

Supporting Information to: Strain Engineering in InP/(Zn,Cd)Se Core/Shell Quantum Dots

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Resonant behavior

The InP core and the (Zn,Cd)Se shells have different electronic transitions. When the incident or scattered light is energetically close to the transition, resonant Raman scattering occurs, enhancing the signal intensity of the component in resonance. However, frequency shifts were not observed, as displayed in Figure SI1.

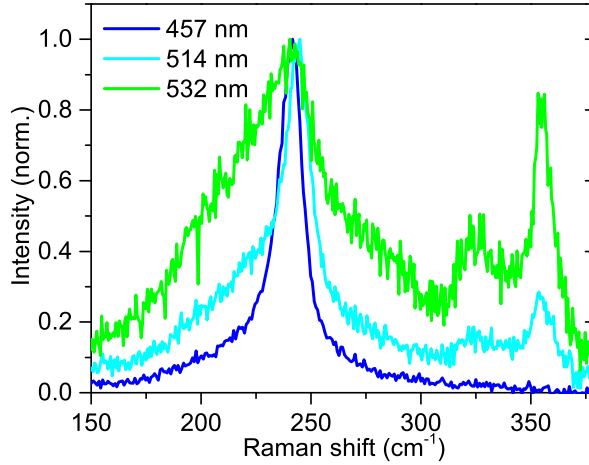


Figure SI1: Raman spectra of InP/Zn_{0.98}Cd_{0.02}Se QDs measured with different excitation wavelengths. Changing the wavelength to 532 nm makes the core-related band well resolvable, whereas changing towards blue wavelengths (shell resonance) enhances the shell-related bands and the core-related band is not not observable any more.

To be able to resolve the core- and the shell-related Raman bands, the excitation wavelength was varied from sample to sample, depending on the shell composition. Table (SI1) summarizes the excitation wavelengths for all samples and the corresponding spectral resolution.

Table SI1: Excitation wavelengths used for the different samples with spectral resolution.

Sample	Excitation wavelength (nm)	Resolution (cm^{-1})
InP	514	2.2
InP/ZnSe 0% Cd	458	4
InP/(Zn,Cd)Se 2.5% Cd	514	2.2
InP/(Zn,Cd)Se 5% Cd	514	2.2
InP/(Zn,Cd)Se 13% Cd	830	2
InP/(Zn,Cd)Se 21% Cd	532	4
InP/(Zn,Cd)Se 42% Cd	633 & 846	2.2
InP/(Zn,Cd)Se 70% Cd	830	2
InP/(Zn,Cd)Se 87% Cd	830	2
InP/(Zn,Cd)Se 98% Cd	830	2
InP/(Zn,Cd)Se 100% Cd	830	2

Raman spectra

Figure SI2-SI11 display the complete Raman spectra of all samples under investigation. All spectra are normalized to the shell-related LO intensity. Please note that silicon, which served as sample substrate, has Raman-active vibrations around 300 cm^{-1} and is sometimes slightly visible in the spectra. The InP LO Raman bands used for the discussion are always well-separated from the Si Raman band.

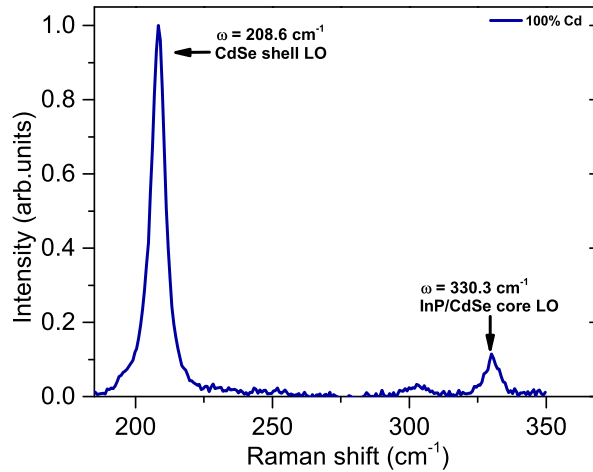


Figure SI2: Raman spectrum of InP/CdSe QDs.

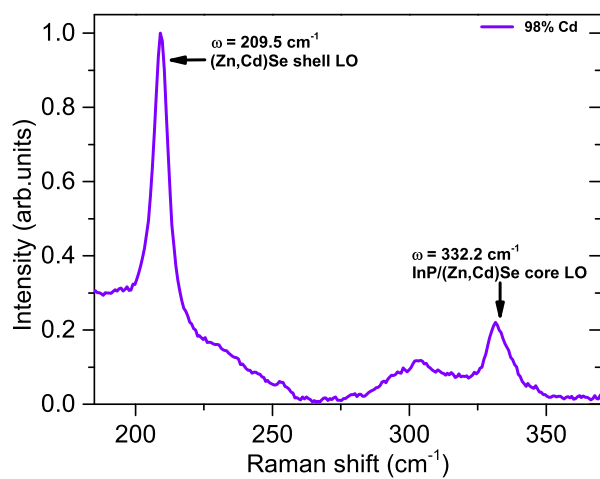


Figure SI3: Raman spectrum of InP/Zn_{0.02}Cd_{0.98}Se QDs.

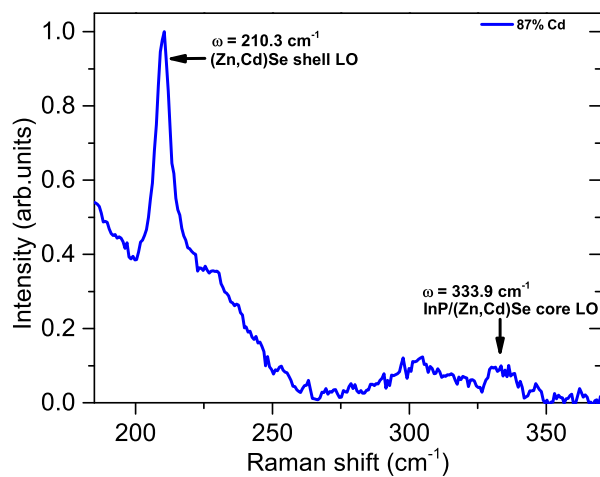


Figure SI4: Raman spectrum of InP/Zn_{0.13}Cd_{0.87}Se QDs.

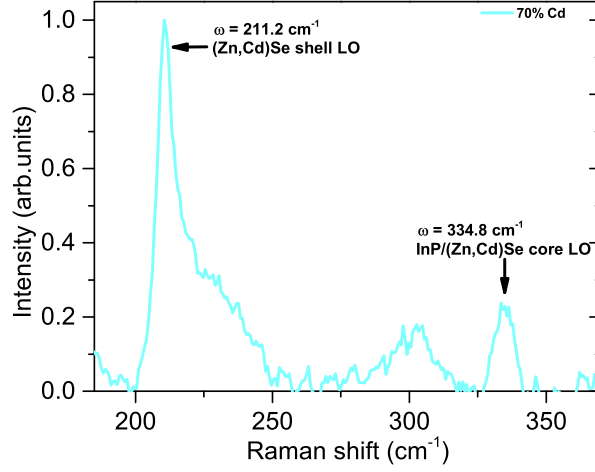


Figure SI5: Raman spectrum of InP/Zn_{0.30}Cd_{0.70}Se QDs.

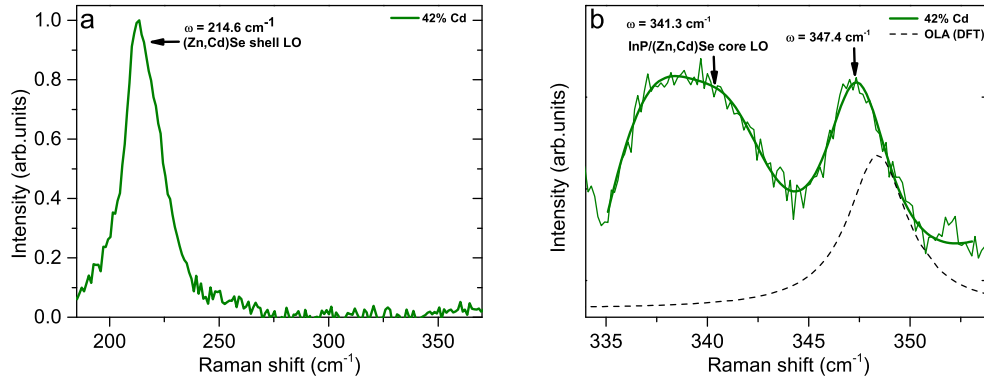


Figure SI6: Raman spectra of InP/Zn_{0.58}Cd_{0.42}Se QDs a) in the region of the shell-related LO, measured with an excitation wavelength of 633 nm. b) In the core-related LO frequency region, measured with an excitation wavelength of 846.163 nm, the dashed curve are DFT calculations of oleic acid.

The shell-related LO of InP/Zn_{0.58}Cd_{0.42}Se QDs (Figure SI6) was measured with an excitation wavelength of 633 nm, while the core-related LO could not be detected with this excitation wavelength. Changing the excitation wavelength towards the infrared (846.163 nm) and integrating for a longer times (30 min) helped to resolve the core-related vibrations. However, under such experimental conditions, the ligand-related organic vibrations, which are also Raman active, are also visible. In order to discuss the spectra, we performed DFT calculations of the organic ligand molecules (oleic acid and dodecanethiol). The vibration

around 347 cm^{-1} can be assigned to oleic acid, while the Raman bands around 340 cm^{-1} are in a frequency region without organic vibrations. We fitted this asymmetric band the same way as the common InP Raman bands with two Lorentzian functions.

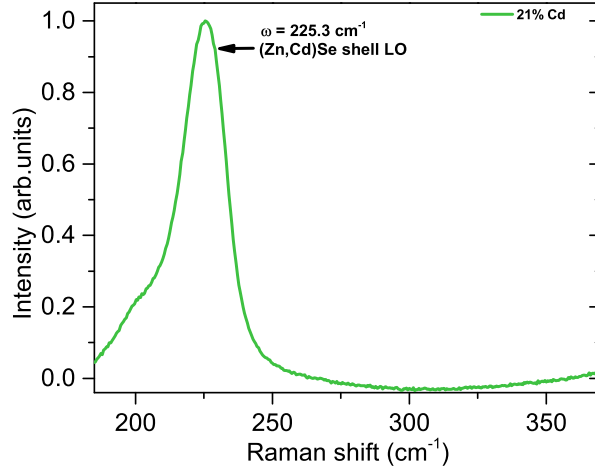


Figure SI7: Raman spectrum of InP/Zn_{0.79}Cd_{0.21}Se QDs. The core-related LO could not be detected.

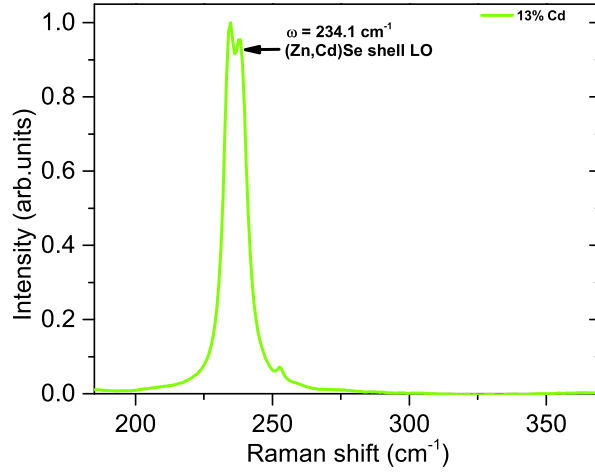


Figure SI8: Raman spectrum of InP/Zn_{0.87}Cd_{0.13}Se QDs. The core-related LO could not be detected.

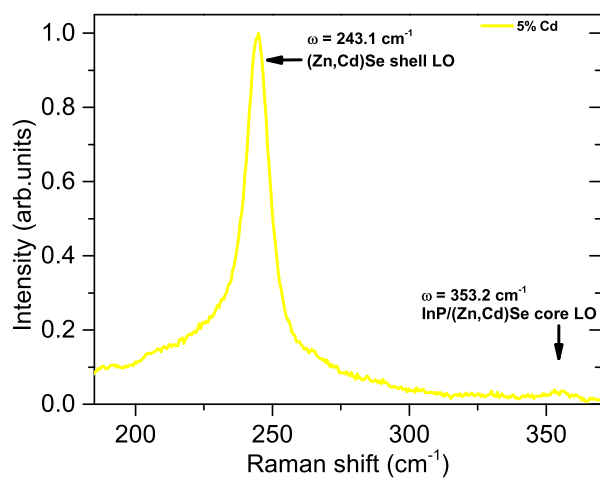


Figure SI9: Raman spectrum of InP/Zn_{0.95}Cd_{0.05}Se QDs.

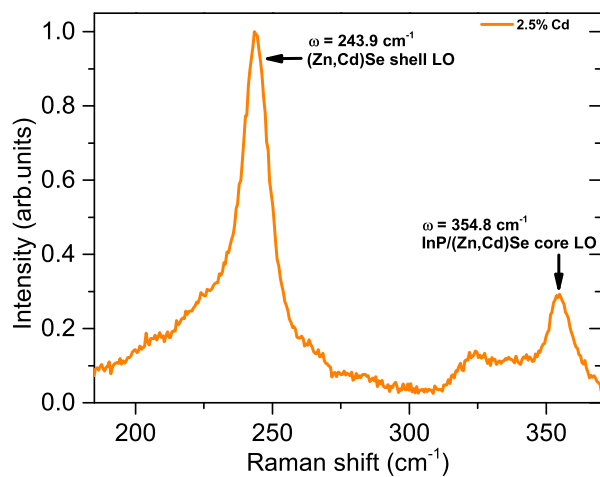


Figure SI10: Raman spectrum of InP/Zn_{0.975}Cd_{0.025}Se QDs.

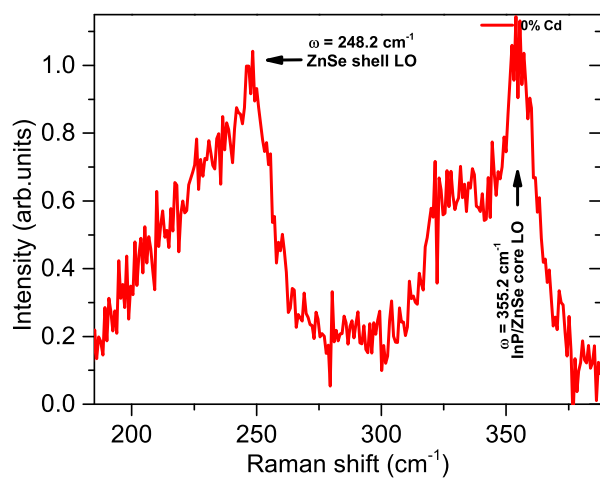


Figure SI11: Raman spectrum of InP/ZnSe core/shell QDs.

Additional TEM images

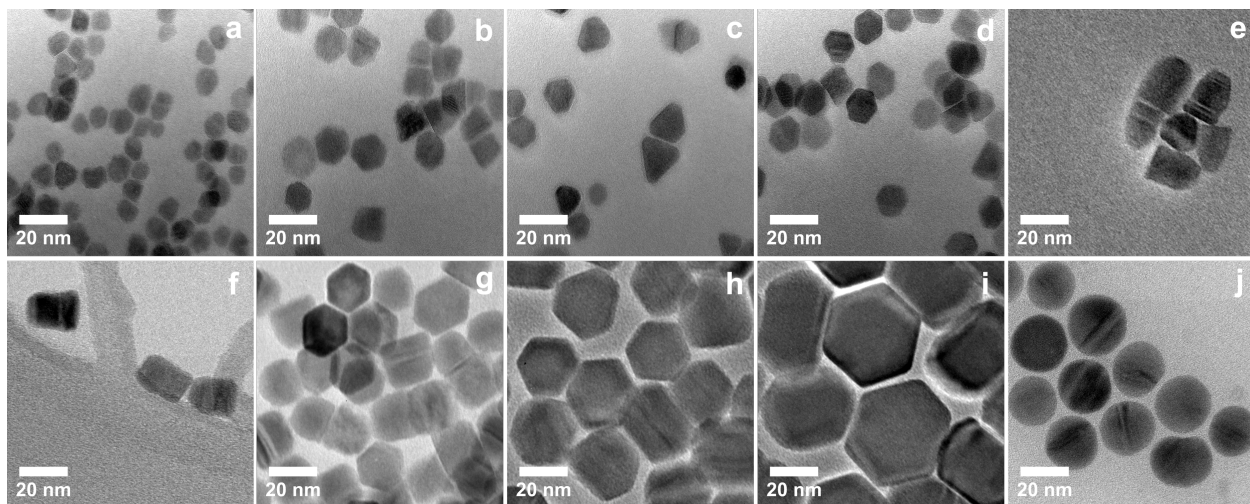


Figure SI12: TEM images of a) InP/ZnSe QD, b) InP/Zn_{0.975}Cd_{0.025}Se QD, c) InP/Zn_{0.95}Cd_{0.05}Se QD, d) InP/Zn_{0.87}Cd_{0.13}Se QD, e) InP/Zn_{0.79}Cd_{0.21}Se QD, f) InP/Zn_{0.58}Cd_{0.42}Se QD, g) InP/Zn_{0.30}Cd_{0.70}Se QD, h) InP/Zn_{0.13}Cd_{0.87}Se QD, i) InP/Zn_{0.02}Cd_{0.98}Se QD, j) InP/CdSe QD.

XRD experiments

Figure SI13 a displays Whereas the InP/ZnSe diffractogram ($x = 0$) points towards a zinc blende structure. Typical wurtzite diffraction peaks appear with increasing Cd content. To assess the influence of Cd admixing, we therefore focus on the zinc blende (220)/ wurtzite (110) diffraction peak. Measuring the cation-cation distance, these coincide for zinc blende and wurtzite CdSe and are only slightly shifted for zinc blende and wurtzite ZnSe. The black markers in Figure SI13 b are the experimental $d_{(exp)}$ as derived from the zinc blende (220)/ wurtzite (110) diffraction peak. The red line correspond to linear interpolation between the zinc blende (220) lattice spacing for ZnSe and CdSe (see equation (3)). The blue line is a linear interpolation between the wurtzite (110) lattice spacing for ZnSe and CdSe (see equation (6)). Although the experimental lattice plane spacing does not fully coincide with either of these trend lines, its variation is comparable to what is predicted based on such linear interpolations.

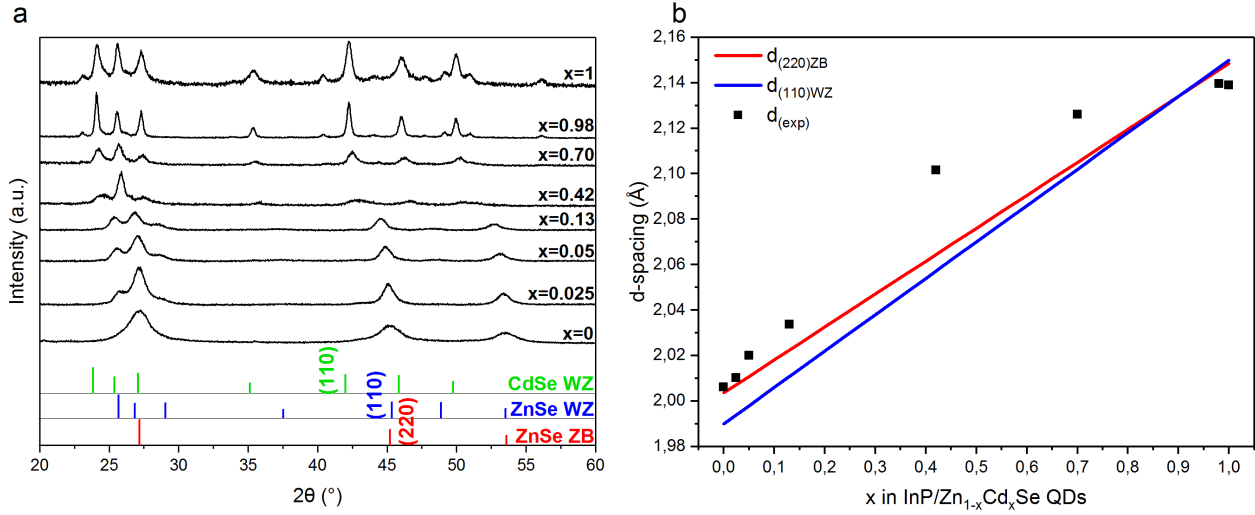


Figure SI13: a) XRD patterns of InP/Zn_{1-x}Cd_xSe QDs for $x = 0, 0.025, 0.05, 0.13, 0.42, 0.70, 0.98, 1$. b) Experimental $d_{(exp)}$ derived from the diffraction peak. linear interpolation between the zinc blende (220) lattice spacing for ZnSe and CdSe is shown with the red line and linear interpolation between the wurtzite (110) lattice spacing for ZnSe and CdSe is shown in blue.

The experimental interplanar distance $d_{(exp)}$ can be calculated from Bragg's law:

$$d_{(exp)} = \frac{\lambda}{2\sin\theta} \quad (1)$$

Here $\lambda = 1.541 \text{ \AA}$ which correspond to the wavelength of the incident Cu K-alpha radiation and θ the scattering angle expressed in radians.

Calculation of $d_{(220)}$ values for zinc blende $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ (see red line in Figure SI13 b):

$$d_{(hkl)ZB} = \frac{a_{(Zn_{1-x}Cd_xSe)ZB}}{\sqrt{h^2 + k^2 + l^2}} = \frac{(1-x)a_{(ZnSe)ZB} + xa_{(CdSe)ZB}}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

Here h , k , and l are the Miller indices of the Bragg plane and $a_{(Zn_{1-x}Cd_xSe)ZB}$ is the lattice spacing of zinc blende $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ material which is expressed according to the Vegard's law. Since $a_{(ZnSe)ZB} = 5.67 \text{ \AA}$ and $a_{(CdSe)ZB} = 6.08 \text{ \AA}$. The $d_{(220)}$ values of zinc blende $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ is given by:

$$d_{(220)ZB} = \frac{(1-x)5.67 + x6.08}{2\sqrt{2}} \quad (3)$$

Calculation of $d_{(110)}$ values for wurtzite $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ (see blue line in Figure SI13 b):

$$d_{(hkl)WZ} = \frac{\sqrt{3}}{2} \frac{a_{(Zn_{1-x}Cd_xSe)WZ}}{\sqrt{h^2 + hk + k^2}} + \frac{c_{(Zn_{1-x}Cd_xSe)WZ}}{l} \quad (4)$$

Here h , k , and l are the Miller indices of the Bragg plane and $a_{(Zn_{1-x}Cd_xSe)WZ}$ and $c_{(Zn_{1-x}Cd_xSe)WZ}$ the lattice constants of wurtzite $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ material which can be expressed according to the Vegard's law. According equation (4), the $d_{(hkl)}$ values of wurtzite $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ material for $h = 1$, $k = 1$ and $l = 0$ is:

$$d_{(110)WZ} = \frac{a_{(Zn_{1-x}Cd_xSe)WZ}}{2} = \frac{(1-x)a_{(ZnSe)WZ} + xa_{(CdSe)WZ}}{2} \quad (5)$$

Since $a_{(ZnSe)WZ} = 3.98 \text{ \AA}$ and $a_{(CdSe)WZ} = 4.30 \text{ \AA}$, the $d_{(110)}$ values of wurtzite $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ is

given by:

$$d_{(110)WZ} = \frac{(1-x)3.98 + x4.30}{2} \quad (6)$$

Theoretical peak positions 2θ of bulk zinc blende ZnSe and wurtzite ZnSe and CdSe (see vertical lines in Figure SI13 a):

ZnSe ZB (red lines) 27.22° , 45.2° , 53.56° .

CdSe WZ (green lines) 23.89° , 25.39° , 27.10° , 35.14° , 42.00° , 45.81° , 49.72° .

ZnSe WZ (blue lines) 25.72° , 26.89° , 29.09° , 37.55° , 45.35° , 48.88° , 53.51° .

Experimental diffraction peaks positions $2\theta_{(exp)}$ of the zinc blende (220)/ wurtzite (110) of InP/Zn_{1-x}Cd_xSe QDs (see Figure SI13 a):

InP/ZnSe QDs: 45.20° .

InP/Zn_{0.975}Cd_{0.025}Se QDs: 45.10° .

InP/Zn_{0.95}Cd_{0.05}Se QDs: 44.87° .

InP/Zn_{0.87}Cd_{0.13}Se QDs: 44.55° .

InP/Zn_{0.58}Cd_{0.42}Se QDs: 43.04° .

InP/Zn_{0.30}Cd_{0.70}Se QDs: 45.52° .

InP/Zn_{0.02}Cd_{0.98}Se QDs: 42.24° .

InP/CdSe QDs: 42.25° .

Focusing on the zinc blende (220)/ wurtzite (110) peak positions of InP/Zn_{1-x}Cd_xSe QDs (values indicated above) and according to equation (1) we can calculate the $d_{(exp)}$ for $x = 0, 0.025, 0.05, 0.13, 0.42, 0.70, 0.98, 1$. (see black markers in Figure SI13 b). These values are listed in Table (SI2).

Table SI2: Calculated values for $d_{(exp)}$.

$d_{(exp)}$ (Å)	x
2.006009323	0
2.010224407	0.025
2.019992511	0.05
2.033755624	0.13
2.101541437	0.42
2.126030100	0.70
2.139472585	0.98
2.13898935	1

Synthesis of InP and InP/Zn_{1-x}Cd_xSe QDs

Full chemical yield synthesis of InP QDs with first exciton at 560 nm (estimated diameter: 3.2 nm): 50 mg (0.225 mmol) of indium(III) chloride, and 150 mg (1.1 mmol) of zinc(II) chloride were mixed in 2.5 mL (7.5 mmol) of technical oleylamine (OLA). The reaction mixture was stirred and degassed at 120 °C for an hour and heated to 180 °C under inert atmosphere. Upon reaching 180 °C, a volume of 0.23 mL (0.8 mmol) of tris(diethylamino)phosphine was quickly injected in the above mixture and InP nanocrystals synthesis was proceeded. The reaction occurs during 30 min. At the end of the reaction, the temperature was down. InP were precipitated in ethanol and suspended in toluene. This synthesis provides InP nanocrystals with a diameter of 3.2 nm (band-edge absorption [first exciton] at 560 nm).

Synthesis of InP/ZnSe Core/Shell QDs: A 3.2 nm InP QD synthesis was performed at 180 °C. After the InP core formation, instead of cooling down the temperature, at 20 min, 0.45 mL of stoichiometric TOP-Se (2.24 M) was injected at 180 °C. After 140 min, a mixture of 2 g (3 mmol) of Zn(stearate)₂, 8 mL of octadecene (ODE) and 2 mL of OLA was injected. The Temperature was increased from 180 °C to 320 °C and 1.4 mL of TOP-Se was injected drop by drop during increasing of the temperature. At 240 min the reaction was stopped and the temperature was lowered down. InP/ZnSe QDs were precipitated once in ethanol and suspended in toluene.

Synthesis of InP/Zn_{1-x}Cd_xSe Core/Shell QDs: A 3.2 nm InP QDs synthesis was performed at 180 °C. After the InP core formation, instead of cooling down the temperature, at 20 min, 0.45 mL of stoichiometric TOP-Se (2.24 M) was injected at 180 °C. At 140 min, a mixture of Cd(acetate)₂ dihydrate and Zn(stearate)₂, was mixed with 8 mL of ODE and 2 mL of OLA was injected. The temperature was increased from 180 °C to 320 °C and 1.4 mL of TOP-Se was injected drop by drop during increasing the temperature. At 240 min the reaction was stopped and the temperature was cooled down. InP/Zn_{1-x}Cd_xSe QDs were then precipitated once in ethanol and suspended in toluene.

Synthesis of InP/Zn_{0.02}Cd_{0.98}Se Core/Shell QDs: 50 mg (0.225 mmol) of indium(III) chloride, and 84 mg (0.62 mmol) of zinc(II) chloride were mixed in 2.5 mL (7.5 mmol) of technical oleylamine (OLA). The reaction mixture was stirred and degassed at 120 °C for an hour and heated to 180 °C under inert atmosphere. Upon reaching 180 °C, a volume of 0.23 mL (0.8 mmol) of tris(diethylamino)phosphine was quickly injected in the above mixture and InP synthesis was proceeded. After the InP core formation, instead of cooling down the temperature, at 20 min, 0.45 mL of stoichiometric TOP-Se (2.24 M) was injected at 180 °C. At 140 min, a mixture of 0.93 g (3.49 mmol) of Cd(acetate)₂ dihydrate, (Cd to Cd+Zn molar ratio=0.85) mixed with 2 mL of ODE and 2 mL of OLA was injected. The temperature was increased from 180 °C to 320 °C and 1.4 mL of TOP-Se was injected drop by drop during increasing the temperature. At 240 min the reaction was stopped and the temperature was cooled down. InP/Zn_{0.02}Cd_{0.98}Se QDs were then precipitated once in ethanol and was suspended in toluene.

Synthesis of InP/CdSe Core/Shell QDs: 50 mg (0.225 mmol) of indium(III) chloride were mixed in 2.5 mL (7.5 mmol) of technical oleylamine (OLA). The reaction mixture was stirred and degassed at 120 °C for an hour and heated to 180 °C under inert atmosphere. Upon reaching 180 °C, a volume of 0.23 mL (0.8 mmol) of tris(diethylamino)phosphine was quickly injected in the above mixture and InP nanocrystals synthesis was proceeded. After the InP core formation, instead of cooling down the temperature, at 20 min, 0.45 mL of stoichiometric TOP-Se (2.24 M) was injected at 180 °C. At 140 min, a mixture of 1.09 g (4.1 mmol) of Cd(acetate)₂ dihydrate were mixed with 8 mL of ODE and 2 mL of OLA was injected. Then temperature was increased from 180 °C to 320 °C. At 240 min the reaction was stopped and the temperature was cooled down. InP/CdSe QDs were precipitated once in ethanol and was suspended in toluene.

Table SI3: Comparison between theoretical and EDX values of Cd/(Cd+Zn) ratio in InP/(Zn,Cd)Se QDs synthesized with the synthesis method outlined in Synthesis of InP/Zn_{1-x}Cd_xSe Core/Shell QDs.

Cd/(Cd+Zn) _{theoretical} (%)	3.2	6.4	13.8	35	36	50	70	85
Cd/(Cd+Zn) _{EDX} (%)	2.5	5	13.3	21.4	42.4	70.1	86.8	98.1