Synthesis of Monodisperse InP Quantum Dots: Use of an Acid-Free Indium Carboxylate Precursor

Léo Angelé,^{[a][b]} Sébastien Dreyfuss,^[b] Benoit Dubertret,^{[b]} and Nicolas Mézailles^{*[a]}*

[a] Laboratoire Hétérochimie Fondamentale et Appliquée (LHFA), Université Toulouse 3-Paul Sabatier and CNRS UMR 5069, 31062 Toulouse Cedex 9, France, France

[b] Nexdot, 102 Avenue Gaston Roussel, 93230 Romainville, France

KEYWORDS: Indium phosphide quantum dots, kinetics, precursors, absorption, size focusing, core-shell

ABSTRACT: The role of indium carboxylate precursors in the synthesis of monodisperse InP quantum dots was investigated. The reaction between acid-free indium palmitate and tris(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$) was monitored using high-temperature ^{31}P -NMR, indicating the presence of a single molecular phosphorus species throughout the duration of the reaction. The addition of varying amounts of carboxylic acid and its effects on both the reaction kinetics and the optical properties of InP QDs was studied. In the presence of acid, rapid protonation of $\text{P}(\text{TMS})_3$ led to the formation of a mixture of four $\text{H}_x\text{P}(\text{TMS})_{3-x}$ species, resulting in the poorer controlled formation of InP nanocrystals. Upon deposition of a graded ZnSeS

shell on the synthesised InP core, luminescent quantum dots were obtained (QY 67%; PL: FWHM 40nm).

INTRODUCTION

Quantum dots (QDs) have already reached applications in the lighting and display markets, with the first-generation of commercially viable QDs based primarily on cadmium.¹ Due to its toxicity, the use of cadmium is drastically limited by international regulations such as the Restriction of Hazardous Substances Directive (RoHS) in Europe. In response to this, academic and industrial researchers have pursued the development of more environmentally friendly materials such as indium phosphide (InP) QDs.^{2,3} So far, the optical properties of InP-based QDs have lagged behind that of Cd-based QDs for several reasons. Cui et al. showed that the broad emission peaks of InP QDs was related to their size polydispersity, since sharp optical properties were obtained with singular QD particles.⁴ More recent work by Janke et al. showed that other factors, such as surface and lattice defects of InP quantum dots, were also contributing to the broadening of the emission linewidth.⁵ Nevertheless, limiting the size distribution of InP QDs remained a critical factor in order to attain these desirable optical properties. Difficulties arising during the synthesis of InP QDs were attributed mainly to the source of phosphorus during the reaction. The pyrophoric, hazardous and readily hydrolysed phosphorus precursor, tris(trimethylsilyl)phosphine ($\text{P}(\text{TMS})_3$), required the use of an inert atmosphere throughout the entire synthesis with a poor control over the reactivity of the compound. In the presence of an *in situ* generated indium carboxylate precursor, $\text{P}(\text{TMS})_3$ was reported to have rapidly depleted, leading to the growth of InP nanocrystals via a poorly controlled ripening process.⁶ To limit this effect, the groups of Bawendi and Cossairt implemented the use of less reactive silylphosphines

and germylphosphines such as $\text{P}(\text{SiPh}_3)_3$ or $\text{P}(\text{GeMe}_3)_3$, leading to slightly better control over polydispersity.^{7,8} Other research groups investigated further into alternative phosphorus sources such as P_4 ,⁹ PCl_3 ,^{10,11} PH_3 ^{12,13}, but with little improvement to the quality of the InP QDs. The most promising recent developments relied on the use of aminophosphines $\text{P}(\text{NR}_2)_3$, providing a more accessible route to InP QD synthesis albeit without improving size polydispersity issues.¹⁴⁻

16

The indium precursor remained another equally important parameter for the reaction which has been rarely addressed. Notably, Bawendi et al. showed the importance of controlling the amount of water present in the reaction and recently Peng et al. demonstrated improvements on optical properties by additional phosphine ligands coordinating the indium centre before the start of the reaction.^{17,18}

However, in most InP QD syntheses an indium carboxylate precursor bearing long aliphatic chains is generated *in situ* from $\text{In}(\text{acetate})_3$.¹⁹ Narayanaswamy et al. showed that under the conditions used, only about two out of three acetate ligands are displaced from the indium centre, implying that approximately one equivalent of the non-volatile long chain carboxylic acid remained in the reaction medium throughout the entire process.²⁰ According to literature, this free fatty acid would have an effect on the synthesis of InP QDs. Firstly, as demonstrated by Cossairt and co-workers, the free fatty acid would rapidly hydrolyse the phosphorus precursor $\text{P}(\text{TMS})_3$ to form mixtures of $\text{H}_x\text{P}(\text{TMS})_{3-x}$ ($x = 1$ to 3) with different reactivities towards the In precursor.²¹ Secondly, Chaudret's group showed that free fatty acids, upon heating at InP QD synthesis temperatures (250°C or more), would undergo ketonization thereby releasing water and ketone molecules in the process. In turn, these water molecules would lead to surface oxidation of the InP QDs.^{22,23} In other words, working under air and water-free conditions would not be

sufficient for good reaction control if free acid was present in the medium either at the beginning of the reaction or generated *in situ*. The working hypothesis for this study consisted of the principle that an $\text{In}(\text{RCOO})_3$ precursor, free of acid, would lead to an improved control over InP QD formation during synthesis.

In the present work, a simple synthesis of such acid free $\text{In}(\text{palmitate})_3$ complex was carried out. InP QDs were synthesized from pure Indium complex with controlled amounts of additional carboxylic acid and compared. The absence of acid was shown to provide a slow growth of QDs without ripening occurring, believed to be linked to the presence of a single molecular P species. In the presence of increasing amounts of acid, faster, less controlled reactions occurred, linked to the presence of four reactive molecular P derivatives. This precise understanding ensured InP QDs were obtained within a controlled, size-focusing regime featuring excellent optical properties after deposition of a protective shell via a simple heat up process. To the best of our knowledge, greater optical properties were only obtained via hot-injection methods or through the use of zinc carboxylates as additives.²³ However, using zinc carboxylates results in irregular and detrimental core doping, whilst hot-injection syntheses are significantly harder to scale up.⁵

RESULTS AND DISCUSSION

As mentioned above, in most InP QDs syntheses the indium carboxylate precursor is generated *in situ*.¹⁹ This first step is performed by reacting indium (III) acetate, a commercial precursor, with three equivalents of myristic, palmitic or oleic acid, at *ca* 120°C for a few hours under dynamic vacuum. This dynamic vacuum speeds up the reaction process by eliminating acetic acid generated as a by-product of the process.^{25,26} However, under these conditions, the

reaction was unable to run to completion and a mixture of $\text{In(RCOO)}_{3-x}(\text{CH}_3\text{COO})_x$ with $x \approx 1$ is formed.²⁰ To carry out the present study, we set out to isolate pure indium palmitate complex In(Palm)_3 . In order to ensure complete substitution of all three acetate ligands, an excess of palmitic acid (10 equiv., solvent of the reaction) was used as well as longer reaction times (4 hours at 110°C under dynamic vacuum) (figure 1). After the reaction, the crude product was thoroughly washed as described in ESI, in order to remove the excess of palmitic acid and any trace remnants of acetic acid.²⁵ Finally, the product was dried under vacuum at 100°C for 6 hours.

Figure 1. Optimized synthesis of In(Palm)_3 ; where palmitic acid is both the solvent and the reactant.

The purity of our In(Palm)_3 sample was demonstrated by NMR and IR spectroscopy. The ^1H NMR spectrum of the isolated complex did not show a singlet corresponding to the CH_3 of the acetate moiety, expected at around 1.8 ppm which suggested the formation of In(Palm)_3 . (ESI, part 1) Note that while our work was in progress, Tamang *et al.* reported the synthesis of In(RCOO)_3 from the reaction of InCl_3 with 3 equiv. of carboxylic acid in the presence of an organic base. This work is dedicated to the development of a general synthesis of a wide variety of metal carboxylate complexes.²⁷ In the IR spectrum, no characteristic signal for the COOH moiety could be found (figure 2). Superposition of spectra for palmitic acid and In(Palm)_3 complex **1** showed the absence of the O=C stretch band from the acid at 1700 cm^{-1} and the presence of two O-C stretch bands at 1580 and 1540 cm^{-1} of In(Palm)_3 .

Figure 2. Infra-red spectra of In(Palm)_3 complex **1** and palmitic acid (2000-1000 cm^{-1} region).

An additional, indirect, proof of purity of complex **1** was performed upon addition of minute amounts of palmitic acid (5% by mass), whereby the signal corresponding to COOH would appear once more at 1700 cm^{-1} (figure S4).²⁸ The complex **1** was subsequently stored in an Ar-filled glovebox in order to prevent possible H_2O coordination at the Lewis acid Indium centre. With this acid and water-free In precursor, the reaction with P(TMS)_3 in a 1:1 ratio in 1-Octadecene (ODE) at 80°C was monitored by ^{31}P NMR spectroscopy (in the presence of PPh_3 as internal standard). The reagents and solvent were mixed in a J-Young NMR tube at room temperature inside an Ar-filled glovebox (see ESI for details). The NMR tube was then inserted into the probe of the NMR spectrometer and heated to 80°C while ^{31}P NMR spectra were recorded every 263s to allow a quantitative analysis of the spectra (see figure S7 and S8 for full spectra at $t = 0$ and $t = 22\text{min } 15\text{s}$). As shown on figure 3, which corresponds to zoomed parts of

the full spectra where $\text{P}(\text{TMS})_{3-x}\text{H}_x$ can be observed, only a single signal corresponding to $\text{P}(\text{TMS})_3$ was observed throughout the reaction.

Figure 3. Monitoring of reaction between $\text{In}(\text{Palm})_3$ and $\text{P}(\text{TMS})_3$ at 80°C , zoom of the spectra collected every 263s. The only signal corresponds to $\text{P}(\text{TMS})_3$

Note that the apparent peak broadness of $\text{P}(\text{TMS})_3$ can be explained by the poor shimming process in NMR resulting from presence of solid material ($\text{In}(\text{Palm})_3$ is poorly soluble in D8-tol needed for the high temperature experiment) inside the NMR tube through most of the reaction²⁹ The intensity of the $\text{P}(\text{TMS})_3$ resonance decreased over time and stabilized after 1hr and 40minutes of reaction to a remaining 15 % of the initial amount (vs triphenylphosphine (TPP), used as an internal standard). This first experiment demonstrated that in the absence of an external source of acid only one molecular phosphorus species, $\text{P}(\text{TMS})_3$, was present during the synthesis of InP, with figure 4 showing the proposed mechanism for that reaction. It also

highlighted that a temperature higher than 80°C was needed in order to fully convert all the phosphorus precursor.

Figure 4. Proposed mechanism for the initial steps of the InP synthesis with likely intermediates, highlighting the formation of RCOOSiMe_3 as the sole by product of the stepwise In-P bond formations.

A control experiment was carried out under the same conditions without the In(Palm)_3 species. ^{31}P NMR showed no evolution of the P(TMS)_3 peak, which implied that the phosphorus precursor reacted solely with the indium carboxylate complex. This suggested that the final stages of crystalline InP QD formation require higher thermal activation. In parallel, an identical reaction was followed by UV-visible spectroscopy. Although the solution took a bright red colour within 15 minutes, no defined absorption peak could be observed (figure S6). This confirms that 80°C was neither enough to obtain crystalline quantum dots, nor to have formed magic-size clusters (MSC).²⁶ The effect of temperature on the reaction was therefore studied using an approach inspired from Lee et al.²⁵. This involved heating a mixture of In(Palm)_3 (1.0 equiv.), P(TMS)_3 (0.8 equiv.) and trioctylphosphine (TOP) in ODE under N_2 . Note that the ratio P/In of 0.8 was selected based on literature syntheses.³⁰ With higher P/In ratios, rapid

aggregation of a dark product was observed rather than well dispersed InP QDs. The mixture was heated to 305°C in 20 min and kept at this temperature for a further 10 minutes. The reaction was monitored using UV-visible spectroscopy by taking aliquots at various temperatures, which are presented in figure 5a.

Figure 5. (a) Absorption spectra of the InP cores at various temperature without acid (b) Absorption spectrum when reaching 305°C and after 10 min at 305°C

At temperatures between 90°C and 150°C, the reaction mixture remained colourless, confirmed by weak absorption in the visible light range. Between 150°C and 200°C, a light colouration was observed, yet no excitonic features distinctive of quantum dots were visible. A broad excitonic peak around 440 nm corresponding to QD formation appeared only at 250°C. When the temperature was increased further, the absorption peak shifted to higher wavelengths and sharpened. Notably, this sharpening of the absorption peak indicated that the growth occurred during a size focusing regime. Once the temperature reached 305°C, the UV-vis spectrum of the reaction mixture stopped evolving, indicating the depletion of the phosphorus precursor. No ripening or degradation processes were observed, even after further heating at 305°C for 10 minutes, as shown in figure 5b. These results strongly differ from those of previous studies on InP QDs synthesized with *in situ* generated Indium carboxylates and $P(TMS)_3$.² Indeed, it has

been reported that the main difficulty for controlling the synthesis of InP QDs was due to a rapid and uncontrollable consumption of $\text{P}(\text{TMS})_3$, and that this growth occurred solely by ripening processes. Therefore, it was considered impossible to reach a size focusing regime without using multi-injection techniques or additives such as zinc carboxylates.^{30,31} This work showed that these detrimental processes can be circumvented using an indium precursor free of carboxylic acid.

To fully understand the role of the carboxylic acid, similar experiments were carried out with controlled, precise amounts of added oleic acid. Oleic acid was chosen over palmitic acid as its liquid state at room temperature simplified the weighing out of minute amounts, around 1 mg, with higher accuracy. For direct comparison, the reactions were also conducted in J-Young NMR tubes and monitored at 80°C by NMR spectroscopy. Note that each reaction was carried out at least twice, with identical results. As reported in the literature, $\text{P}(\text{TMS})_3$ was readily hydrolysed in a fast and non-selective process in the absence of an In precursor.²⁰ With sub-stoichiometric amounts of acid, a mixture of four compounds $\text{HP}(\text{TMS})_2$, $\text{H}_2\text{P}(\text{TMS})$ and PH_3 together with $\text{P}(\text{TMS})_3$ was observed. The relative proportions of these compounds depended on the initial amount of acid and these ratios did not change in solution, even when heated. Reactions between $\text{In}(\text{palm})_3$: $\text{P}(\text{TMS})_3$:oleic acid with ratios 1.0:0.8:x, with $x = 0.1$ to 1.0 were followed by ^{31}P NMR spectroscopy. As a representative example, the spectra collected from the experiment with $x = 1.0$ are presented in Figure 6.

Figure 6. Monitoring of reaction between $\text{In(Palm)}_3\text{:P(TMS)}_3\text{:oleic acid}$ in 1.0:0.8:1.0 ratio at 80°C : $^{31}\text{P}\{^1\text{H}\}$ NMR spectra recorded each 263 s.

The experiments carried out with different ratios are presented in the ESI (figures S9 to S13). Integration of all four signals throughout the reaction was used to gauge the evolution of precursor concentrations. The spectra highlight that each of the phosphorus derivatives possessed a different reactivity towards the indium complexes formed during the reaction. Specifically, it appeared that the HP(TMS)_2 species decreased faster than the P(TMS)_3 and H_2PTMS , themselves faster than PH_3 in accord with previously reported literature.⁷ Importantly, the monitoring showed no further evolution of the total amount of P derivatives after 15 minutes, with only the PH_3 remaining. The time needed to reach this plateau depended on the amount of free carboxylic acid, ranging from 15 minutes when 1.0 equivalent of acid was present, to 100 minutes without acid (ESI figures S5 and S9 to S12). This demonstrated the difference in reactivity of the four phosphorus derivatives. This led to reasonably postulate that such differences in reactivity already seen at 80°C would have an impact on the growth control of InP QDs at higher

temperatures. A UV-visible spectrum of the mixture resulting from the reaction of In(Palm)_3 , P(TMS)_3 , oleic acid in a 1.0:0.8:1.0 ratio at 80°C for 2 h was recorded (figure S13) which did not show any excitonic features corresponding to QDs. Higher temperatures were clearly needed to achieve QDs formation as a result. Considering these results, the effect of the amount of added oleic acid (0.1, 0.3, 0.5, and 1.0 equivalents) on the outcome of the standard QD synthesis at high temperatures was studied. The reactions were monitored by UV-visible spectroscopy of aliquots taken at various temperatures.

A broad absorption feature could already be detected when the temperature reached 90°C when only more than 0.3 equiv. acid was used (figure 7a). In comparison, without the presence of acid, excitonic features only appeared at temperatures of 250°C (figure 5a.). Surprisingly at 90°C, the reaction with 1.0 equiv. acid seemed to result in smaller-size QDs than the reaction with 0.5 equiv. acid. It was hypothesised that this might have been due to the production of MSCs, as these conditions were similar to the ones used by Cossairt et al. to produce MSCs absorbing at 386 nm.³² To test this hypothesis, further experiments were performed at 80°C. Without acid, no MSCs were observed while with 1.0 eq of oleic acid, a sharp excitonic feature centred at 365 nm corresponding to MSCs was observed (Figure S15). These experiments confirmed that with an initial amount of 1.0 equiv. of free acid, MSCs were likely intermediates for the formation of InP QDs, which is consistent with previous literature reports.²¹ At 210°C, the differences between reactions with various acid amounts were particularly significant as seen in figure 7b.

Figure 7. Absorption spectra of reactions at 90°C (a), 210°C (b) and final products ((c), 10 minutes at 305°C) with various amounts of added acid.

Without acid or with 0.1 equiv., nucleation had barely started and no excitonic feature was present. On the other hand, reactions with 0.3-1.0 equiv. acid displayed a far more defined absorption peak showing QD formation, whereby the signal was even sharper for 1.0 equiv. of acid. Undoubtedly, free acid accelerated the formation of QDs and at this point appeared to be a strongly inducing parameter. The QDs in figure 7c obtained after 10 minutes at 305°C, presented very different absorption spectra.

To understand this, the full reaction monitoring for each acid amount was studied in greater detail (figure S16 to S21). The profile of the reaction with one equiv. of acid (figure 8a) was particularly significant. At 90°C, a broad excitonic feature around 390 nm was already present, which as mentioned above, could have been attributed to the growth of the 365 nm absorbing MSCs. Between 90°C and 250°C, a shift of the absorption peak was observed, consistent with InP QD growth. At 250°C, optimal size dispersity was obtained, as seen by the

sharpness of the excitonic feature, with a half width at half maximum (HWHM) of 34 nm, taken from the higher wavenumber side of the peak and a peak/valley ratio of 1.29. Upon further heating, InP QDs continued to grow with a shift in the absorption peak from 470nm to 500 nm. Although, at the same time the peak broadened, implying an increase in size dispersity due to a detrimental ripening process.

Figure 8. (a) Absorption spectra of the InP cores at various temperature with 1 equiv. acid (b) Absorption spectrum when reaching 305°C and after 10 min at 305°C.

Importantly, this ripening process continued when the mixture was held at 305°C for an additional 10 minutes (figure 8b) leading to a HWHM increase from 42 nm to 47 nm, and a peak/valley ratio decrease from 1.23 to 1.11. The reactions with 0.3 and 0.5 equiv. acid (figures S18 and S19 respectively) presented a similar behaviour. They reached an optimal size dispersity at 275°C and 295°C respectively before a ripening process took place. Conversely, in the absence of added acid, the reaction profile showed a broad excitonic feature at 250°C that sharpened with an increase in temperature, showing the growth of QDs with size focusing and without ripening after 10 minutes at 305°C (figures 5a and b). Most importantly, the absence of ripening allowed for greater control over the reaction as no quenching was required. The reaction with 0.1 equiv. of acid differed from the others with the absence of a well-defined peak between

210°C and 305°C (figure S17). This result was consistent with a recent report by Peng *et al.* who obtained a similar reaction profile for a reaction through a heat-up setup while working with 10% free acid in the medium.¹⁷ This could be due to the presence of two nucleation regimes: a first one starting at temperatures below 100°C due to the free acid, and a second one occurring at temperatures higher than 200°C comparable to the conditions without free acid. This could imply a prolonged nucleation, leading to greater size polydispersity, consistent with results by Cossairt *et al.* who demonstrated that longer nucleation times for InP quantum dots during synthesis was detrimental to reaching a homogenous size dispersity.⁸ Thus, even trace amounts of free acid does lead to significant size dispersity during the heat-up process, counteracting the prior isolation of the In(Palm)₃ precursor.

These findings on the influence of the amount of acid present during the synthesis of InP QDs could be rationalized by the initial steps proposed in figure 9. The acid partly hydrolyses P(TMS)₃ to four different compounds P(TMS)_{3-x}H_x (with 0 < x < 3) which react at different rates with the In(Palm)₃ precursor, to form three possible indium complexes, featuring the first In-P bond. For each P-H bond reaction, one equivalent of palmitic acid would be formed, and this acid could in turn react with the mixture of phosphines to once again modify their relative proportion. The acid could equally react with the (RCOO)₂InP(SiMe₃)_{2-x}(H)_x (x = 0.1) as well. Further reaction of the three indium complexes would occur with different kinetics due to the significant differences in steric environments at the phosphorus centre. Therefore, this would explain the poor conditions for controlling growth when fatty acid would be present in the medium. Importantly, the proposed mechanism does show that the overall quantity of acid would not change throughout the reaction, which would also be consistent with the ripening process that does occur only in the presence of acid.

Figure 9. Proposed mechanism of the initial steps of the InP synthesis with likely intermediates, highlighting the formation of RCOOH as an extra by-product of the stepwise In-P bond formations

A final experiment was carried out to compare these results to a classic procedure from literature using an *in situ* generated indium precursor.¹⁹ Anhydrous indium(III) acetate and three equivalents of palmitic acid were mixed at 120°C in ODE for 2h under vacuum (0.3 mbar). P(TMS)₃ and TOP were added to this precursor solution, then the mixture was heated up to 305°C under conditions identical to above. As shown in figure S4.6, the UV-visible monitoring showed an evolution nearly identical to the one when 1.0 equiv. of acid was added to the pure In(Palm)₃ complex. Thus, it is believed that some reproducibility issues with the InP QD syntheses were due to the way the indium precursor was generated (time under vacuum, temperature, pressure, amount of initial acid), and therefore on the amount of remaining free fatty acid within the mixture. Having obtained InP QDs from different syntheses we proceeded to evaluate their emissive properties after deposition of a ZnSeS gradient shell which displayed good luminescent properties due to reduced lattice mismatching. For the deposition of the ZnSeS shell, zinc stearate was introduced into a crude mixture of the InP cores at room temperature

under stringent air-free conditions. Then, the solution was heated to 310 °C with successive injections of TOP-Se and TOP-S in order to form a gradient ZnSeS shell. Emission spectra were recorded and shown below in figure 10, and PL data presented in table 1. For the acid-free synthesis, the InP/ZnSeS core-shell quantum dot showed an emission wavelength of 550 nm with a full width at half maximum (FWHM) of 40 nm, and a photoluminescence quantum yield (QY) of 67%. An identical ZnSeS shell deposition procedure was carried out on an InP cores synthesized with varied amounts of acid. All the final core/shell quantum dots displayed a quantum yield between 60 and 67%.

Table 1. Optical properties of InP/ZnSeS core shell QD depending on the amount of free acid

Indium precursor	Emission (nm)	Emission FWHM (nm)	QY (%)
In(Palm) ₃	550	40	67
In(Palm) ₃ + 0.1 equiv. acid	550	46	62
In(Palm) ₃ + 0.3 equiv. acid	544	44	60
In(Palm) ₃ + 0.5 equiv. acid	552	43	67
In(Palm) ₃ + 1 equiv. acid	570	51	65
In(Ac) ₃ + 3 equiv. acid	567	62	60

Figure 10. Photoluminescence spectra of core shell InP@ZnSeS QDs.

The quantum yields of the final QDs were similar, therefore implying that the QY was reliant solely on the nature of the shell, and not the presence of acid during the synthesis of the core. Conversely, the FWHM clearly depended on the amount of acid used during synthesis, with the lowest FWHM obtained using an acid-free protocol. This demonstrated that preventing ripening was clearly important for the optical properties of the final material.

CONCLUSION

In summary, the purity of the indium precursor, i.e. acid free, was demonstrated to be key in obtaining high quality InP QDs from the reaction of $\text{P}(\text{TMS})_3$ and $\text{In}(\text{Palm})_3$. As shown by the subsequent NMR studies, it was linked to the inhibition of competitive pathways resulting from an uncontrolled partial hydrolysis of the $\text{P}(\text{TMS})_3$ precursor by carboxylic acids. Nucleation was shown to only have occurred above 210°C in the absence of acid, whereas substoichiometric amounts of acid were able to initiate nucleation at temperatures as low as 90°C . Without the presence of acid, a slower growth occurred without a competitive ripening process. In this sense, acid free synthesis provided desirable growth conditions, as found in CdSe QD synthesis. Further studies are currently underway to lower FWHM and tune emission wavelength while maintaining a size focusing regime. This study was able to show that the presence of variable amounts of free acid as found in “classical” InP syntheses amounted for their poorer reproducibility in addition to their variable and worse optical properties. This work has hoped to contribute to the improvement of available methodologies for the synthesis of luminescent InP QDs. For instance, synthesizing larger InP nanocrystals in order to make red luminescent objects with sharp emission spectra remains a major challenge. The most efficient way to achieve this as

described in the literature would be to slowly add, after initial QD formation, an $\text{In(RCOO)}_3\text{-P(TMS)}_3$ complex prepared at low temperatures.^{18,32} This process, however, often results in the broadening of the emission spectrum when compared with green QDs. This work suggests that these complexes might in fact be mixtures of different species due to the amount of free acid in solution. Using a clean indium carboxylate precursor to prepare these complexes could lead to a far greater control over growth and substantial increase in size focusing, thus, paving the way for the synthesis of greatly enhanced red-light emitting InP quantum dots.

ASSOCIATED CONTENT

Supporting Information contains experimental procedures, NMR, IR as well as absorption spectra of products and reactions; TEM pictures of InP/ZnSeS QD.

AUTHOR INFORMATION

Corresponding Author

*Nicolas Mézailles : mezailles@chimie.ups-tlse.fr

*Benoit Dubertret : benoit.dubertret@nexdot.fr

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by the “Agence nationale de la recherche et des technologies” under convention CIFRE N° 2017/0502.

ACKNOWLEDGMENT

We would like to acknowledge Stéphane Massou for assistance with NMR. We would like to acknowledge Wilfried Solo Ojo for helpful discussion and critical reading of the manuscript. We would like to acknowledge Félix Boussoufi for assistance in collecting Powder X-ray diffraction patterns and Scott Willis for proof-reading of the manuscript. Solvay is acknowledged for a generous gift of phosphines.

ABBREVIATIONS

QDs, quantum dots; P(TMS)₃, tris(trimethylsilyl)phosphine; ODE, 1-Octadecene; TPP, triphenylphosphine; MSC, magic-size clusters; TOP, trioctylphosphine; HWHM, half width at half maximum; FWHM, full width at half maximum; QY, quantum yield.

REFERENCES

- (1) Murray, C. B.; Norris, D. J.; Bawendi, M. G. Synthesis and Characterization of Nearly Monodisperse CdE (E = Sulfur, Selenium, Tellurium) Semiconductor Nanocrystallites. *J. Am. Chem. Soc.* **1993**, *115* (19), 8706–8715. <https://doi.org/10.1021/ja00072a025>.
- (2) Reiss, P.; Carrière, M.; Lincheneau, C.; Vaure, L.; Tamang, S. Synthesis of Semiconductor Nanocrystals, Focusing on Nontoxic and Earth-Abundant Materials. *Chem. Rev.* **2016**, *116* (18), 10731–10819. <https://doi.org/10.1021/acs.chemrev.6b00116>.
- (3) Marşan, D.; Şengül, H.; Özdil, A. M. A. Comparative Assessment of the Phase Transfer Behaviour of InP/ZnS and CuInS/ZnS Quantum Dots and CdSe/ZnS Quantum Dots under Varying Environmental Conditions. *Environmental Science: Nano* **2019**, *6* (3), 879–891. <https://doi.org/10.1039/C8EN01073K>.
- (4) Cui, J.; Beyler, A. P.; Marshall, L. F.; Chen, O.; Harris, D. K.; Wanger, D. D.; Brokmann, X.; Bawendi, M. G. Direct Probe of Spectral Inhomogeneity Reveals Synthetic Tunability of Single-

Nanocrystal Spectral Linewidths. *Nature Chemistry* **2013**, *5* (7), 602–606. <https://doi.org/10.1038/nchem.1654>.

(5) Janke, E. M.; Williams, N. E.; She, C.; Zhrebetskyy, D.; Hudson, M. H.; Wang, L.; Gosztola, D. J.; Schaller, R. D.; Lee, B.; Sun, C.; Engel, G. S.; Talapin, D. V. Origin of Broad Emission Spectra in InP Quantum Dots: Contributions from Structural and Electronic Disorder. *J. Am. Chem. Soc.* **2018**, *140* (46), 15791–15803. <https://doi.org/10.1021/jacs.8b08753>.

(6) Allen, P. M.; Walker, B. J.; Bawendi, M. G. Mechanistic Insights into the Formation of InP Quantum Dots. *Angewandte Chemie International Edition* **2010**, *49* (4), 760–762. <https://doi.org/10.1002/anie.200905632>.

(7) Cossairt, B. M. Shining Light on Indium Phosphide Quantum Dots: Understanding the Interplay among Precursor Conversion, Nucleation, and Growth. *Chem. Mater.* **2016**, *28* (20), 7181–7189. <https://doi.org/10.1021/acs.chemmater.6b03408>.

(8) Gary, D. C.; Glassy, B. A.; Cossairt, B. M. Investigation of Indium Phosphide Quantum Dot Nucleation and Growth Utilizing Triarylsilylphosphine Precursors. *Chem. Mater.* **2014**, *26* (4), 1734–1744. <https://doi.org/10.1021/cm500102q>.

(9) Harris, D. K.; Bawendi, M. G. Improved Precursor Chemistry for the Synthesis of III–V Quantum Dots. *J. Am. Chem. Soc.* **2012**, *134* (50), 20211–20213. <https://doi.org/10.1021/ja309863n>.

(10) Liu, Z.; Kumbhar, A.; Xu, D.; Zhang, J.; Sun, Z.; Fang, J. Coreduction Colloidal Synthesis of III–V Nanocrystals: The Case of InP. *Angewandte Chemie International Edition* **2008**, *47* (19), 3540–3542. <https://doi.org/10.1002/anie.200800281>.

(11) An, S.; Cho, H.; Jeon, H. B.; Kim, S.-W. InPZnS Alloy Quantum Dots with Tris(Hexylthio)Phosphine as a Dual Anionic Precursor. *Nanoscale* **2018**, *10* (6), 3014–3019. <https://doi.org/10.1039/C7NR08211H>.

(12) Mordvinova, N.; Vinokurov, A.; Dorofeev, S.; Kuznetsova, T.; Znamenkov, K. Phosphine Synthetic Route Features and Postsynthetic Treatment of InP Quantum Dots. *Journal of Alloys and Compounds* **2014**, *582*, 43–49. <https://doi.org/10.1016/j.jallcom.2013.08.003>.

(13) Li, L.; Protière, M.; Reiss, P. Economic Synthesis of High Quality InP Nanocrystals Using Calcium Phosphide as the Phosphorus Precursor. *Chem. Mater.* **2008**, *20* (8), 2621–2623. <https://doi.org/10.1021/cm7035579>.

(14) Tessier, M. D.; Dupont, D.; De Nolf, K.; De Roo, J.; Hens, Z. Economic and Size-Tunable Synthesis of InP/ZnE (E = S, Se) Colloidal Quantum Dots. *Chem. Mater.* **2015**, *27* (13), 4893–4898. <https://doi.org/10.1021/acs.chemmater.5b02138>.

- (15) Matsumoto, T.; Maenosono, S.; Yamaguchi, Y. Organometallic Synthesis of InP Quantum Dots Using Tris(Dimethylamino)Phosphine as a Phosphorus Source. *Chem. Lett.* **2004**, 33 (11), 1492–1493. <https://doi.org/10.1246/cl.2004.1492>.
- (16) Buffard, A.; Dreyfuss, S.; Nadal, B.; Heuclin, H.; Xu, X.; Patriarche, G.; Mézailles, N.; Dubertret, B. Mechanistic Insight and Optimization of InP Nanocrystals Synthesized with Aminophosphines. *Chem. Mater.* **2016**, 28 (16), 5925–5934. <https://doi.org/10.1021/acs.chemmater.6b02456>.
- (17) Xie, L.; Harris, D. K.; Bawendi, M. G.; Jensen, K. F. Effect of Trace Water on the Growth of Indium Phosphide Quantum Dots. *Chem. Mater.* **2015**, 27 (14), 5058–5063. <https://doi.org/10.1021/acs.chemmater.5b01626>.
- (18) Xu, Z.; Li, Y.; Li, J.; Pu, C.; Zhou, J.; Lv, L.; Peng, X. Formation of Size-Tunable and Nearly Monodisperse InP Nanocrystals: Chemical Reactions and Controlled Synthesis. *Chem. Mater.* **2019**, 31 (14), 5331–5341. <https://doi.org/10.1021/acs.chemmater.9b02292>.
- (19) Battaglia, D.; Peng, X. Formation of High Quality InP and InAs Nanocrystals in a Noncoordinating Solvent. *Nano Lett.* **2002**, 2 (9), 1027–1030. <https://doi.org/10.1021/nl025687v>.
- (20) Narayanaswamy, A.; Xu, H.; Pradhan, N.; Kim, M.; Peng, X. Formation of Nearly Monodisperse In₂O₃ Nanodots and Oriented-Attached Nanoflowers: Hydrolysis and Alcoholysis vs Pyrolysis. *J. Am. Chem. Soc.* **2006**, 128 (31), 10310–10319. <https://doi.org/10.1021/ja0627601>.
- (21) Gary, D. C.; Cossairt, B. M. Role of Acid in Precursor Conversion During InP Quantum Dot Synthesis. *Chem. Mater.* **2013**, 25 (12), 2463–2469. <https://doi.org/10.1021/cm401289j>.
- (22) Cros-Gagneux, A.; Delpech, F.; Nayral, C.; Cornejo, A.; Coppel, Y.; Chaudret, B. Surface Chemistry of InP Quantum Dots: A Comprehensive Study. *J. Am. Chem. Soc.* **2010**, 132 (51), 18147–18157. <https://doi.org/10.1021/ja104673y>.
- (23) Virieux, H.; Le Troedec, M.; Cros-Gagneux, A.; Ojo, W.-S.; Delpech, F.; Nayral, C.; Martinez, H.; Chaudret, B. InP/ZnS Nanocrystals: Coupling NMR and XPS for Fine Surface and Interface Description. *J. Am. Chem. Soc.* **2012**, 134 (48), 19701–19708. <https://doi.org/10.1021/ja307124m>.
- (24) Won, Y.-H.; Cho, O.; Kim, T.; Chung, D.-Y.; Kim, T.; Chung, H.; Jang, H.; Lee, J.; Kim, D.; Jang, E. Highly Efficient and Stable InP/ZnSe/ZnS Quantum Dot Light-Emitting Diodes. *Nature* **2019**, 575 (7784), 634–638. <https://doi.org/10.1038/s41586-019-1771-5>.

- (25) Ramasamy, P.; Kim, N.; Kang, Y.-S.; Ramirez, O.; Lee, J.-S. Tunable, Bright, and Narrow-Band Luminescence from Colloidal Indium Phosphide Quantum Dots. *Chem. Mater.* **2017**, *29* (16), 6893–6899. <https://doi.org/10.1021/acs.chemmater.7b02204>.
- (26) Gary, D. C.; Terban, M. W.; Billinge, S. J. L.; Cossairt, B. M. Two-Step Nucleation and Growth of InP Quantum Dots via Magic-Sized Cluster Intermediates. *Chem. Mater.* **2015**, *27* (4), 1432–1441. <https://doi.org/10.1021/acs.chemmater.5b00286>.
- (27) Franke, D.; Harris, D. K.; Xie, L.; Jensen, K. F.; Bawendi, M. G. The Unexpected Influence of Precursor Conversion Rate in the Synthesis of III-V Quantum Dots. *Angew. Chem. Int. Ed.* **2015**, *54* (48), 14299–14303. <https://doi.org/10.1002/anie.201505972>
- (28) Basel, S.; Bhardwaj, K.; Pradhan, S.; Pariyar, A.; Tamang, S. DBU-Catalyzed One-Pot Synthesis of Nearly Any Metal Salt of Fatty Acid (M-FA): A Library of Metal Precursors to Semiconductor Nanocrystal Synthesis. *ACS Omega* **2020**, *5* (12), 6666–6675. <https://doi.org/10.1021/acsomega.9b04448>.
- (29) Moreels, I.; Fritzinger, B.; Martins, J. C.; Hens, Z. Surface Chemistry of Colloidal PbSe Nanocrystals. *J. Am. Chem. Soc.* **2008**, *130* (45), 15081–15086. <https://doi.org/10.1021/ja803994m>.
- (30) Ramasamy, P.; Ko, K.-J.; Kang, J.-W.; Lee, J.-S. Two-Step “Seed-Mediated” Synthetic Approach to Colloidal Indium Phosphide Quantum Dots with High-Purity Photo- and Electroluminescence. *Chem. Mater.* **2018**, *30* (11), 3643–3647. <https://doi.org/10.1021/acs.chemmater.8b02049>.
- (31) Kim, Y.; Ham, S.; Jang, H.; Min, J. H.; Chung, H.; Lee, J.; Kim, D.; Jang, E. Bright and Uniform Green Light Emitting InP/ZnSe/ZnS Quantum Dots for Wide Color Gamut Displays. *ACS Appl. Nano Mater.* **2019**, *2* (3), 1496–1504. <https://doi.org/10.1021/acsanm.8b02063>.
- (32) Friedfeld, M. R.; Johnson, D. A.; Cossairt, B. M. Conversion of InP Clusters to Quantum Dots. *Inorg. Chem.* **2019**, *58* (1), 803–810. <https://doi.org/10.1021/acs.inorgchem.8b02945>.

For table of content only