Supporting Information for:

Redox Brightening of Colloidal Semiconductor Nanocrystals using Molecular Reductants

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Methods

Synthesis. Colloidal Mn^{2+}:ZnSe nanocrystals (NCs) were synthesized by modification of a previously published procedure.[1] To briefly summarize, 10.8 g of hexadecylamine ($C_{16}H_{35}N$, 90%, Acros) and 8 mg $MnCl_2 \cdot 6H_2O$ were degassed under vacuum at 130 °C for 1.5 h. The reaction vessel was placed under N_2 and the temperature reduced to 60 °C, at which point 0.2 g of $(Me_4N)_2[Zn_4(SePh)_{10}]$ and 20 mg of selenium (99.9%, Aldrich) were introduced. The temperature was increased to 130 °C under vacuum, maintained for 2 h, and then increased to 275 °C under nitrogen and kept constant until the desired NC size was achieved. After growth, the solution was rapidly cooled to <100 °C, and the particles were isolated by addition of ~5 mL of toluene and ~30 mL of ethanol. The isolated NCs were then resuspended in toluene. The process of precipitation with ethanol followed by resuspension in toluene was repeated three times to remove excess reagents. The precipitated nanocrystals were then gently heated in 6 g of 1-octadecene (90%, Aldrich), 1.5 g oleylamine (70%, Aldrich), and 3 mL TOP (TOP, 97%, Strem) at 120 °C under nitrogen for ~3 days.

For low quantum yield samples, the NCs were then precipitated with ethanol, resuspended in toluene, and stored in air for several months until a stable quantum yield of ϕ = 0.4% was obtained. For high quantum yield samples, the NCs were precipitated with ethanol and resuspended in toluene under an inert atmosphere for storage.

Analytical Characterization. Manganese and zinc concentrations were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Perkin Elmer Optima 8300). Photoluminescence data was collected by exciting the nanocrystals using an unfocused 405 nm, 5 mW laser diode and detecting emitted photons using an Ocean Optics 2000+ fiber-coupled spectrometer.

Redox Brightening. In a typical experiment with sodium-potassium alloy on silica gel (NaK_2; Stage 1, Aldrich, main text Figure 2), 100 µL of a 26 µM toluene solution of colloidal Mn^{2+}:ZnSe NCs was placed in an air-free 1 cm quartz cuvette with 2 mL tetrahydrofuran (THF) and a small Teflon stir bar. For experiments with a molecular electron shuttle, 1 mg 2,2' bipyridine was dissolved as well. Photoluminescence was monitored before and after addition of ~5 mg NaK_2 with vigorous stirring.

In a typical brightening titration experiment (main text, Figure 3), 20 µL of a 26 µM toluene solution of colloidal Mn^{2+}:ZnSe NCs was placed in an air-free 1 cm quartz cuvette with 2 mL tetrahydrofuran (THF) and a small Teflon stir bar. To eliminate potential complications from photobrightening, prior to titration experiments each sample was excited with a cw 405 nm laser until no further changes in PL intensity were observed. Subsequently, aliquots of reductant

(anthracene radical, cobaltocene) were added by microliter syringe with vigorous stirring. Photoluminescence was measured shortly after each addition of reductant.

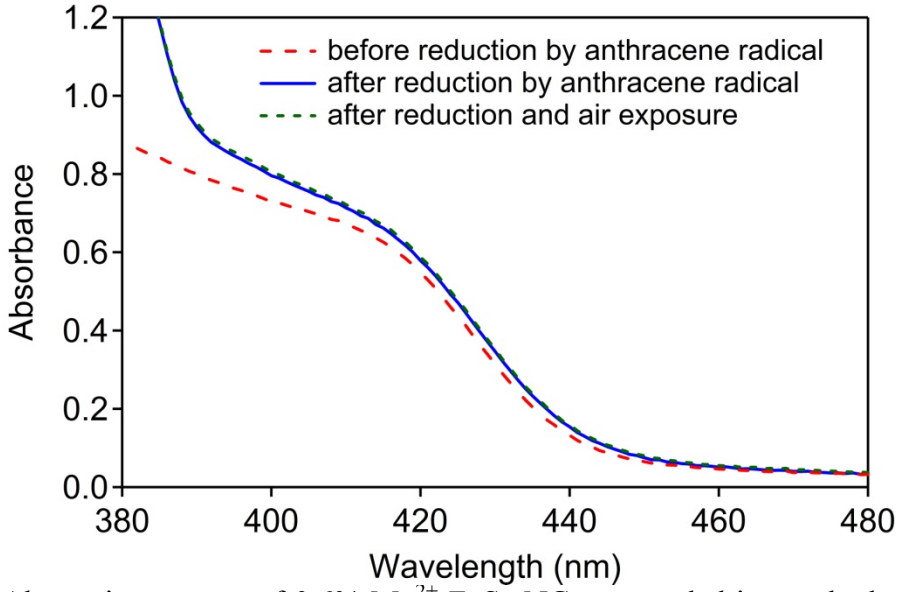

Figure S1. Absorption spectra of 0.6% Mn^{2+}:ZnSe NCs suspended in tetrahydrofuran collected before and after brightening using anthracene radical, and again following air exposure of the brightened nanocrystals. The difference between spectra collected before and after brightening is due to absorption by oxidized anthracene radical (anthracene).

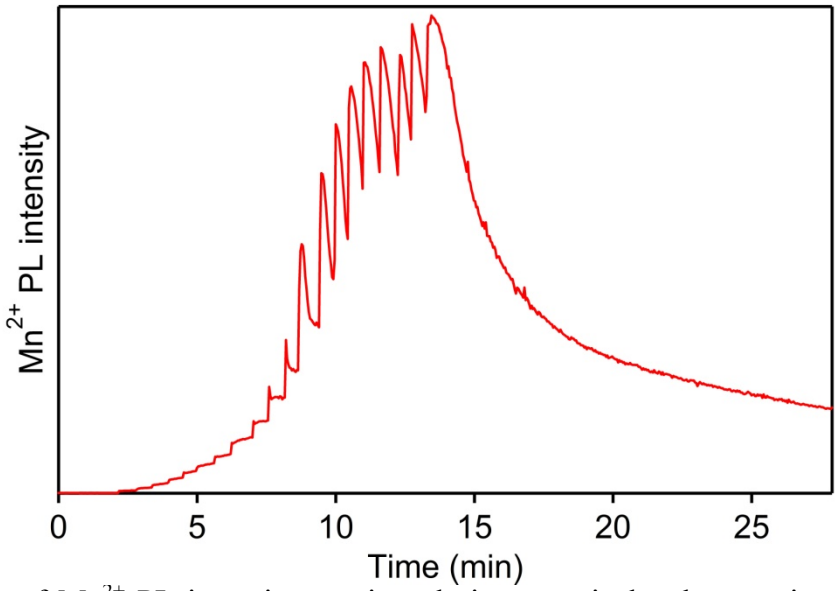

Figure S2. Plot of Mn^{2+} PL intensity vs. time during a typical reductant titration experiment. Spikes in the PL intensity mark additions of anthracene radical as described in the main text.

References

1. P. I. Archer, S. A. Santangelo, D. R. Gamelin, *J. Am. Chem. Soc.* **2007**, *129*, 9808.