

Supporting Information

Selenium Redox Reactivity on Colloidal CdSe Quantum Dot Surfaces

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Experimental Methods

General Considerations. Unless stated otherwise, all measurements and synthetic manipulations were carried out using standard Schlenk techniques under a nitrogen atmosphere, or in M. Braun or Vac gloveboxes under an atmosphere of purified nitrogen. Anhydrous THF and toluene were purified through columns of dried alumina. Unless stated otherwise, reagents were purchased from Sigma-Aldrich and used without further purification. Tributyltin hydride was distilled before use. Cadmium oxide was purchased from Strem and used without further purification. Lithium triethylborodeuteride (1.0 M in THF) was prepared from triethylborane (1.0 M in THF) and lithium deuteride. Cadmium oleate was prepared according to published procedures.¹

Nanocrystal Synthesis. Zinc blende CdSe nanocrystals of various diameters were prepared by an adaptation of a previously reported heat-up synthesis method.² As an example: CdO (0.195 g, 1.52 mmol), oleic acid (1.6 mL, 5 mmol), and octadecene (36 g) were combined in a three-necked round bottom flask equipped with a stir bar and condenser and degassed under vacuum at 115 °C for 30 min. Under nitrogen, the mixture was heated to 300 °C until it became optically clear and colorless. The mixture was cooled to 115 °C, and SeO₂ (0.170 g, 1.53 mmol) was added under nitrogen flow, and the mixture was heated to 240 °C for 10 min., becoming an orange solution. The reaction mixture was cooled to room temperature, and the nanocrystals were precipitated using ethanol and then washed via redispersion/precipitation with toluene/ethanol. For nanocrystals purified under air-free, anhydrous conditions, the crude reaction mixture was distilled to remove octadecene, then dispersed in anhydrous pentane and precipitated with anhydrous methyl acetate.

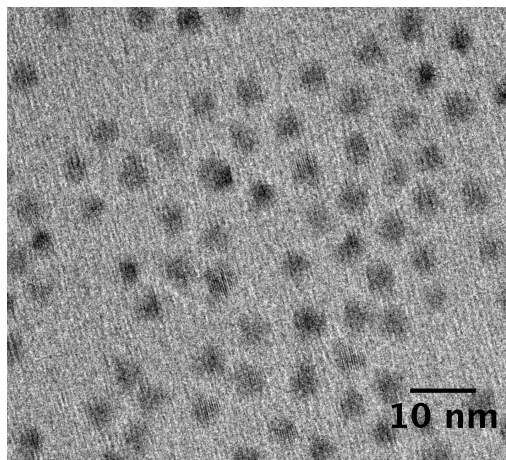


Figure S1. Representative TEM image of CdSe QDs.

General Characterization. Nanocrystals were dried under vacuum, dispersed in anhydrous toluene or in anhydrous benzene- d_6 , and stored in a dinitrogen glovebox. UV-vis spectra were measured of solutions in 1 cm air-free cuvettes sealed with Teflon stoppers using a Varian Cary 5000 spectrophotometer. For photoluminescence measurements, a sealable cuvette containing 3 mL of nanocrystal solution (band gap absorption = 0.1–0.2) and 0, 30, 60, or 90 equiv Li[Et₃BH] added as a 0.01 M THF solution was prepared in a nitrogen-filled glovebox. Photoluminescence decay curves were measured by exciting the nanocrystals with the frequency-doubled output of a Ti:sapphire laser at a 2.53 MHz repetition rate (400 nm, 200 μ W). Decay curves were recorded using a monochromator and streak camera with an instrument response function of \sim 15 ps.

NMR spectra were recorded on Bruker AV300 or Bruker AV500 instruments. ¹H NMR spectra were referenced to the solvent residual peak (7.16 ppm for C₆D₆), ¹¹B NMR spectra were referenced to an external standard of neat BF₃•OEt₂ (0.0 ppm), and ³¹P NMR spectra were referenced to an external standard of 85% H₃PO₄ (0.0 ppm). EPR spectra were recorded on a Bruker EMX spectrometer at liquid nitrogen temperatures.

XPS spectra were taken on a Surface Science Instruments S-Probe photoelectron spectrometer. This instrument has a monochromatized Al K α X-ray source which was operated at 20 mA and 10 kV. The samples were prepared by dropcasting toluene solutions of the functionalized colloidal CdSe QDs onto silicon wafers. X-ray analysis area for these acquisitions was approximately 800 μ m across. Pressure in the analytical chamber during spectral acquisition was less than 5×10^{-9} torr. Pass energy for survey and detail spectra (to calculate composition) was 150 eV. The take-off angle (the angle between the sample normal and the input axis of the energy analyzer) was 0°, (0° take-off angle \approx 100 Å sampling depth). Service Physics Hawk version 7 data analysis software was used to calculate the elemental compositions from peak areas above an inelastic scattering (Shirley) background.

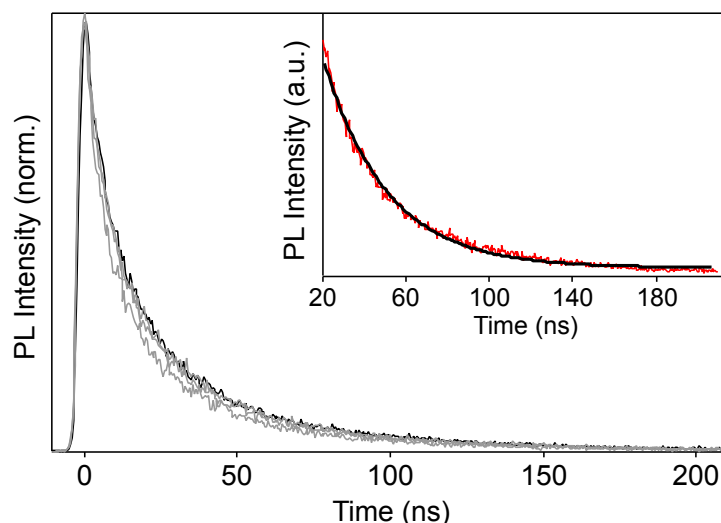


Figure S2. Normalized time-resolved PL from Figure 2 (main text). Inset: Time-resolved PL from a representative decay trace (red) with a single-exponential fit from 20–200 ns (black) to remove potential contributions from fast Auger decay processes. Decay time constants plotted in Figure 2 (main text) were fit using this time window for all decay traces.

Photodoping. CdSe nanocrystals were photodoped as described previously.³ Typically, solutions of QDs in anhydrous toluene with 30-50 equivalents/QD of Li[Et₃BH] (added as a 0.01 M solution in THF) were prepared anaerobically and loaded into an air-free cuvette. The nanocrystals were photodoped by illumination with a 100 W Hg/Xe Oriel photolysis lamp (~2 W/cm², ~1.5 cm illumination diameter) using a 480 nm longpass filter. Absorption spectra were monitored during photodoping until the band-edge absorption stopped decreasing.

The data presented in Table 1 were collected as follows: in a nitrogen-filled glovebox, an air-free cuvette equipped with a stir bar was charged with a solution of CdSe QDs ($d \sim 3.6$ nm, 1.8 μ M in toluene, 3 mL). The corresponding reducing agent was added to the solution in the dark, and the cuvette was capped with a Teflon stopper. Using a Cary 5000 UV-vis-NIR spectrophotometer, spectra were collected at 1 min. intervals while the sample was perpendicularly excited using a 5-mW 405-nm diode, typically for 15 min. In some cases, photoexcitation was for a longer period of time, or a 100-W photolysis lamp equipped with a 480-nm long pass filter was used instead.

Thermal tributyltin hydride reduction of CdSe QDs. In the glovebox, a Schlenk tube equipped with a stir bar was charged with a solution of CdSe QDs in toluene (0.36 mM, 3 mL, 1.1 μ mol). Bu₃SnH (60 μ L, 0.22 mmol, 200 equiv.) and AIBN (2 mg, 0.011 mmol, 10 equiv) were added. The tube was sealed with a Teflon stopper, then heated in the dark at 60 °C for 22 h. The mixture was cooled to room temperature than dried *in vacuo*. Under nitrogen, the QDs were purified by two pentane-redispersion/methyl acetate-precipitation cycles and filtered to remove tin-containing side products. Figs. S11 and S12 plot XPS characterization and photodoping of these functionalized QDs.

Surface alkylation of CdSe QDs. Under ambient conditions, CdSe QDs described above (10 mL, 1.4×10^{-4} M in toluene, $d \sim 3.6$ nm) were treated with octadecylphosphonic acid (80 mg, 0.24 mmol, 170 equiv). The mixture was stirred for 3 h at room temperature, then the QDs were purified by 3 ethanol-precipitation/toluene-redispersion cycles. The QDs were dried under vacuum, brought into the glovebox, and resuspended in toluene. A sample of 0.7 μ mol of QDs in 4 mL toluene was treated with 100 μ L MesMgBr (1.0 M in ether, 140 equiv), and the mixture was stirred for 10 min. at room temperature. 6-bromo-1-hexene (5 μ L, 0.04 mmol, 50 equiv/QD) was added, and the mixture was transferred to a Schlenk tube equipped with a stir bar. The mixture was heated in the dark at 70 °C for 18 h, then dried *in vacuo*. The residue was dissolved in dichloromethane (1 mL), then precipitated from solution with ethanol. Concentrated HCl (4 mL) was added to the pellet, then the mixture was sonicated for 1 h. The acid solution was diluted using 5 mL H₂O, and the organics were extracted using dichloromethane, dried over MgSO₄, and filtered through a plug of silica gel. The filtrate was then analyzed using GC-MS, and the presence of the corresponding alkylated diselenide was confirmed using an authentic sample.⁴ No unreacted 6-bromo-1-hexene was observed. The same procedure performed without treating the QDs with MesMgBr forms a small amount of diselenide (GC-MS), but in a much smaller ratio to unreacted 6-bromo-1-hexene.

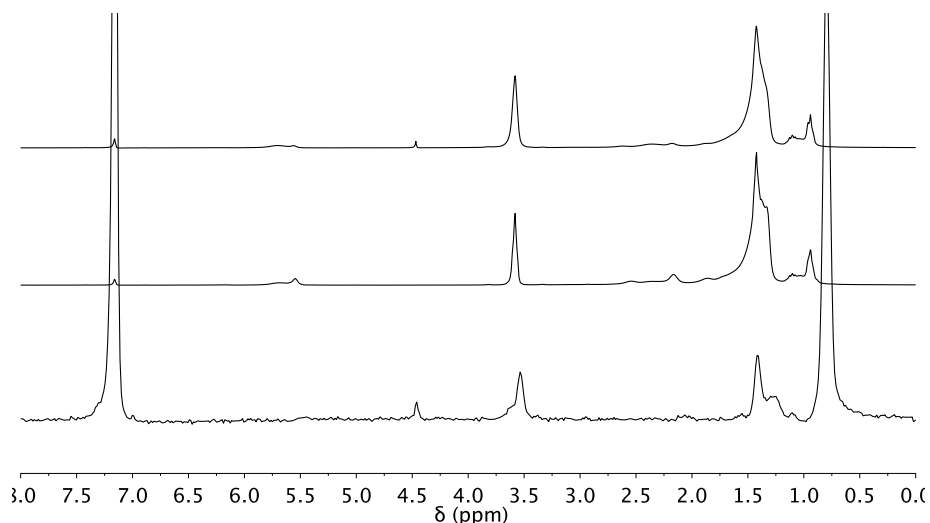


Figure S3. ^1H NMR spectrum at 25 °C of CdSe QDs in C_6D_6 after addition of $\text{Li}[\text{Et}_3\text{BH}]$ (100 equiv) (top). ^1H NMR spectrum at 25 °C of CdSe QDs in C_6D_6 after addition of $\text{Li}[\text{Et}_3\text{BD}]$ (100 equiv) (middle). ^2H NMR spectrum at 25 °C of CdSe QDs in C_6H_6 after addition of $\text{Li}[\text{Et}_3\text{BD}]$ (100 equiv). D_2 is visible at 4.45 ppm, while other peaks arise from naturally abundant deuterium occurring in solvent (benzene and THF). Signal at 0.8 ppm arises from an impurity in the $\text{Li}[\text{Et}_3\text{BD}]$.

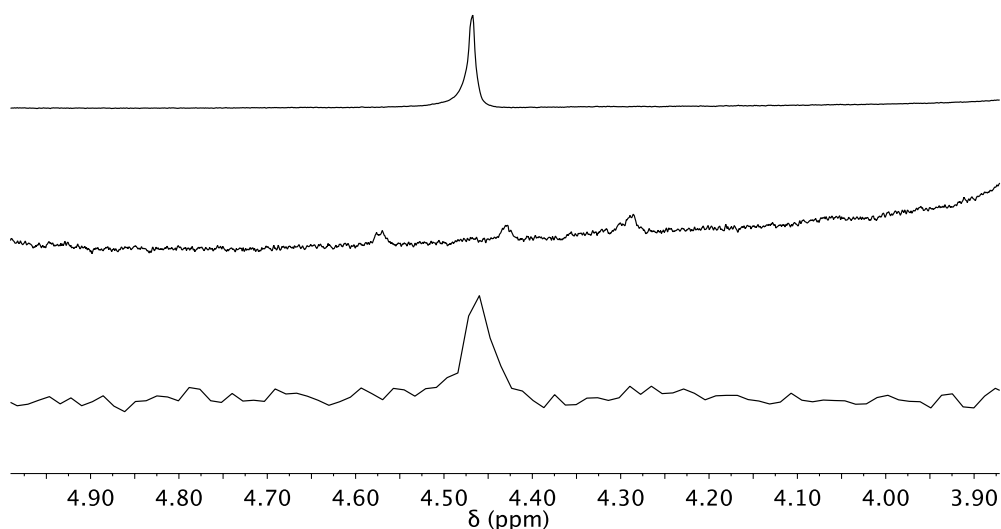


Figure S4. Expanded NMR spectra from Figure S1 showing H_2 (top), HD (middle), and D_2 (bottom). Only the singlet corresponding to D_2 is observed in the ^2H NMR spectrum of CdSe QDs treated with $\text{Li}[\text{Et}_3\text{BD}]$. No doublet corresponding to HD is detected, suggesting that D_2 is formed preferentially to HD.

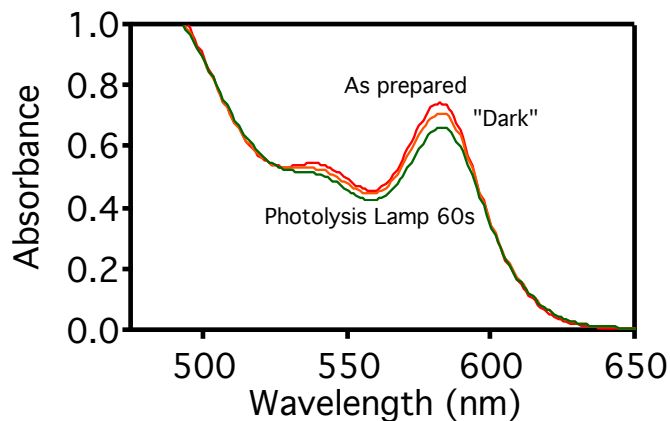


Figure S5. Absorption spectra of a mixture of CdSe QDs with excess sodium ethoxide (10,000 equiv./QD) in the dark and after photoexcitation.

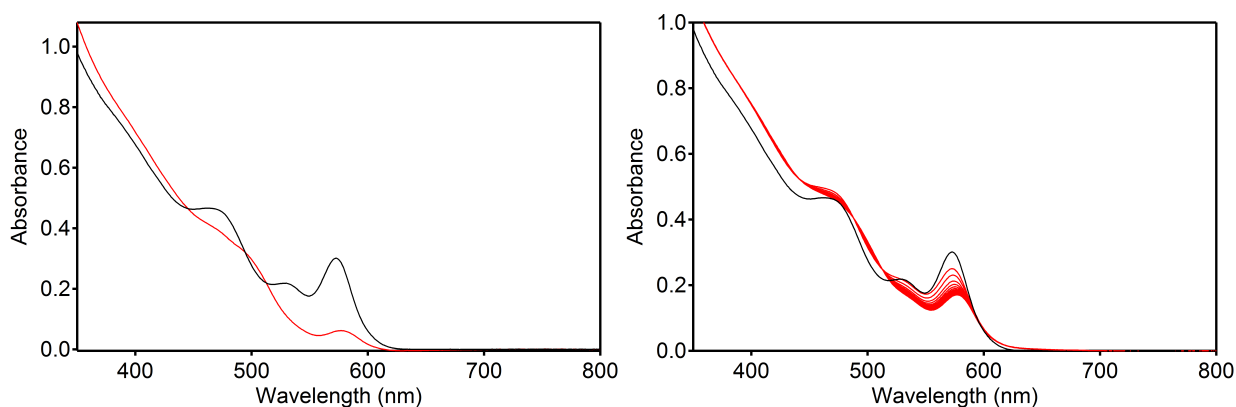


Figure S6. Absorption spectrum of CdSe QDs ($d \sim 3.6$ nm, $1.8 \mu\text{M}$ in 2:1 THF/toluene) before (black) and after (red) treatment with 60 equiv./QD of sodium naphthalenide in the dark (left). Absorption spectrum of CdSe QDs ($d \sim 3.6$ nm, $1.8 \mu\text{M}$ in 2:1 THF/toluene) before (black) and after (red) treatment with 40 equiv./QD of sodium naphthalenide in the dark followed by photoexcitation (right).

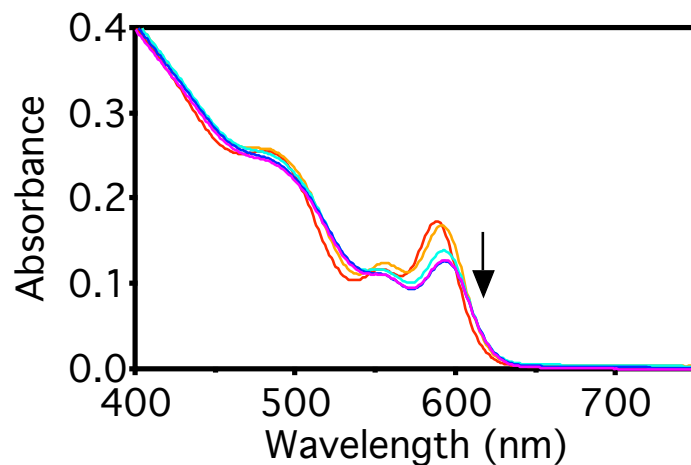


Figure S7. Absorption spectra of CdSe QDs after treatment with tributylphosphine (5000 equiv./QD) and a degassed aqueous solution of NaOH (10,000 equiv./QD) followed by photoexcitation.

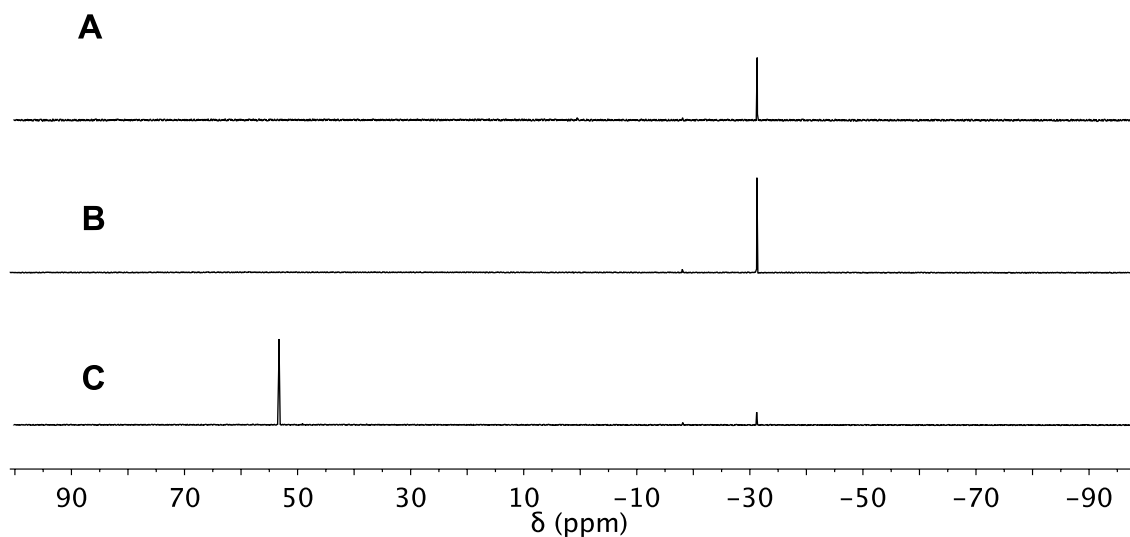


Figure S8. (A) ^{31}P NMR spectrum of PBu_3 in THF. (B) ^{31}P NMR spectrum of a mixture of PBu_3 and PhSeSePh in THF. (C) ^{31}P NMR spectrum of a mixture of PBu_3 , PhSeSePh (1 equiv), and NaOH (1.0 M in degassed H_2O , 2 equiv) after 20 min. at room temperature. The signal at 53 ppm corresponds to Bu_3PO .

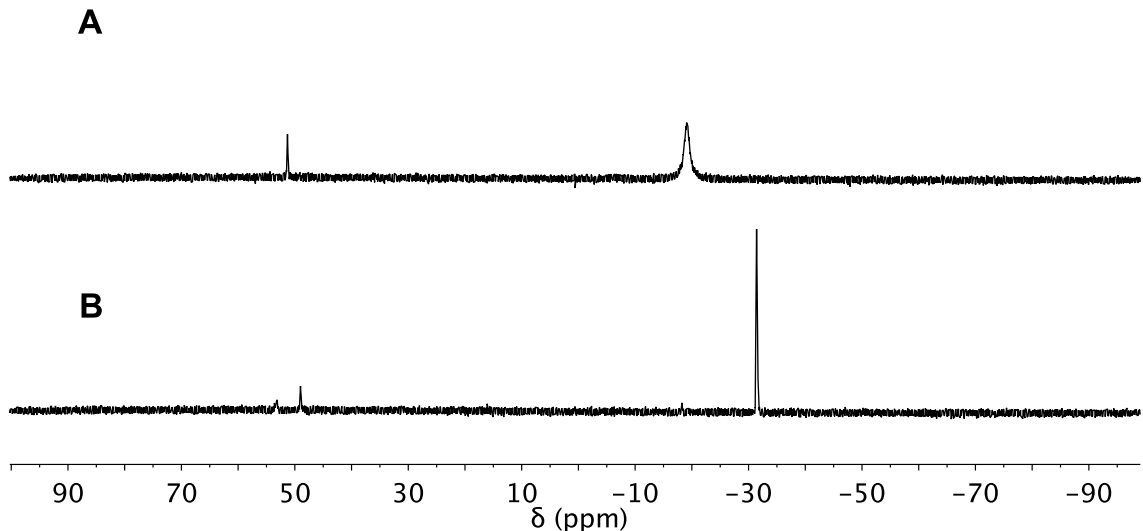


Figure S9. (A) ^{31}P NMR spectrum of a 2:1 THF/toluene mixture of cadmium oleate and PBu_3 (2 equiv). (B) ^{31}P NMR spectrum of the same mixture with added NaOH (1.0 M in degassed H_2O , 4 equiv) after 20 min. at room temperature. By integration, the mixture contains ca. 70% free Bu_3P , and an upper limit of 14% Bu_3PO .

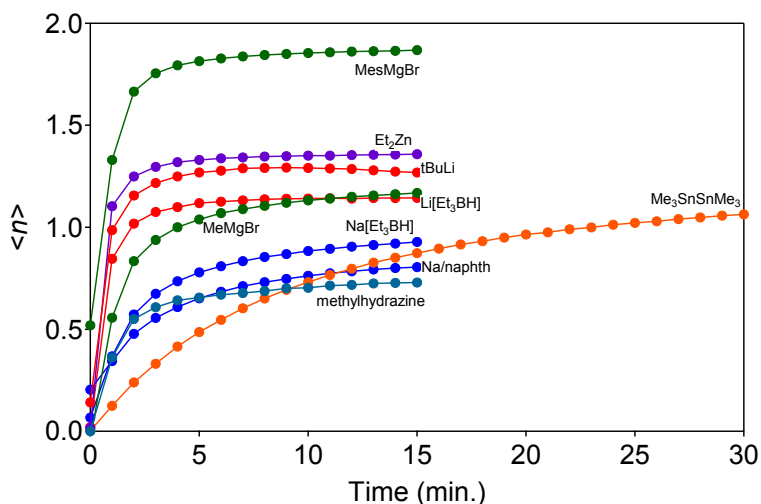


Figure S10. Average number of electrons per QD $\langle n \rangle$ estimated from $\langle n \rangle = 2(A_0 - A)/A_0$ during photodoping of CdSe QDs ($d \sim 3.6$ nm, $1.8 \mu\text{M}$ in toluene or 2:1 THF/toluene) using different reductants over time under excitation with a 5-mW 405-nm diode.

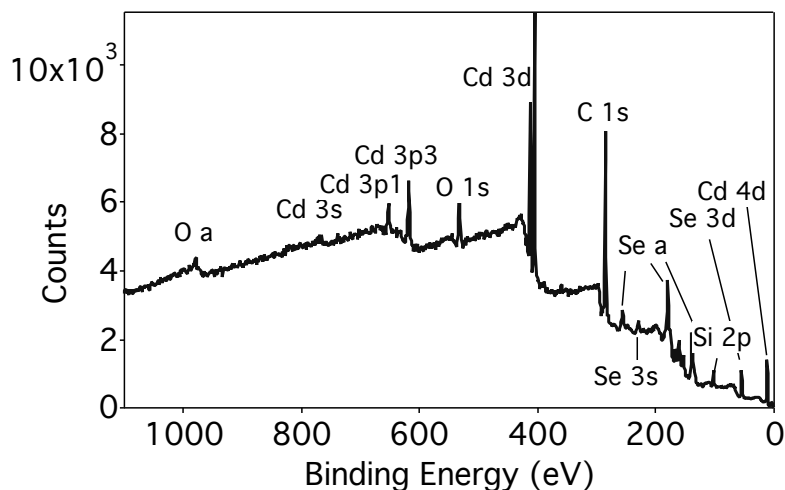


Figure S11. XPS survey spectrum of tin-functionalized CdSe QDs after washing and filtration to remove excess tin. CdSe QDs ($d \sim 3.6$ nm, $1.1 \mu\text{mol}$) were treated with Bu_3SnH (200 equiv) and AIBN (10 equiv), then heated in the dark at 60°C for 22 h.

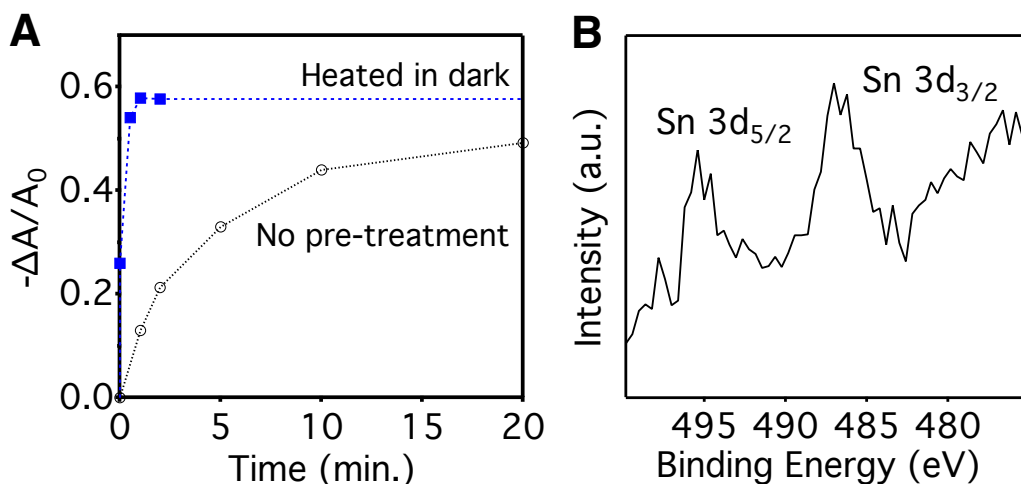


Figure S12. (A) Normalized first-exciton differential absorbance ($-\Delta A/A_0$, $\lambda = 582$ nm) plotted vs irradiation time for a solution of CdSe QDs in toluene ($1\text{--}2 \mu\text{M}$, $d \sim 3.9$ nm) with added AIBN (10 equiv./QD) and Bu_3SnH (5000 equiv./QD). Samples were irradiated immediately after mixing (black) or after first stirring in the dark at 60°C for 22 h (blue). Dashed lines are guides to the eye. (B) Sn 3d X-ray photoelectron spectra (XPS) of Bu_3SnH -functionalized CdSe QDs on a Si substrate. XPS results indicate a $\sim 200:1$ Cd:Sn ratio, or approximately 2–3 Sn atoms per QD.

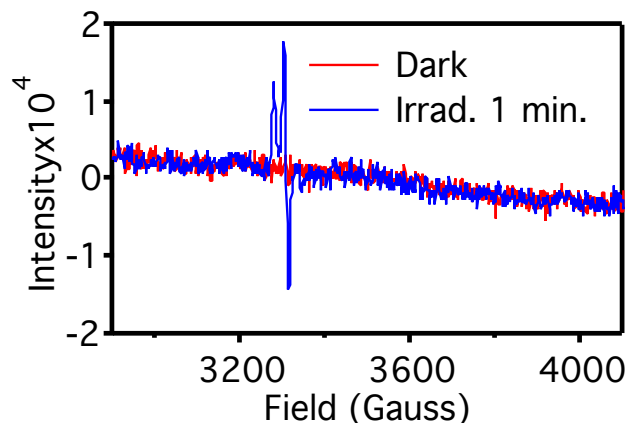


Figure S13. EPR spectra of a mixture of CdSe QDs ($d \sim 3.6$ nm, 22 μ M) and phenyl *tert*-butylnitron (0.25 M, 10,000 equiv) in toluene before (red) and after photoexcitation (blue).

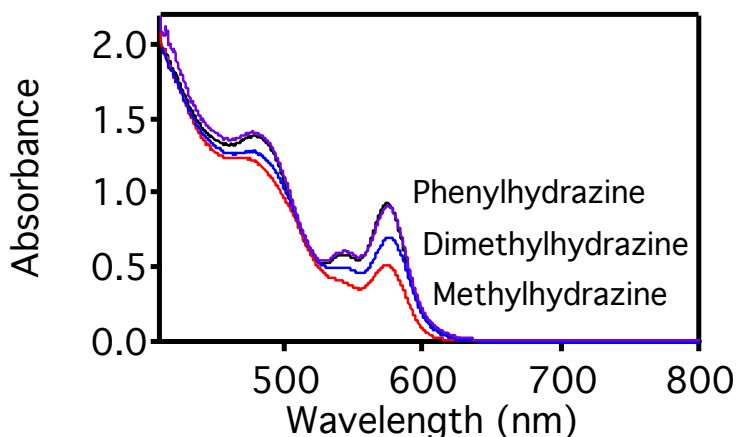


Figure S14. Absorption spectra of mixtures of CdSe QDs ($d \sim 5.7$ nm, 20 μ M, 0.7 mL) and 10 μ L neat substituted hydrazine reagent after photoexcitation.

References

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