

**Supporting Information for:**

**Tailoring ZnSe-CdSe Colloidal Quantum Dots *via***

**Cation-Exchange: from Core/Shell to Alloy**

**Nanocrystals**

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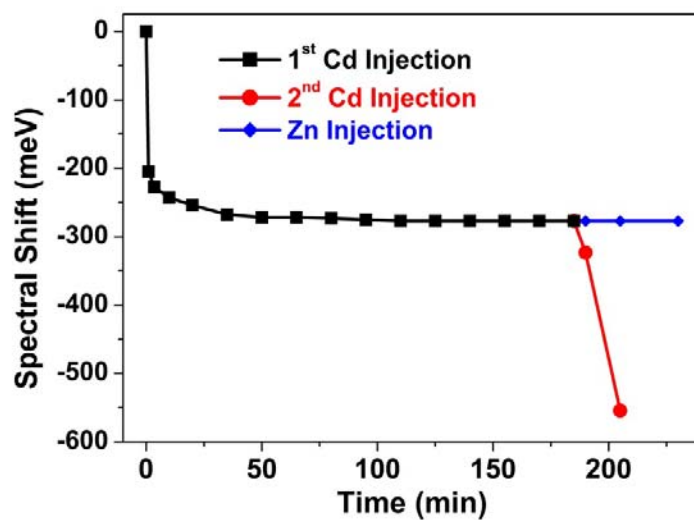
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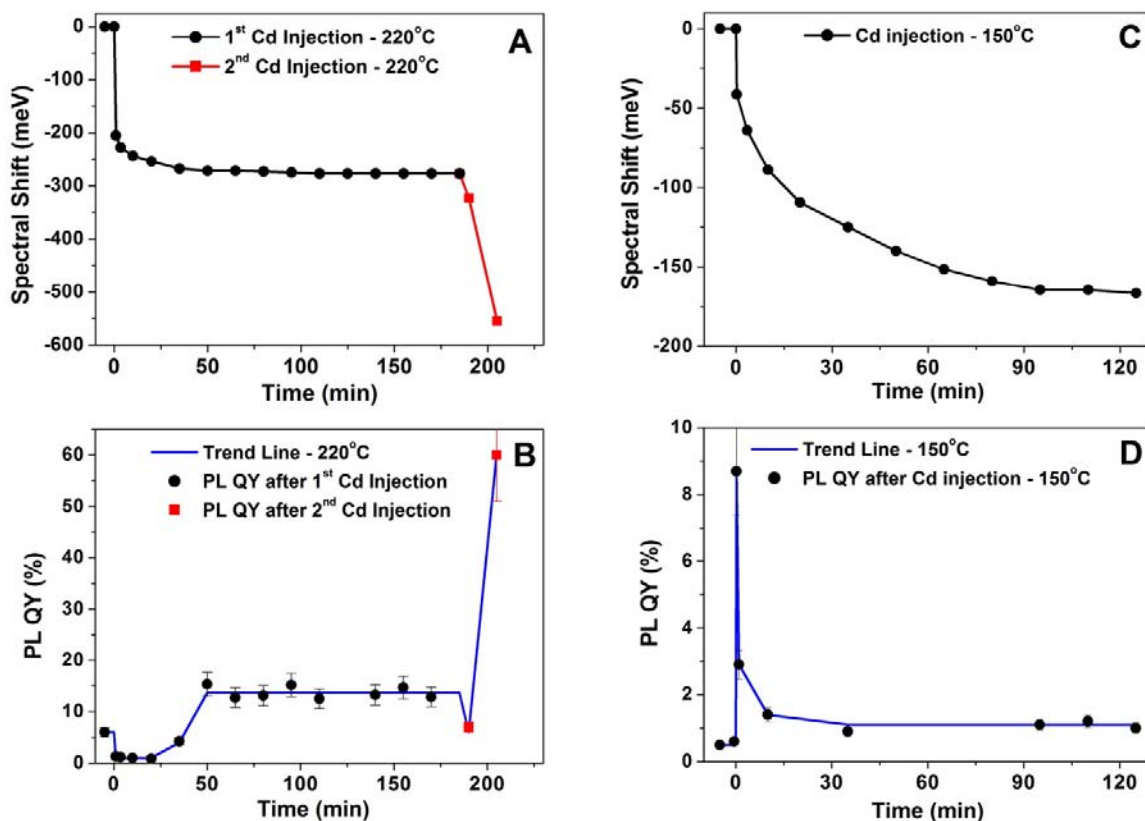
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**Table S1.** Elemental composition of  $(\text{Zn}_{1-x}\text{Cd}_x)\text{Se}$  NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange in 5.6 nm diameter ZnSe NCs at different reaction temperatures. In some cases, multiple sequential temperatures were used. The elements were quantified by Scanning Transmission Electron Microscopy Energy Dispersive X-Ray Spectroscopy (STEM-EDS). To ensure that the elemental concentrations were statistically valid and representative of the whole NC ensemble, EDS analyses were performed on wide areas ( $\sim 10^4$ – $10^5$  nm<sup>2</sup>,  $\sim 100$  to  $\sim 1000$  NCs), and averaged over several observation spots.

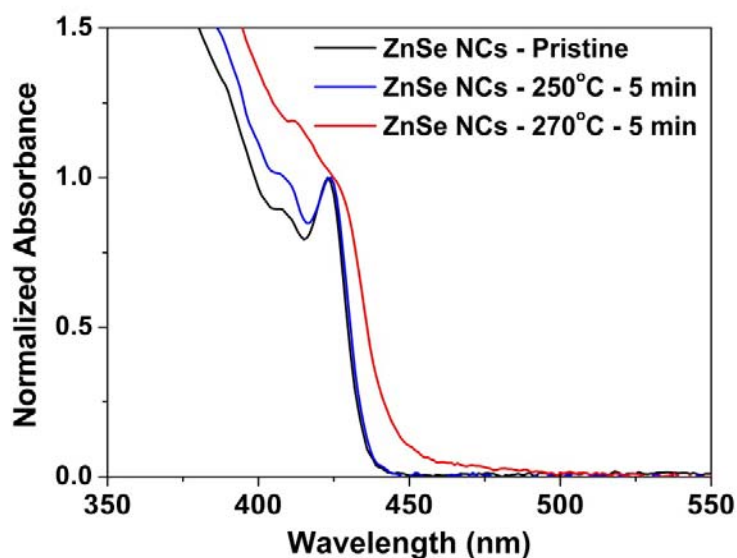
<b>Sample</b>	<b>T (°C)</b>	<b>Cd (at%)</b>	<b>Zn (at%)</b>	<b>Se (at%)</b>	<b>x</b>
<b>S150</b>	150	13.7±3.5	39.7±3.3	46.5±6.8	0.26
<b>S150-220</b>	150+220	21.0±2.0	28.9±1.4	50.1±3.0	0.42
<b>S220</b>	220	22.4±0.9	28.4±0.8	49.2±0.1	0.44
<b>S250</b>	250	33.8±2.9	18.8±1.7	47.4±4.5	0.64
<b>S150-250</b>	150+220+250	20.7±0.2	33.0±1.9	45.8±2.1	0.39



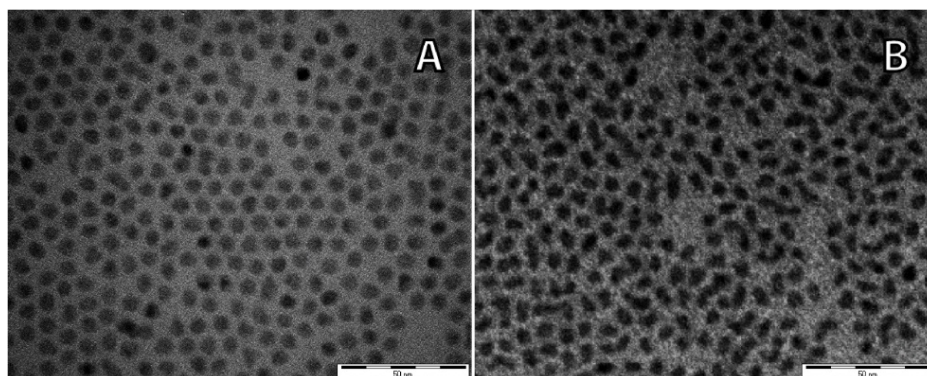
**Figure S1.** Temporal evolution of the spectral shift observed for the lowest energy absorption transition of (Zn,Cd)Se NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  exchange in 5.6 nm ZnSe NCs at 220 °C. The reaction was started by a single Cd-oleate injection (0.5 mL of 0.04 M solution,  $\text{Cd}_{\text{added}}/\text{ZnSe} = 0.23$ ) at  $t = 0$ . A second injection of Cd-oleate (0.5 mL, 0.04 M solution) was performed at 189 min, while keeping all other reaction parameters constant. A control experiment in which the second injection consisted of Zn-oleate (5 mL, 0.04 M solution) instead of Cd-oleate was also carried out.



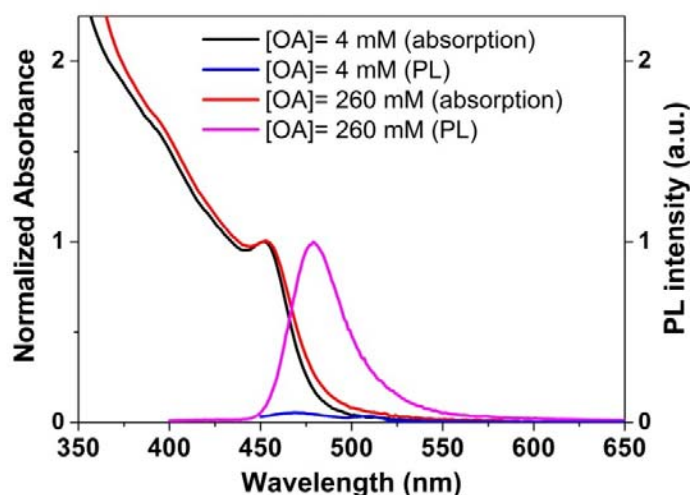
**Figure S2.** Temporal evolution of the spectral shift observed for the lowest energy absorption transition of (Zn,Cd)Se NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  exchange in 5.6 nm ZnSe NCs at two different temperatures: (A) 220 °C and (C) 150 °C. The evolution of the photoluminescence (PL) quantum yields (QY) for the same series of samples is shown in panels (B) and (D) (220 °C and 150 °C, respectively) (error bars:  $\pm 15\%$ ). The reaction was started by a single Cd-oleate injection (0.5 mL of 0.04 M solution,  $\text{Cd}_{\text{added}}/\text{ZnSe} = 0.23$ ) at  $t = 0$  for both reaction temperatures. In the case of the reaction at 220 °C, a second injection of Cd-oleate (0.5 mL, 0.04 M solution) was performed at 189 min, while keeping all other reaction parameters constant.



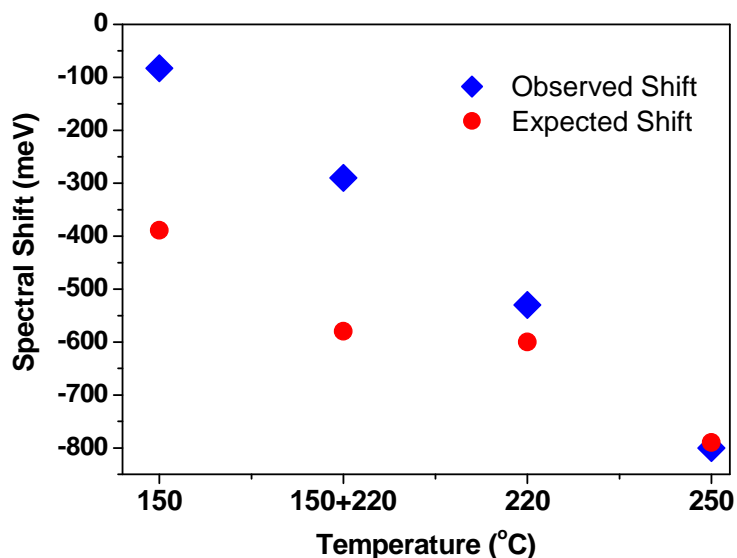
**Figure S3.** Absorption spectra of 5.6 nm ZnSe NCs heated for 5 min at two different temperatures under the same conditions used for the cation exchange reactions, but without addition of Cd precursors (coordinating solvent: 1.477 g octadecylamine and 6.3 mL octadecene,  $6 \times 10^{-5}$  mmol ZnSe NCs, see experimental section in the main text for additional details). The absorption spectrum of the parent ZnSe NCs prior to any thermal treatment is also given for comparison. The spectrum observed after heating at 250 °C for 5 min is also representative for the control experiments carried out at lower temperatures (150, 220, and 240 °C) and longer times (20 min).



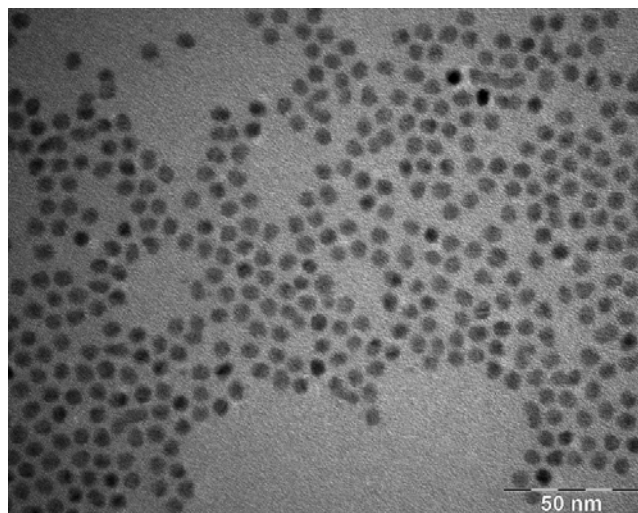
**Figure S4.** Representative TEM images of (Zn,Cd)Se NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  exchange in 5.6 nm ZnSe NCs at 220 °C. In (A) the cation exchange was driven by three sequential injections of 0.5 mL of 0.04 M Cd-oleate at 0, 20, and 40 min, while in (B) 1.5 mL of 0.04 M Cd-oleate was injected at  $t=0$ . The total reaction time (80 min) and all other reaction parameters were identical in both cases. The scale bar corresponds to 50 nm. The spectral shift was -530 meV and -740 meV for the samples shown in (A) and (B), respectively.



**Figure S5.** Absorption and photoluminescence (PL) spectra of (Zn,Cd)Se NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  exchange in 5.6 nm ZnSe NCs at 220 °C. The cation exchange was driven by a single Cd-oleate injection at  $t=0$  ( $\text{Cd}_{\text{added}}/\text{ZnSe} = 0.23$ ;  $[\text{Cd}(\text{Ol})_2]_0 = 90 \text{ mM}$ ), and the reaction was allowed to proceed for 100 min in both cases. All other reaction parameters were identical, except for the concentration of free oleic acid ([OA]), which originated from the excess used in the conversion of Cd acetate to Cd oleate (see experimental section in the main text for additional details).

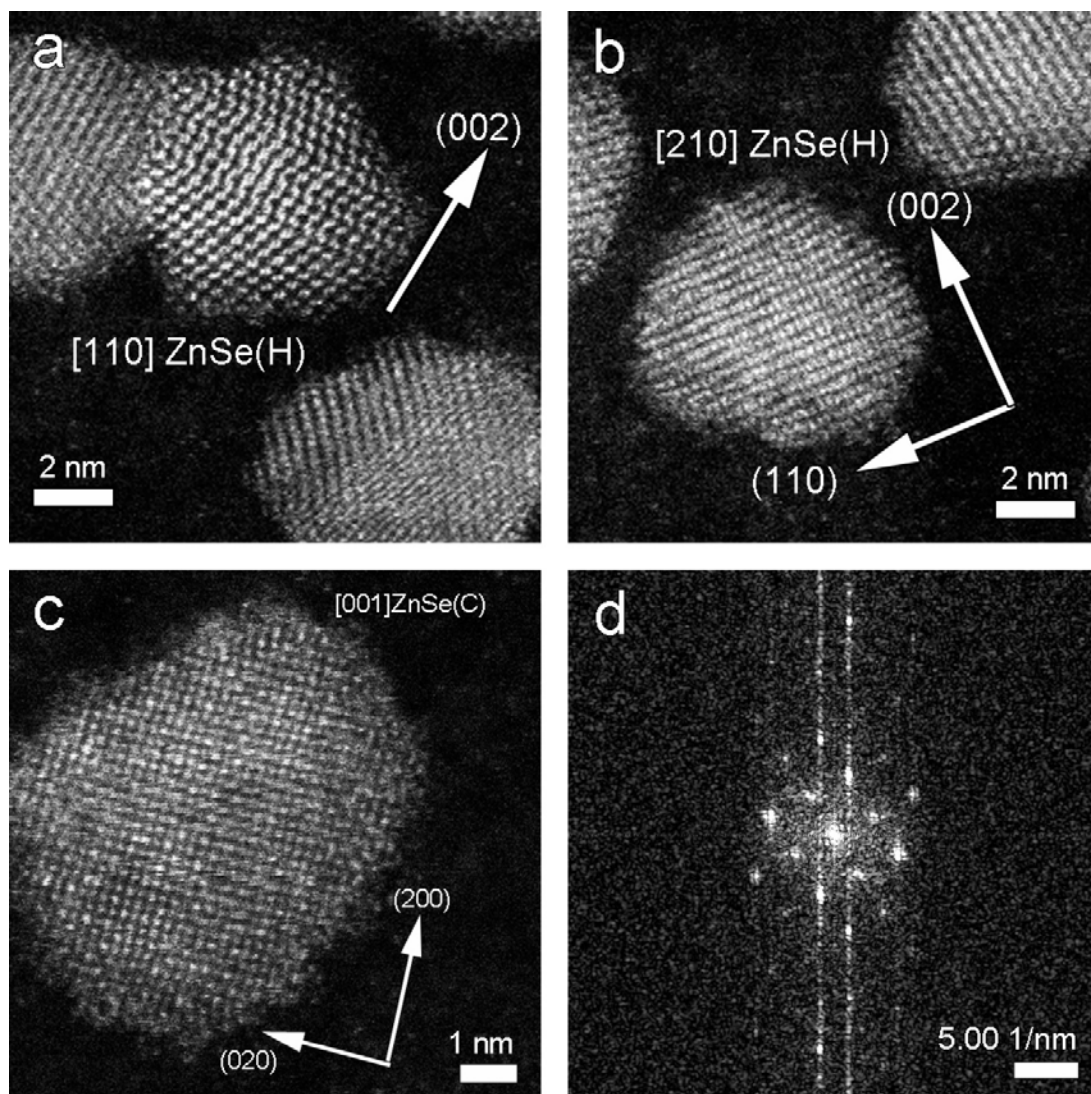


**Figure S6.** Observed and expected spectral shifts for the lowest energy absorption transition of (Zn,Cd)Se NCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange in 5.6 nm ZnSe NCs at different reaction temperatures (150, 220, 250 °C). A sample obtained by carrying out the exchange reaction at two consecutive temperatures is also included (80 min at 150 °C, followed by heating to 220 °C in 20 min, and 5 min at 220 °C). The cation exchange was driven by three sequential injections of Cd-oleate at 0, 20, and 40 min. The total reaction time was 80 min for all samples except S150-220. All other reaction parameters were identical. The observed spectral shift corresponds to the difference between the position of the lowest energy absorption transition of the product (Zn,Cd)Se NCs and that of the parent ZnSe NCs. The expected spectral shift is calculated assuming that the product NCs are  $(\text{Zn}_{1-x}\text{Cd}_x)\text{Se}$  homogeneous alloy NCs and using Eq. (1) in the main text. The  $x$  values are 0.26, 0.42, 0.44, and 0.64, for samples S150, S150-220, S220, and S250, respectively (see Table 1 in the main text for details). The band gap of 5.6 nm ZnSe NCs is taken to be 2.93 eV (Figure 1A in the main text). The band gaps of CdSe NCs are taken to be 1.99, 1.98, 1.975, and 1.97 eV, from S150 to S250, respectively [35].

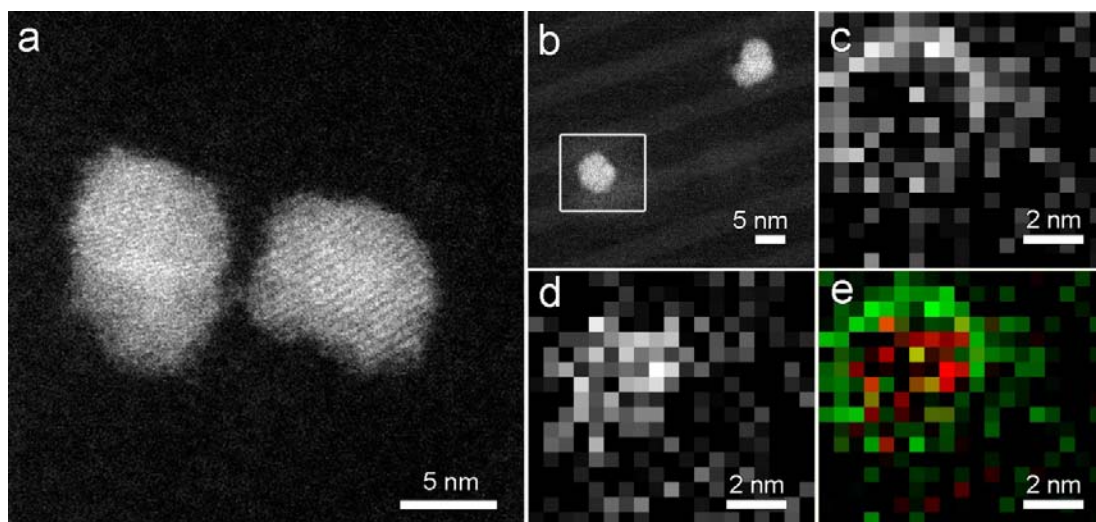


**Figure S7.** Representative TEM image of (Zn,Cd)Se NCs obtained by thermally treating sample S150-220 at 250 °C for 20 min. Sample S150-220 consisted of ZnSe/CdSe core/shell HNCs obtained by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange in 5.6 nm ZnSe NCs at two consecutive reaction temperatures: 80 min at 150 °C, followed by heating to 220 °C in 20 min, and 5 min at 220 °C (see main text for details).

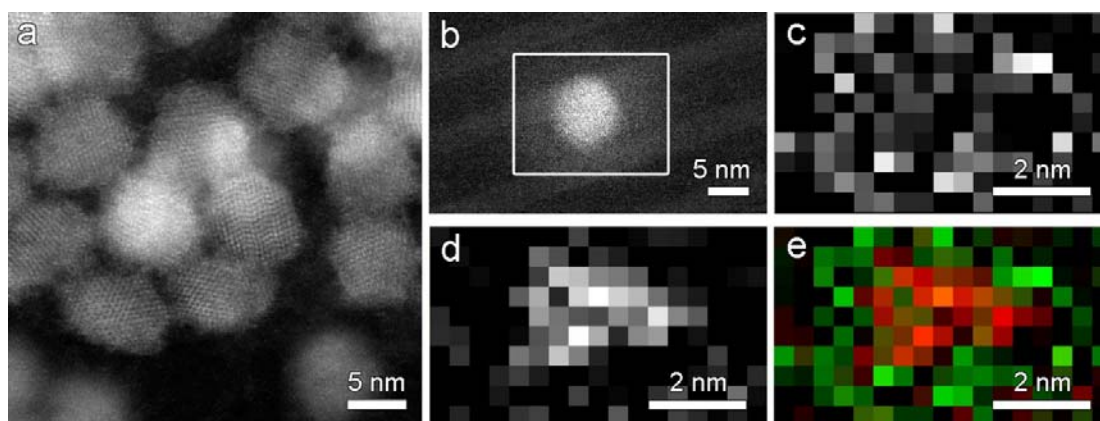




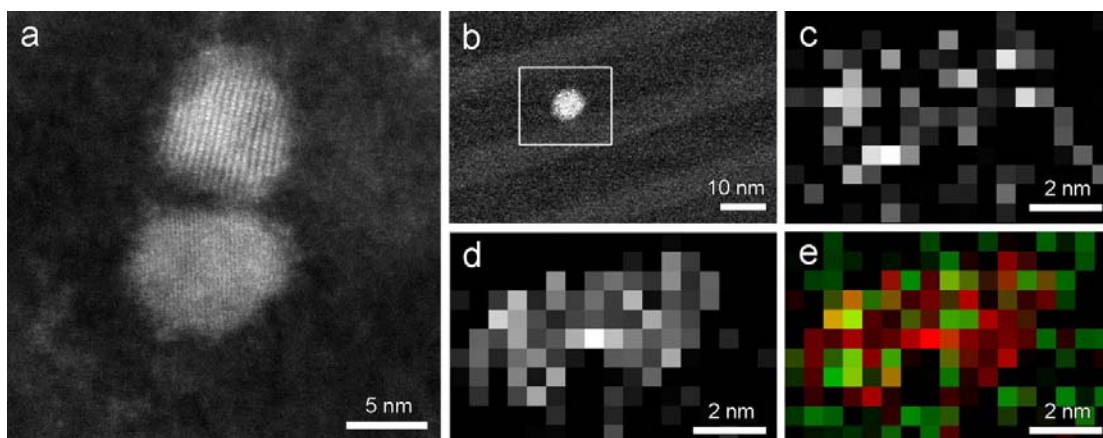
**Figure S8.** HR-STEM images of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at two consecutive temperatures (80 min at 150 °C, followed by heating to 220 °C in 20 min, and 5 min at 220 °C). 0.5 mL Cd-oleate solution (0.04 M) were injected at 0, 20, and 40 min. The NCs possess a ZnSe/CdSe core/shell architecture (see Figure 6 in the main text), but only the lattice parameters of ZnSe are observed. The NCs crystallize in both the wurtzite (**a,b**) and zincblende (**c,d**) structures of ZnSe.



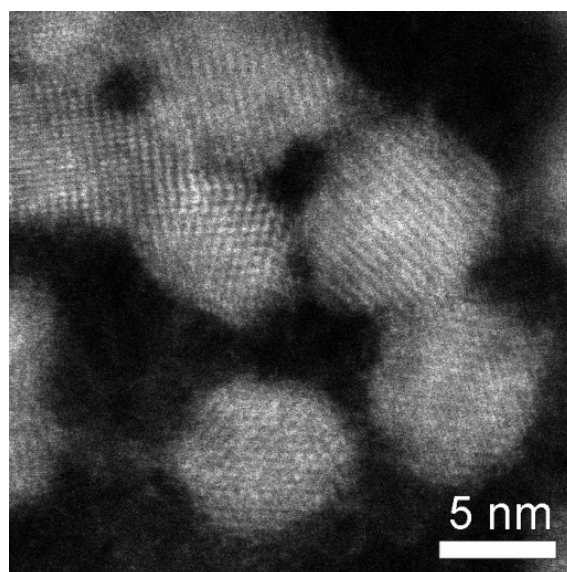
**Figure S9.** (a) HR-STEM images of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at 220 °C (80 min). 0.5 mL Cd-oleate solution (0.04 M) were injected at 0, 20, and 40 min. (b) The square indicates the region selected for EELS analysis. The chemical distribution profiles of Zn (red) and Cd (green) shown in (e) were constructed from the chemical maps for Cd (c) and Zn (d).



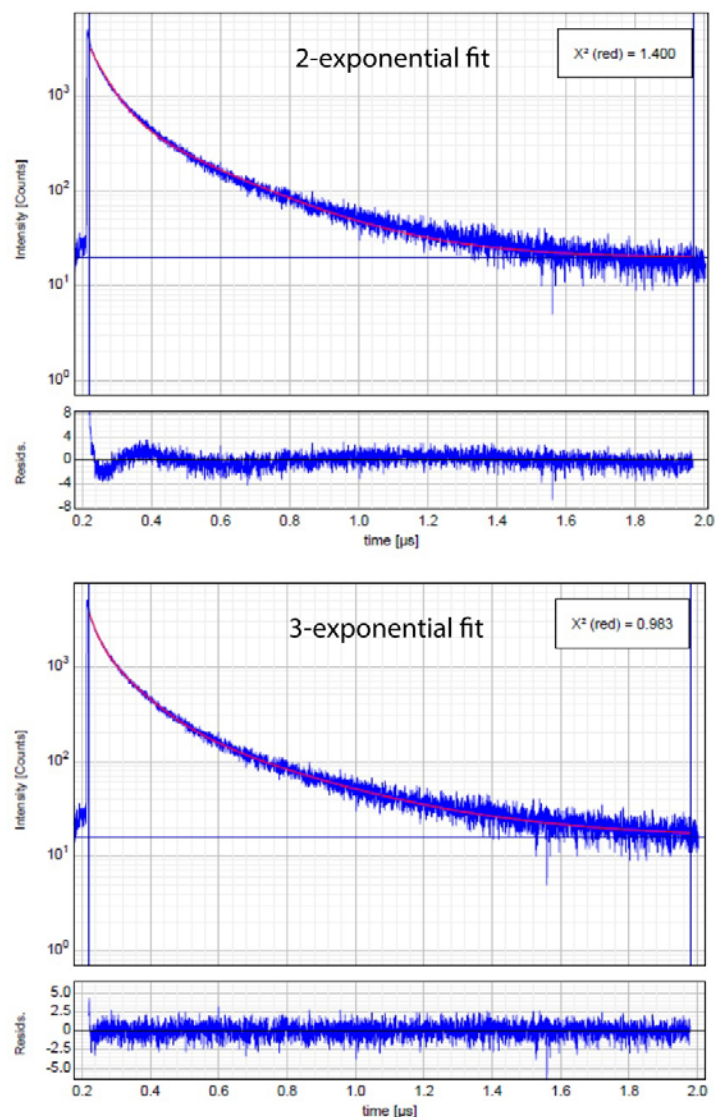
**Figure S10.** (a) HR-STEM images of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at 200 °C (80 min). 0.5 mL Cd-oleate solution (0.04 M) were injected at 0, 20, and 40 min. (b) The square indicates the region selected for EELS analysis. The chemical distribution profiles of Zn (red) and Cd (green) shown in (e) were constructed from the chemical maps for Cd (c) and Zn (d).



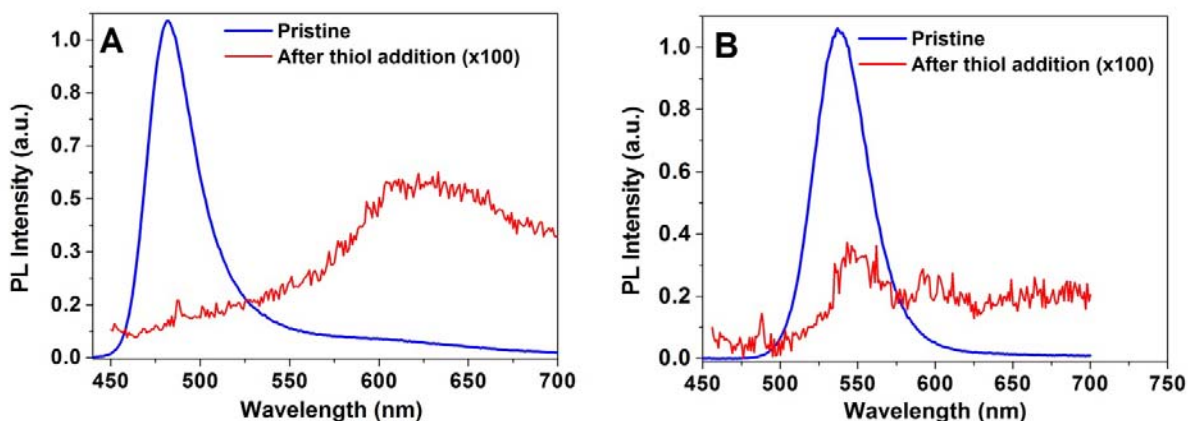
**Figure S11.** (a) HR-STEM images of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange. The NCs were obtained by heating sample 150-220 (see Figure 6 (A-E) in the main text and Figure S8) at 250 °C for 20 min. The sample was separated from the reaction mixture and purified prior to being heated to 250 °C. (b) The square indicates the region selected for EELS analysis. The chemical distribution profiles of Zn (red) and Cd (green) shown in (e) were constructed from the chemical maps for Cd (c) and Zn (d).



**Figure S12.** HR-STEM images of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at 150 °C (80 min). 0.5 mL Cd-oleate solution (0.04 M) were injected at 0, 20, and 40 min. The amount of Cd present was too small to be reliably analyzed by EELS.

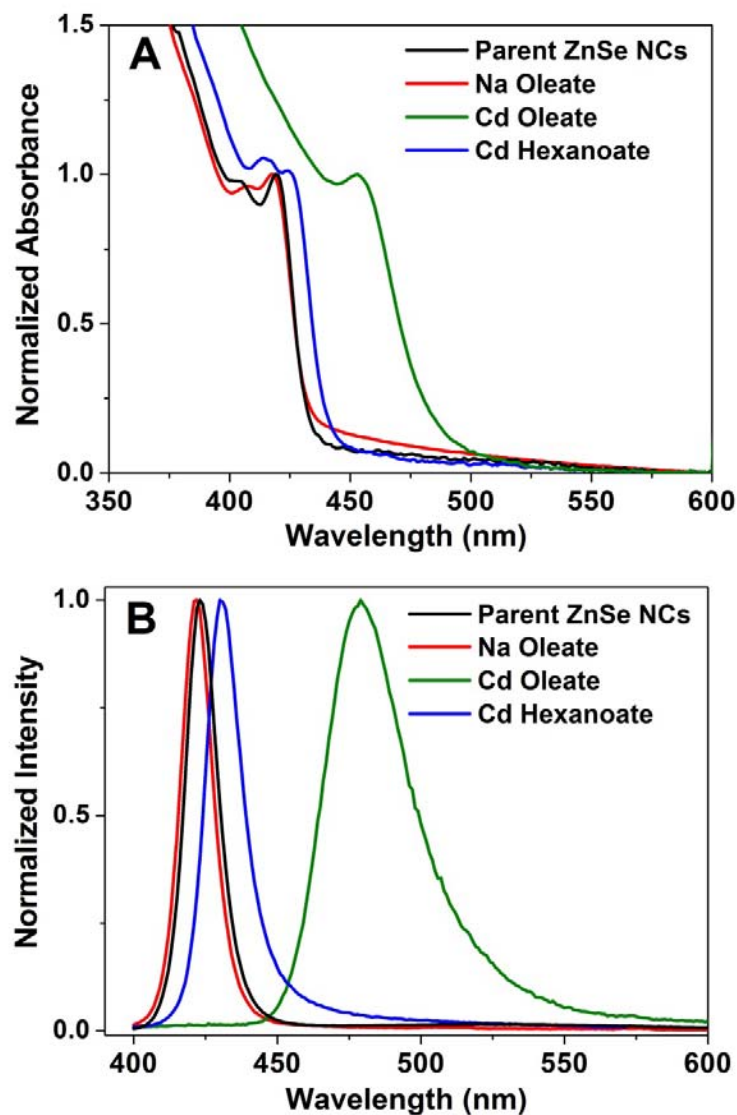


**Figure S13.** Comparison between two- and three-exponential fits of the PL decay curve of (Cd,Zn)Se NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at two consecutive temperatures (80 min at 150 °C, followed by heating to 220 °C in 20 min, and 5 min at 220 °C, sample S150-220). This PL decay curve is also shown in Figure 7 in the main text (blue curve). The residuals are shown at the bottom of each panel. The decay constants are 49 ns (Amplitude: 79%) and 240 ns (Amplitude: 21%) for the 2-exponential fit; and 23 ns (Amplitude: 45%), 89 ns (Amplitude: 45%), and 337 ns (Amplitude: 10%) for the 3-exponential fit.



**Figure S14.** Photoluminescence spectra ( $\lambda_{\text{exc}} = 400$  nm) of two different samples of (Cd,Zn)Se NCs prior to and after addition of hexanedithiol to solutions of the NCs in toluene under inert atmosphere conditions and immediately before the PL measurements. **(A)** Sample S150-220 (ZnSe/CdSe core/shell HNCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at two consecutive temperatures, 150 °C and 220 °C, Figures 6 in the main text and S8 above). **(B)** Sample S220 ((Cd,Zn)Se gradient alloy NCs obtained from 5.6 nm diameter ZnSe NCs by  $\text{Zn}^{2+}$  for  $\text{Cd}^{2+}$  cation exchange at 220 °C, Figures 6 in the main text and S9 above).





**Figure S15.** Absorption (A) and photoluminescence (B) spectra of (Zn,Cd)Se NCs obtained by Zn<sup>2+</sup> for Cd<sup>2+</sup> cation exchange in 5.6 nm ZnSe NCs at 220 °C using two different Cd-precursors (Cadmium hexanoate and Cadmium oleate). A control experiment in which the Cd-precursor was replaced by Sodium oleate is also presented. The reaction was driven by a single metal-precursor injection at t=0. Other than the metal precursor, all reaction parameters were identical. The total reaction time was 120 min. The spectra of the parent ZnSe NCs are also shown.