 0.21 ml, 1.34 mmol, 1 equiv), CdSe QDs water solution (0.1 ml, 10 ppm) and p-toluidine (7.1 mg, 0.07 mmol, 0.05 equiv.). The mixture was then irradiated under blue LED light (10 mW/cm^2). b.[M] stands for monomer (1,5-hexadiene) molar concentration c.Conversion determined by ^{1}H NMR d.Determined by GPC in THF, based on linear polystyrene as calibration standard e. The reaction was performed in the dark, covered with aluminum foil.

Table S3. Results of photoinduced free radical polymerization initiated by CdSe QDs obtained by ligand exchange method A[a]

Entry	[QD]:[M][b] (ppm)	Ligand exchange method	Conv (%)[c]	M_n (kDa)[d]	Đ
1[e]	3	Method A	100	34.1	1.70
2	3	Method A	65.1	32.1	2.05

a. Reaction condition: QDs solution in water was directly used for polymerization. 0.54 ml OEGMEM, 2 ml water, were mixed in a 20 ml silicon vial under 3 hours irradiation by the blue LED household lamp (λ max = 460 nm) b.[M] stands for monomer molar concentration c.Conversion determined by ^{1}H NMR d.Determined by GPC in THF, based on linear polystyrene as calibration standard e. reaction operated with AET ligand capped QDs

Mechanism of ligand stripping methods

Ligand stripping involves a reaction of EDA with the QDs surface followed by a ligand exchange with MPA. Essentially, ethylenediamine strips off the original oleic acid ligand from the QDs surface and reversibly binds to the QDs. Addition of a ligand such as MPA with a thiol group is expected to form stronger Lewis-acid base interactions compared to the amine group in EDA, thus replacing EDA and stabilizes the QDs in aqueous media.

Reference:

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