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Supporting Information for Charge trapping versus exciton delocalization in CdSe quantum dots

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Sample preparation

Cadmium oxide (CdO, 99.5%), oleylamine (technical grade, 70%), octylamine (99%), cadmium acetate dihydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, 98.0%), trioctylphosphine (TOP, 97%), octadecene (ODE, 90%), methanol (MeOH, 98%), toluene (99%), chloroform (CHCl_3 , 99.5%), oleic acid (OA, 90%), tellurium (Te, 200 mesh, 99.8%), 4-methylbenzenethiol (MBT, 98%), sodium diethyldithiocarbamate trihydrate ($\text{NaDDTC} \cdot 3\text{H}_2\text{O}$), methyl viologen dichloride hydrate (MV, 98%), and phenothiazine (PTZ, 98%) were obtained from Aldrich. Selenium (Se, 200 mesh, 99%) and hexanes (98%) were obtained from Alfa Aesar. Acetonitrile (99.9%) was obtained from Fisher Scientific. TOP and ODE were purified by vacuum distillation. Methanol was purified by distillation from magnesium turnings and iodine. All other chemicals were used as received.

Synthesis of zincblende CdSe quantum dots. A mixture of 5 mL ODE, 2 mL oleic acid, and 1 mmol CdO (128 mg) were added to a 25 mL three-neck flask. The solution was stirred under vacuum for 5 min and bubbled with nitrogen gas for 5 min, then heated to 280°C to form a transparent solution. A well-mixed suspension of selenium powder (0.4 mmol, 31 mg) in 1 mL ODE was then quickly added to the solution and the temperature was held at 280°C for one minute. The solution was then removed from heat and allowed to gradually cool to 50°C. The quantum dots were purified by extracting with 4 mL hexane, 6 mL methanol, and 0.5 mL TOP. After stirring for two minutes, the colorless methanol layer was removed by syringe and discarded, then the quantum dots were extracted two more times with just hexane and methanol. Hexane was removed from the ODE/quantum dot solution by heating slightly under vacuum. Finally, the quantum dots were precipitated by centrifugation using chloroform and acetonitrile, and re-suspended in the solvent appropriate for the given ligand exchange or shelling

Addition of methyl viologen ligands. A 1 mM solution of MV was made by mixing 2.5 mg MV into a mixture of 7 mL chloroform and 3 mL methanol. 1 mL of this solution was then added to a solution of 1×10^{-7} moles QDs in 2 mL of chloroform. This was allowed to stir at room temperature under nitrogen for 30 minutes. The final solution was dried under vacuum. The QDs were re-suspended in chloroform to obtain absorbance and emission spectra and drop cast onto a coverslip to obtain Raman data.

Addition of phenothiazine ligands. 1 mL QDs in toluene ($\sim 1 \times 10^{-7}$ moles QDs) was combined with a solution of 1×10^{-4} moles PTZ (~ 19.9 mg) in 4 mL toluene and stirred at room temperature under nitrogen for 4 hours. To eliminate most of the excess PTZ ligands, the QDs were precipitated by centrifugation after adding methanol to the solution. Finally, the QDs were re-suspended in toluene to obtain absorbance and emission spectra and drop cast onto a coverslip to obtain Raman data.

Addition of 4-methylbenzenethiol ligands. 1 mL QDs in toluene ($\sim 1 \times 10^{-7}$ moles QDs) was combined with a solution of 1×10^{-5} moles MBT (~ 1.25 mg) in 4 mL toluene, stirred while

heating to 80°C, and then stirred under nitrogen for another 1 hour. The solution was cooled to room temperature before directly obtaining absorbance and emission spectra and drop cast onto a coverslip to obtain Raman data.

Addition of CdS shell. The cadmium diethyldithiocarbamate (Cd(DDTC)₂) precursor synthesis and CdS shelling were carried out as described in ref. 1.

Addition of CdTe shell. The cadmium precursor was formed by adding 0.5 mL octylamine and 0.3 mmol cadmium acetate dihydrate (~80 mg) to 2.5 mL ODE and sonicating until colorless. The tellurium precursor was formed by adding to a 15 mL vial 0.1 mmol tellurium powder, 100 mesh (~12.5 mg), and 0.6 mL ODE. The vial was capped with a septum and put under vacuum to remove air, then repressurized with nitrogen gas. Then, 0.2 mmol TOP (~0.4 mL) was added through the septum and sonicated for about 1 hr until the tellurium powder was fully dissolved. For the shelling reaction, to a 25 mL three-neck flask with a stir bar was added 1 mL ODE, 1 mL oleylamine, and 1×10^{-7} moles zincblende CdSe QDs (~1 mL). The solution was stirred under vacuum for 5 minutes, then bubbled with nitrogen gas for 5 min. The solution was heated to 80°C while stirred under nitrogen. Four drops of cadmium precursor were added to the solution, heated to 130°C, and held at that temperature for 10 min. The sample was cooled back down to 80°C and four drops of tellurium precursor were added. The sample was heated back up to 130°C and held for 10 minutes. This process was repeated several times until a 1 monolayer shell was grown. The solution was cooled to 50°C and extracted three times with hexane and methanol. The QDs were then precipitated out by centrifuging after adding an equal part of chloroform and enough acetonitrile to make the solution look opalescent. The QDs were resuspended in hexane to obtain absorbance and emission spectra and drop cast onto a coverslip to obtain Raman data.

Resonance Raman spectra over larger range of Raman shifts

Figure S1 shows the resonance Raman spectra of all six samples over the full Raman shift range 100-1700 cm⁻¹. No emission backgrounds have been subtracted. The PZT, MV, and MBT ligands, and the CdTe shell, largely quench the emission, and the CdS shell shifts the emission to much longer wavelengths. Only the original CdSe cores exhibit significant emission, increasing rapidly beyond ~800 cm⁻¹, at the 457.9 nm excitation wavelength.

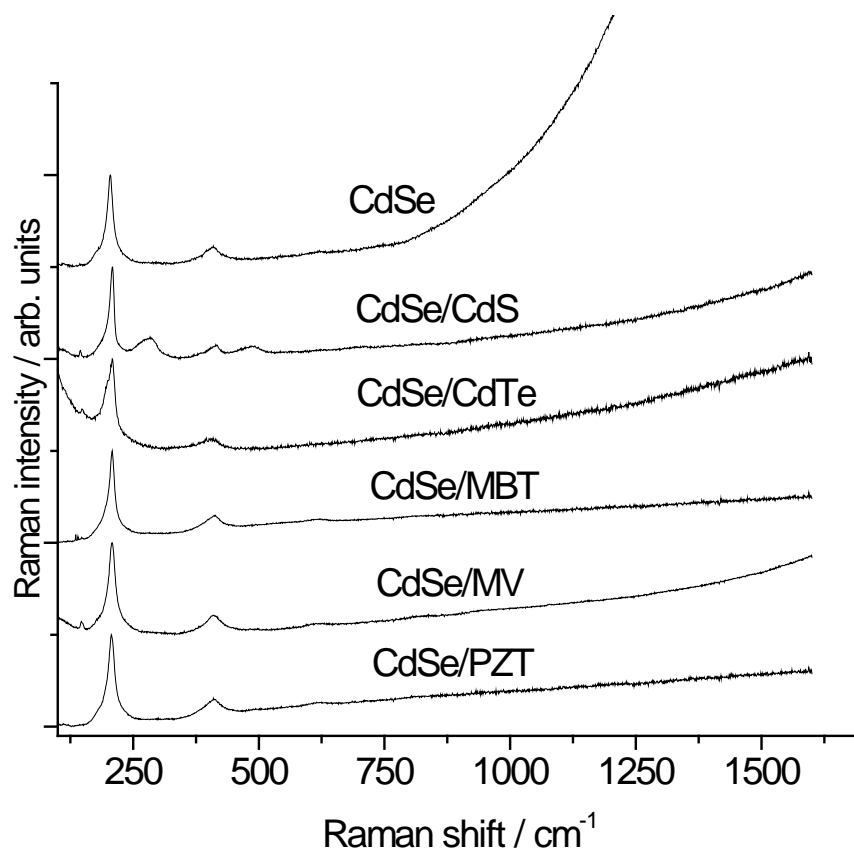


Figure S1. Resonance Raman spectra of, top to bottom, CdSe QDs, CdSe/CdS core/shells, CdSe/CdTe core shells, and CdSe QDs with 4-methylbenzenethiol, methyl viologen, and phenothiazine ligands. Spectra have been scaled to the CdSe LO phonon and shifted vertically.

(1) Gong, K.; Martin, J. E.; Shea-Rohwer, L. E.; Lu, P.; Kelley, D. F. Radiative Lifetimes of Zincblende CdSe/CdS Quantum Dots. *J. Phys. Chem. C* **2015**, *119*, 2231-2238.