Quantum Dots

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Mechanistic Insights into the Formation of InP Quantum Dots**

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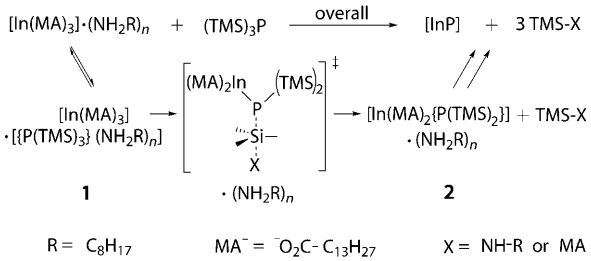
In memory of Peter Curtin

InP QDs (InP quantum dots)[1–3] are of increasing technological interest as a replacement for CdSe QDs in visible-light applications. However, the synthetic methods used for InP QDs have not produced QDs with the narrow size distributions attained for CdSe and PbSe QDs.[1–5] Studies of the molecular mechanisms involved in the formation of QDs have only recently been reported for CdSe and PbSe QDs,[6,7] and the mechanisms underlying InP QD formation are essentially unknown. We investigated the reactions involved in InP QD formation to understand the broad size distributions in current InP QD syntheses.

In a simplified view of the formation of monodisperse colloids, two general events should occur: 1) an initial nucleation of colloids, followed by 2) subsequent growth of these nuclei from molecular precursors.[8,9] Studies on the growth of CdSe and PbSe QDs have shown that these systems fulfill both events.[6,7] For InP QDs, we have found that molecular phosphorus precursors are completely depleted following InP nucleation, indicating that subsequent QD growth is due exclusively to ripening from non-molecular InP species. The inability of InP QD syntheses to satisfy (2) owing to depletion of molecular precursors may explain the broad size distributions of InP QDs relative to CdSe or PbSe QDs.

Colloidal InP QDs are synthesized by the injection of precursors into a hot solution of surfactants, or by mixing precursors at room temperature followed by heating.[1–3] In these reactions, indium(III) myristate, $In(MA)_3$, reacts with tris(trimethylsilyl)phosphine, $(TMS)_3P$, at elevated temperatures to produce trimethylsilyl myristate (TMS-MA) and InP QDs (Scheme 1). By operating at reduced temperatures with amines, it is possible to monitor the evolution of molecular species during InP formation. Amines inhibit precursor decomposition, which is contrary to previous claims that amines act as activating agents in InP QD synthesis.[2,10–13]



Scheme 1. Proposed mechanistic pathway for amine-inhibited InP synthesis. Both the formation of outer-sphere complex **1** and the irreversible formation of intermediate **2** are inhibited by increased solvation. A charge-dispersion S_N2 transition state for TMS–X bond formation and P–TMS bond cleavage is inferred from the large negative activation entropy and the large rate decrease with added amine.

We propose the mechanism for amine-inhibited InP QD synthesis given in Scheme 1. Initially, $In(MA)_3$ is coordinated to Lewis base(s), such as octylamine (OA), in the outer (solvation) sphere. In the reversible first step, one $(TMS)_3P$ molecule becomes incorporated into the solvation sphere (**1**). Complex **1** then loses a myristate ligand, a stable In–P bond forms, and the coordinated phosphine loses a TMS group, thereby irreversibly forming a molecular intermediate (**2**). Intermediate **2** reacts further to form [InP] clusters and nanocrystals. Evidence that supports this mechanism will be described below.

To probe the evolution of molecular species during InP QD synthesis, we used ^{1}H NMR spectroscopy to investigate species with TMS substituents. In this reaction, the TMS group is the only likely ligand for molecular phosphines, so the high ^{1}H NMR sensitivity of the TMS group permits the observation of any phosphorus-containing molecules or decomposition products present at significant concentration. Reactions were performed in sealed NMR tubes with 0.02 M $In(MA)_3$, 0.01 M $(TMS)_3P$, 0.0–1.44 M octylamine, and 0.03 M diphenylmethane as an internal standard in [D_8]toluene.

In the absence of octylamine, a ^{1}H NMR spectrum taken within three minutes of mixing $In(MA)_3$ and $(TMS)_3P$ at room temperature showed quantitative conversion of $(TMS)_3P$ into TMS-MA (Figure 1a,b). The rapid decomposition of $(TMS)_3P$ is due to the direct approach of $(TMS)_3P$ to the indium center, circumventing outer-sphere equilibria en route to the production of a stable Si–O bond in the TMS-MA product. The exceedingly fast conversion of $(TMS)_3P$ into TMS-MA at room temperature occurs on a timescale that is not practical for monodisperse QD synthesis or kinetic analysis by NMR.[6–9]

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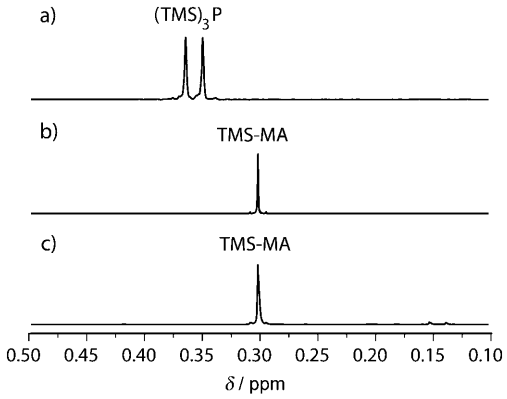

Figure 1. ^{1}H NMR spectra of a) $(TMS)_3P$ at 20 °C before injection, b) the reaction mixture of $In(MA)_3$ and $(TMS)_3P$ in [D_8]toluene three minutes after mixing at 25 °C, and c) the reaction mixture of $(TMS)_3P$ and 6:1 octylamine/$In(MA)_3$ in 1,2-[D_4]dichlorobenzene after heating at 178 °C for one minute. Both (b) and (c) show quantitative conversion of $(TMS)_3P$ into TMS-MA shortly after the reactions are initiated.

Using literature procedures at elevated temperatures containing octylamine, we find that no molecular precursors remain shortly after reaction initiation at high temperature. A sealed NMR tube with a composition similar to those previously reported was heated at the published reaction temperature (178 °C)[2] and showed no $(TMS)_3P$ after 1 min (Figure 1c). Our findings, with and without octylamine, demonstrate that previously reported reaction conditions for InP QDs are based on ripening of non-molecular InP species, similar to those used for InAs,[14] and do not fulfill the requirements for the formation of monodisperse colloids.

However, when octylamine-containing InP reaction mixtures were run at 40 °C, the reaction rate slowed sufficiently to permit kinetic analysis. From time-resolved ^{1}H NMR spectra (Figure 2), four species account for all of the TMS groups throughout the reaction. $(TMS)_3P$ and TMS-MA together account for over 90 % of all TMS groups; the remaining TMS groups are either associated with the intermediate **2** (Figure 2a, inset) or the silated octylamine (TMS-OA) that occurs in less than 5 % yield under standard conditions. The relative rates of $(TMS)_3P$ depletion and of TMS-MA growth are consistent with near quantitative conversion of $(TMS)_3P$ into TMS-MA (Figure 2b). Linear evolution at early times facilitated the analysis of initial rates.

We attribute the doublet at $\delta = 0.26$ ppm ($^3J_{HP} = 4.4$ Hz) to **2**,[15] as this signal suggests a phosphorus-containing species that retains at least one TMS group. We corroborated this assignment with a heteronuclear multiple bond coherence (HMBC) experiment, which showed that ^{1}H resonances of $(TMS)_3P$ and **2** were cross-coupled to respective ^{31}P resonances (Supporting Information, Figure S10). The ^{1}H NMR resonance of **2** has a linewidth comparable to that of molecular $(TMS)_3P$ and TMS-MA noted above, thus indicating that the species has a distinct molecular structure. Finally, the time evolution of the **2** resonance shows the characteristic growth and depletion of a reaction intermediate (Supporting Information, Figure S1).

Upon increasing the octylamine concentration from 6:1 to 18:1, the rate of $(TMS)_3P$ depletion continued to decrease

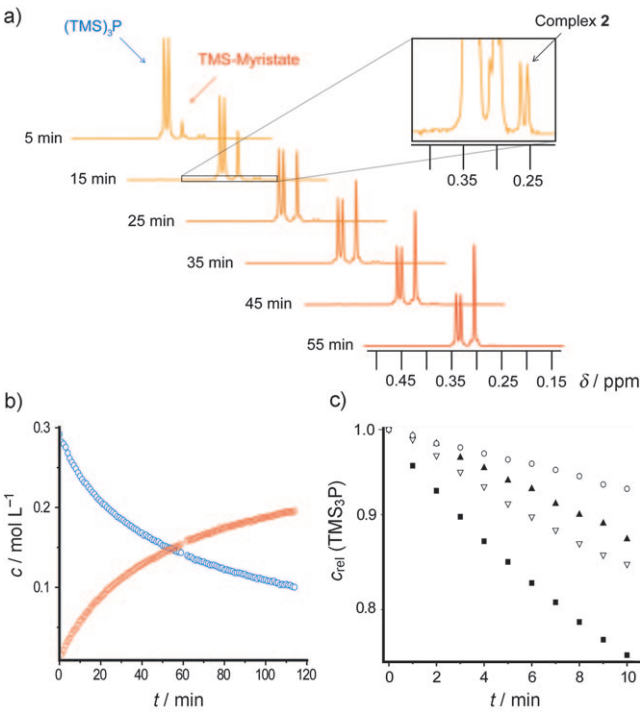

Figure 2. a) Time-resolved ^{1}H NMR spectra at 40 °C, showing evolution of $(TMS)_3P$ (blue) and TMS-MA signals (red) during standard conditions for InP QD synthesis with amines. Inset: Detail of the spectrum at 15 minutes. The doublet at $\delta = 0.26$ ppm is assigned to **2**. b) Concentration (c) profiles of $(TMS)_3P$ and TMS-MA protons determined at 1 min intervals by integration of spectra represented in Figure 2a. c) Concentration profiles of $(TMS)_3P$ for InP QD syntheses with varying amine concentrations at 40 °C, normalized at $t = 0$. [amine]/[In]: ○ 36:1, ▲ 18:1, ▽ 12:1, ■ 6:1. Reaction rate decreases with increasing amine concentration; reactions without amines reach completion too rapidly to be resolved with our method.

(Figure 2c); thus amines inhibit rather than activate[2,10–13] InP synthesis. As a change in amine ratio influences the rate even at high concentrations, and as the rates do not have a clear power dependence on octylamine concentration in either this or prior studies,[13] the amine does not have a well-defined stoichiometry during the rate-determining step. For ratios of octylamine to indium of greater than 18:1, we observed a diminishing change in the rate with added amine. The reactions with high octylamine content also yielded an increase in the TMS-OA product, which complicates kinetic analysis.

We find no evidence for other molecular phosphorus compounds, such as P–H-containing species. The only resonances in the ^{31}P NMR spectra correspond to $(TMS)_3P$ and **2** (Supporting Information, Figure S11). When monitoring the depletion of $(TMS)_3P$ at various octylamine concentrations, we do not observe doublets in the ^{1}H NMR spectrum that would indicate the formation of P–H species, so this reaction does not appear to be a significant pathway in the decomposition of $(TMS)_3P$.

To account for the mechanism of amine inhibition, we measured the initial reaction rate at various temperatures; these data are summarized in an Eyring plot (Figure 3). The activation entropy indicates that the reaction proceeds via an

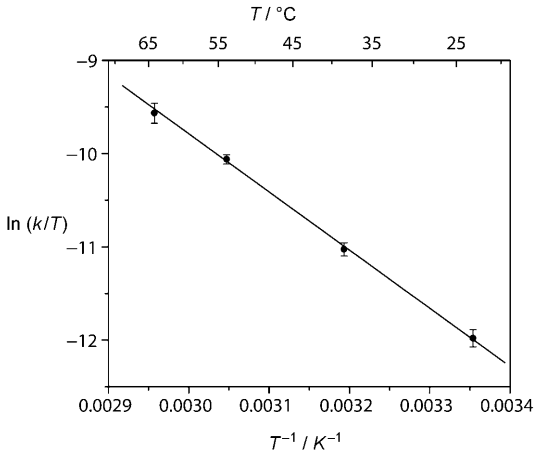

Figure 3. Eyring plot for amine-based synthesis of colloidal InP QDs, with $\Delta H^{\ddagger} = 51.9 \pm 1.3$ kJ mol^{-1} and $\Delta S^{\ddagger} = -126 \pm 4$ J mol^{-1} K^{-1}. Each data point was acquired three times, and temperature error was negligible.

ordered transition state, which is likely from an arrangement of two or more species. The activation enthalpy ($\Delta H^{\ddagger} = (51.9 \pm 1.3)$ kJ mol^{-}) is about 10 kJ mol^{-1} less than that measured by Liu et al. for CdSe nanocrystal formation,[7] which is plausible for the highly reactive precursors used during InP QD synthesis. The addition of octylamine may decrease the rate (and increase $\Delta G^{\ddagger}$) by stabilizing the enthalpy of precursors (increasing $\Delta H^{\ddagger}$), but octylamine may also influence the activation entropy.

The amine inhibition of InP synthesis results from solvation effects during the steps that lead to complex **1**, **2**, or both. As the concentration of a competing Lewis base increases, the sterically hindered $(TMS)_3P$ molecule is less likely to approach the indium center. Therefore, an increase in amine concentration decreases the formation of **1**, and the observed saturation behavior may arise from crowding of the $In(MA)_3$ ligand sphere.

The large negative $\Delta S^{\ddagger} = (-126 \pm 4)$ J mol^{-1} K^{-1} and the more than thousandfold decrease in rate upon addition of amines are also consistent with solvation changes during nucleophilic substitution.[16] Strong solvation effects are rarely observed for isopolar transition states (e.g. for pericyclic reactions), so it is unlikely that the route from **1** to **2** occurs in a single step. A potential step for this reaction is via a S_N2 transition state that results in charge dispersion. During charge-dispersive S_N2 reactions, charged species react to form uncharged products. Because octylamine can hydrogen-bond more strongly with the attacking nucleophiles than with **2**, an increase in amine concentration hinders the formation of the transition state, and thus decreases the formation of **2**.

In conclusion, we find that currently reported InP QD syntheses are based on non-molecular ripening processes. We demonstrated that amines inhibit precursor decomposition, which we rationalize by one or more solvation effects. It is apparent that the challenges in the synthesis of III–V (Group 13/15) QDs are not due to differences in the bonding between II–VI or IV–VI and III–V semiconductors, but instead result from the depletion of molecular precursors following QD nucleation in current III–V QD syntheses.

Experimental Section

Reactions were performed in 600 MHz J-Young NMR tubes. $[D_8]$-toluene, $[D_4]$-1,2-dichlorobenzene (C.I.L.), diphenylmethane, octylamine (Fluka), and all the reaction solutions were stored over 4 Å molecular sieves prior to use. $(TMS)_3P$ (Strem) was used without further purification, and $In(MA)_3$ was prepared as previously reported.[17] NMR samples were prepared in $[D_8]$toluene by mixing 0.35 mL of 0.04 M $In(MA)_3$, 0.06 M diphenylmethane, and 0.0–1.44 M octylamine with 0.35 mL of 0.02 M $(TMS)_3P$ in a nitrogen-filled glovebox, under minimal lighting, and then immediately transferred into a variable-temperature 500 MHz Varian NMR for ^{1}H and ^{31}P spectroscopic analysis. A detailed explanation of the kinetic analysis and additional experimental details can be found in the Supporting Information.

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