Supplementary Information

One-Step Synthesis of Alloyed Dual-Emitting Semiconductor Nanocrystals

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Methods.

Synthesis. The tetrameric cluster $(Me_4N)_2[Zn_4(SePh)_{10}]$ was prepared as described previously.[1] Alloyed $Zn_{1-x-y}Cd_xMn_ySe$ nanocrystals (NCs) were synthesized from this cluster as follows: In a three-neck flask, hexadecylamine (HDA, 10.8 g), $MnCl_2•4H_2O$ (0.006 g), and the desired amount of $CdCl_2•2.5H_2O$ (0.015 g for dual emission at room temperature) were heated at 100 °C under vacuum for 90 min. This solution was then placed under nitrogen atmosphere and the temperature was dropped to below 80 °C. With nitrogen overpressure, the cluster (0.2 g) and elemental selenium (Se, 0.01 g) were added to the reaction flask. The flask was quickly evacuated and then heated under vacuum at 100 °C for 60 minutes. The reaction mixture was then placed under nitrogen atmosphere and the temperature was ramped to 280 °C. Aliquots were collected every 5 minutes and isolated from solution by precipitation and washing. NC growth was complete within 60 to 120 minutes. Unreacted precursors were removed by repeated precipitation of the product NCs with ethanol, acetone, and methanol, followed by resuspension of the NCs in toluene. These conditions were chosen to yield $x \sim 0.01$ based on previous experience.[1]

For ZnSe shell growth, precursors were prepared by adapting previously described methods.[2, 3] For addition of ZnSe to the NC surfaces, core NCs suspended in a small amount of toluene (0.01 mmol in M^{2+}, as estimated by absorption)[4] were added to a three-neck flask containing octadecene (ODE, 1.5 g) and oleylamine (OLA, 1.5 g). The reaction flask was kept under vacuum at 100 °C for 30 minutes. Under nitrogen atmosphere, the reaction was heated to 220 °C, at which point an ODE solution containing zinc oleate (0.2 M) was added to the NC suspension over a period of 3-4 minutes, by syringe. The zinc precursor was allowed to react for 15 minutes prior to the addition of the selenium precursor. Trioctylphosphine selenide (TOPSe), formed by combining elemental selenium (1 mmol) and trioctylphosphine (5 ml, 97%, Strem), was added to the core solution over a period of 5 minutes using a syringe pump. The precursors were allowed to react for 25 minutes prior to the addition of more zinc precursor. Alternate addition of Zn^{2+} and Se^{2-} precursors was continued until the desired shell thickness was reached. Rod formation was observed when attempting to perform a similar shell growth procedure at a lower temperature (180 °C). Following synthesis, these NCs were washed by repeated precipitation with ethanol, acetone, and methanol, followed by resuspension in toluene.

Characterization. Room-temperature absorption spectra were collected using a Cary 500 (Varian) spectrophotometer. Room- and low-temperature continuous-wave photoluminescence (PL) measurements were performed on colloidal suspensions of NCs in toluene. High-temperature continuous-wave PL measurements were performed on colloidal suspensions of NCs in octadecene under an inert atmosphere. Steady-state PL spectra were collected using a continuous-wave 405 nm laser pointer as the excitation source and a USB2000 Miniature Fiber Optic Spectrometer (Ocean Optics) for detection. Sample temperatures were varied using a CN7800 microprocessor based temperature process controller and a thermocouple (Omega). PL quantum yields were measured using an Absolute Photoluminescence Quantum Yield Measurement System C9920-02 (Hamamatsu). ICP-AES measurements were made using an Optima 8000 (Perkin Elmer). Room-temperature EPR spectra were collected on an EMX X-band spectrometer (Bruker) operating at 9.8 GHz. Variable-temperature time-resolved PL measurements were performed on NC films cooled using a Displex closed-cycle refrigerator and excited using either the frequency-doubled output of a pulsed Ti:Sapphire laser (Coherent) or a square-wave-pulsed 365 nm LED. Time-resolved luminescence data were collected using a streak camera combined with a grating spectrometer (Ti:Sapphire excitation) or an R928 PMT with a monochromator (Acton) (LED excitation). TEM images were collected using an FEI Tecnai G2 F20. NC sizes were estimated from TEM images of ~100 particles using ImageJ software. X-ray diffraction patterns were collected using a Bruker D8 Discover with GADDS XRD system at the University of Washington NanoTechnology User Facility.

Luminescence of core vs core/shell NCs. The exciton blue-shift in $Zn_{1-x-y}Cd_xMn_ySe$/ZnSe vs $Zn_{1-x-y}Cd_xMn_ySe$ is likely due to a small amount of Zn^{2+} diffusion into the $Zn_{1-x-y}Cd_xMn_ySe$ NC during shell growth (*i.e.*, a change in the alloy composition towards ZnSe). The Mn^{2+} PL red-shift is tentatively attributed to the same change in composition, which alters the distribution of local Mn^{2+} environments to make it more Zn^{2+} rich. Because the emissive excited state of Mn^{2+} has a negative dependence on ligand field strength, it moves to lower energy when the lattice becomes more Zn^{2+} rich.

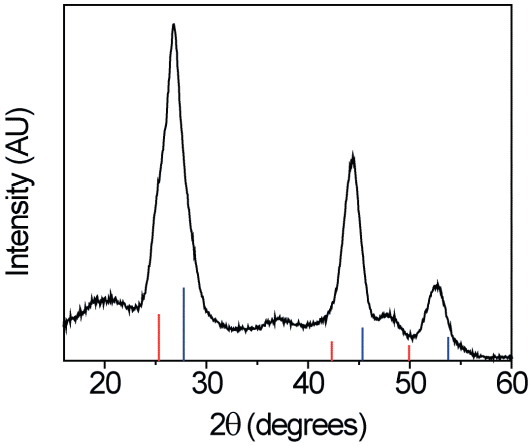


Figure S1. X-ray diffraction for $Zn_{0.829}Cd_{0.168}Mn_{0.003}Se$ nanocrystals. X-ray diffraction pattern of NCs (Fig. 2a,b) isolated after 60 minutes of reaction time, exhibiting a zinc-blende structure with peak positions between those of CdSe (red) and ZnSe (blue).

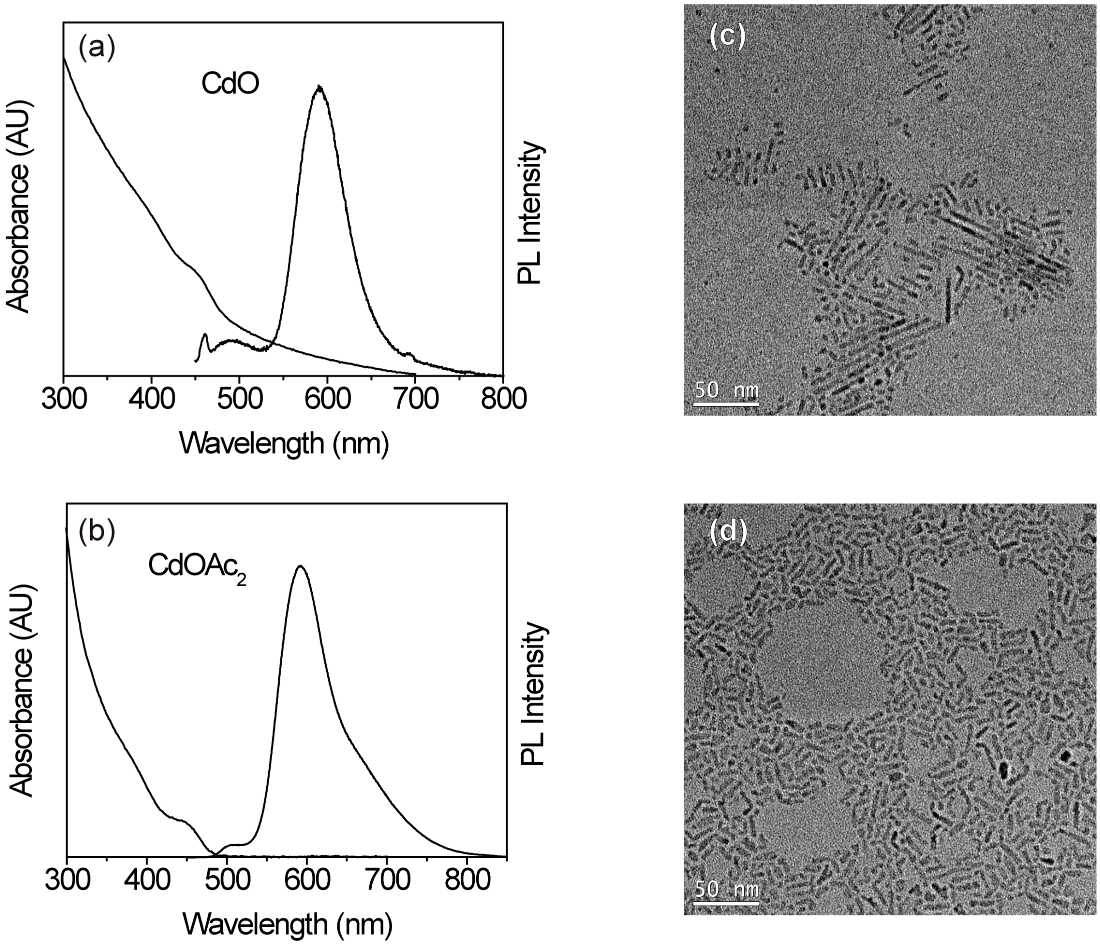


Figure S2. Nanocrystals obtained using different Cd^{2+} precursors. Absorption and PL spectra of $Zn_{1-x-y}Cd_xMn_ySe$ NCs using (a) CdO and (c) Cd(OAc)$_2$ as the Cd^{2+} precursor. TEM images of the NCs using (b) CdO and (d) Cd(OAc)$_2$ as the Cd^{2+} precursor. Scale bars = 50 nm.

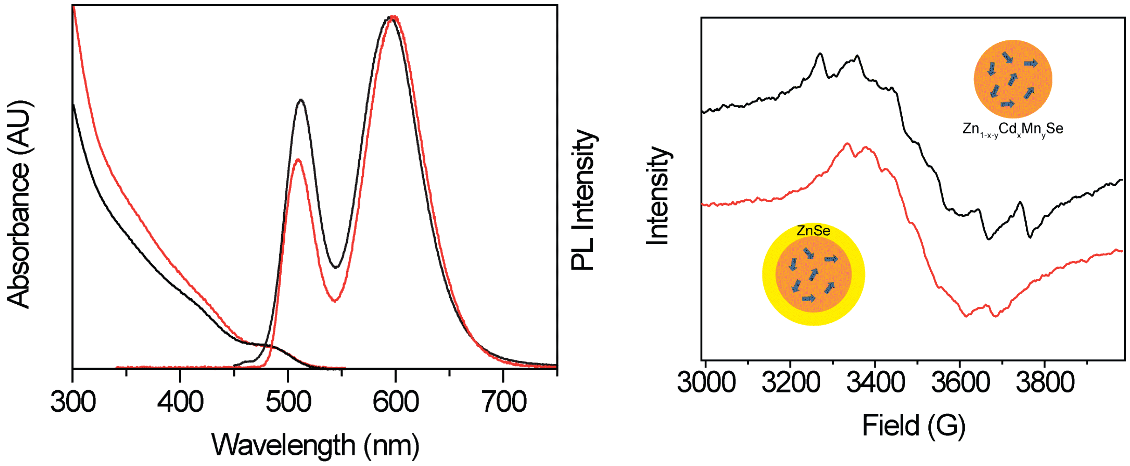


Figure S3. Comparison of $Zn_{0.784}Cd_{0.209}Mn_{0.007}Se$ core and $Zn_{0.784}Cd_{0.209}Mn_{0.007}Se$ /ZnSe nanocrystals. (a) Absorption and PL spectra of the NCs before (black, Fig. 3) and after (red, Fig. 2c,d) ZnSe shell growth. (b) EPR spectra of the same NCs. The core/shell NCs show a hyperfine coupling constant of $61.8 \times 10^{-4}cm^{-1}$ consistent with substitutional Mn^{2+} in the internal volume of the NC.

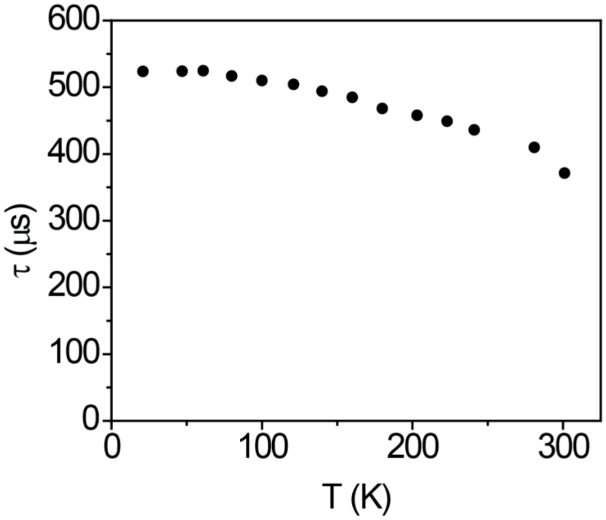


Figure S4. Average Mn^{2+} photoluminescence decay time vs temperature. The Mn^{2+} PL decay time of $Zn_{0.784}Cd_{0.209}Mn_{0.007}Se$ core NCs (monitored at 600 nm, Fig. 3) increases from ~350 µs at room temperature to ~525 µs at ~60 K and below.

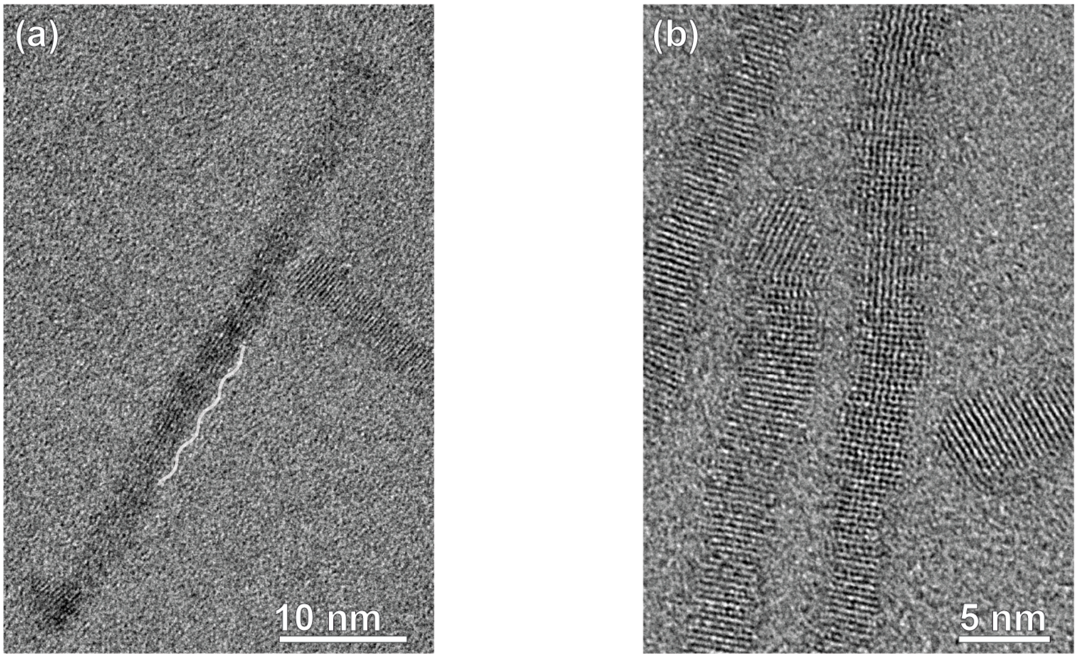
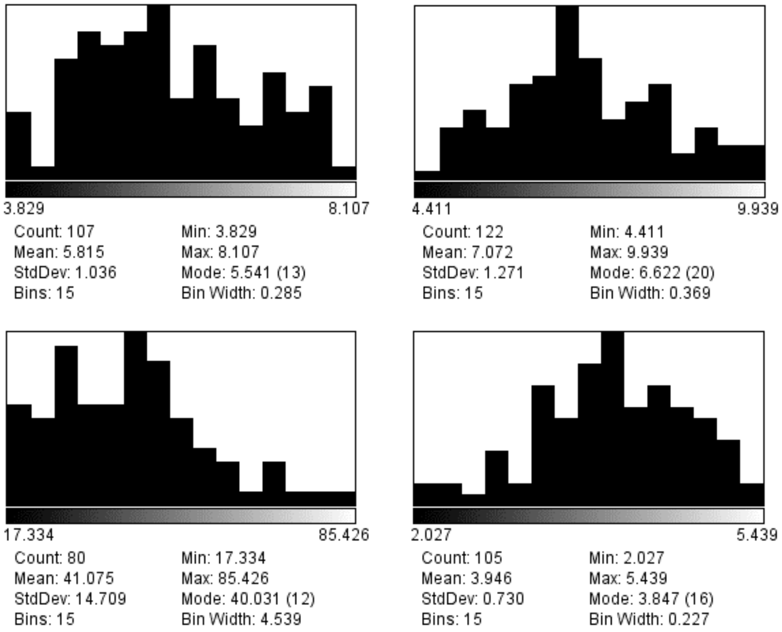


Figure S5. High-resolution TEM images of dual-emitting nanorods. (a) The nanorods show necking between bulges indicative of formation by oriented attachment of spherical particles. The white line is drawn as a guide for the eye to emphasize this property. Scale = 10 nm. (b) Nanorods from the same sample shown at higher magnification. The nanorods again exhibit a curved outline, suggesting they formed through concatenation of spherical particles. Scale = 5 nm.



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Count: 107        Min: 3.829
Mean: 5.815       Max: 8.107
StdDev: 1.036     Mode: 5.541 (13)
Bins: 15          Bin Width: 0.285

Count: 122        Min: 4.411
Mean: 7.072       Max: 9.939
StdDev: 1.271     Mode: 6.622 (20)
Bins: 15          Bin Width: 0.369

Count: 80         Min: 17.334
Mean: 41.075      Max: 85.426
StdDev: 14.709    Mode: 40.031 (12)
Bins: 15          Bin Width: 4.539

Count: 105        Min: 2.027
Mean: 3.946       Max: 5.439
StdDev: 0.730     Mode: 3.847 (16)
Bins: 15          Bin Width: 0.227
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Figure S6. Size-distribution histograms of alloy nanocrystals. (a) $Zn_{0.829}Cd_{0.168}Mn_{0.003}Se$ NCs (Fig. 2a,b) with *d* ~ 5.8 nm. (b) $Zn_{0.784}Cd_{0.209}Mn_{0.007}Se/ZnSe$ NCs (Fig. 2c,d) with *d* ~ 7.0 nm. (c and d) $Zn_{0.64}Cd_{0.35}Mn_{0.01}Se$ nanorods (Fig. 4) with length of ~41 nm and *d* of ~4.0 nm. The histograms plot the dimensions in nanometers.

References.

1 V. A. Vlaskin, R. Beaulac and D. R. Gamelin, *Nano Lett.*, 2009, **9**, 4376.
2 J. J. Li, Y. A. Wang, W. Guo, J. C. Keay, T. D. Mishima, M. B. Johnson and X. Peng, *J. Am. Chem. Soc.*, 2003, **125**, 12567.
3 H.-S. Chen, B. Lo, J.-Y. Hwang, G.-Y. Chang, C.-M. Chen, S.-J. Tasi and S.-J. J. Wang, *J. Phys. Chem. B*, 2004, **108**, 17119.
4 N. Norberg, G. Parks, G. Salley and D. R. Gamelin, *J. Am. Chem. Soc.*, 2006, 13195.