Supporting Information

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Indium Phosphide-Based Quantum Dots with Shell-Enhanced Absorption for Luminescent Down-Conversion

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Indium Phosphide-Based Quantum Dots with Shell-Enhanced Absorption for Luminescent Down-Conversion

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S1 Synthesis protocols of InP and InP/(Zn,Cd)Se QDs

S1.1. Reference 1 - InP QDs with first exciton at 560 nm (estimated diameter: 3.2 nm)

50 mg (0.225 mmol) of indium(III) chloride, as indium raw materials, and 150 mg (1.1 mmol) of zinc(II) chloride, as zinc raw materials, are mixed in 2.5 mL (7.5 mmol) of technical oleylamine (OLA). The reaction mixture is stirred and degassed at 120 °C for an hour and then heated to 180 °C under inert atmosphere. Upon reaching 180 °C, a volume of 0.23 mL (0.8 mmol) of tris(diethylamino)phosphine is quickly injected in the above mixture and InP nanocrystals synthesis proceeded. The reaction occurs during 30 min. At the end of the reaction, the temperature is lowered. InP nanocrystals are then precipitated in ethanol and suspended in toluene. This synthesis provides InP nanocrystals with a diameter of 3.2 nm (first excitonic absorption peak at 560 nm).

S1.2. Reference 2 - 634 nm Emitting Core/Shell InP/Cd$_{0.025}$Zn$_{0.975}$Se QDs

A 3.2 nm InP QDs synthesis is performed at 180°C. Instead of cooling down the temperature, at 20 min, 0.45 mL of stoichiometric TOP-Se (2.24 M) is injected. At 140 min, a mixture of 0.035 g (0.13 mmol) of Cd(acetate)$_2$ dihydrate and 1.794 g (2.84 mmol) of Zn(stearate)$_2$, (Cd to Cd+Zn fraction = 0.032) mixed with 8 mL of ODE and 2 mL of OLA is injected. Then temperature is increased from 180°C to 320°C and 1.4 mL of TOP-Se is injected drop by drop during the rise of temperature. At 240 min the reaction is stopped and the temperature is cooled down. InP/Cd$_{0.025}$Zn$_{0.975}$Se QDs are then precipitated once in ethanol and suspended in toluene.

S1.3. Reference 3 - 644 nm Emitting Core/Shell InP/Cd$_{0.05}$Zn$_{0.95}$Se QDs

The synthesis of InP/Cd$_{0.05}$Zn$_{0.95}$Se QDs follows the same protocol as outlined above but 0.035 g (0.13 mmol) of Cd(acetate)$_2$ dihydrate and 1.794 g (2.84 mmol) of Zn(stearate)$_2$ are replaced by 0.069 g (0.26 mmol) of Cd(acetate)$_2$ dihydrate and 1.706 g (2.70 mmol) of Zn(stearate)$_2$, (Cd to Cd+Zn fraction = 0.064).

S1.4. Reference 4 - 664 nm Emitting Core/Shell InP/Cd$_{0.13}$Zn$_{0.87}$Se QDs

The synthesis of InP/Cd$_{0.13}$Zn$_{0.87}$Se QDs follows the same protocol as outlined above but 0.035 g (0.13 mmol) of Cd(acetate)$_2$ dihydrate and 1.794 g (2.84 mmol) of Zn(stearate)$_2$ are replaced by 0.15 g (0.56 mmol) of Cd(acetate)$_2$ dihydrate and 1.52 g (2.4 mmol) of Zn(stearate)$_2$, (Cd to Cd+Zn fraction = 0.138).
S2  InP/(Zn,Cd)Se synthesis – effect of initial addition of CdCl₂

Figure S1. (a) Absorbance spectra of aliquots using reference 1 protocol but the 150 mg (1.1 mmol) of ZnCl₂ are replaced by 22 mg (0.11 mmol) of CdCl₂ and 135 mg (0.99 mmol) of ZnCl₂. (b) Absorbance spectra of aliquots using reference 1 protocol. Admixing CdCl₂ during the initial InP core synthesis induces an undesired redshift and a broadening of the first exciton transition. All spectra have been normalized relative to the absorbance maximum $A_{1S}^{1S}$ of the band-edge feature.

Figure S2. Absorption spectra during shell growth using reference 2 protocol but 150 mg (1.1 mmol) of ZnCl₂ is replaced by 22 mg (0.11 mmol) of CdCl₂ and 135 mg (0.99 mmol) of ZnCl₂. Admixing CdCl₂ during the initial InP core synthesis induces an undesired redshift and a broadening of the first exciton transition.
S3 Statistics on InP/(Zn,Cd)Se QDs diameter

| QDs               | Mean Diameter (nm) | Standard Deviation (nm) | Minimum Diameter (nm) | Median Diameter (nm) | Maximum Diameter (nm) |
|-------------------|--------------------|-------------------------|------------------------|----------------------|-----------------------|
| InP/ZnSe          | 10.2               | 0.88                    | 8.22                   | 10.29                | 12.12                 |
| InP/Zn_{0.975}Cd_{0.025}Se | 13.5              | 1.13                    | 10.31                  | 13.89                | 15.19                 |
| InP/Zn_{0.95}Cd_{0.05}Se   | 13.2              | 1.43                    | 10.01                  | 13.38                | 16.43                 |
| InP/Zn_{0.87}Cd_{0.13}Se   | 13.3              | 1.22                    | 10.23                  | 13.45                | 15.44                 |

Table S1. Diameter statistics of InP/(Zn,Cd)Se QDs for $x_{Cd}=0, 0.025, 0.05, 0.13$ (referred to as InP/Zn$_{1-x}$Cd$_x$Se) as derived from the bright field TEM images.

S4 Shell composition as determined by EDX measurements of InP/(Zn,Cd)Se QDs

| Element   | Atom% QDs Reference 2 Protocol | Atom% QDs Reference 3 Protocol | Atom% QDs Reference 4 Protocol |
|-----------|-------------------------------|-------------------------------|-------------------------------|
| Zn K      | 48.3                          | 49.4                          | 42.1                          |
| Se L      | 50.5                          | 48.0                          | 51.4                          |
| Cd L      | 1.2                           | 2.6                           | 6.5                           |
| Cd/(Cd+Zn)| 0.025                         | 0.050                         | 0.13                          |

Table S2. Overview of the outcome of EDX analyses on InP/(Zn,Cd)Se QDs synthesized using the synthesis protocols outlined in S1, focusing on the Zn, Cd and Se content. One sees that the Cd/(Cd+Zn) atom ratio closely follows the molar ratio of the Cd and Zn precursors used during synthesis.
S5. XRD patterns of InP/(Zn,Cd)Se QDs

Figure S3. (a) XRD patterns of InP/Cd$_x$Zn$_{1-x}$Se QDs for $x=0$, 0.025, 0.05, 0.13. 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 zincblende (220) / wurtzite (110) diffraction peak.
Measuring the cation-cation distance, these coincide for zincblende and wurtzite CdSe and are only slightly shifted for zincblende and wurtzite ZnSe. (b) (black markers) experimental \(d_{(exp)}\) as derived from the zincblende (220) / wurtzite (110) diffraction peak; (red line) linear interpolation between the zinc blende (220) lattice spacing for ZnSe and CdSe; (blue line) linear interpolation between the wurtzite (110) lattice spacing for ZnSe and CdSe. Although the experimental lattice plane spacing does not fully coincide with either of these trendlines, its variation is comparable to what is predicted based on such linear interpolations.

**Calculation of \(d_{(exp)}\) values with XRD angles:**

\[
2d_{(exp)}\sin\theta_{(exp)} = n\lambda
\]

\[
d_{(exp)} = \frac{n\lambda}{2\sin\theta_{(exp)}}
\]

\(n = 1, \ \lambda = 0.15418\text{nm}\)

**Calculation of \(d_{(220)}\) values for zincblende crystal lattice:**

\[
d_{(220)} = \frac{a}{2\sqrt{2}}, \ a = [(1-x)a_{CdSe} + x a_{ZnSe}]
\]

\(n = 1, \ \lambda = 0.15418\text{nm}, \ a_{CdSe} = 0.608\text{nm}, \ a_{ZnSe} = 0.567\text{nm}\)

**Calculation of \(d_{(110)}\) values for wurtzite crystal lattice:**

\[
d_{(110)} = \frac{a}{2}, \ a = [(1-x)a_{CdSe} + x a_{ZnSe}]
\]

\(n = 1, \ \lambda = 0.15418\text{nm}, \ a_{CdSe} = 0.430\text{nm}, \ a_{ZnSe} = 0.398\text{nm}\)

**Experimental peak positions (2θ):**

- InP/ZnSe QDs: 27.19°, 45.20°, 53.52°.
- InP/Zn_{0.975}Cd_{0.025}Se QDs: 27.17°, 45.10°, 52.38°.
- InP/Zn_{0.95}Cd_{0.05}Se QDs: 27.06°, 44.89°, 53.11°.
- InP/Zn_{0.87}Cd_{0.13}Se QDs: 26.85°, 44.55°, 52.68°.

**Theoretical peak positions (2θ):**

- ZnSe bulk cubic (red lines): 27.22°, 45.2°, 53.56°.
- ZnSe bulk wurtzite (blue lines): 25.72°, 26.89°, 29.09°, 37.55°, 45.35°, 48.88°, 53.51°.
- CdSe bulk wurtzite (green lines): 23.89°, 25.39°, 27.10°, 35.14°, 42.00°, 45.81°, 49.72°.