

Supplementary Information for:

Tuning Equilibrium Compositions in Colloidal $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ Nanocrystals Using Diffusion Doping and Cation Exchange

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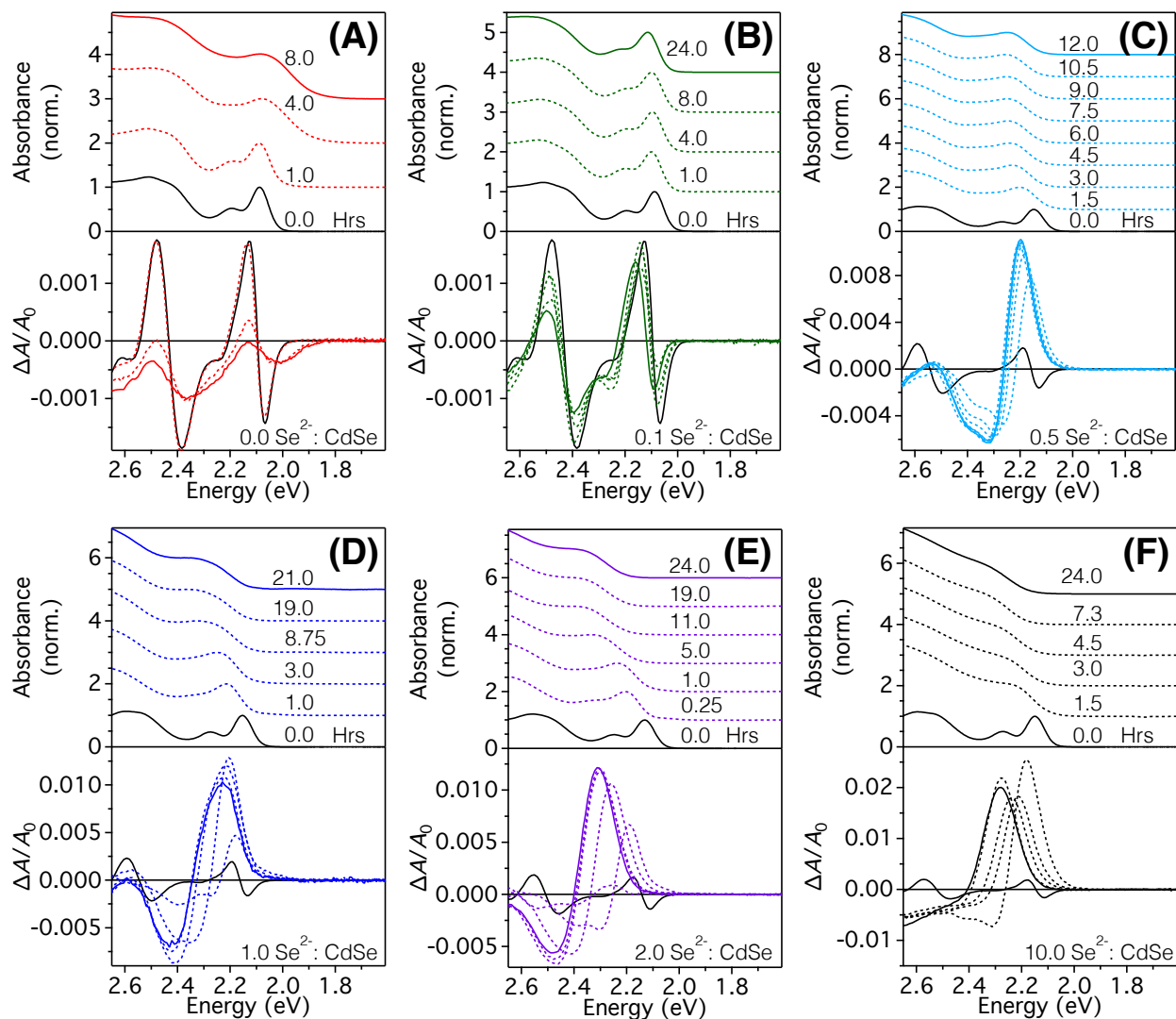


Figure S1. Representative electronic absorption (top) and MCD (bottom) spectra of aliquots removed during various diffusion-doping reactions at 300 °C with added Se^{2-} :added Mn^{2+} :lattice Cd^{2+} in CdSe NC (Se^{2-} : Mn^{2+} :CdSe) ratios of (A) 0:1:1, (B) 0.1:1:1, (C) 0.5:1:1, (D) 1:1:1, (E) 2:1:1, and (F) 10:1:1 corresponding to the data plotted in Figure 2A of the main text. Vertical offsets of the absorption spectra are included for clarity of presentation.

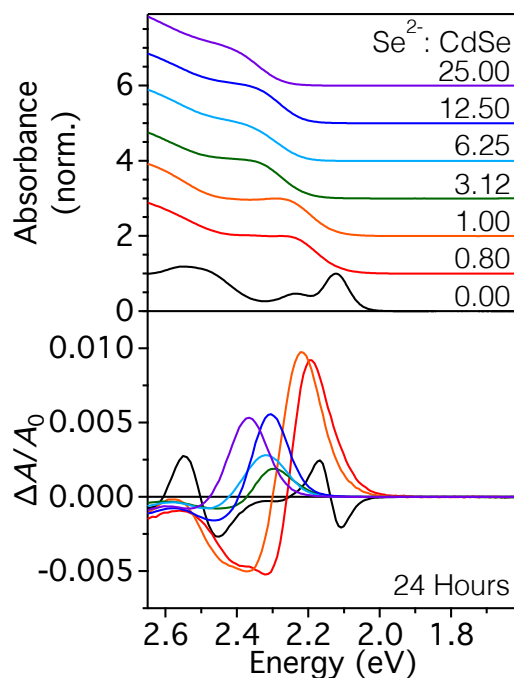


Figure S2. Representative electronic absorption (top) and MCD (bottom) spectra of $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ NCs after 24 hours of diffusion doping at 300 °C with the indicated $\text{Se}^{2-}:\text{CdSe}$ ratios, yielding the data plotted in Figure 2B of the main text. All reactions were performed at a ratio of 1:1 added Mn^{2+} to Cd^{2+} in CdSe (1:1 $\text{Mn}^{2+}:\text{CdSe}$). Vertical offsets of the absorption spectra are included for clarity of presentation.

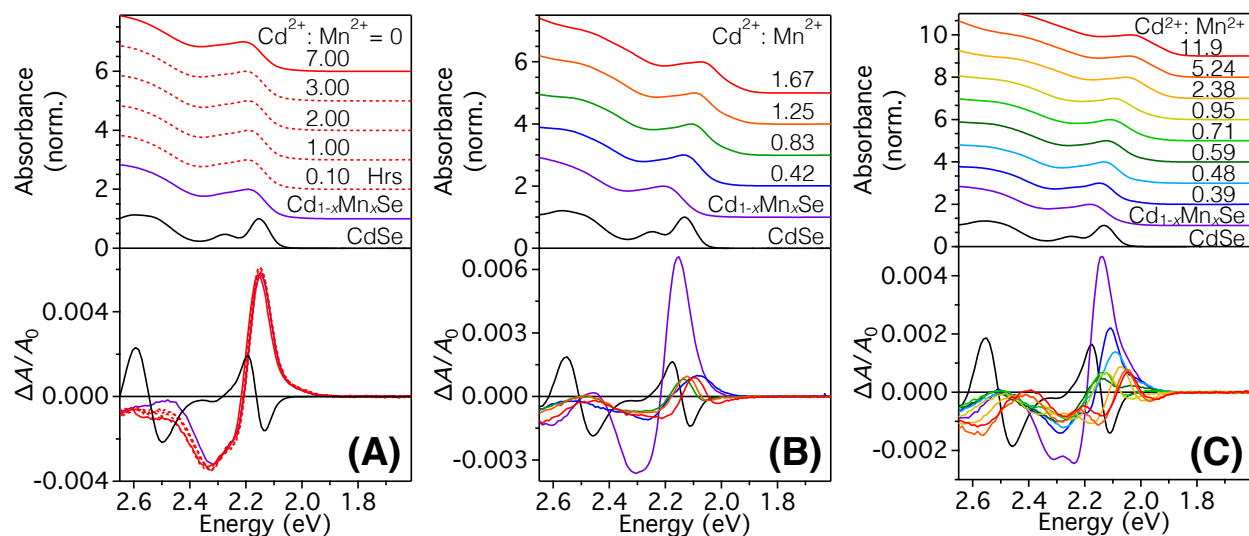


Figure S3. (A) Electronic absorption (top) and MCD (bottom) spectra of aliquots removed during diffusion doping and the control "purification" reaction performed with no added Cd^{2+} , yielding the control data plotted in Figure 4A in the main text. Undoped CdSe (black) was diffusion doped with added $\text{Se}^{2-}:\text{Mn}^{2+}:\text{CdSe}$ at a ratio of 0.5:1:1 at 280 °C for 24 hr (purple). After equilibrating, oleic acid dissolved in ODE was injected, and aliquots (red) were removed from the reaction at the indicated times after injection. (B) Electronic absorption (top) and MCD (bottom) spectra of diffusion doped $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ NCs partially and fully purified by cation exchange reactions with Cd^{2+} , yielding the data plotted in Figure 4B in the main text. Undoped CdSe (black) was diffusion doped with added $\text{Se}^{2-}:\text{Mn}^{2+}:\text{CdSe}$ at a ratio of 0.5:1:1 at 280 °C for 24 hr (purple). After equilibrating, cadmium oleate was added in a ratio of 0.42 (blue), 0.83 (green), 1.25 (orange), and 1.67 (red) added $\text{Cd}^{2+}:\text{lattice Mn}^{2+}$. (C) The experiment of panel B was repeated with the indicated added $\text{Cd}^{2+}:\text{lattice Mn}^{2+}$ ratios.

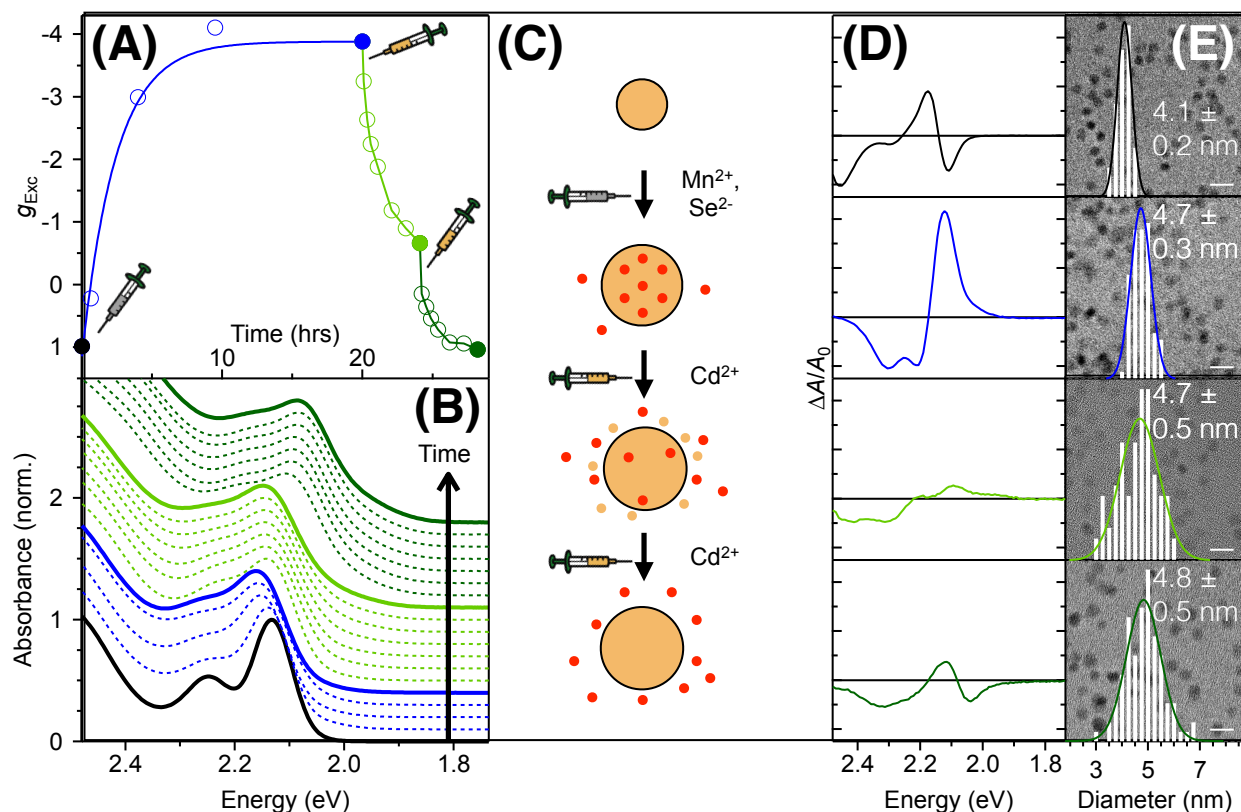


Figure S4. (A) g_{Exc} (from analysis of data in panels B, D, and other aliquots) of aliquots removed over the course of diffusion doping (blue) at 280 °C with 0.5:1:1 added Se^{2-} : Mn^{2+} :CdSe NCs and purified by cation exchange (green) triggered after 20 hr by injection of 1.20 equivalents of Cd^{2+} per lattice Mn^{2+} , split evenly into two injections of 0.60 equivalents 4 hr apart. The cation exchange portion of this experiment corresponds to the blue traces of Figure 4A in the main text. The curves are guides to the eye. (B) Electronic absorption spectra of undoped CdSe (black), diffusion doped (blue), partially purified (light green), and fully purified (dark green) NCs. (C) Scheme illustrating the four equilibrated aliquots indicated by dark circles in panel A and bold traces in panel B. (D) MCD spectra of the same four equilibrated aliquots representing undoped CdSe (black), diffusion doped $\text{Cd}_{1-x}\text{Mn}_x\text{Se}$ after 20 hr (blue), partially purified (light green), and fully purified (dark green) NCs. Zero lines are plotted in black, and the major tick marks correspond to increments of 0.002 $\Delta A/A_0$. (E) TEM images and corresponding size histograms from analysis of ≥ 100 NCs from each of the four equilibrated aliquots. The scale bar in each image represents 10 nm. These data were not shown in the main text because some Ostwald ripening is evident from slight broadening of the distribution from 5% to 10%. TEM samples were prepared by submerging a 200 mesh copper grid (Ted Pella, Inc.) in a 1 μM colloidal suspension of nanocrystals in toluene and allowing this substrate to dry in air. TEM images were obtained on an FEI TECNAI F20, 200 kV microscope at the UW NanoTech User Facility.

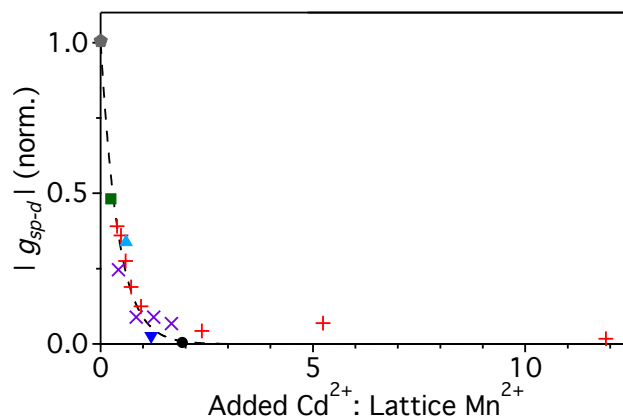


Figure S5. Extension of Figure 4B in the main text to larger ratios of added Cd²⁺:lattice Mn²⁺ during cation exchange at 280 °C. Dependence of the extent of purification by cation exchange at equilibrium on added Cd²⁺, monitored as $|g_{sp-d}|$ of re-equilibrated samples after cation exchange from diffusion-doped Cd_{1-x}Mn_xSe QDs (normalized to the initial equilibrated, diffusion-doped values of $|g_{sp-d}|$ for each sample) and plotted vs the number of equivalents of Cd²⁺ added relative to the amount of lattice Mn²⁺ in the diffusion-doped NCs. The black dashed line is a guide to the eye.