

Supporting Information

EPR Spin Trapping of Nucleophilic and Radical Reactions at Colloidal Metal Chalcogenide
Quantum Dot Surfaces

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Supporting Information
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General Considerations. Unless otherwise indicated, all procedures were carried out in oven-dried glassware in an MBraun glovebox under an atmosphere of purified nitrogen or using standard Schlenk techniques. Anhydrous tetrahydrofuran (THF), toluene, and hexanes were purified using a J.C. Meyer solvent system.¹ C₆D₆ was purchased from Cambridge Isotope Laboratories, dried over sodium/benzophenone ketyl radical, and vacuum transferred before use. 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO) was purchased from ChemImpex, distilled under vacuum, and stored in the glovebox at -30 °C. Unless otherwise indicated, other commercial reagents were used as received. Octadecylphosphonic acid was purchased from AmBeed. *Cis*-3-hexene was purchased from TCI America. *Trans*-3-hexene was purchased from Sigma-Aldrich. Dibenzyl disulfide and dibutyl disulfide were synthesized following previously published procedures.² Benzyl bromide was degassed, passed through a plug of dry alumina, and stored under nitrogen in the glovebox. Tetramethylethylenediamine (TMEDA) was dried over CaH₂, distilled, and stored in the glovebox.

Sample Characterization. ¹H NMR spectra were recorded on a Bruker 400 MHz instrument, a Bruker 500 MHz instrument, or a Varian 600 MHz instrument, with shifts reported relative to the residual solvent peak (δ 7.16 ppm for C₆D₆, 7.27 ppm for CDCl₃). EPR spectra were recorded at room temperature as solution samples in 4 mm quartz tubes using a Bruker EMX instrument with a frequency of 9.36 GHz. EPR spectra were simulated using EasySpin³ (5.2.35) in Matlab (R2021b). Electronic absorption spectra were collected on solution samples in sealable 1 cm quartz cuvettes using an Agilent Cary 60 instrument. Powder X-ray diffraction (XRD) data were collected on samples drop-cast on a glass slide, using a Bruker AXS D8 Advance diffractometer at a step rate of 0.2° from a 2 θ value of 20–80°. TEM samples were drop-cast onto a copper grid (Ultrathin Carbon Type-A, 400 mesh, Ted Pella) and dried under vacuum overnight. TEM images were collected on a JEOL 2011 microscope or a Talos F200i microscope. Quantum dots (QDs) were sized by TEM (>200 particles). Photoluminescence (PL) emission spectra were measured using an Ocean Optics USB+2000 spectrometer with excitation using a 405 nm laser pointer.

Photoirradiation Experiments. Single color surface mount StarBoard LEDs were purchased from DigiKey (405 and 530 nm) and Mouser Electronics (310, 365, and 445 nm). Each LED was attached to an aluminum heat sink (Newark, SA-LED-113E) using Thermalcote Thermal Grease (Newark). The optical power was measured with a Standa power meter. Alternatively, single wavelength lamps were purchased from Kessil (PhotoReaction PR160L, 370 and 440 nm). A 300 W Xe lamp (Newport 67005) equipped with a 515 nm longpass filter (Newport FSQ-0G515) was used for longer wavelength irradiation. USB-powered fans were used to maintain the temperature of the samples.

Gel Permeation Chromatography (GPC). To prepare the column, Bio-Beads SX-1 (200–400 mesh; 4 g) were dried under vacuum at room temperature for 3 days. The beads were brought into the glovebox and stored in THF for 12 h. The beads were transferred into a column ($d \sim 2$ cm) and flushed to remove any residual contaminants. The unpurified QD sample (ca. 0.4 mL, ca. 0.5 mM) was loaded onto the column and eluted with THF using gravity. The first red band to elute was collected and dried under vacuum. The second band was collected until no yellow residue remained on the column and dried under vacuum.

Synthesis of CdSe, CdS, ZnSe, and PbS QDs

Synthesis of zinc blende CdSe QDs ($d \sim 3.6$ nm). In a representative procedure, a 500 mL 3-neck round-bottom flask equipped with a stir bar was charged with CdO (3.0 g, 22.9 mmol, 1 equiv), oleic acid (24 mL, 69.7 mmol, 3 equiv), and 1-octadecene (ODE, 300 mL). The flask was fitted with a reflux condenser and the stirring mixture was degassed under vacuum at 90 °C for 30 min. Under N₂, the mixture was heated to 300 °C with vigorous stirring until it turned colorless and homogeneous, indicating the formation of Cd(OA)₂ (OA⁻ = oleate). The solution was cooled below 60 °C and SeO₂ (2.904 g, 22.86 mmol, 1 equiv) was added as a solid under N₂ flow. The mixture was heated with stirring to 240 °C under N₂ until the mixture turned red, then the flask was removed from heat and cooled to room temperature. The ODE was removed by vacuum distillation. The resulting red residue was taken up in hexanes and centrifuged. The pellet was discarded, and ethanol was added to the supernatant. The mixture was centrifuged again to collect the precipitated CdSe QDs. This step was repeated twice. The purified QD sample was suspended in a minimal volume of hexanes (ca. 5 mL) and dried under vacuum before storing in the glovebox.

Synthesis of OA-capped zinc blende CdSe QDs ($d \sim 6.2$ nm). A 500 mL 3-neck round-bottom flask equipped with a stir bar was charged with CdO (5.0 g, 39 mmol, 1 equiv), oleic acid (25 mL, 78 mmol, 2 equiv), and ODE (300 mL). The flask was fitted with a reflux condenser and the stirring mixture was degassed under vacuum 100 °C for 1 h. Under N₂, the reaction mixture was then heated to 300 °C until the solution turned colorless and homogeneous. The solution was cooled to 60 °C and SeO₂ (4.3 g, 39 mmol, 1 equiv) was added as a solid under an N₂ flow. The mixture was heated while stirring to 240 °C under N₂. After the solution turned red, the reaction was monitored by aliquoting samples for UV-vis measurements until the desired size was reached. The solution was heated at 240 °C for 45 min. The flask was then removed from heat and cooled to room temperature. The ODE was removed by vacuum distillation. The resulting reddish-brown residue was taken up in hexanes and centrifuged. The pellet was discarded, and ethanol was added to the supernatant. The mixture was centrifuged and the pellet, CdSe QDs, was collected and the supernatant was discarded. This step was repeated three times. The purified QD sample was dried under vacuum and the resulting residue was brought into a nitrogen glovebox. The CdSe QDs were resuspended in THF and stored in the freezer.

Synthesis of OA-capped zinc blende CdS QDs ($d \sim 2.7, 3.5, 3.8$ nm). A 3-necked round bottom flask with a stir bar was charged with CdO (0.385 g, 3.0 mmol, 1 equiv), oleic acid (7.37 mL, 9.0 mmol, 3 equiv) and ODE (35 mL). The mixture was degassed under vacuum with stirring and heated to 100 °C for 30 min. The mixture was put under a N₂ atmosphere and heated to 300 °C with vigorous stirring until it turned colorless and homogeneous. The temperature of the solution was then cooled to 240 °C and a hot solution of O-phenyl-O'-(p-tolyl) thiocarbonate (0.596 g, 2.44 mmol, 0.82 equiv) in toluene (5 mL) was injected by syringe. The reaction was stirred for 120 minutes before removing the flask from heat and cooling to room temperature. The ODE was distilled off under vacuum without heating past 160 °C. The resulting yellow residue was taken up in hexanes and centrifuged. The pellet was discarded, and ethanol was added to the supernatant. The mixture was centrifuged again to collect the precipitated CdS QDs. This step was repeated twice. The purified CdS sample was suspended in hexanes (ca. 10 mL) and dried under vacuum before storing in the glovebox.

OA-for-octadecylphosphonate (ODPA) ligand exchange for CdSe or CdS QDs. In a representative procedure, a 20 mL scintillation vial equipped with a stir bar was charged with octadecylphosphonic acid (0.2 g, 0.6 mmol, 100 equiv/QD) and a benzene suspension of OA-capped CdS QDs ($d \sim 3.0$ nm, 1.5 mM, 4 mL, 6 μ mol). The mixture was stirred for 5 h under ambient conditions. The QD sample was precipitated by addition of methanol (20 mL) and centrifuged. The solvent was decanted, and the pellet was purified by two resuspension/precipitation steps using benzene/methanol. The purified sample was dried under vacuum and stored in a 4:1 THF/C₆D₆ mixture. A similar procedure was used for ligand exchange of a benzene suspension of OA-capped CdSe QDs ($d \sim 3.6$ nm, 0.5 mM, 6 mL, 0.72 μ mol) with octadecylphosphonic acid (0.24 g, 0.72 mmol, 200 equiv/QD).

OA-for-decanethiolate ligand exchange for CdS QDs. In a representative procedure, in the glovebox, a 20 mL scintillation vial equipped with a stir bar was charged with 1-decanethiol (76 μ L, 0.4 mmol, 200 equiv/QD) and a hexanes suspension of OA-capped CdS QDs ($d \sim 3.5$ nm, 0.6 mM, 3 mL, 1.8 μ mol). The mixture was stirred for 20 min at room temperature. The QD sample was precipitated by addition of methyl acetate (10 mL) and centrifuged. The solvent was decanted, and the pellet was purified by two resuspension/precipitation steps using hexanes/methyl acetate. The purified sample was dried under vacuum and stored in hexanes.

Removal of Cd(OA)₂ from OA-capped CdS QDs. In a representative reaction, in the glovebox, a scintillation vial equipped with a stir bar was charged with a hexanes solution of CdS QDs ($d \sim 3.5$ nm, 0.6 mM, 1.5 mL, 0.9 μ mol) and TMEDA (1.3 mM, 0.5 mL 0.63 mmol, 700 equiv). The mixture was allowed to stir for 0.5 h, precipitated with methyl acetate (10 mL), and centrifuged. The solvent was decanted, and the pellet was purified by two resuspension/precipitation steps using hexane/methyl acetate. The purified sample was dried under vacuum and stored in hexanes.

Synthesis of ZnSe QDs ($d \sim 3.0$ nm). A 250 mL 3-neck round bottom flask equipped with a stir bar was charged with Zn₅(CO₃)₂(OH)₆ (550 mg, 1.00 mmol, 1 equiv), oleic acid (5 mL, 15 mmol, 15 equiv), and ODE (100 mL). The flask was fitted with a reflux condenser. Under N₂, the mixture was heated to 270°C. Then, 10 mL of a separately prepared Se-ODE mixture (selenium (197 mg, 2.5 mmol, 2.5 equiv) in ODE (10 mL)) were injected and the reaction was heated at 260 °C for 20 min. The ODE was removed by vacuum distillation. The resulting residue was taken up in toluene and centrifuged. The pellet was discarded, and methanol was added to the supernatant in a 2:1 ratio toluene/methanol. The mixture was centrifuged again to collect the precipitated ZnSe QDs. This step was repeated twice. The purified QD sample was suspended in a minimal volume of hexanes (ca. 5 mL) and dried under vacuum before storing in the glovebox.

Synthesis of OA-capped PbS QDs ($d \sim 3.4$ nm).⁴ In the glovebox, a 250 mL 3-neck round bottom flask equipped with a stir bar was charged with Pb(OA)₂ (8.81 g, 11.4 mmol) and octane (150 mL). A separate 25 mL 3-neck round bottom flask equipped with a stir bar was charged with *N,N'*-diphenylthiourea (1.74 g, 7.62 mmol) and diglyme (5 mL). Each flask was fitted with a reflux condenser, placed under a N₂ atmosphere, heated to 95 °C in an oil bath, and stirred for 30 min. The *N,N'*-diphenylthiourea/diglyme solution was then quickly injected into the Pb(OA)₂ solution with vigorous stirring. After 1 min, the solution turned a dark brown. The reaction mixture was cooled to room temperature, then concentrated under vacuum. In the glovebox, the resulting brown residue was taken up in toluene and centrifuged. The pellet was discarded, and

methyl acetate was added to the supernatant. The mixture was centrifuged again to collect the precipitated PbS QDs. This step was repeated twice. The purified QD sample was suspended in hexanes and dried under vacuum. The resulting solution was resuspended in hexanes and stored in the glovebox at $-30\text{ }^{\circ}\text{C}$.

QD Sample Characterization

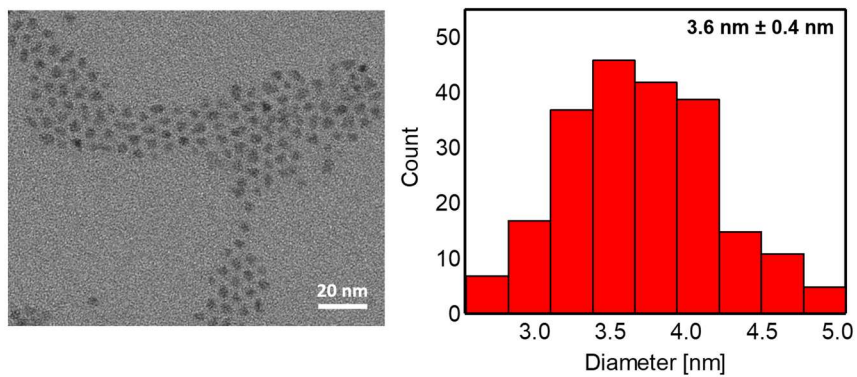


Figure S1. TEM image and size distribution of zinc blende OA-capped CdSe QDs ($d \sim 3.6\text{ nm}$).

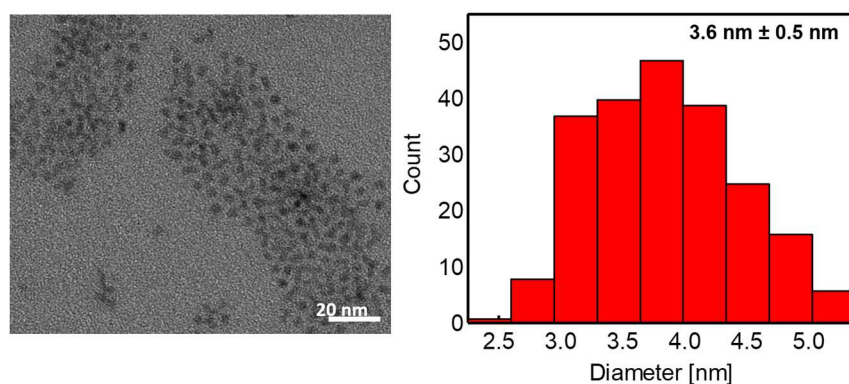


Figure S2. TEM image and size distribution of CdSe QDs after DMPO reaction and purification.

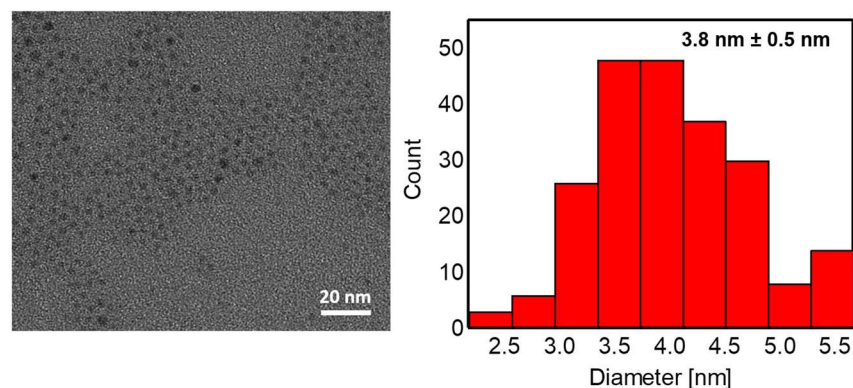


Figure S3. TEM image and size distribution of zinc blende OA-capped CdS QDs ($d \sim 3.8\text{ nm}$).

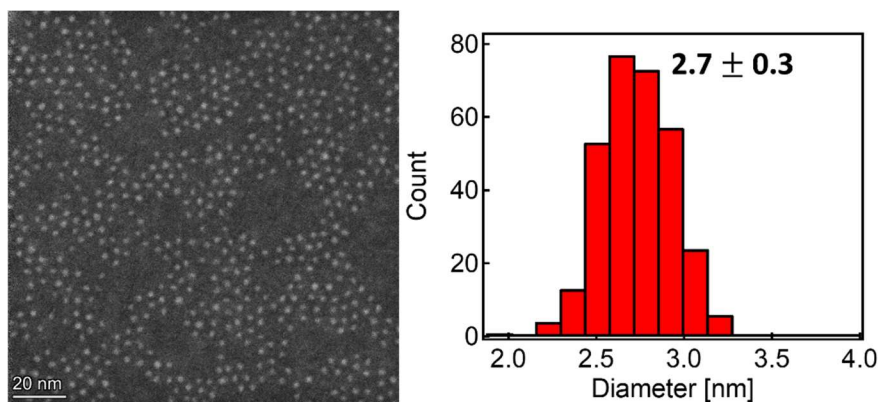


Figure S4. TEM image and size distribution of zinc blende OA-capped CdS QDs ($d \sim 2.7$ nm).

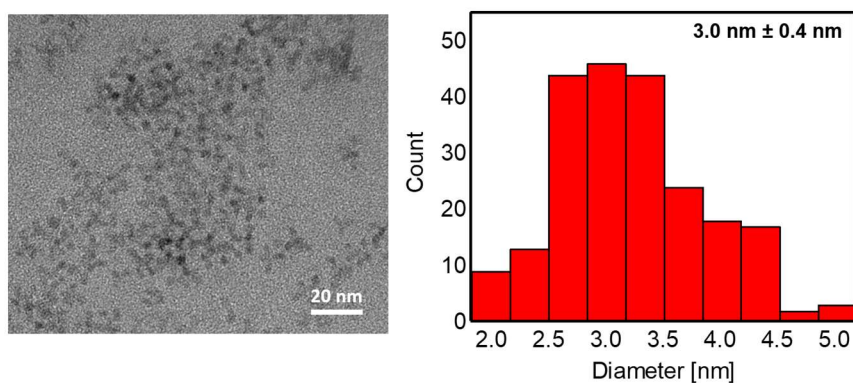


Figure S5. TEM image and size distribution of zinc blende ZnSe QDs ($d \sim 3.0$ nm).

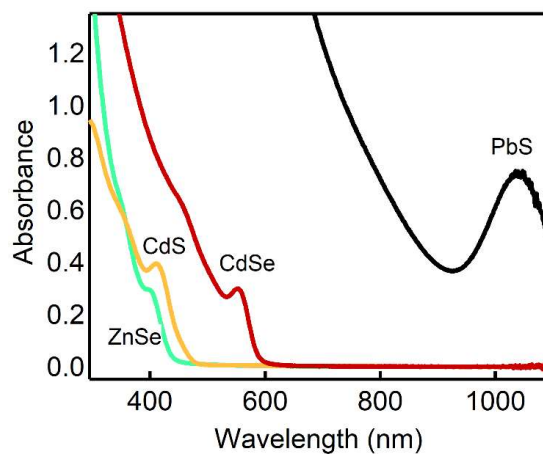


Figure S6. Absorption spectra of toluene solutions of CdSe, CdS, PbS, and ZnSe QD samples studied.

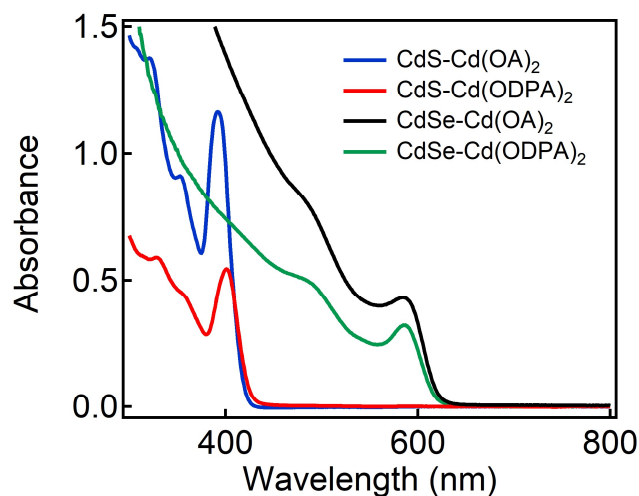


Figure S7. Electronic absorption spectra of THF solutions of OA-capped CdS ($d \sim 2.7$ nm) and CdSe ($d \sim 3.6$ nm) QDs, as well as of ODPA-capped QD samples after ligand exchange.

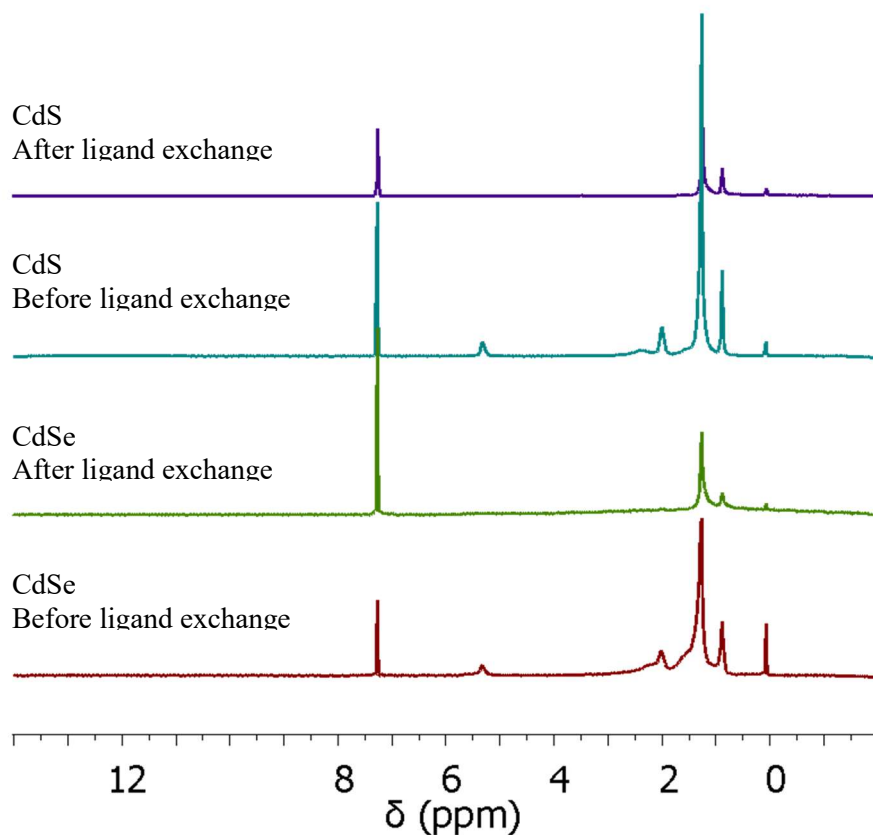


Figure S8. ^1H NMR spectra of CDCl_3 solutions of CdS ($d \sim 2.7$ nm) and CdSe QDs ($d \sim 3.6$ nm) before and after ligand exchange from OA^- with octadecylphosphonic acid and after purification by precipitation/centrifugation, showing removal of surface bound oleate species after purification.

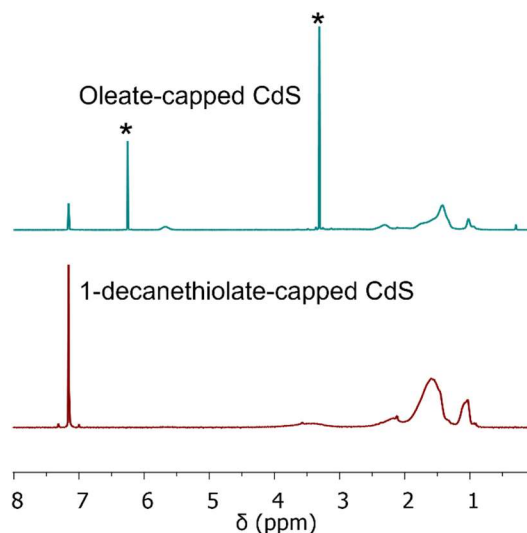


Figure S9. ^1H NMR spectra of C_6D_6 solutions of oleate-capped CdS QDS ($d \sim 3.5$ nm) before (top) and after (bottom) ligand exchange with 1-decanethiol and purification by precipitation/centrifugation, showing removal of surface-bound OA^- . (*) indicates the 1,3,5-trimethoxybenzene internal standard.

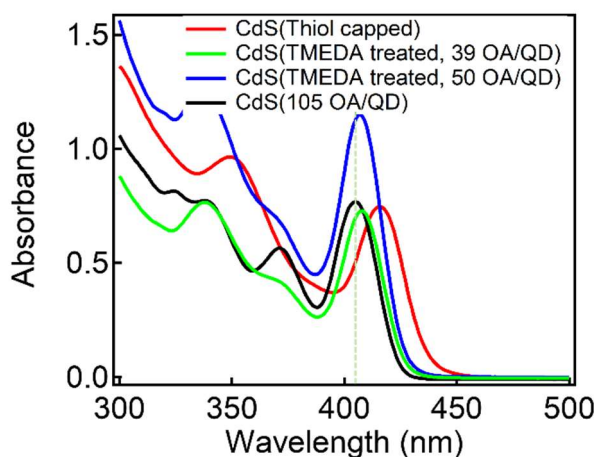
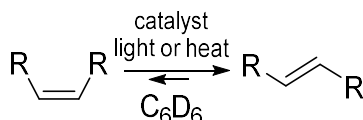


Figure S10. Electronic absorption spectra of hexanes solutions of OA-capped CdS QD samples ($d \sim 3.5$ nm) as-prepared (black), after treatment with TMEDA to remove $\text{Cd}(\text{OA})_2$ ligands (blue and green), and after exchange with 1-decanethiol (red).

Table S1. Ligand concentrations of OA-capped CdS QDs used in these studies quantified by ^1H NMR spectroscopy using a 1,3,5-trimethoxybenzene internal standard.

QD sample (size)	d (nm)	OA/QD	OA/nm ²
CdS (2.7 nm)	2.7	49	2.1
CdS (3.5 nm)	3.5	105	2.7
CdS after TMEDA treatment (1)	3.5	50	1.3
CdS after TMEDA treatment (2)	3.5	39	1.0



Photoisomerization of alkenes. In a representative procedure, an NMR tube was charged with a C_6D_6 suspension of CdS QDs ($d \sim 2.7$ nm, 0.5 mL, 0.75 mM, 0.375 μmol) and sealed with a septum-lined screwcap in the glovebox. To this tube, *trans*-3-hexene (4.7 μL , 38 μmol , 100 equiv/QD) was added via syringe. The tube was irradiated using a 370 nm Kessil lamp at room temperature and analyzed using ^1H NMR spectroscopy over 40 h.

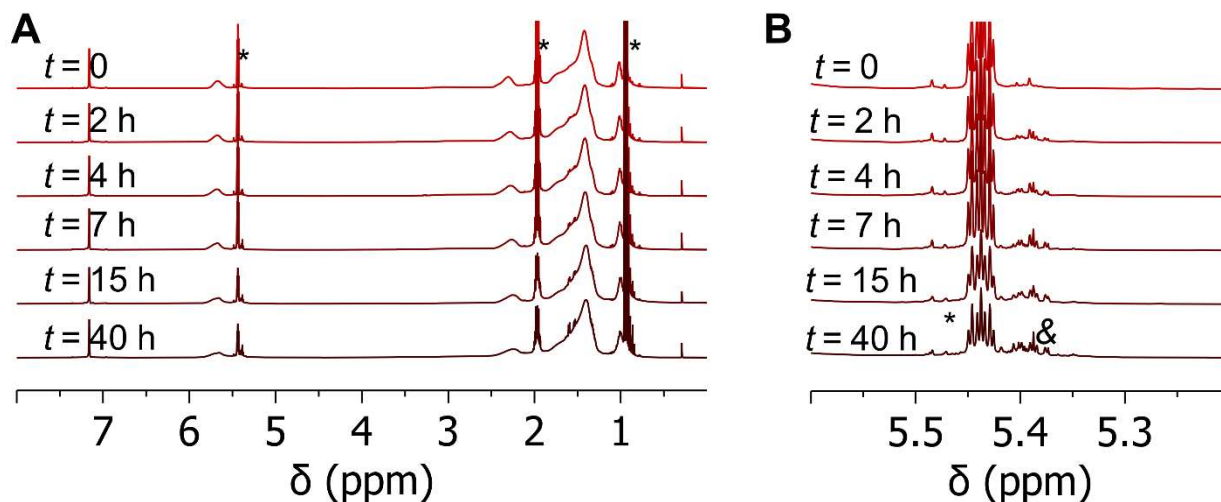


Figure S11. (A) ^1H NMR spectra of a C_6D_6 suspension of OA-capped CdS QDs ($d \sim 2.7$ nm) with *trans*-3-hexene (*, 80 equiv/QD) taken after irradiation ($\lambda_{\text{exc}} = 370$ nm), showing the formation of *cis*-3-hexene. (B) Truncated spectra indicating the alkenyl proton resonances of *trans*-3-hexene (*) and *cis*-3-hexene (&).

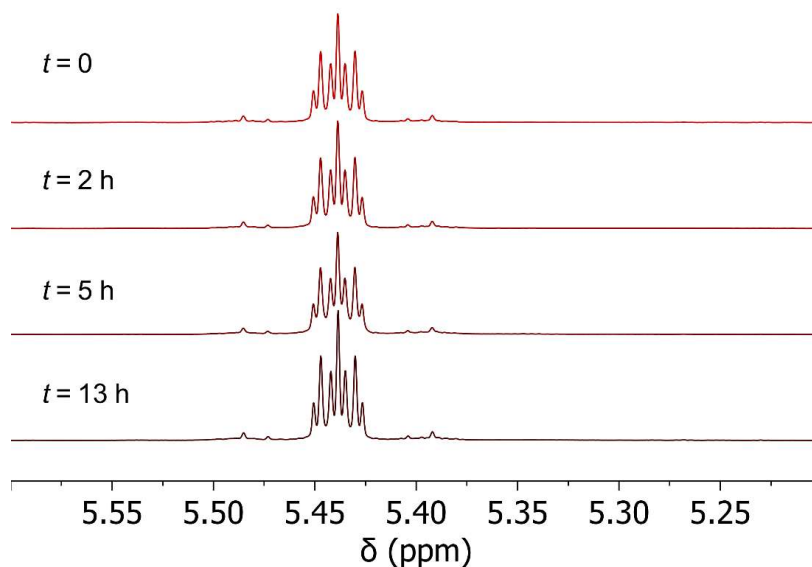


Figure S12. ^1H NMR spectra of a C_6D_6 solution of *trans*-3-hexene under irradiation ($\lambda_{\text{exc}} = 370$ nm, 100 mW/cm^2), showing that no *cis-trans* photoisomerization occurs without CdS QDs.

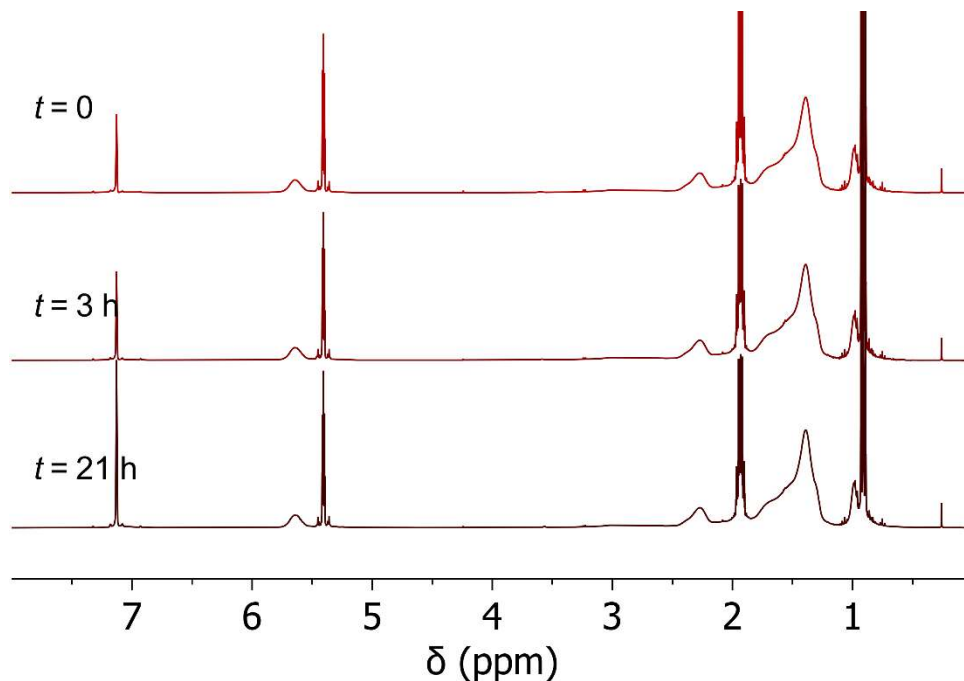


Figure S13. ^1H NMR spectra of a C_6D_6 suspension of CdS QDs ($d \sim 2.7$ nm) and *trans*-3-hexene (80 equiv/QD) heated at 90°C for 21 h, showing no *cis-trans* isomerization of 3-hexene.

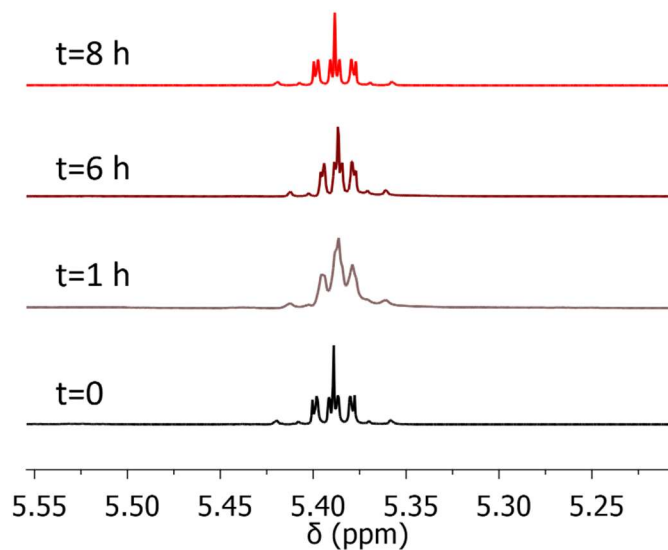


Figure S14. ^1H NMR spectra of a C_6D_6 mixture of CdS QDs ($d \sim 3.5$ nm) and *cis*-3-hexene (100 equiv/QD) after irradiation with sub-band-gap light ($\lambda > 515$ nm, 100 mW/cm 2), showing that no *cis-trans* photoisomerization occurs over 8 h.

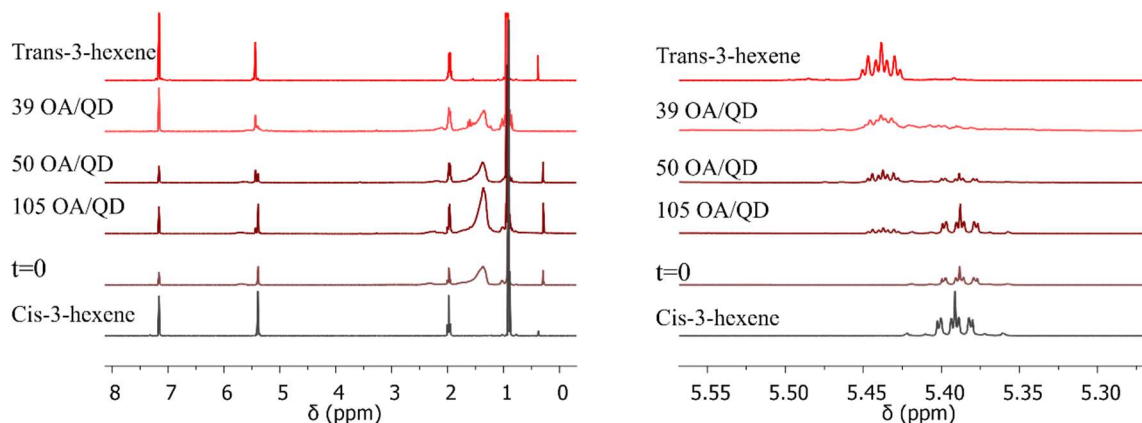


Figure S15. Comparison of ^1H NMR spectra of C_6D_6 solutions of *cis*-3-hexene treated with CdS QDs ($d \sim 3.5$ nm, 1 mol %) with different $\text{Cd}(\text{OA})_2$ densities (1.7, 1.3, and 1.0 OA/nm^2) after irradiation ($\lambda = 370$ nm, 100 mW/cm^2) for 15 h.

Alkene isomerization–UV/Vis studies. In a nitrogen-filled glovebox, a 1-cm quartz Schlenk cuvette equipped with a stir bar was charged with a hexanes suspension of OA-capped CdS QDs (5 μM , 3.0 mL, 0.015 μmol). *Cis*-3-hexene (2 μL , 1.5 μmol , 100 equiv/QD) was added by syringe. The cuvette was sealed and irradiated at 25 $^\circ\text{C}$ with a 370 nm Kessil lamp (100 mW/cm^2) outside the glovebox for 24 h with stirring and simultaneous absorption measurement. After 24 h, the sealed cuvette was opened to expose the solution to atmospheric oxygen and an absorption spectrum of the content collected without irradiation. A similar procedure was repeated for the control reactions. Briefly, in a separate experiment, a hexanes suspension of CdS QDs was irradiated 370 nm lamp at room temperature for 20 h, with no added alkene.

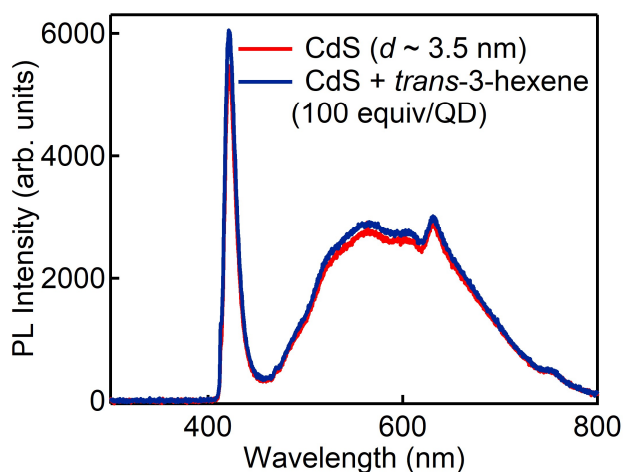
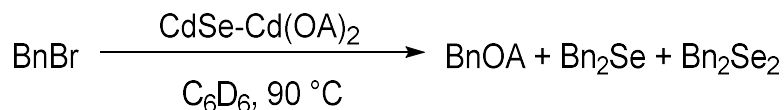


Figure S16. PL emission of OA-capped CdS QDs ($d \sim 3.5$ nm) before and after addition of *trans*-3-hexene (100 equiv/QD), showing no PL quenching by alkene addition.



Benzyl bromide substitution. In a representative procedure, in the glovebox, a J. Young NMR tube was charged with a C_6D_6 suspension of OA-capped CdSe QDs ($d \sim 3.6$ nm, 0.5 mM, 0.6 mL, 0.3 μmol). Benzyl bromide (2 μL , 50 equiv/QD) was added, and the NMR tube was sealed with a Teflon-lined cap. The tube was then heated at 90 $^\circ\text{C}$ in the dark and analyzed by ^1H NMR spectroscopy over 20 h. Similar procedures were followed for OA-capped CdS QDs ($d \sim 3.5$ nm) and ODPA-capped CdSe QDs ($d \sim 3.6$ nm). Assignments to products were made by GC-MS of the mixture and by comparison to literature data (benzyl oleate [BnOA],⁵ dibenzyl sulfide and dibenzyl selenide,⁵ dibenzyl diselenide⁶). For the related reaction with CdS QDs, BnOA, dibenzyl trisulfide,⁷ and dibenzyl disulfide⁸ were identified by ^1H NMR spectroscopy. Dibenzyl sulfide was also observed by GC-MS.

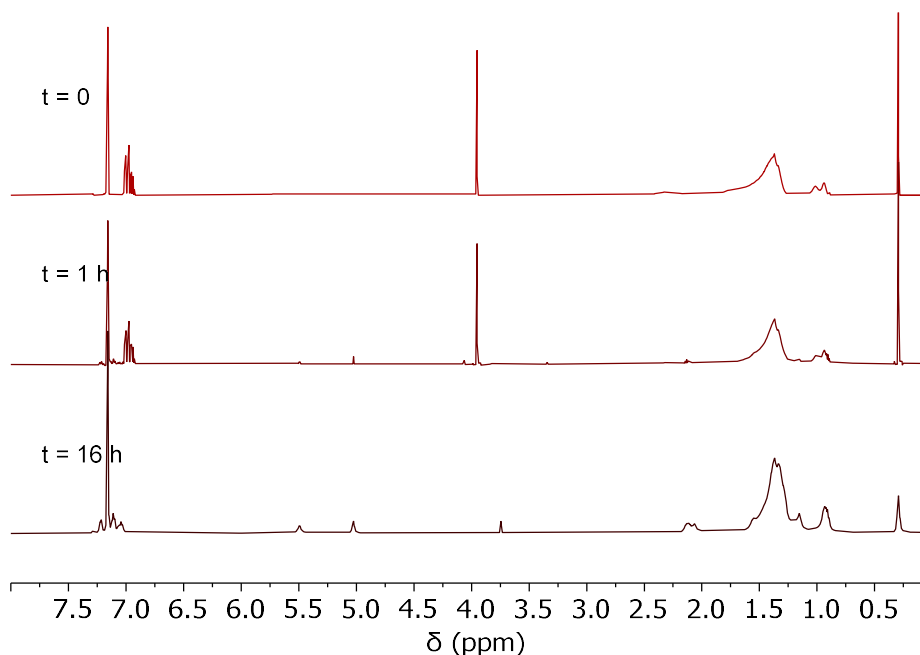


Figure S17. ^1H NMR spectra of a C_6D_6 mixture of OA-capped CdSe QDs ($d \sim 3.6$ nm) and benzyl bromide (30 equiv/QD) during heating at 90 $^\circ\text{C}$, showing consumption of benzyl bromide (δ 3.95 ppm) and formation of new benzylic products.

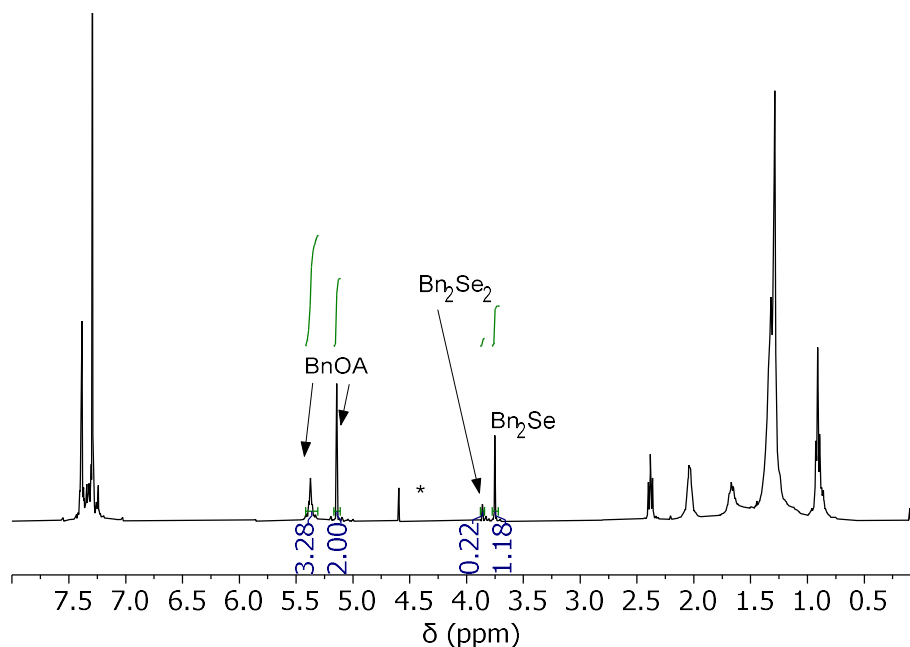


Figure S18. ^1H NMR spectrum of a CDCl_3 solution of the reaction mixture of OA-capped CdSe QDs after treatment with benzyl bromide and heating at $90\text{ }^\circ\text{C}$ for 15 h, followed by separation of the QDs by precipitation. The spectrum is of the QD-free supernatant, indicating molecular, unbound products.

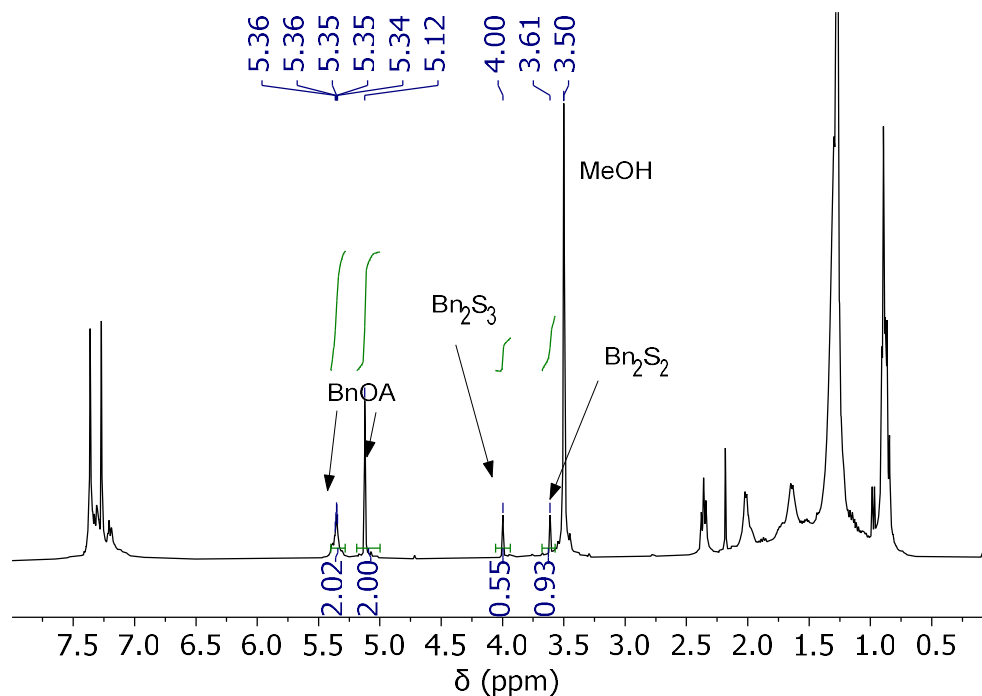


Figure S19. ^1H NMR spectrum of a CDCl_3 solution of the reaction mixture of OA-capped CdS QDs after treatment with benzyl bromide and heating at $90\text{ }^\circ\text{C}$ for 18 h, followed by separation of the QDs by precipitation using methanol. The spectrum is of the QD-free supernatant, indicating molecular, unbound products.

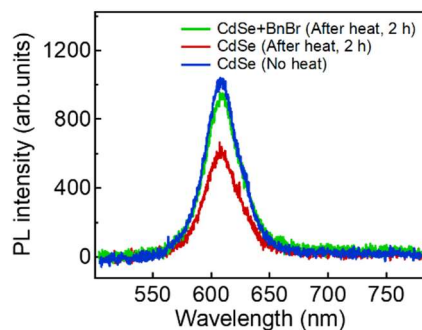
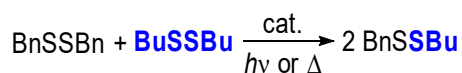


Figure S20. PL emission of toluene solutions of OA-capped CdSe QDs ($d \sim 3.6$ nm, $1.32 \mu\text{M}$) when treated benzyl bromide (50 equiv/QD,) before and after heating at 80°C for 2 h. While heating in the absence of BnBr results in PL quenching, the sample treated with BnBr exhibits the same PLQY due to Se^{2-} alkylation.



Disulfide scrambling. In a representative procedure, in the glovebox, an NMR tube was charged with a C_6D_6 suspension of CdSe QDs ($d \sim 3.6$ nm, 0.5 mM, 0.6 mL, $0.3 \mu\text{mol}$). Dibenzyl disulfide ($15 \mu\text{mol}$, $18.5 \mu\text{L}$, 50 equiv/QD) and dibutyl disulfide ($15 \mu\text{mol}$, $2.3 \mu\text{L}$, 50 equiv/QD) were added and the NMR tube was sealed with a septum-lined screwcap. The tube was then heated at 100°C and analyzed by ^1H NMR spectroscopy over 17 h.

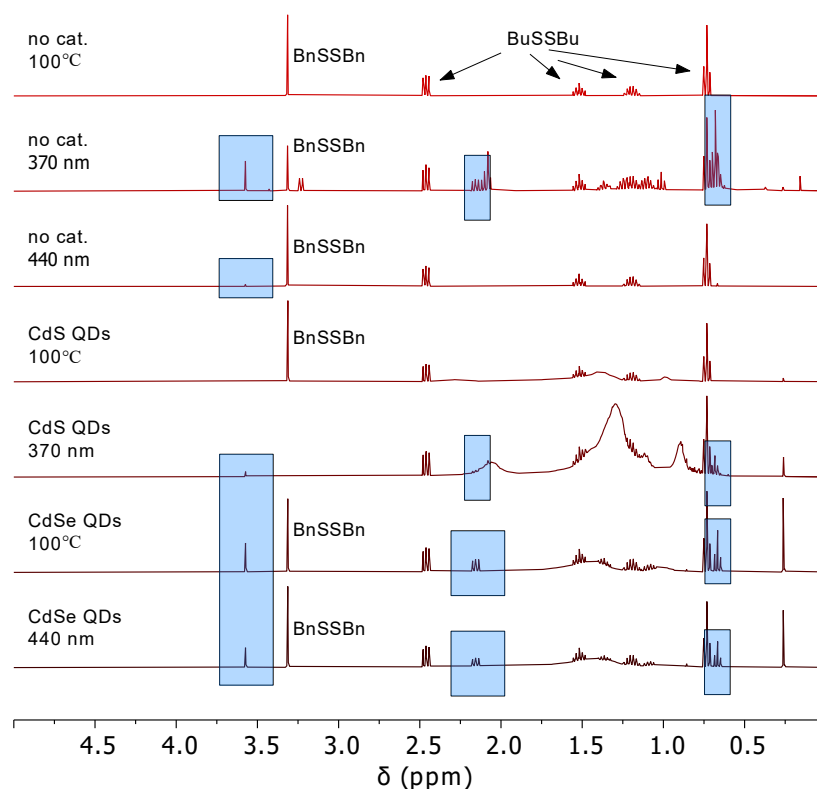


Figure S21. ^1H NMR spectra of C_6D_6 solutions of 1:1 BnSSBn/BuSSBu after irradiation or heating with and without QD catalysts. Blue boxes indicate the mixed disulfide product BnSSBu.

DMPO spin trapping. In a representative procedure, 400 μL of a 0.5 mM (0.212 μmol , 1 equiv) CdSe QD suspension in hexanes was added to a 20 mL scintillation vial and dried under vacuum inside the glovebox. 400 μL of a toluene solution of DMPO (240 mg in 4 mL toluene, 0.212 mmol, 0.5 mM, 1000 equiv) in toluene was added and the reaction mixture transferred to an EPR tube. The EPR tube was sealed with Parafilm and heated (70–110 $^{\circ}\text{C}$) or irradiated for 16 h. After 12 h, an EPR spectrum was taken of the unpurified reaction mixture. All reactions were subsequently purified by GPC using a THF eluent. The QD fraction was diluted with 420 μL toluene. 10 μL were used for determining the QD concentration by absorption spectroscopy, and 400 μL were transferred to an EPR tube. The supernatant fraction was diluted with 400 μL toluene and an EPR spectrum was taken of both fractions in parafilm-sealed EPR tubes. The parafilm-sealed EPR tubes were stored inside the glovebox.

Spin quantification. Stock solutions of TEMPO radical in toluene were prepared at different concentrations in the glovebox. EPR spectra were measured, and a calibration curve was prepared by double integration of the spectra following baseline correction.

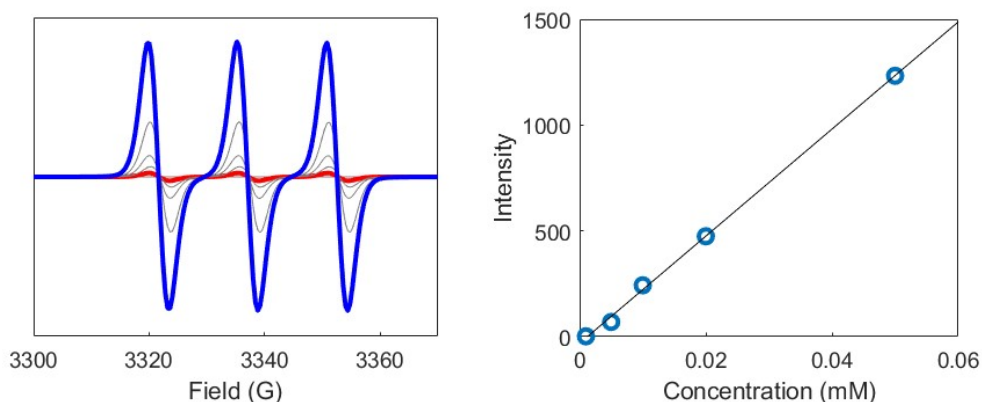


Figure S22. X-band EPR spectra of toluene solutions of TEMPO radical (0–0.05 mM, left). Plot of doubly integrated EPR signals vs. TEMPO radical concentration, with included linear fit (right). Slope = 25,000 mM^{-1} , $R^2 = 0.99$. This calibration line was used to quantify nitroxide radical species in the described experiments.

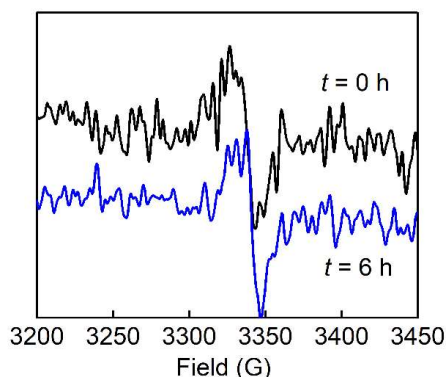


Figure S23. EPR spectra of a toluene solution of DMPO before and after irradiation for 6 h ($\lambda_{\text{exc}} = 440 \text{ nm}$), showing that no nitroxide radical is formed in the absence of QDs.

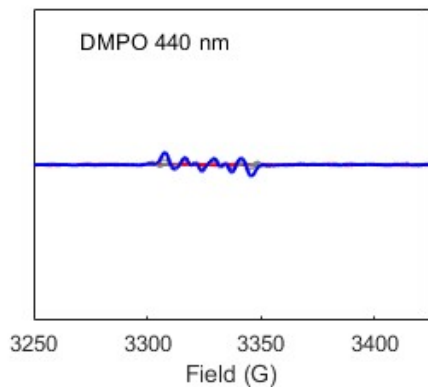


Figure S24. EPR spectra of a THF solution of DMPO before and after irradiation over 40 h ($\lambda_{\text{exc}} = 440$ nm). A weak multi-line signal is observed.

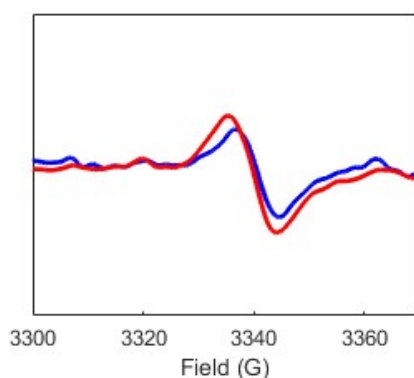


Figure S25. EPR spectra of a toluene solution of OA-capped CdSe QDs before (blue) and after (red) irradiation for 12 h ($\lambda_{\text{exc}} = 440$ nm), showing that no nitroxide radical is formed in the absence of DMPO.

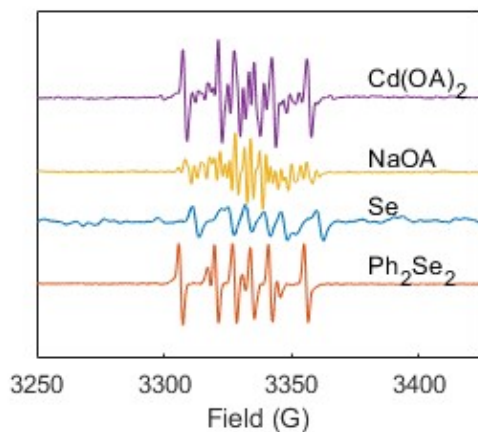


Figure S26. EPR spectra of mixtures of DMPO and Cd(OA)_2 , NaOA, Se, or Ph_2Se_2 after heating at 80–100 °C for 12 h.

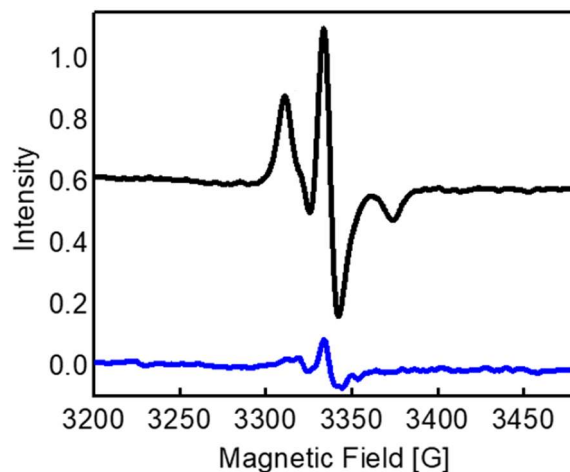


Figure S27. EPR spectra of purified QD samples from the reaction of OA-capped CdSe QDs with DMPO (black) and PBN (blue) under 445 nm irradiation.

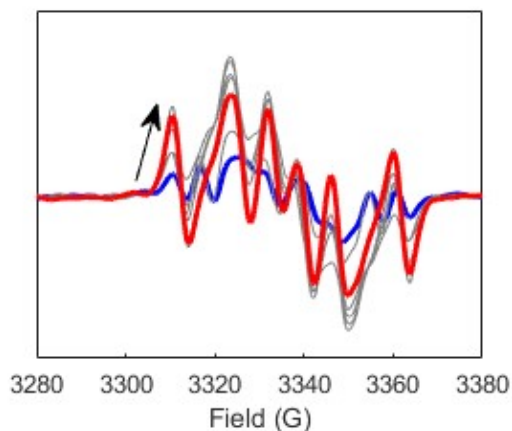


Figure S28. EPR spectra of a toluene mixture of OA-capped CdSe ($d \sim 3.6$ nm) and DMPO (1000 equiv/QD) upon irradiation ($\lambda_{\text{exc}} = 440$ nm, 0 (blue) to 90 min (red)).

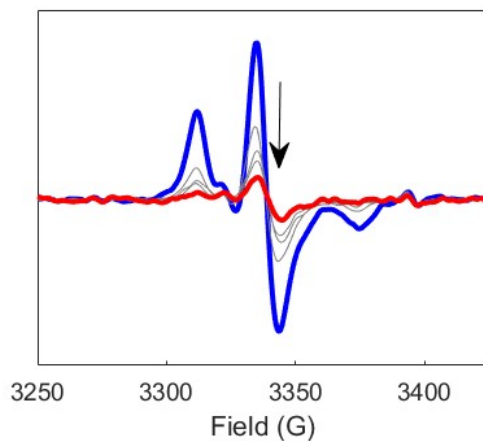


Figure S29. Decay of purified CdSe QD-bound nitroxide radical under irradiation over 5 h ($\lambda_{\text{exc}} = 440$ nm, from $t = 0$ (blue) to 90 min. (red)).

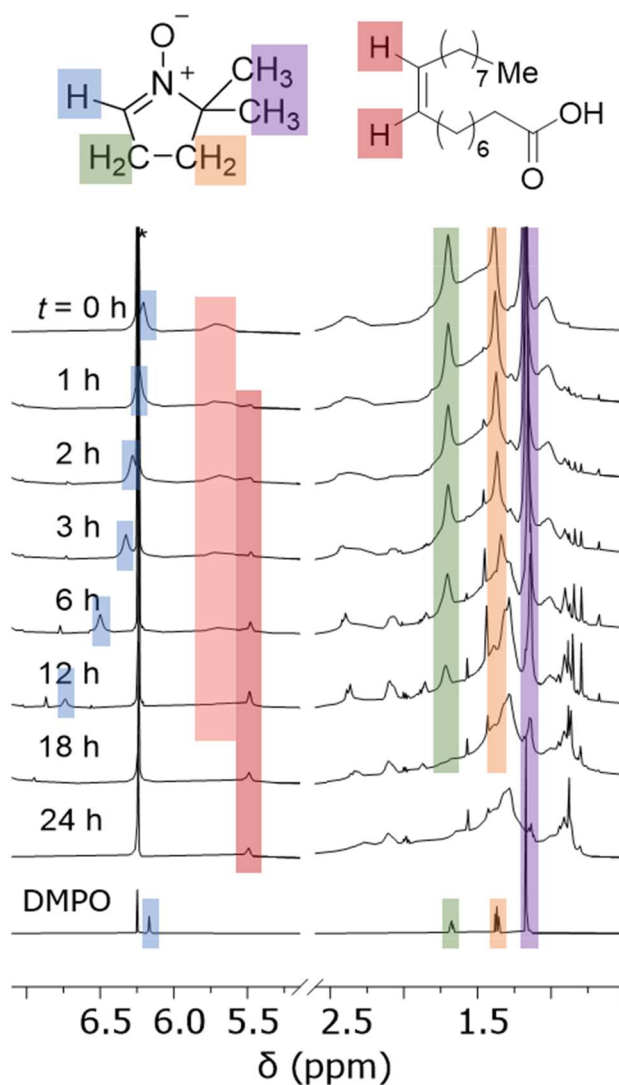


Figure S30. ^1H NMR spectra of a C_6D_6 mixture of zinc blende OA-capped CdSe QDs ($d \sim 3.6$ nm) and DMPO (300 equiv/QD) during irradiation ($\lambda = 440$ nm, 200 mW/cm 2).

Photodoping procedure. In the glovebox, a toluene suspension of OA-capped CdSe QDs ($d \sim 3.6$ nm, 1.3 μM , 3.0 mL) was treated with DMPO (0.001 g, 1000 equiv/QD) and transferred to a 1-cm quartz four-sided cuvette equipped with a stir bar. The cuvette was sealed with a screw cap and irradiated with a LED ($\lambda = 440$ nm, 200 mW/cm 2) with simultaneous absorption measurements.

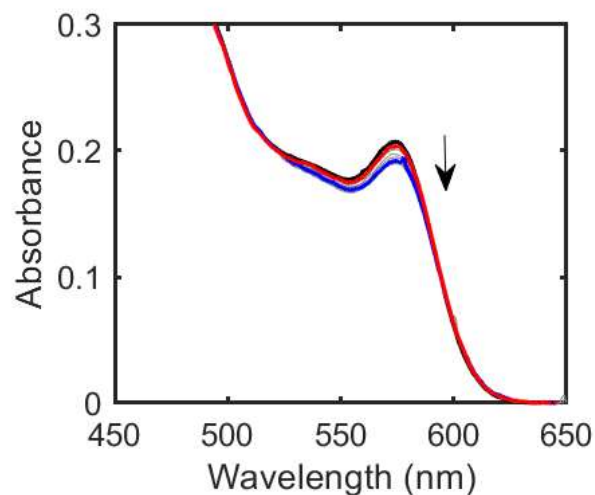


Figure S31. Electronic absorption spectra of a toluene mixture of OA-capped CdSe QDs ($d \sim 3.6$ nm) and DMPO (1000 equiv/QD) before (black) and after (blue) irradiation for 5 min. The red trace is the spectrum of the sample post-photoexcitation and after exposure to air, indicating that the bleach is reversible upon oxidation, consistent with sample photodoping.

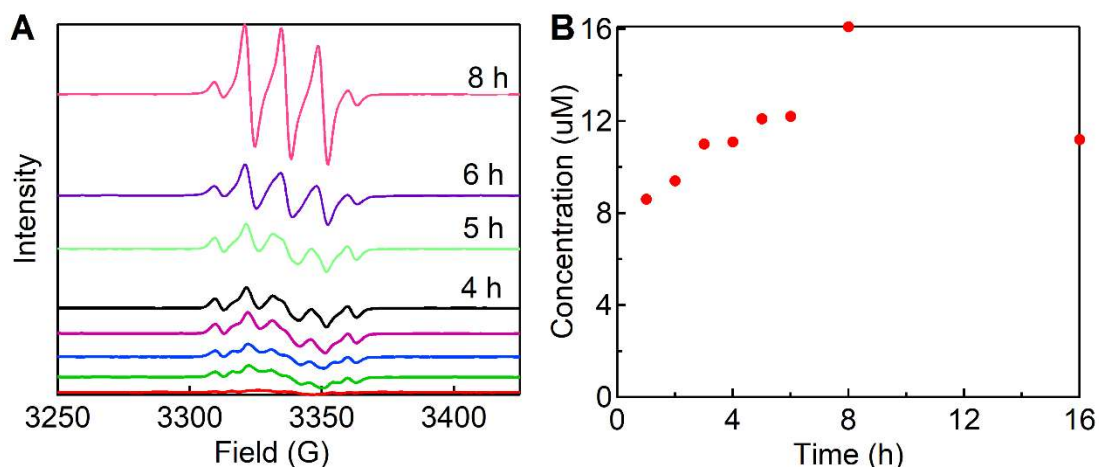


Figure S32. (A) EPR spectra of a toluene mixture of OA-capped CdSe ($d \sim 3.6$ nm) and DMPO (1000 equiv/QD) after heating to 90 °C. (B) Concentration of nitroxide radicals calculated by spin quantification over time while heating to 90 °C.

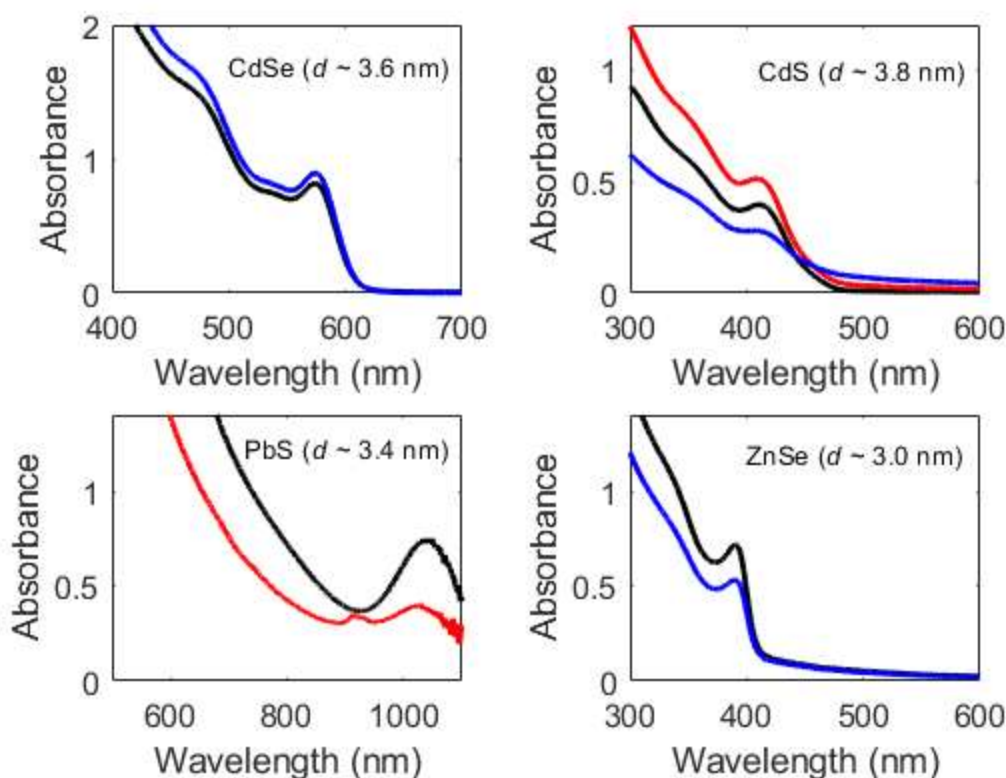


Figure S33. Electronic absorption spectra of QD samples before (black) and after addition of DMPO followed by heating (red) or photoirradiation (blue). For all samples, some slight broadening is observed with no significant etching or changes in QD size.

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