Economic and Size-tunable Synthesis of InP/ZnE (E = S,Se) Colloidal Quantum dots.

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Supporting Information

S1 InP, InP/ZnS and InP/ZnSe QDs synthesis protocols

S1.1 Chemicals

Indium(III) chloride (99.999 %), indium(III) bromide (99.999 %), indium(III) iodide (99.998 %), zinc(II) chloride (≥ 98 %), zinc(II) bromide (≥ 98 %), zinc(II) iodide (≥ 98 %), tris(diethylamino)phosphine (97 %), selenium powder 100 mesh (99.99 %) and zinc stearate (technical grade, 65 %) were purchased from Sigma Aldrich. Trioctylphosphine (> 97 %) and sulfur powder were purchased from Strem Chemicals. Oleylamine (80-90 %) was purchased from Acros Organics. Octadecene (technical 90 %) was purchased from Alfa Aesar.

S1.2 Reference 1 – InP QDs with first exciton at 570 nm (estimated diameter: 3.2 nm)

100 mg (0.45 mmol) of indium(III) chloride, as indium raw materials and 300 mg (2.2 mmol) of zinc(II) chloride, as zinc raw materials are mixed in 5.0 mL (15 mmol) of technical oleylamine which is a coordinating solvent. 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 0.45 mL (1.6 mmol) of tris(diethylamino)phosphine (phosphorous:indium ratio = 3.6:1) are quickly injected in the above mixture. After the phosphorous precursor injection, the InP nanocrystals synthesis proceeded. The reaction occurs during 30 minutes. At the end of the reaction, the temperature is cooled down. InP nanocrystals are then precipitated in ethanol and suspended in chloroform. This synthesis provides InP nanocrystals with a diameter of 3.2 nm (first excitonic absorption peak at 570 nm).

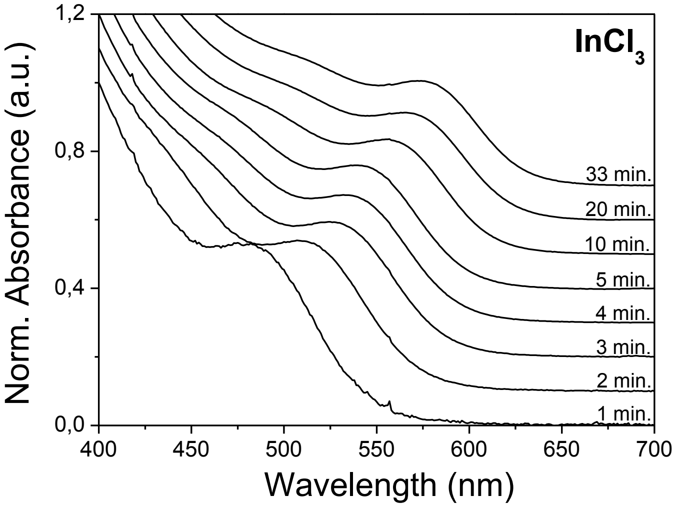

Figure S1a. Absorbance spectra of aliquots taken during the reference 1 synthesis

S1.3 Reference 2 – InP QDs with first exciton at 550 nm (estimated diameter: 3.0 nm)

Same protocol as for reference 1 but indium chloride is replaced by 160 mg (0.45 mmol) of indium(III) bromide

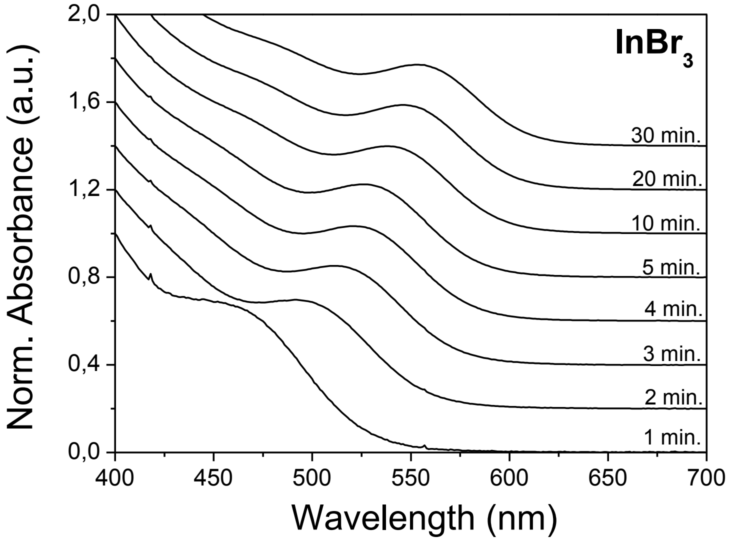

Figure S1b. Absorbance spectra of aliquots taken during the reference 2 synthesis

S1.4 Reference 3 – InP QDs with first exciton at 520 nm (estimated diameter: 2.8 nm)

Same protocol as for the reference 1 synthesis but the indium chloride is replaced by 224 mg (0.45 mmol) of indium(III) iodide.

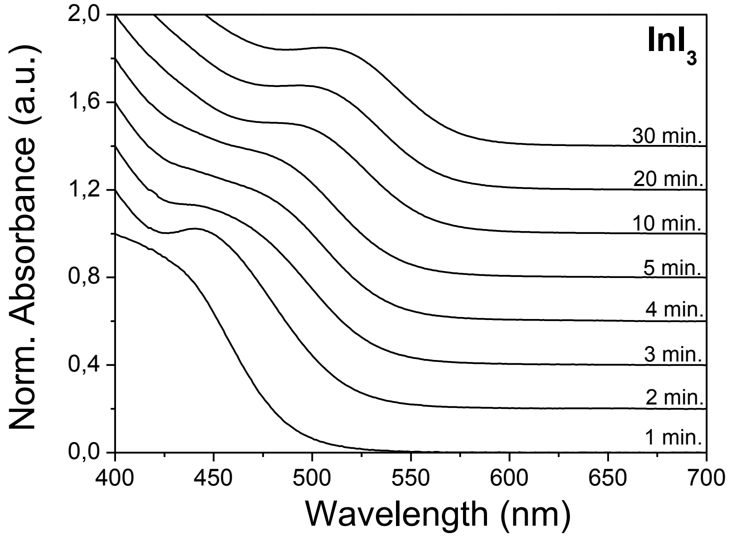

Figure S1c. Absorbance spectra of aliquots taken during the reference 3 synthesis

S1.5 Shell growth procedures

Saturated TOP-S – 0.72 g of sulfur powder is dissolved in 10 mL of TOP.
Saturated TOP-Se – 1.77 g of selenium powder is dissolved in 10 mL of TOP.

S1.5.1 InP/ZnS QDs

An InP QDs synthesis is performed at 180°C. Instead of cooling down the temperature, at 20 minutes: slow injection of 1 mL of saturated TOP-S (2.2 M). At 60 minutes: temperature is increased from 180 °C to 200 °C. At 120 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of octadecene (ODE). Temperature is increased from 200 °C to 220 °C. At 150 minutes: injection of 0.7 mL of saturated TOP-S (2.2 M). Temperature is increased from 220 °C to 240 °C. At 180 minutes: slow injection of 0.5 g of Zn(stearate)$_2$ in 2 mL of ODE. Temperature is increased from 240 °C to 260 °C. At 210 minutes: end of reaction. At the end of the reaction, the temperature is cooled down. InP/ZnS nanocrystals are then precipitated in ethanol and suspended in chloroform.

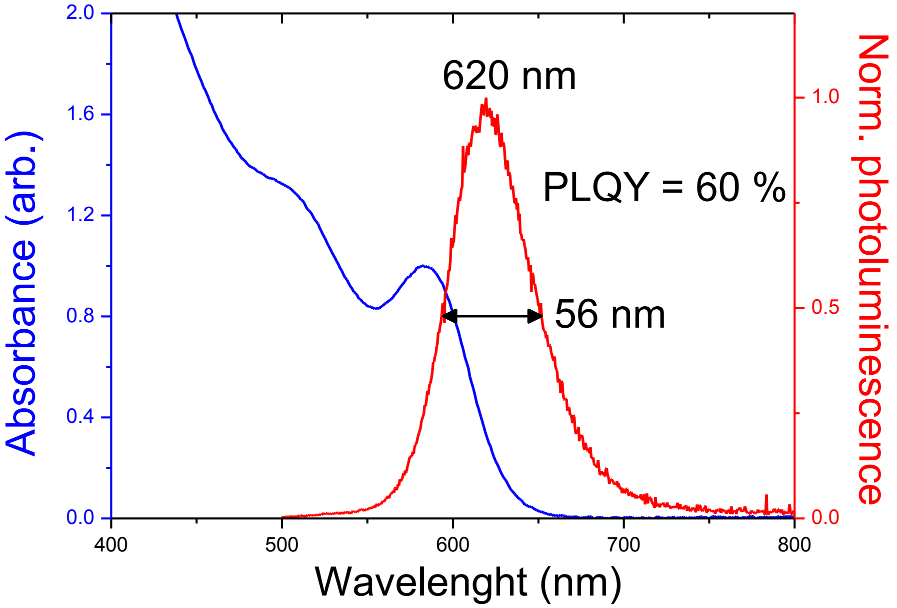

Figure S1d. Absorbance and emission spectra obtained at the end of the InP/ZnS synthesis

S1.5.2 InP/ZnSe

An InP QDs synthesis is performed at 180°C. Instead of cooling down the temperature, after 20 minutes: slow injection of 1 mL of saturated TOP-Se (2.2 M). At 60 minutes: temperature is increased from 180 °C to 200 °C. At 120 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of ODE. Temperature is increased from 200 °C to 220 °C. At 150 minutes: injection of 0.7 mL of saturated TOP-Se (2.2 M). Temperature is increased from 220 °C to 240 °C. At 180 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of ODE. Temperature is increased from 240 °C to 280 °C. At 210 minutes: slow injection of 0.7 mL of saturated TOP-Se (2.2 M). Temperature is increased from 280 °C to 320 °C. After 240 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of ODE. 300 minutes: end of reaction. At the end of the reaction, the temperature is cooled down. InP/ZnSe nanocrystals are then precipitated in ethanol and suspended in chloroform.

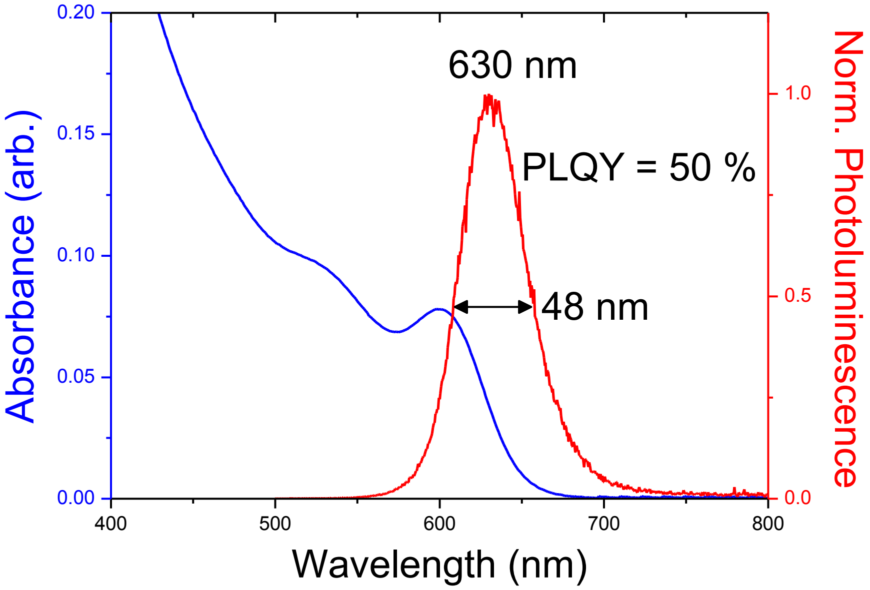

Figure S1e. Absorbance and emission spectra obtained at the end of the InP/ZnSe synthesis

S2 Influence of $ZnCl_2$ on the size-dispersion

S2.1 Experimental Data

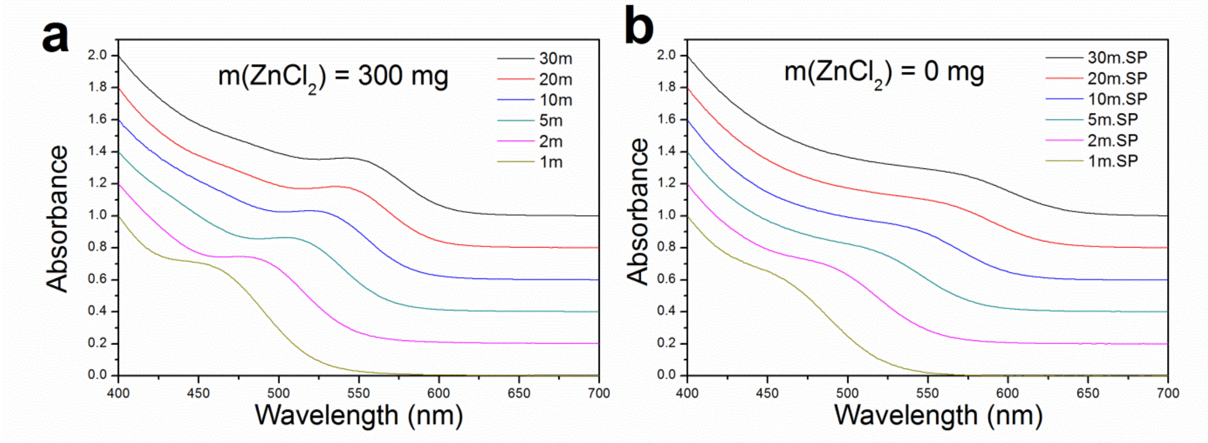

Figure S2a: Influence of the $ZnCl_2$ on the size-dispersion. a. Absorbance spectra of aliquots using ref.1 protocol with 300 mg of $ZnCl_2$. b. Absorbance spectra of aliquots using ref. 1 protocol with 0 mg of $ZnCl_2$.

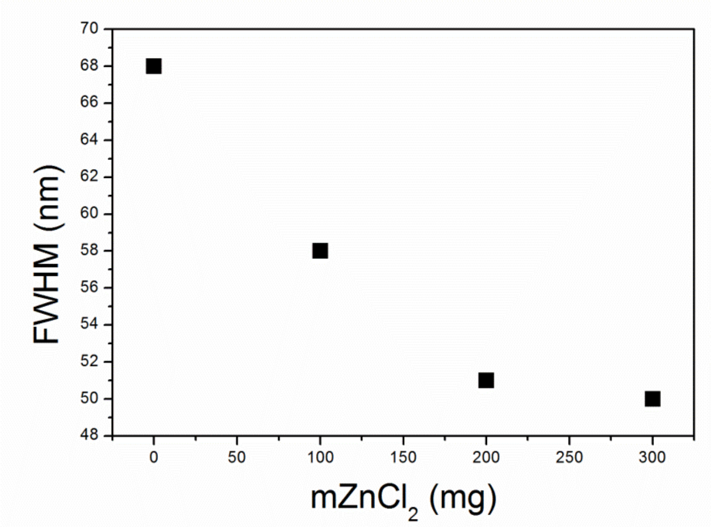

Figure S2b: Estimated full width at half maximum of the 1st absorption excitonic peak as a function of the added $ZnCl_2$ amount.

S2.2 Full Width at Half Maximum Estimation

Generally, the exciton linewidth is estimated by fitting the absorption spectrum to a sum of Gaussians and a background that accounts for the systematic increase of the absorbance at shorter wavelengths. However, as the first exciton transition in the InP spectra are not well pronounced, this method is not easy to implement and the final result may strongly depend on the particular functional form of the background correction. Hence, instead of fitting the absorbance spectrum to a sum of Gaussians and a background, we choose to plot the first derivative of the absorption spectrum. Then, the two extrema can be used to estimate the width of the first exciton transition by using the known relation between these extrema and the full width at half maximum (FWHM) of a Gaussian:

$$\mathrm{FWHM} = \sqrt{2\ln 2}\,(\lambda_{max} - \lambda_{min})$$

Here, λ_{max} and λ_{min} refer to the wavelength where the derivative of the absorption spectrum attains a maximum and a minimum, respectively. This method is not perfect as it will only be accurate if the absorption background depends linearly on wavelength, yet it is easier to implement than a Gaussian and it does not require one to assume a particular functional form for the background.

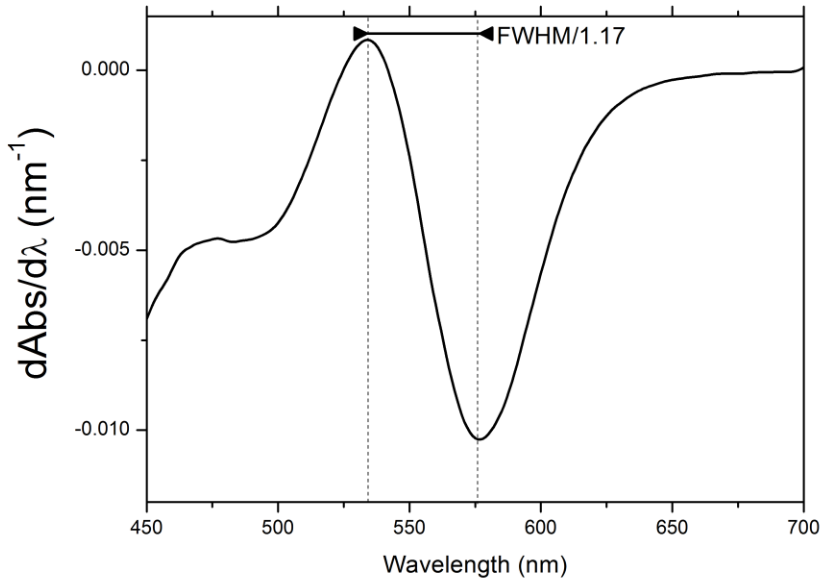

Figure S2c: First derivative of a InP QDs absorbance spectrum. Curve has been smoothed. The two stationary points allow to estimate the full width at half maximum of the absorbance exciton.

S3 Size histogram of InP QDs with a first absorbance excitonic peak at 570 nm.

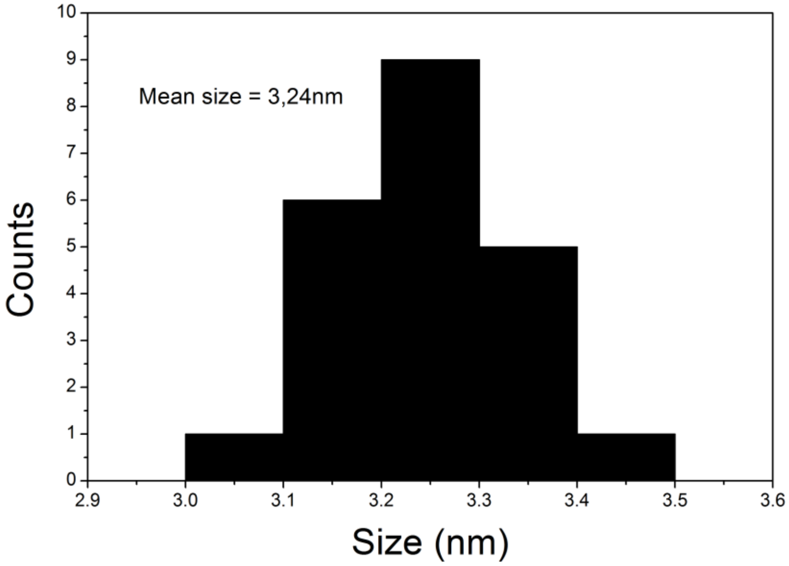

Figure S3: diagrams of size distribution of InP QDs with a first absorbance excitonic peak at 570 nm.

S4 XRD patterns of InP, InP/ZnS and InP/ZnSe QDs

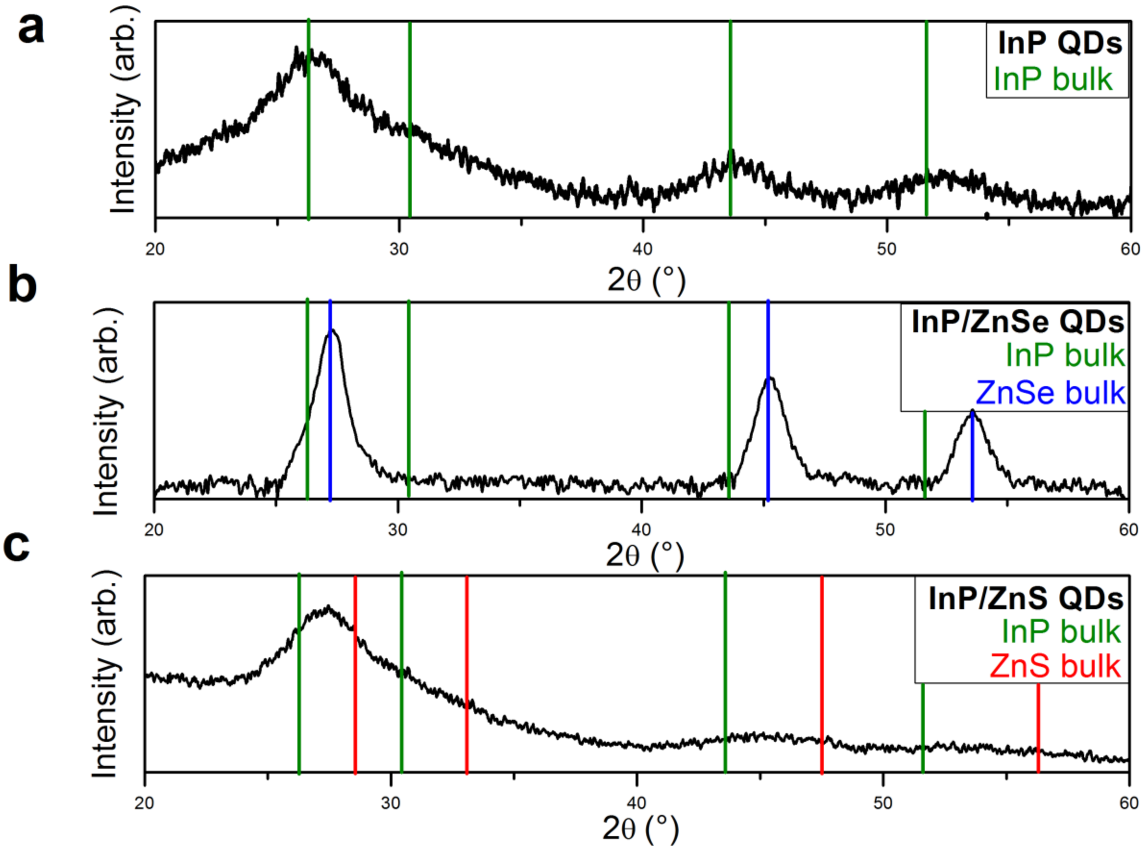

Figure S4: XRD diagrams of a. InP QDs, b InP/ZnSe QDs and c. InP/ZnS QDs.

Peaks position:

InP QDs: 26.3 °, 44.0 °, 52.3 °
InP/ZnSe QDs: 27.3 °, 45.3 °, 53.6 °
InP/ZnS QDs: 27.3 °, 45.9 °

InP zinc-blende bulk: 26.28 °, 30.44 °, 43.58 °, 51.61 °
ZnSe zinc-blende bulk : 27.22 °, 45.19 °, 53.57 °ZnS zinc-blende bulk: 28.56 °, 33.09 °, 47.51 °, 56.29 °

S5 InP, InP/ZnS and InP/ZnSe QDs absorbance spectra comparison

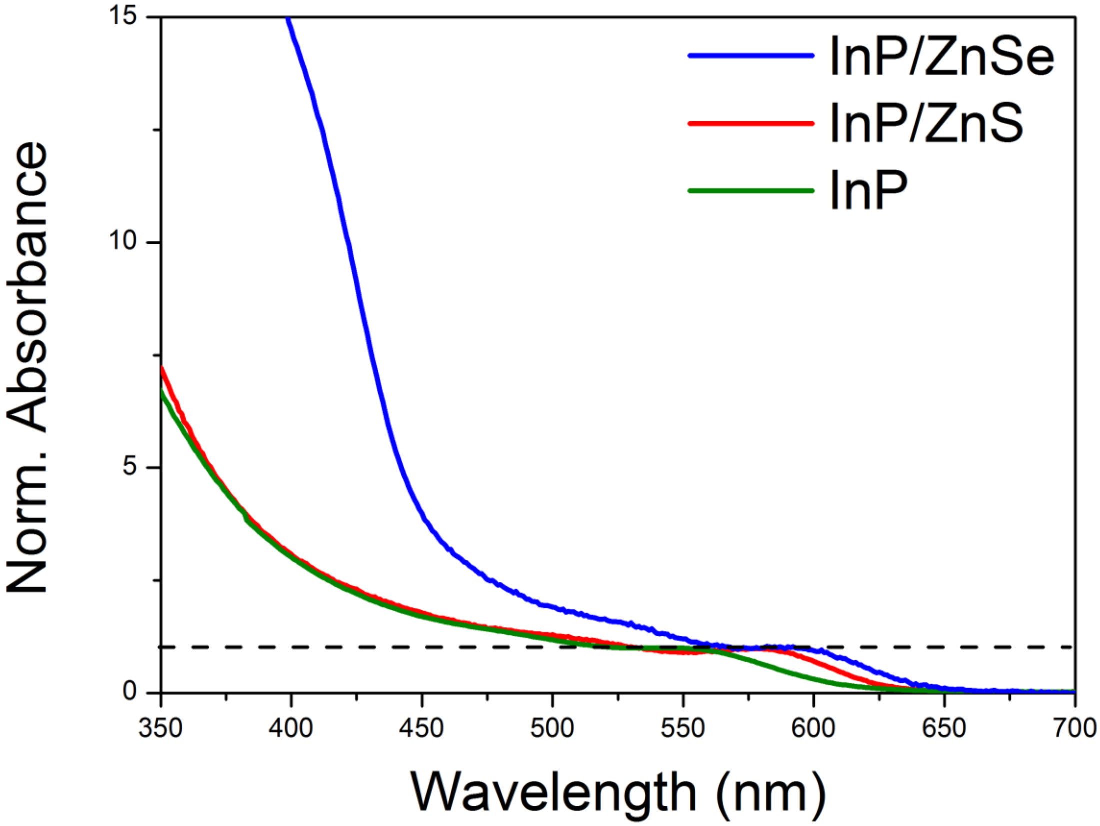

Figure S5: Absorbance spectra normalized at the first exciton of InP, InP/ZnS and InP/ZnSe QDs.

S6 Chemical yield evaluation method

The chemical yield is estimated by measuring the absorbance of a known dilution of the reaction mixture in the short wavelength range. The dilution is estimated by first measuring the mass of the aliquot withdrawn from the mixture. Then a known volume of toluene is added to the aliquot. The absorbance of the provided solution is then measured. It is well-known that the intrinsic absorption coefficient of colloidal nanocrystals are close to those of bulk materials in the short wavelength range.[1–4] Knowing the intrinsic absorption coefficient of bulk InP, we can then use these values to calculate the chemical yield of InP nanocrystals solution.

Example:

An aliquot with a measured mass $m_{aliquats} = 20$ mg is withdrawn from reaction the mixture (total mass of the reaction mixture: $m_{Total} = 4.5$ g). Then, 3.0 mL of toluene is added to the aliquot and it is loaded in an absorbance cuvette. An absorbance A of 0.45 is measured at $\lambda = 413$ nm for the aliquot in toluene solution. According to literature,[3] the intrinsic absorption coefficient is given by:

$$\mu_{i,th} = \frac{4\pi nk|f_{LF}|^2}{n_S\lambda}$$

Here, n and k are the real and imaginary part of the refractive index of bulk zinc-blende InP and n_S is the refractive index of toluene. The local field factor f_{LF} is given by:[3]

$$|f_{LF}|^2 = \frac{9n_S^4}{(n^2 - k^2 + 2n_S^2)^2 + 4(nk)^2}$$

We can have access to n, k and n_s from the literature,[5,6] which yields at $\lambda = 413$ nm: $n = 4.395$, $k = 1.247$, $n_s = 1.52$. Then $|f_{LF}|^2 = 0.078$ and $\mu_{i,th} = 8.5 \cdot 10^6\ \mathrm{m}^{-1}$.

We can then deduce the volume fraction f of InP in the aliquot with the measured absorbance A and the theoretical intrinsic absorption coefficient $\mu_{i,th}$:[3]

$$f = \frac{A.\ln(10)}{\mu_{i,th} \cdot L} = 1.2 \cdot 10^{-5}$$

Where L is the cuvette length (m). The amounts of InP units can then be deduced from f and the InP molar volume V_M.

$$n_{cuvette} = f \cdot \frac{V_{cuvette}(m^3)}{V_M\ (\frac{m^3}{mol})} = 1.2 \cdot 10^{-5} \cdot \frac{3.0 \cdot 10^{-6}}{3.0 \cdot 10^{-5}} = 1.2 \cdot 10^{-6}\ \mathrm{mol}$$

The total amount of InP units in the reaction mixture can be calculated with the ratio between the mass of the aliquot $m_{aliquats}$ and the mass m_{Total} of the reaction mixture.

$$n_{Total} = n_{cuvette} \cdot \frac{m_{Total}}{m_{aliquats}} = 1.2 \cdot 10^{-6} \cdot \frac{4.5}{20 \cdot 10^{-3}} = 0.27 \text{ mmol}$$

We have defined the chemical yield C.Y. as a percentage between InP units in the reaction mixture n_{Total} and the In quantity n_{In}that we have initially put in the reaction mixture.

$$C.Y. = \frac{n_{Total}}{n_{In}} \cdot 100 = \frac{0.27}{0.45} \cdot 100 = 60\ \%$$

For this particular example we have measured a chemical yield of 60 %. It means that 60 % of the initially used indium precursor has been effectively converted into InP nanocrystals at the moment of the reaction we have taken the aliquot.

S7 Cost estimation of InP syntheses

Unit: unit of the precursor.

Unit cost: cost in euro of a number of unit of the precursor (€). Based on suppliers prices.

Unit/g InP: unit of the precursor needed to make 1 g of InP QDs.

Cost/g InP: cost attributed to the precursor to make 1g of InP QDs.

$(TMS)_3P$-based synthesis[7]

Chemical Yield : 80 % assumed	unit cost	unit	units/g InP	cost/g InP
$(TMS)_3P$	232.5	G	1,8	502
Indium Acetate	5,15	G	2	12
Octadecene	42.8	L	0,1	5
Methanol	50	L	0,3	18
Total Cost				€537

$(DMA)_3P$-based synthesis (P:In = 1.5).[8]

Chemical Yield : 20% measured	unit cost	unit	units/g InP	cost/g InP
$P(DMA)_3$	7,55	G	8,6	65
Indium Chloride	12,36	G	7,6	94
Oleylamine	0.16	mL	191,5	31
Ethanol	0.023	mL	383,1	9
Total Cost				€199

$(DEA)_3P$-based synthesis (P:In = 1).

Chemical Yield : 20% measured	unit cost	unit	units/g InP	cost/g InP
P(DEA)3	6	G	8,5	51
Indium Chloride	12,36	G	7,6	94
Oleylamine	0,16	mL	382,6	61
Ethanol	0,023	mL	765,3	18
Total Cost				€ 224

(DEA)$_3$P-based synthesis (P:In = 3.6).

Chemical Yield : 80% measured	unit cost	unit	units/g InP	cost/g InP
P(DEA)$_3$	6	G	7.7	46
Indium Chloride	12,36	G	1,9	23
Oleylamine	0.16	mL	94.8	15
Ethanol	0.023	mL	189.5	4
Total Cost				€88

S8 X-Ray fluorescence analysis (instrument: Rigaku Nex CG)

Sample 1 – InP QDs made with $InCl_3$ (100 mg $InCl_3$, 5 mL OLA, 0.40 mL $(DEA)_3P$). InP QDs were washed 3 times with ethanol and re-suspended in toluene. InP QDs was drop-casted on paper filter to make XRF measurements.

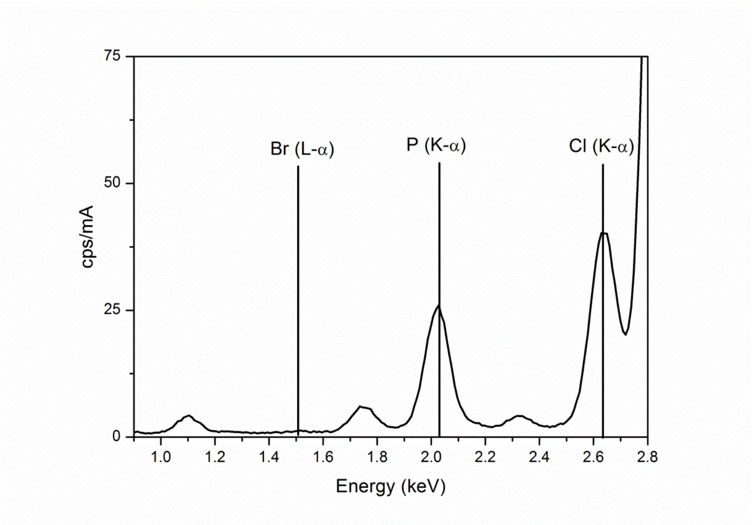

Figure S8a. XRF analysis of InP QDs made using $InCl_3$ as the indium precursor, with a zoom an the spectral region containing P, Cl and Br signals. Deduced atomic percentages: In (72 %), P (15 %), Cl (13 %), Br (0 %).

Sample 2 – InP QDs made with $InBr_3$ (160 mg $InBr_3$, 5 mL OLA, 0.40 mL $(DEA)_3P$). InP QDs were washed 3 times with ethanol and re-suspended in toluene. InP QDs was drop-casted on paper filter to make XRF measurements.

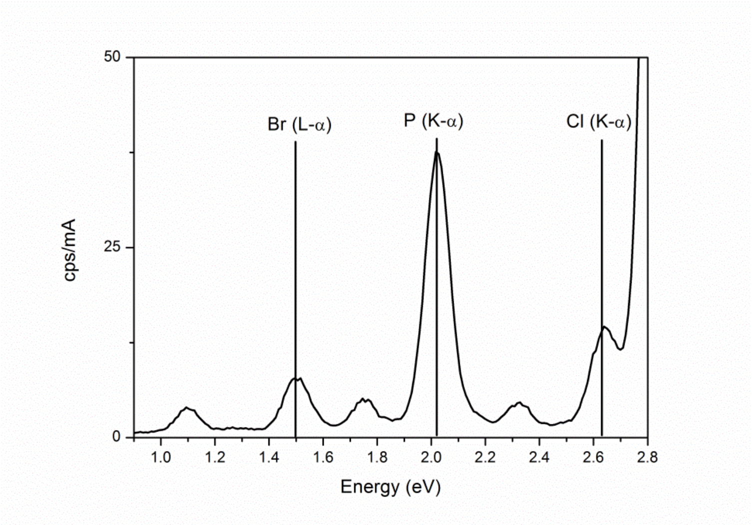

Figure S8b. XRF analysis of InP QDs made using $InBr_3$ as the indium precursor, with a zoom on the spectral region containing P, Cl and Br signals. Deduced atomic percentages: In (77 %), P (16 %), Cl (1 %), Br (6 %).

S9 Growth rate for surface-reaction controlled growth

A comprehensive expression for the nanocrystal growth rate comprising both the effects of solute supply by diffusion and the surface reaction was derived by Talapin et al.:[9]

$$j_G = \frac{dr}{dt} = DV_m[\mathrm{M}]_0 \left\{ \frac{S - \exp\left(\frac{2\gamma V_m}{rRT}\right)}{r + \frac{D}{k_g(r)}} \right\} \approx V_m k_g(r)[\mathrm{M}]_0 \left(S - \exp\left(\frac{2\gamma V_m}{rRT}\right)\right)$$

Here, r denotes the nanocrystal radius, D is diffusion coefficient of the solute, V_m the molar volume of the material formed, $[\mathrm{M}]_0$ the solute solubility, S the supersaturation, γ the surface tension of the material formed, R the gas constant, T the absolute temperature and $k_g(r)$ the rate constant for solute adsorption at a nanocrystal with radius r. The last expression holds for surface reaction controlled growth, *i.e.*, when $D/k_g(r)$»r. It thus follows that the growth rate will increase if the product $k_g(r)[\mathrm{M}]_0$ goes up.

S10 Emission linewidth evolution of InP/ZnE QDs during shell growth

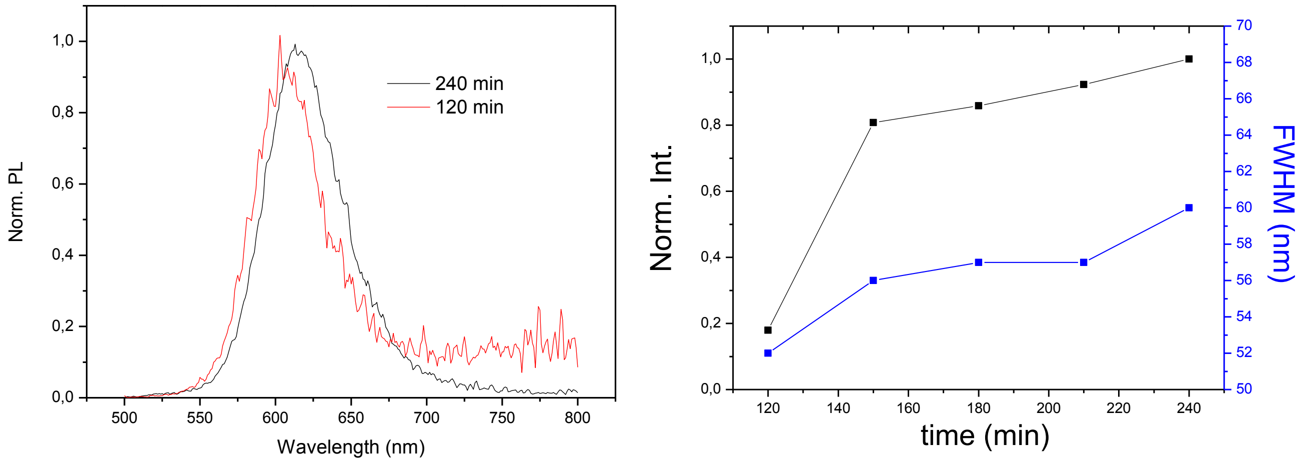

Figure S10a. Evolution of InP/ZnS QDs photoluminescence during the shell growth procedure. *Left:* PL spectra *Right:* Emission linewidth and intensity

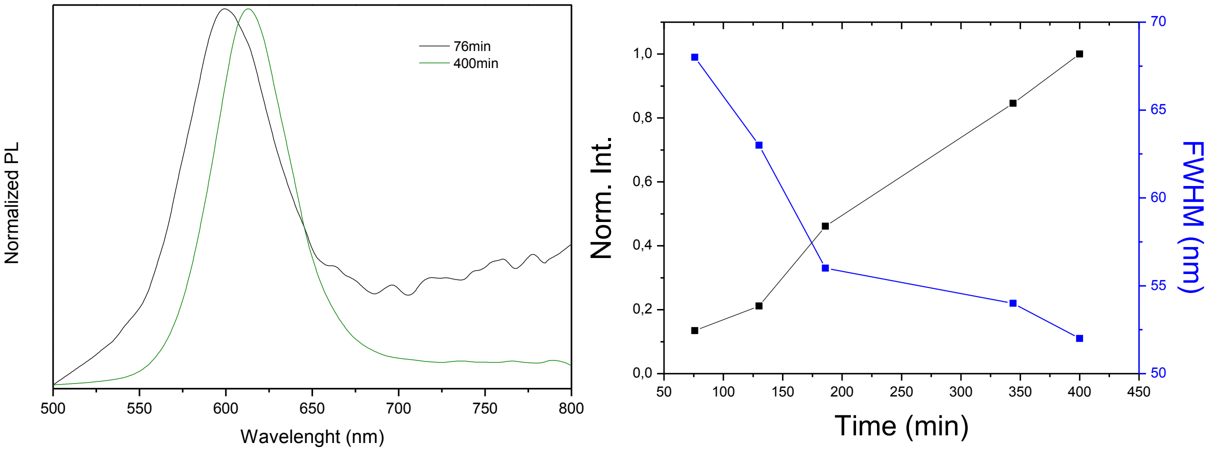

Figure S10b. Evolution of InP/ZnSe QDs photoluminescence during the shell growth procedure. *Left:* PL spectra *Right:* Emission linewidth and intensity

S11 Absorption and emission spectra of InP/ZnS QDs with high PLQY

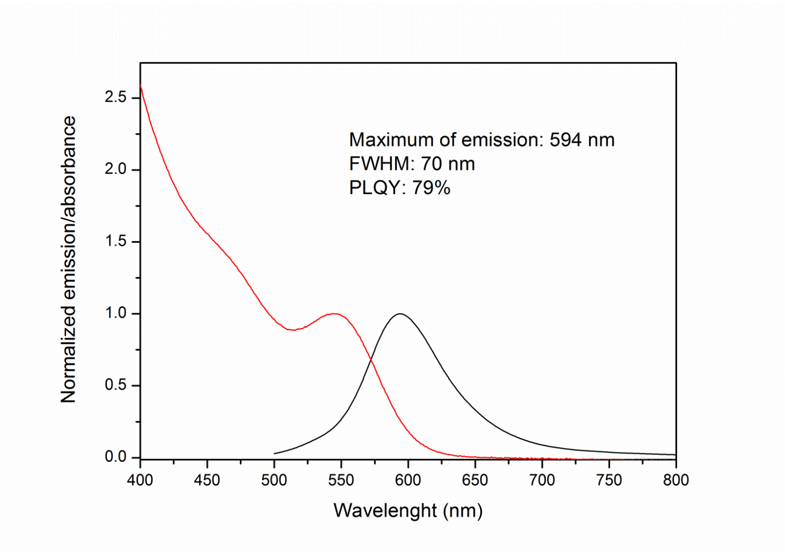

Figure S11. Absorption (red lines) and emission spectra (black line) of InP/ZnS QDs with high PLQY

Protocol

160 mg (0.45 mmol) of $InBr_3$ and 300 mg (2.2 mmol) of $ZnCl_2$ are mixed in 5.0 mL (15 mmol) of technical oleylamine. 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 0.45 mL (1.6 mmol) of $(DEA)_3P$ are quickly injected in the above mixture. 20 minutes after: slow injection of 1 mL of saturated TOP-S (2.2 M). At 70 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of octadecene (ODE). Temperature is increased from 180 °C to 220 °C. At 160 minutes: injection of 0.7 mL of saturated TOP-S (2.2 M). Temperature is increased from 220 °C to 240 °C. At 240 minutes: slow injection of 1 g of Zn(stearate)$_2$ in 4 mL of ODE. Temperature is increased from 240 °C to 260 °C. At 290 minutes: injection of 0.7 mL of saturated TOP-S (2.2 M). Temperature is increased from 260 °C to 280 °C. At 335 minutes: slow injection of 1g of Zn(stearate)$_2$ in 4 mL of octadecene (ODE). Temperature is increased from 280 °C to 300 °C. At 347 minutes: injection of 0.7 mL of saturated TOP-S (2.2 M). Temperature is increased from 300 °C to 320 °C. 360 minutes: end of reaction. At the end of the reaction, the temperature is cooled down. InP/ZnS nanocrystals are then precipitated in ethanol and suspended in chloroform.

S12 PLQY evolution with aging

Sample	FWHM @ max. of em. (nm)	PLQY after synthesis (%)	PLQY after aging (%)
InP/ZnSe	48 @ 630	50	20 after 3 months
InP/ZnS	55 @ 618	50	50 after 1 year
InP/ZnSe/ZnS	47 @ 624	50	40 after 3 months

Conditions: QDs dispersed in chloroform stored in the dark and at room temperature.

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