Supporting Information for

Characterization of Indium Phosphide Quantum Dot Growth Intermediates Using MALDI-TOF Mass Spectrometry

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Experimental Details

Indium acetate (99.99% metals basis) was purchased from Alfa Aesar. Trioctylphosphine (min, 90%), trioctylphosphine oxide (99%) and tris(trimethylsilyl)phosphine (10 wt% in hexane, >98%) were purchased from Strem Chemicals. Myristic acid (>99%), 1-octadecene (technical grade, 90%), toluene (anhydrous, 99.8%), hexane (anhydrous, 95%), *trans*-2-[3-(4-*tert*-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (≥98%), and ferrocene (98%) were purchased from Sigma Aldrich. Toluene-d₈ (D, 99.5%) was obtained from Cambridge Isotope Laboratories, Inc. Bio-Beads S-X1 GPC medium was purchased from Bio-Rad Laboratories, Inc. UV-Vis spectra were taken in Shimadzu UV-3101PC UV-VIS-NIR scanning spectrometer. Photoluminescence spectra were taken on a FluoroMax3 by HORIBA Jobin Yvon. All the synthetic or analytical procedures of InP QDs were performed under nitrogen or vacuum in a Schlenk line or glove box.

HT/HP reactors. Both the high temperature/high pressure microchemical system and the chip reactors are the same as previously reported¹. The HT/HP tube reactor was made out of supersmooth stainless steel tubes purchased from McMaster-Carr (type 304 stainless steel, OD=1/16", ID=0.02"). The reactor volume is approximately 355 uL. The tubes were wrapped around an aluminum rod (OD=2") with a heating cartridge inserted into the center of the rod. All connections, tubes, and devices were made out of type-316 stainless steel, and heating cartridges were made of multipurpose aluminum. Two syringe pumps (Harvard apparatus, PhD Ultra) were used for solution injections.

Synthesis of In(My)₃. In a typical synthesis, 10.3 mmol In(Ac)₃ (3 g) and 31.1 mmol pre-dried MA (7.10 g) were mixed in 40 mL pre-dried 1-octadecene in a glove box. The mixture was transferred to a Schlenk line and heated up to 110 °C to form a clear solution under vacuum (90 mtorr) for three hours. The reactant solution was maintained under argon and then cooled down to room temperature. Protected under argon, the slurry was transferred into the glove box and washed with anhydrous hexane 6 times. The white solids were vacuum dried overnight, stored in the glove box and characterized by FT-IR spectra as previously described¹.

HT/HP synthesis of InP QDs. Caution: Air free handling of P(SiMe₃)₃ solution is required since P(SiMe₃)₃ is pyrophoric. Similar to previous studies¹, the synthesis of InP QDs was performed at 900 psi with the temperatures ranging from 105 – 300 °C under inert conditions. Anhydrous toluene was chosen as the solvent. In general, indium precursor stock solution was prepared by adding 1.5938 g In(My)₃ and 2 mL TOP into 48 mL toluene (40 mM In, 4 vol% TOP). Phosphorus precursor solution was prepared by adding 3.75 mL 10 wt% P(SiMe₃)₃ in hexane into 46.25 mL toluene (20 mM P). Two syringe pumps were used to pump indium and phosphorus precursors with identical flow rates. Therefore, the In/P ratio was set as 2 for all conditions. The two-stage syntheses were performed using previously reported chip reactor systems¹. The temperature of the first stage was set at 130 °C and the temperature of the second stage was varied accordingly. The flow rates of both indium and phosphorus precursors were set as 30 uL/min.

Calculation of residence time in HT/HP reactors: Calculation of residence time in the HT/HP reactors should include the effect of solvent expansion at high temperatures. According

to the NIST website², the densities of toluene at 22 °C, 240 °C and 270 °C at 900 psi are 0.8697 g/mL, 0.6415 g/mL and 0.5958 g/mL. Since the fluids are pumped at 22 °C, the residence time can be calculated using the following formula:

$$\tau = \frac{V_{\text{reactor}} / F_{\text{total}}}{\rho_{22^{\circ}C} / \rho_T}$$

Where V_{reactor} is the heated reactor volume (e.g., μ L), F_{total} is the total flow rate (e.g., μ L/min), $\rho_{22^{\circ}C}$ is the density of toluene at 22 °C and ρ_T is the density of toluene at T °C.

Table S1. Example residence time calculations

Reactor type	Conditions	Residence time / min
	30 uL/min, 270 °C	8.1
	40 uL/min, 270 °C	6.1
	60 uL/min, 270 °C	4.1
	20 uL/min, 240 °C	13.1
355 uL tube reactor	30 uL/min, 240 °C	8.7
	40 uL/min, 240 °C	6.5
	60 uL/min, 240 °C	4.4
	120 uL/min, 240 °C	2.2
	180 uL/min, 240 °C	1.5

HT/HP synthesis of cluster-free InP QDs. The synthesis of cluster-free InP QDs was performed in the 355 μ L tube reactor system at 270 °C and 8.1 min. The concentration of indium and phosphorus precursor is set as 40 mM and 20 mM in toluene respectively. Their flow rates are set as the same (15 μ L/min). 1-4 vol% TOP or equivalent molar amount of TOPO were added into the In(My)₃ solution to tune the absorption spectra. All precursor-handling processes were carried out in a glove box. Here are the details of the experimental conditions we have used:

Table S2. Experimental details to synthesize cluster-free InP QDs

First absorption peak (nm)	Surfactant Addition		
520.5	4 equiv. % TOPO		
531.0	2 equiv. % TOPO		
546.5	1 vol% TOP + 1 equiv. % TOPO		
570.5	4 vol% TOP		
579.5	2 vol% TOP		

Batch synthesis of InP QDs. Caution: Air free handling of $P(SiMe_3)_3$ solution is required since $P(SiMe_3)_3$ is pyrophoric. The batch synthesis procedure was adapted from literature³. 358.5 mg In(My)₃ (0.45 mmoles) was added to 9 mL 1-ODE in a 3-neck flask. The reaction mixture was heated at 110 °C under vacuum for 45 min. The atmosphere was switched to N_2 and the temperature was raised to 150 °C. 94 mg $P(SiMe_3)_3$ (0.375 mmoles) dissolved in 2.25 mL TOP were swiftly injected into the flask and the temperature was raised to 230°C. 1 mL aliquots were

taken at 1 min (150 °C) and 14 min (230°C). These samples were transferred into a glove box and purified using GPC before MALDI characterization. As this batch synthesis utilized 1-ODE as the solvent, which permanently damages the GPC column, a freshly packed GPC column was used for both samples.

Purification of InP QDs by GPC. The preparative GPC column was packed inside a glove box following a previous reported procedure⁴. 4 g of Bio-beads were first swollen in anhydrous toluene overnight. All of the swollen beads were then transferred to a glass column with a filter and glass fret disk. After the gel settled down and formed a column with approximately 28 mL volume, a small layer of sand was carefully placed at the top of the column and anhydrous toluene was used to rinse the column. The as-synthesized InP QDs in toluene from the HT/HP reactor system were first concentrated in a Schlenk line and then transferred into the glove box. A portion of the InP QD sample (less than 1 mL) was then injected into the column with anhydrous toluene as the eluent, and all the purified samples were collected when the elution volume was close to 1/3 of the total volume of the column. The column was carefully rinsed before the next injection. The purified samples were used for further MALDI MS, NMR and STEM characterization.

MALDI Characterization. MALDI-TOF mass data were collected on a Bruker Microflex MALDI-TOF mass spectrometer in the Biopolymers and Proteomics Laboratory in Koch Institute at MIT. DCTB was used as a matrix and the concentration of the stock solution is 78 mM in toluene (i.e., 10 mg in 0.5 mL toluene). Purified InP growth mixtures were diluted so that their absorbance at 310 nm was about 0.05-0.25 AU. The matrix solution and InP solution was mixed in a 1:1 volume ratio to maximize the mass signal detection. The sample-matrix mixture was then spotted onto a MALDI plate in a glove box. The plate was sealed in a home-made box under N₂ and then loaded into the mass spectrometer for characterization. Desorption and ionization of InP growth mixtures were achieved by absorbing pulsed nitrogen laser. For low mass characterization, tripsinogen was used as the external standard (11999 and 23981 Da) to calibrate the spectrometer and the laser intensity was set between 20-30% for sample characterization. The detector gain (linear detector, positive mode) was set as 7.2x. Stability test of clusters upon lasing at different powers is shown in Figure S5. For high mass characterization, albumin (bovine serum, BSA) was used as the external standard (33216 and 66431 Da) for the calibration and the laser intensity was set between 30-40% for sample characterization. Stability test of QDs upon lasing at different powers is shown in Figure S5. The detector gain (linear detector, positive mode) was set as 20.0x. No background subtraction was performed on the spectra. The mass spectra were smoothed with simple average of 10 data points.

NMR analysis of QDs. The quantitative ¹H NMR spectra was recorded on Bruker Avance-400 NMR spectrometer with ferrocene as the internal standard and 30 s relaxation delay. ³¹P NMR spectra were recorded on Varian Inova-500 NMR spectrometer. All of measurements on the airsensitive InP QDs were performed in a J-Young NMR tube.

Mass Weighing. 1 mL concentrated purified InP QD solution with a known absorption spectra was carefully pumped dry under vacuum. The mass of the dried QD sample was recorded on an electrobalance (MC 215, Sartorius). The mass of each sample was close to 15 mg and the mass values were measured multiple times to ensure accuracy.

STEM Characterization of InP QDs. The scanning transmission electron microscope (STEM) samples were prepared by drop casting the solutions containing the purified InP QDs onto a carbon coated 200-mesh holey TEM copper grid. The copper grid was dried and kept in a dry pumped vacuum specimen box. Afterwards the grid was loaded into a double-tilt sample holder. Aberration corrected scanning transmission electron microscopy (Cs-corrected STEM) images were acquired at LMA-INA-UNIZAR using a high angle annular dark field detector in a FEI XFEG TITAN electron microscope operated at 300 kV equipped with a CETCOR Cs-probe corrector from CEOS Company allowing formation of an electron probe of 0.08 nm.

XPS Characterization of InP QDs. To mimic the conditions used for MALDI characterization, after GPC purification, we drop casted concentrated InP QD samples onto a gold electrode, and used vacuum to remove the solvent. The gold electrode was then stored in a home-made box, sealed under nitrogen and brought to the XPS measurement. XPS measurements were performed on PHI Versaprobe II XPS.

Quantification of extinction coefficients, inorganic core mass and the number of InP units per particle in the core

(1) The extinction coefficient at 310 nm (ε) is calculated according to the following formula:

$$\varepsilon = \frac{\lambda}{(m_1 - m_2) / m_{\rm M} / V}$$

Where λ is the measured absolute absorbance at 310 nm of the QD solution, m_1 is the total dried mass of the above QD solution together with the measurement bottle, m_2 is the mass of the bottle, m_M is the average mass of the QDs measured through MALDI-TOF MS, V is the volume of the QD solution. To calculate the propagation error of the extinction coefficient calculation, the following formula is used:

$$\Delta \varepsilon = \sqrt{\left(\frac{\partial \varepsilon}{\partial \lambda}\right)^2 \Delta \lambda^2 + \left(\frac{\partial \varepsilon}{\partial m_1}\right)^2 \Delta m_1^2 + \left(\frac{\partial \varepsilon}{\partial m_2}\right)^2 \Delta m_2^2 + \left(\frac{\partial \varepsilon}{\partial m_M}\right)^2 \Delta m_M^2}$$

 $\Delta\lambda$, Δm_1 and Δm_2 are the standard deviation calculated from multiple measurements. For the MALDI mass, $\Delta m_{\rm M}$ is determined through

$$\Delta m_{\rm M} = \sqrt{(m_{\rm M,L} - \overline{m_{\rm M}})^2 + (m_{\rm M,H} - \overline{m_{\rm M}})^2}$$

Where $m_{\rm M,L}$ is the average mass obtained for the QD ensemble at the lowest laser power possible and $m_{\rm M,H}$ is the average mass obtained for the QD ensemble at the lowest laser power plus 5% more laser power.

(2) After the GPC purification, since we only observed bound myristate signal from ^{1}H NMR spectra and no signal from the ^{31}P NMR spectra, the structure of the InP QDs can be written as $In_{x}P_{y}(My)_{z}$. The $In_{x}P_{y}$ part was considered as the inorganic core, which should be observed in the STEM-HAADF images. Myristate is considered as the only ligand on the QD surface, which is also attributed as the only proton source on the nanoparticle.

The ligand population on the particle was calculated based on ¹H NMR (with ferrocene as the internal standard) and the extinction coefficient described above. The total concentration of ligands was determined by the ¹H NMR peak integrals; the QD concentration is measured by UV-Vis absorption spectra and the calculated extinction coefficient. By dividing these two numbers, the ligand/QD ratio in each sample can be obtained.

The volume of the inorganic core ($V_{\rm inorganic}$) is determined through the following formula:

$$V_{ ext{inorganic}} = \frac{m_{ ext{M}} - N_{ ext{L}} imes M_{ ext{[MA]}}}{
ho_{ ext{InP}}}$$

Where $N_{\rm L}$ is the ligand population on the nanoparticle, $\rho_{\rm InP}$ is the density of InP bulk crystals and $M_{\rm [MA]}$ is the molecular weight of myristate. Different estimated projected areas corresponding to this inorganic core volume can be obtained depending the shape of the nanoparticle.

If assuming spherical shape,
$$S_{\text{spherical}} = \pi r^2 = \pi (\frac{3}{4\pi} V_{\text{inorganic}})^{2/3}$$

If assuming tetrahedron shape,
$$S_{\text{tetrahedron}} = \frac{\sqrt{3}}{4}a^2 = \frac{\sqrt{3}}{4}(6\sqrt{2}V_{\text{inorganic}})^{2/3}$$

In this work, these two projected areas are used to compare against that obtained from STEM analysis.

(3) The number of InP units (N_{IInPl}) in a particle is determined through the following formula:

$$N_{\rm [InP]} = \frac{m_{\rm M} - N_{\rm L} \times M_{\rm [MA]} - N_{\rm L} / 3 \times M_{\rm [In]}}{M_{\rm [InP]}}$$

Where $M_{\rm [In]}$ is the molecular weight of an indium atom. To balance the charge of all the myristate ligand, the QDs should have an indium rich surface. By subtracting out those extra indium atoms, a neutral inorganic core made out of InP units could be obtained. Regarding the error propagation, using a similar method as described above, $\Delta N_{\rm [InP]}$ can be quantified using $\Delta m_{\rm M}$ and $\Delta N_{\rm L}$. A 5% error is estimated for the ligand population quantification process, giving $\Delta N_{\rm L} = 0.05 N_{\rm L} \sqrt{2}$.

(4) The extinction coefficients per InP unit (ε) for a particle is determined through the following formula:

$$\varepsilon' = \frac{\varepsilon}{N_{\text{InP}}}$$

Regarding the error propagation, using a similar method as described above, $\Delta \varepsilon$ can be quantified using $\Delta \lambda$, Δm_1 , Δm_2 , $\Delta m_{\rm M}$ and $\Delta N_{\rm L}$.

Table S3. Ligand population, inorganic core mass and projected areas assuming different shapes of InP QDs with different first absorption peaks

First absorption peak (nm)	Particle mass (kDa)	Ligand population	Inorganic core mass (kDa)	Projected area (spherical shape,nm ²)	Projected area (tetrahedron shape,nm ²)	In/P ratio	Extinction coefficients at 350 nm (M ⁻¹ cm ⁻¹)
520.5	46.5	111	21.3	4.6	6.8	1.32	2.2×10 ⁵
531.0	55.0	130	25.5	5.2	7.7	1.31	3.1×10^{5}
546.5	70.5	157	34.8	6.3	9.4	1.27	3.8×10^{5}
570.5	89.0	185	47.0	7.7	11.5	1.22	5.8×10^{5}
579.5	99.0	201	53.3	8.4	12.6	1.21	8.7×10^5

To compare the QD optical property with the bulk InP property, we first calculated the average extinction coefficient per InP unit at 310 nm from our five QD samples, which is 5135 M⁻¹cm⁻¹. As a result, the absorption cross section can be calculated according to ref. 21, using

$$C_{abs,QD} = \frac{2303\varepsilon_{310}}{N_A}$$

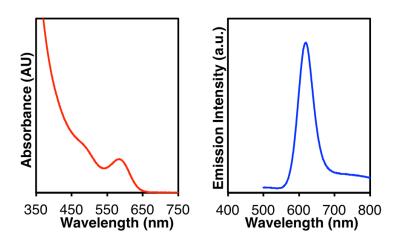
We obtained the absorption cross section ($C_{abs,QD}$) as 1.96×10^{-17} cm².

According to Aspnes and Studna's work⁵, the absorption coefficient of the bulk InP at 310nm is 7.0×10^5 cm⁻¹. We obtained the absorption cross section of bulk InP material using the following formula:

$$C_{abs,bulk} = \frac{\alpha_{310}}{N}$$

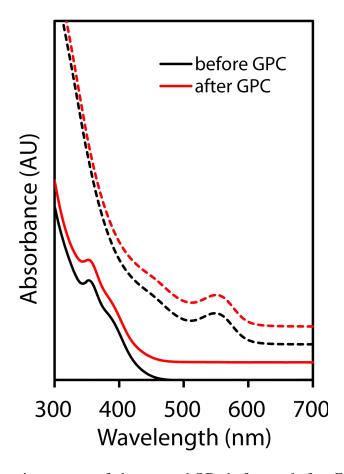
Where the atomic number density is $N = 3.96 \times 10^{22} \text{cm}^3$. Therefore, the absorption cross section of bulk InP material ($C_{abs,bulk}$) is equal to $1.77 \times 10^{-17} \text{cm}^2$. As a result, our InP QD optical property at 310 nm and bulk InP property are very similar (10% absorption cross section difference).

Figure S1.



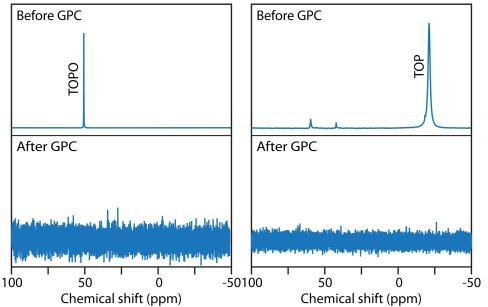
Exemplary absorption and PL measurement of InP QDs. The corresponding QDs emit at 619 nm and the emission line width (FWHM) is 52 nm. Generally, the InP QDs synthesized in this work exhibit low quantum yields (fractions of a percent) and show a significant amount of red-shifted trap emission which is in good agreement with other literature on InP core-only QDs.

Figure S2.

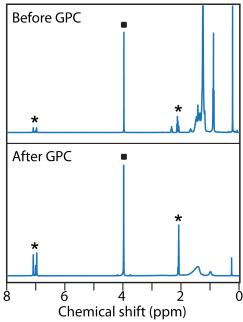


Example UV-Vis absorption spectra of clusters and QDs before and after GPC purification.

Figure S3.

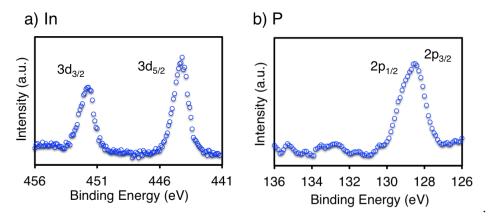


(a) ³¹P NMR spectra showing the completely removal of TOPO (left) and TOP (right) in two example samples of InP QDs using GPC.



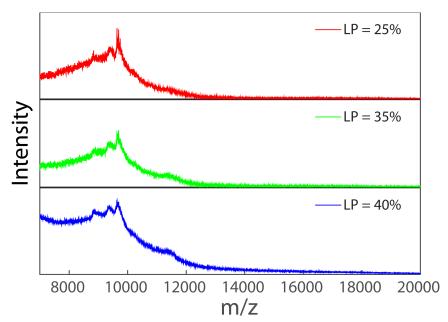
(b) ¹H NMR spectra of InP QDs before and after GPC purification. The asterisks marked in the spectra indicate peaks associated with the toluene solvent. The square indicates the signal from the internal standard ferrocene. After GPC, the proton-to-particle ratio decreased by 94%.

Figure S4.

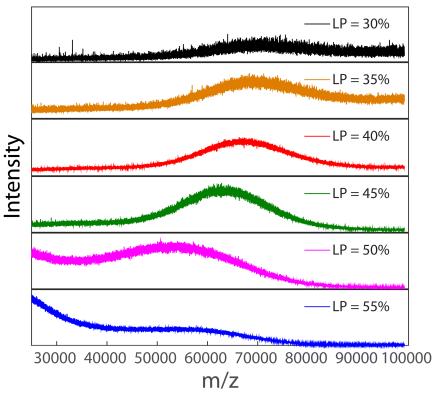


We used XPS to study the oxidation level of InP QDs prepared by the one-solvent protocol. The InP QD sample was synthesized using TOP as coordination ligands and purified by GPC. XPS has been widely used to characterize the oxidation of phosphorus in InP QDs.⁶⁻⁸ As shown in Figure S4-b, we observed negligible oxidized phosphorus signals, and this result is comparable to the oxygen-free InP QDs reported.^{7,8}

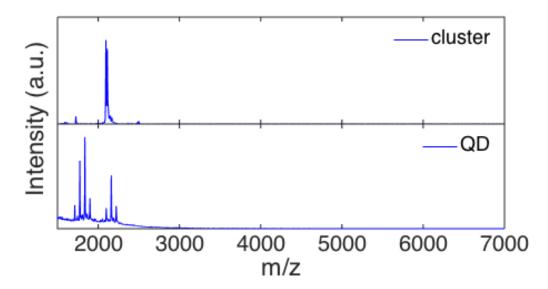
Figure S5.



(a) Clusters stability upon MALDI lasing at different lasing powers (LP) set in the MALDI instrument.

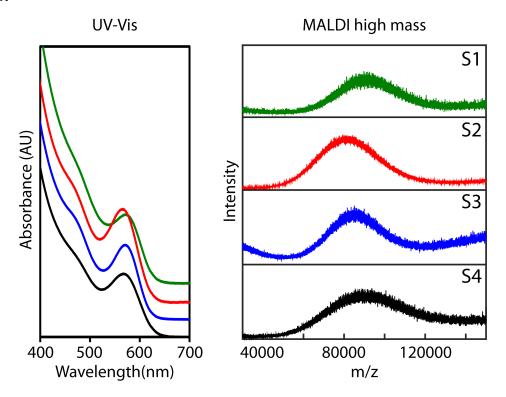


(b) QDs stability upon MALDI lasing at different lasing powers set in the MALDI instrument. Size distribution of QD samples remain unchanged for lasing powers below 40%.



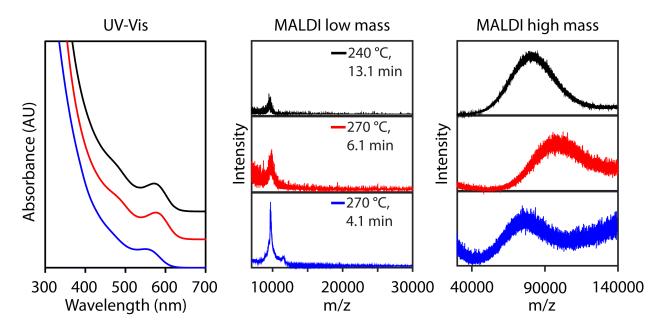
(c) MALDI low mass (1.5 - 7 kDa) characterization of cluster mixtures and QDs. For the cluster mixture sample, the observed peaks are attributed as indium precursors¹ that are desorbed from the cluster surface due to the thermal heating in the characterization. For the QDs ("cluster-free"), different from the signal of the cluster mixture sample, there is a clear pattern among the peaks and the mass difference between each peak is around 62 Da, which should be two P atoms. Therefore, these signals are attributed to the fragmentation of QDs. As we shown in a), QDs can be fragmented depending on the intensity of laser powers. We have considered the inaccuracy caused by the fragmentation in the calculation of the extinction coefficients.

Figure S6.

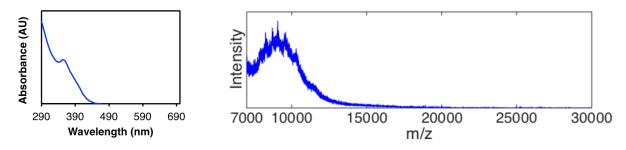


Comparison of UV-Vis and MALDI resolution in characterizing the size and size distribution of four different QD samples.

Figure S7.

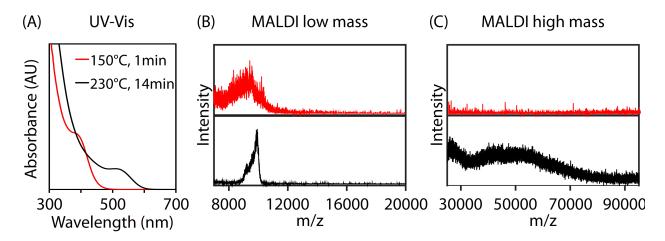


(a) Additional MALDI low and high mass spectra of InP growth intermediates synthesized at 240 and 270 °C in reference to Figure 2 in the main text. The clusters were not fully consumed at the above conditions.



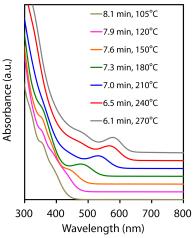
(b) UV-Vis absorption measurement (left) and MALDI low mass characterization (right) of InP clusters synthesized at 130 °C in the first stage of the two-stage chip reactor system in reference to Figure 3 in the main text.

Figure S8.

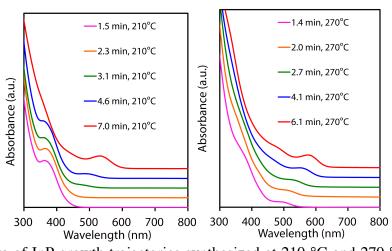


UV-Vis and MALDI characterization of InP growth intermediates prepared in batch synthesis. Consistent with the syntheses in tube reactor and chip reactors, we also observed clusters around 10 kDa in this batch synthesis.

Figure S9.

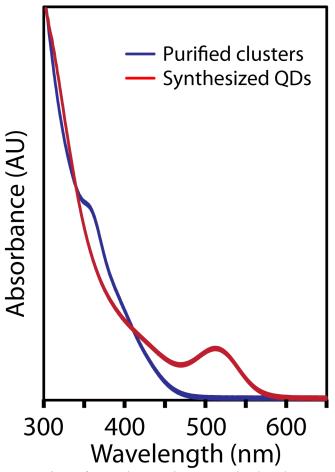


(a) UV-Vis spectra of InP growth trajectories synthesized at different temperatures in the HT/HP tube reactor. The total flow rate is set as 40 uL/min. The growth time is calculated based on the effect of solvent expansion. The absorption features of clusters are visible in temperatures below and at 180 °C. While clusters are still present at 240 and 270 °C characterized by MALDI as shown in Figure 2 and S7, their absorption signals are overshadowed by that of larger InP nanocrystals.



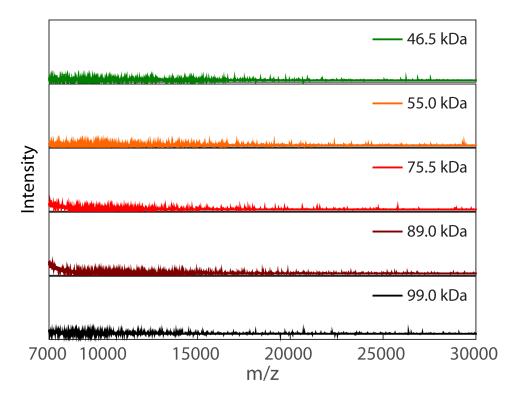
(b) UV-Vis spectra of InP growth trajectories synthesized at 210 °C and 270 °C under different growth times in the HT/HP tube reactor. The growth time is adjusted by changing the flow rate of the precursors. For growth at 270 °C, the absorption features of clusters are visible in flow rates above and at 90 uL/min. Clusters are still present at the 40uL/min condition characterized by MALDI as shown in Figure S7, while their absorption signals are overshadowed by that of larger InP nanocrystals. Similar growth trends are observed for conditions at 210 °C.

Figure S10.



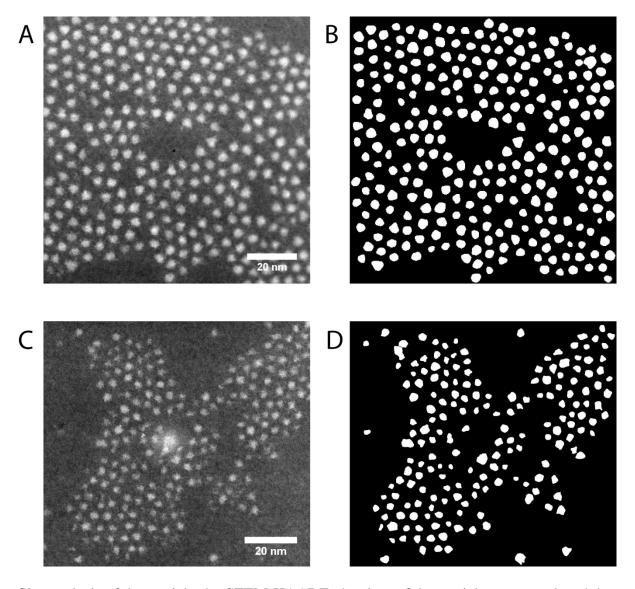
UV-Vis spectra of the conversion of InP clusters into QDs in the absence of any precursors. The clusters were prepared using indium myristate and P(SiMe₃)₃ as the precursors at 110 °C utilizing toluene as the solvent in a tube reactor (residence time: 5.4 min) and purified by GPC in the glovebox. The InP QDs were synthesized at 270 °C with the purified clusters as the only source for growth (residence time: 6.1 min).

Figure S11.



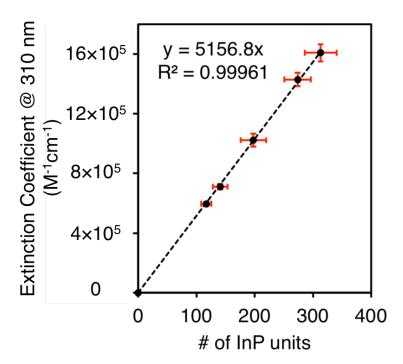
MALDI low mass characterization of cluster-free InP QDs synthesized in reference to Figure 4 in the main text. The high mass of the corresponding QDs is indicated in the legend.

Figure S12.

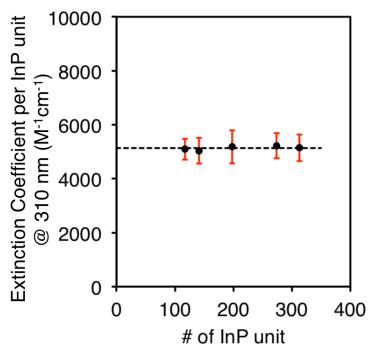


Size analysis of the particles by STEM-HAADF: the sizes of the particles were analyzed through imageJ. B and D display the binary count mask of the A and C. The average projected area of the InP QDs in A is 10.4 nm² based on the analysis of 262 different particles. And the average projected area of InP QDs in C is 5.9 nm² based on the analysis of 379 different particles (for the InP sample shown in C, another image with the same magnification is also analyzed, but not displayed).

Figure S13.

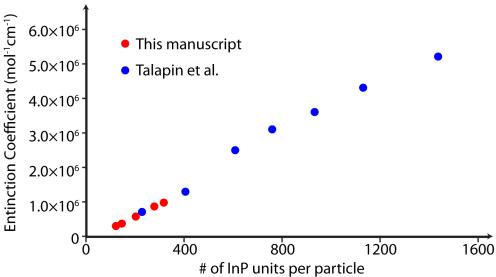


Relation between InP units per particle and their extinction coefficients with error bars calculated using methods described above.



Relation between the number of InP units per particle and their extinction coefficients per InP unit. The dashed line value corresponds to the average value of the five points. As a first order approximation¹⁰, the extinction coefficients remain constant for the InP QDs studied in our work.

Figure S14.



Comparison between the extinction coefficients measured in this manuscript at 350 nm and the ones from Talapin et al¹¹. The number of InP units per particle in the work of Talapin et al. was calculated by assuming that: (1) the particles are spherical in shape; (2) the In-to-P-ratio equals to 1 (the QDs are passivated by neutral ligands such as TOP and TOPO); (3) the density of the particles is the same as the bulk materials.

Reference

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