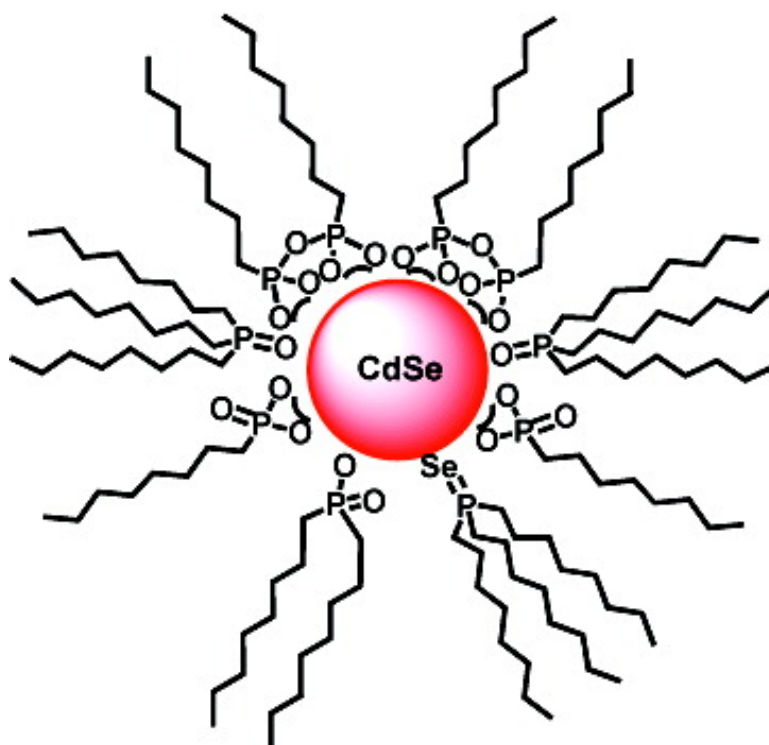


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Identification of Acidic Phosphorus-Containing Ligands Involved in the Surface Chemistry of CdSe Nanoparticles Prepared in Tri-*n*-octylphosphine Oxide Solvents

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Abstract: The surface ligand composition of CdSe nanoparticles prepared using technical grade tri-*n*-octylphosphine oxide (TOPO) was investigated using a nucleophilic ligand displacement methodology and ^{31}P $\{^1\text{H}\}$ NMR spectroscopy. 4-(*N,N*-Dimethylamino)pyridine (DMAP) and benzyltrimethylammonium propionate were added to tetrahydrofuran solutions of CdSe nanoparticles prepared in technical grade TOPO. DMAP was shown to be a sufficiently strong nucleophile to displace the more weakly coordinating ligands, TOPO, TOPSe, di-*n*-octylphosphinate, and *n*-octylphosphonate (OPA). Benzyltrimethylammonium propionate was shown to be a stronger nucleophile than DMAP in that it could displace all the aforementioned surface-bound ligands as well as a previously unidentified surface-bound phosphorus species. Independent synthesis and ^{31}P $\{^1\text{H}\}$ NMR spectral matching confirmed that the new species was *P,P'*-(di-*n*-octyl) dihydrogen pyrophosphonic acid (PPA). The PPA was shown to form during the nanoparticle synthesis via the dehydrative condensation of OPA. CdSe nanoparticle syntheses were performed using pure TOPO and added OPA, and subsequent displacement experiments showed that OPA and PPA were the predominant surface-bound ligands. CdSe nanoparticle syntheses were performed using pure TOPO and added PPA, and subsequent displacement experiments showed that PPA was the predominant surface-bound ligand. PPA was also shown to have the greatest affinity for the nanoparticle surface of all the ligands investigated. Thus, a model for the surface ligand composition could be developed for nanoparticles prepared using technical grade TOPO or other high-boiling solvents with added acidic phosphorus compounds.

Introduction

Semiconductor nanoparticles, such as CdSe, display intense and narrow photoemission profiles, and due to quantum confinement, the emission maximum can be tuned in correspondence with particle diameter.^{1–5} The shape of the nanoparticle also can be controlled through changes in the synthetic conditions.^{6–9} Consequently, these nanoparticles are envisioned for use in various electronic, optical, and biological applications.^{10–15} The ligand layer on the nanoparticle is the key parameter to

controlling particles' solvent dispersibility, effective volume, adhesion to substrates, functionalization, and surface charge. As such, it is important to understand the precise composition of the nanoparticle ligand layer and how variations in the synthetic procedure influence this final composition.

Many synthetic pathways have been reported for obtaining focused particle size distributions and different shapes of CdSe nanoparticles. Typical preparations of CdSe nanoparticles involve the high-temperature reaction of inorganic Se and Cd precursors, such as trioctylphosphine selenide (TOPSe) and CdO, Cd(OAc)₂, or Cd(CH₃)₂.^{1,16} High-boiling-point solvents are used for this procedure, and technical grade tri-*n*-octylphosphine oxide (TOPO) has been one of the most widely used. Because technical grade TOPO has a purity of ~90%, the species comprising the other 10% can play a significant role during the synthesis. Indeed, the "lore" associated with using technical grade TOPO is that CdSe nanoparticle syntheses utilizing different commercial batches of this solvent can yield significantly varying results. Consequently, there have been reports on variants of this synthesis utilizing pure TOPO, or other high-boiling solvents, with added surface stabilizers, such

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as long aliphatic chain amines or carboxylic acids, to control particle growth and to prevent particle coalescence.^{1,17,18}

There are many literature models for the surface ligand composition of CdSe nanoparticles prepared in TOPO solvent. Some describe the surface as being coated with TOPO molecules, rendering it hydrophobic.³ Other publications affirm that when carboxylic acid stabilizers are used, only carboxylic acids are found on the particle surface. In a recent publication, Wang et al. prepared CdSe nanorods using phosphonic acid additives in the synthesis, digested the products in aqua regia, and then studied the ³¹P {¹H} NMR spectra of the organic extracts.⁹ The results showed that the predominant phosphorus species obtained were phosphonic acids.

The surface ligand layer can be rather labile. Literature reports^{19–21} (as well as our own observations) indicate that multiple precipitation and centrifugation cycles often cause the nanoparticles to aggregate and precipitate from solution, presumably due to the loss of surface passivating ligands. Many reported methods on the assembly or application of CdSe nanoparticles take advantage of the lability of the surface ligands to derivatize the nanoparticle surface. Perhaps the most widely used surface functionalization procedure involves displacement of the surface ligands (typically assumed to be TOPO) with a difunctional molecule containing a surface-binding functional group at one end and a desired functional group at the other end. Examples include ω -thiol- α -carboxylic acids,²² 4-substituted pyridines,²³ glutathione,¹³ ω -thiol- α -siloxanes,²⁴ and alkyl phosphine oxides that contain a functional group in one of the alkyl “tails”.²⁵ Polymeric ligands have also been employed in this manner.²⁶

A very different approach also has been developed that involves assembling a polymer about the nanoparticle surface and then cross-linking the polymer into a network cage. It is presumed but not confirmed that the surface ligand layer on the CdSe nanoparticle remains intact. In one such system, amphiphilic copolymers with random sequences of carboxylic acid and long alkyl side chains along the backbone were used in the assembly step, and cross-linking was achieved using a diamine and amide-forming conditions.^{27,28} Excess unreacted functional groups within the polymer network were used for further conjugation.

Despite its central role in applications of CdSe nanoparticles, much remains to be learned about the chemistry of the surface ligand layer. Information such as precise surface ligand compositions, chemistries that govern surface ligand displacement, and factors that govern amphiphilic polymer assembly onto the nanoparticle surface must be obtained for further study. Such

knowledge would allow a more rational approach to surface functionalization methodologies with retention of the inorganic core's desirable optical properties.^{29–31} Here we report ³¹P {¹H} NMR spectroscopic analysis of the ligand layer on the surface of CdSe nanoparticles prepared using technical grade TOPO as the solvent and pure TOPO with various surface-stabilizing additives. The nature of the ligands covering the particle surface was deduced by sequential displacement under mild conditions (in order to avoid chemical alteration of the ligands) using nucleophiles of increasing strength. The results were used to design a new synthetic procedure to generate directly CdSe nanoparticles with well-defined, single-ligand surface layer compositions.

Experimental Section

Chemicals. Technical grade (90%) tri-*n*-octylphosphine oxide (tech TOPO), high-purity (99%) tri-*n*-octylphosphine oxide (TOPO), technical grade (90%) tri-*n*-octylphosphine (TOP), technical grade (90%) 1-octadecene (ODE), cadmium acetate hydrate (Cd(OAc)₂, 99.99+%), *N,N'*-dicyclohexylcarbodiimide (DCC, 99%), and selenium powder (100 mesh) were purchased from Aldrich. 4-(*N,N*-Dimethylamino)pyridine (DMAP, 99%), propionic acid (99%), and benzyltrimethylammonium hydroxide (Triton B, 40 wt % in methanol) were purchased from Acros. *n*-Octylphosphonic acid (OPA, 99%) was purchased from Lancaster Chemical. All materials were used without further purification, and all solvents were obtained from commercial sources as reagent grade and used as received.

For all nanoparticle syntheses, the reagents and reaction solutions were handled under nitrogen atmospheres using Schlenk and glovebox techniques.

Characterization. ³¹P {¹H} NMR spectra were recorded in CDCl₃, CD₃OD, or C₆D₆ and at 121 MHz on a Varian spectrometer. Chemical shift values, δ (ppm), were referenced to H₃PO₄ (0 ppm) as an external standard. ¹H and ¹³C {¹H} NMR spectra were recorded on a Varian 300 or 400 MHz spectrometer using the residual proton or carbon signals from the indicated solvent as a referencing standard. Transmission electron microscopy (TEM) was performed using a Phillips CM-12 microscope. Samples were diluted and dropped directly onto carbon-coated copper grids. Elemental analyses were performed by Midwest Microlabs (Indianapolis, IN).

Synthesis of CdSe Nanoparticles Using Technical Grade TOPO. CdSe nanoparticles were synthesized using modifications of previously reported syntheses.²² A sealed 50 mL round-bottom Schlenk flask containing a stir bar, Cd(OAc)₂ (0.100 g, 0.434 mmol), and tech TOPO (10.0 g, ~26.0 mmol) was subjected to three successive vacuum/backfill degassing cycles. A heating mantle equipped with a thermocouple was used to heat the solution to 310 °C under a N₂ flow. A solution of trioctylphosphine selenide (TOPSe), prepared by combining Se (0.206 g, 2.60 mmol) and TOP (2.33 g, 6.28 mmol), was then swiftly injected via syringe into the rapidly stirred reaction solution. The reaction temperature dropped to 285–300 °C, and the nanoparticle growth proceeded in this temperature range until the solution turned dark red, which usually occurred in a period ranging from 3 to 13 min. Nanoparticle growth was terminated by removing the heat source and allowing the solution to cool to room temperature.

Isolation and purification of the CdSe nanoparticles was performed by first precipitating the nanoparticles from the reaction mixture using equal amounts of acetone and methanol (~25 mL of each). After centrifugation and separation of the solids from the

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supernatant, the pellet of nanoparticles was dispersed in 10 mL of tetrahydrofuran (THF). This precipitation and redispersion cycle was completed a total of three times, and the nanoparticles were stored as dilute solutions in THF.

Synthesis of CdSe Nanoparticles Using a Mixture of High-Purity TOPO and OPA. Using a synthetic route identical to that described above, Cd(OAc)₂ (0.100 g, 0.434 mmol), pure TOPO (8.39 g, 21.7 mmol), OPA (250 to 20 mg, 1.29 to 0.100 mmol), and a stir bar were loaded into a 50 mL round-bottom Schlenk flask that was then sealed with a rubber septum. The TOPO/OPA mixtures used ranged from 0.50 to 5.6 mol % of OPA. The solution was degassed via three vacuum/backfill cycles, and the components were heated at 330 °C. Once the solution became optically transparent, a solution of TOPSe, prepared from 0.104 g (1.30 mmol) of Se dissolved in TOP (3.99 g, 10.8 mmol), was taken from the drybox and swiftly injected via syringe into the rapidly stirred reaction mixture. Nanoparticle growth proceeded in the temperature range 295–310 °C until the reaction turned red (3–6 min). Purification of the resulting nanoparticles followed the above procedure.

Synthesis of CdSe Nanoparticles Using 1-Octadecene Solvent. Following a synthetic procedure similar to that described above, CdSe nanoparticles were prepared using ODE in place of TOPO as follows: Cd(OAc)₂ (0.100 g, 0.434 mmol), ODE (10.0 g, 39.7 mmol), OPA (0.300 g, 1.55 mmol), and a stir bar were loaded into a 50 mL round-bottom Schlenk flask, which was sealed using a rubber septum. The mixture was heated at 80 °C under vacuum for 30 min. The solution was degassed via three vacuum/backfill cycles, and the temperature of the solution was increased to 300 °C. Once the temperature had stabilized, a solution of TOPSe, prepared from 0.104 g (1.30 mmol) of Se dissolved in TOP (3.99 g, 10.8 mmol), was swiftly injected via syringe into the reaction flask. The temperature dropped 20 °C immediately after injection and was maintained at 280 °C for a growth period of 4 min. Purification of the resulting nanoparticles followed the procedure described above.

Synthesis of P,P'-(Di-n-octyl) Dihydrogen Pyrophosphonic Acid (PPA). This compound was prepared following a literature method used to synthesize other pyrophosphonic acid derivatives.³² In a 50 mL round-bottom flask, 0.647 g (3.33 mmol) of OPA was dissolved in 40 mL of anhydrous diethyl ether. A solution of 0.378 g (1.83 mmol) of DCC in 5 mL of anhydrous diethyl ether was added, and the mixture was stirred at room temperature for 25 min. A white precipitate of N,N'-dicyclohexylurea formed almost immediately and afterward was removed by gravity filtration. The filtrate was reduced to 10 mL via rotary evaporation. A white solid formed upon cooling the concentrated solution to 0 °C, and the solid was isolated by vacuum filtration. Recrystallization from diethyl ether yielded PPA as colorless crystals (0.545 g, 57%). ¹H NMR (CDCl₃): δ 11.8 (br s, 2H, OH), 1.8 (m, 4H, P-CH₂), 1.5–1.7 (br m, 24H, CH₂), 0.9 (t, 6H, CH₃). ¹³C{¹H} NMR (CDCl₃): δ 32.0, 30.5, 29.2, 27.4, 25.2, 22.9, 22.1, 14.3 (CH₂). ³¹P{¹³C} NMR (CDCl₃): δ 25.3. Anal. Calcd for C₁₆H₃₆O₅P₂: C, 51.97; H, 9.73; P, 17.01. Found: C, 51.88; H, 9.80; P, 16.71.

Synthesis of CdSe Nanoparticles Using High-Purity TOPO and PPA. In a typical synthesis, PPA (92 to 25 mg, 0.25 to 0.068 mmol), Cd(OAc)₂ (0.100 g, 0.434 mmol), and TOPO (8.39 g, 21.7 mmol) were loaded into a 50 mL round-bottom Schlenk flask containing a stir bar. The TOPO/OPA mixtures used ranged from 0.30 to 1.1 mol % of OPA. The solution was degassed by sequential vacuum/backfill cycles and heated at 330 °C. A solution of TOPSe, prepared from 0.206 g (2.60 mmol) of Se dissolved in 2.33 g (6.28 mmol) of TOP, was swiftly injected via syringe into the reaction flask. Nanoparticle growth proceeded for 3–5 min at the temperature range 292–315 °C. Purification of the resulting nanoparticles followed the procedure described above.

General Procedure for the Displacement of CdSe Surface

Ligands. In a typical surface ligand displacement experiment, 30–40 mg of purified CdSe nanoparticles was dissolved in 4 mL of THF in a 15 mL round-bottom flask equipped with a stir bar. A THF/methanol solution of the nucleophile (DMAP or carboxylate salt) was added directly to the stirred nanoparticle dispersion, and the components were stirred for 12 h at room temperature.

In a typical DMAP experiment, 70 mg of DMAP was dissolved in 2 mL of THF and 0.5 mL of methanol. For the DMAP titration experiment, DMAP was added in 20 mg increments, beginning with the addition of 10 mg, directly to the THF solution of nanoparticles. After each addition of DMAP, the solution was stirred at room temperature for 2 h. Between each DMAP addition, the THF was removed via rotary evaporation and replaced with either CDCl₃ or CD₃OD for ³¹P {¹H} NMR spectroscopic analysis. After analysis, the NMR solvent was removed via rotary evaporation and replaced with 3–4 mL of THF for the next DMAP addition.

In a typical carboxylate displacement experiment, 20 mg of propionic acid was diluted with methanol (2 mL). A stoichiometric amount of Triton B (119 μL) was added to this solution, and solvent was removed by rotary evaporation to yield a clear gel. This residue was dissolved in 2 mL of THF and added to a 1 mL solution of the nanoparticles in THF. The mixture was stirred for 12 h. For analysis, THF was removed via rotary evaporation, and the residue was dissolved in CDCl₃ for ³¹P {¹H} NMR spectroscopic analysis.

Experiments in which DMAP-treated particles were subsequently reacted with the propionate salt were performed by first isolating the DMAP-treated particles by concentrating the THF mixture down to 1 mL volume and then precipitating the particles via the addition of 5 mL of hexane. The particles were then isolated by centrifugation. The absence of free ligands was confirmed by dissolving the pellet in CD₃OD and recording a ³¹P {¹H} NMR spectrum. The CD₃OD was removed by rotary evaporation and replaced with 4 mL of THF. A propionate salt solution (20 mg of propionic acid and 119 μL of Triton B in 1 mL of THF) was then added, and the solution was stirred for 12 h. The reaction solvent was removed by rotary evaporation and replaced with CDCl₃ for ³¹P {¹H} NMR spectroscopic analysis.

Similar to the propionate displacement reactions, decanoic acid (150 mg) was dissolved in THF and methanol (0.5 mL of each) and neutralized with a stoichiometric amount of Triton B (230 μL). The solvent was removed via rotary evaporation, and then the solid was dissolved in 1 mL of THF. This decanoate salt solution was added to the nanoparticle suspension, and the solution either was stirred at room temperature for 12 h or was heated at reflux for 2 h.

CdSe nanoparticle samples for elemental analysis were prepared by concentrating the reaction volume to 1 mL and adding 5 mL of hexane (or methanol for the decanoic acid displacement workup) to precipitate the particles. After centrifugation, the solid pellet was isolated and dried under vacuum for 4 h.

Results and Discussion

Becerra and co-workers used ³¹P {¹H} NMR spectroscopy to characterize CdSe nanoparticle surfaces prepared in TOPO solvent, and the spectra displayed broadened signals attributed to surface-bound phosphorus ligands in nonhomogeneous nuclear environments.^{33,34} A duplicate ³¹P {¹H} NMR spectrum of CdSe nanoparticles synthesized using technical grade TOPO is shown in Figure 1A. The most prominent signal is centered at 30 ppm, and smaller signals are centered around 15 and –5 ppm. The number and position of these signals is consistent with the presence of at least three types of surface-bound phosphorus ligands, as smaller signals may be obscured by the

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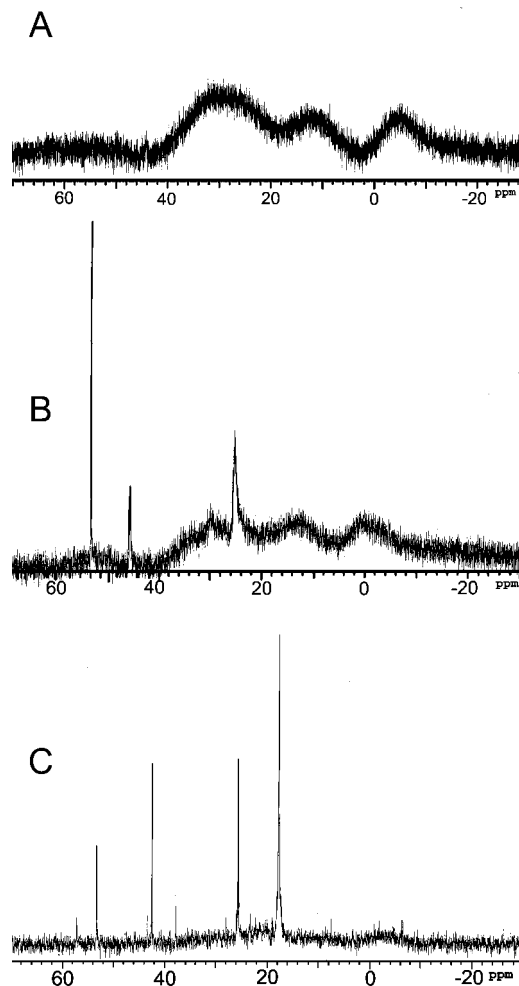


Figure 1. ^{31}P $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 25°C of (A) a solution of CdSe nanoparticles synthesized using technical grade TOPO; (B) the solution after treatment of the nanoparticles in (A) with DMAP; and (C) the solution after treatment of the nanoparticles in (A) with propionate salt solution.

larger ones. An exact assignment of these signals to species used during the synthesis (TOPO, TOPSe, and tri-*n*-octylphosphine [TOP]) could not be made, because there is little experimental data on the chemical shifts of phosphorus-based ligands coordinated to CdSe surfaces. A TEM image of the nanoparticles is shown in Figure 2A, and the average diameter of the nanoparticles was 4.8 ± 0.5 nm, consistent with literature results.

To facilitate analysis and assignment of the surface-bound species, we opted to displace the ligands using nucleophilic reagents of varying strengths.^{19,35} In a typical experiment, the nucleophile was added to a nanoparticle solution in THF solvent, and after a given amount of time the solvent was evaporated and NMR solvent was added to the residue. After all of the residue had dissolved, the solution was transferred to an NMR tube, and an NMR spectrum was recorded. Solution NMR spectra of the free ligands would give sharp signals with distinct chemical shifts and therefore make for easier and more meaningful assignments. Additionally, if a significant amount of phosphorus species was still on the nanoparticles, then the corresponding broad signals would be observed in the spectrum. The possibility of chemical deterioration of the ligands during

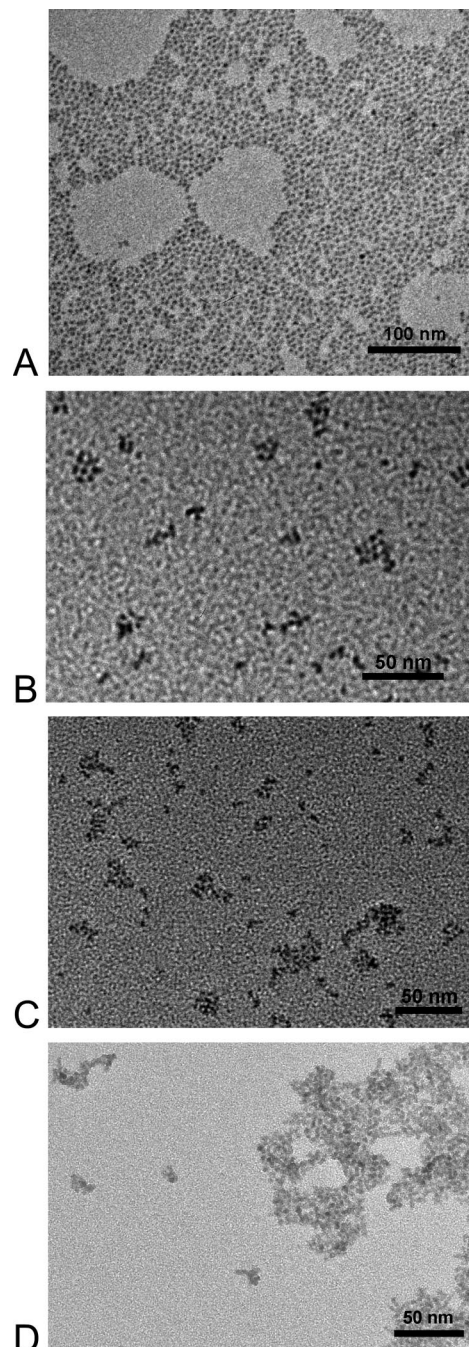


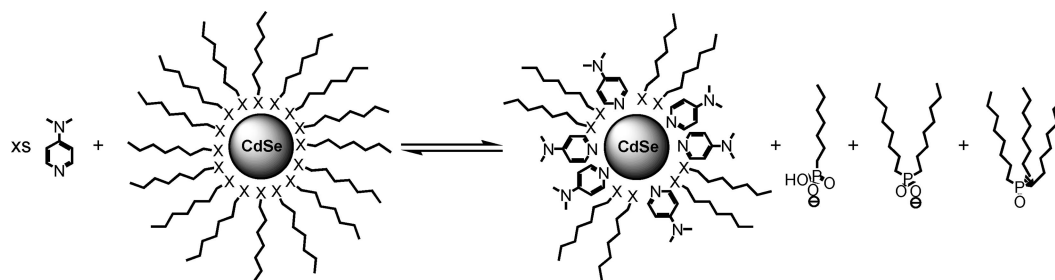
Figure 2. TEM images of (A) CdSe nanoparticles synthesized using technical grade TOPO; (B) CdSe nanoparticles synthesized using high-purity TOPO and 5.6 mol % of added OPA; (C) CdSe nanoparticles synthesized using high-purity TOPO and 1.1 mol % of added PPA; and (D) CdSe nanoparticles synthesized using 1-octadecene and 3.7 mol % of added OPA.

room-temperature nucleophilic displacement is small, affording minimal ambiguity. Furthermore, the relative strength of the interaction between the ligand and the surface could be judged qualitatively by the type of nucleophilic reagent needed to displace it from the surface.

Heating CdSe nanoparticles at reflux in pyridine is a frequently used method to displace the surface ligands.^{35–37} Our attempts at using this procedure failed to yield solutions with any detectable sharp ^{31}P $\{^1\text{H}\}$ NMR signals, a result likely attributable to the variability of the CdSe synthesis using different batches of technical grade TOPO. Treatment of the

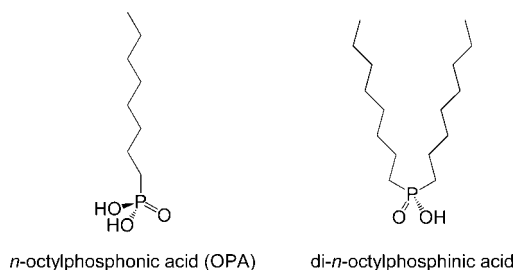
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Scheme 1



CdSe nanoparticles with a stronger nucleophile, 4-(*N,N*-dimethylamino)pyridine (DMAP), was successful in displacing ligands from the surface. A ^{31}P $\{^1\text{H}\}$ spectrum of the residue after reaction for several hours in THF solution at room temperature showed three prominent sharp peaks at 25, 44, and 52 ppm (Figure 1B). Before assignment of the signals, we repeated the experiment with the DMAP added in small increments. After an initial addition of 10 mg of DMAP, the signal at 44 ppm was observed. After a total of 20 mg of DMAP was added, a second peak was observed in the NMR spectrum at 52 ppm. Finally, after the addition of a total of 70 mg of DMAP (roughly a 10-fold excess relative to the theoretical number of TOPO that could coordinate to the surface of the average sized nanoparticle), a third sharp peak was observed at 25 ppm. The broad peaks associated with surface-bound ligands were still observed in the ^{31}P $\{^1\text{H}\}$ NMR spectra of CdSe nanoparticles, even after stirring them with a large concentration of DMAP for several days. This observation was consistent with earlier literature reports of incomplete CdSe ligand exchange reactions using amine nucleophiles.^{26,34,38}

Tabulated ^{31}P $\{^1\text{H}\}$ NMR data were used to assist in the assignment of the sharp signals (Scheme 1).³⁹ The peak at 52 ppm was assigned to free TOPO, while we suspected that the peak at 25 ppm was due to an alkylphosphonate salt. The latter assignment was confirmed by acquiring a ^{31}P $\{^1\text{H}\}$ NMR spectrum of *n*-octylphosphonic acid (OPA) neutralized with either a stoichiometric amount of benzyltrimethylammonium hydroxide (Triton B) or DMAP in CDCl_3 .



Both spectra exhibited chemical shift values at 25 ppm, consistent with the chemical shift of the second signal and with literature ^{31}P $\{^1\text{H}\}$ NMR data on various phosphonates in the pH range above 7.0.^{40–42} The peak at 44 ppm was assigned as

a dialkylphosphinate salt, which is known to be one of the major impurities in technical grade TOPO.⁴³ This chemical shift assignment was confirmed through independent synthesis of a sample of di-*n*-octylphosphinic acid⁴⁴ and the inspection of its ^{31}P $\{^1\text{H}\}$ NMR spectrum after neutralization with a stoichiometric amount of either Triton B or DMAP. We also note that dialkylphosphinates were observed previously to be a strongly binding ligand for CdSe.⁶

Because the surfaces contained anionic phosphorus ligands, we decided to employ a stronger, negatively charged nucleophile in the displacement experiments: alkyl carboxylates. Qu et al.¹ showed that long-chain carboxylic acids can be used as stabilizers in the preparation of CdSe nanoparticles, so carboxylate salts should display good affinity for the nanoparticle surface. The same protocol used for the DMAP displacement experiments was used in these NMR procedures, except that a stoichiometric amount of base (Triton B) was added to the carboxylic acid (in this case, propionic acid) in THF to generate the carboxylate salt *in situ*. The nanoparticle and benzyltrimethylammonium propionate solution was allowed to sit for 12 h before a ^{31}P $\{^1\text{H}\}$ NMR spectrum was recorded.

The same CdSe nanoparticles used for the DMAP displacement experiments were treated with the propionate salt solution (Scheme 2), and the ^{31}P $\{^1\text{H}\}$ NMR spectrum (Figure 1C) of the residue exhibited four primary sharp peaks. Three of these signals were the same as those observed in the aforementioned DMAP displacement experiments (i.e., 53, 44, and 25 ppm, assigned as free TOPO, di-*n*-octylphosphinate, and *n*-octylphosphonate, respectively); however, a new signal at 18 ppm was observed. Furthermore, in contrast to the DMAP-experiment spectra, the broadened phosphorus signals underlying the sharper signals were not observed, which suggests that higher surface ligand exchange efficiency was achieved using benzyltrimethylammonium propionate.

On a side note, ω -thiol- α -carboxylic acids often are used to modify the surface of CdSe nanoparticles and provide an exterior containing carboxylic acid functional groups. Also, amphiphilic random copolymers with long alkyl side chains interspersed with carboxylic acid groups have been used to form a polymer assembly around the nanoparticle with the carboxylic acid groups exposed to the exterior solution. Considering the affinity of carboxylate functional groups to the surface of CdSe nanoparticles, it might be of value to determine the extent to which the carboxylate group is associated with the surface versus the other desired functional groups.

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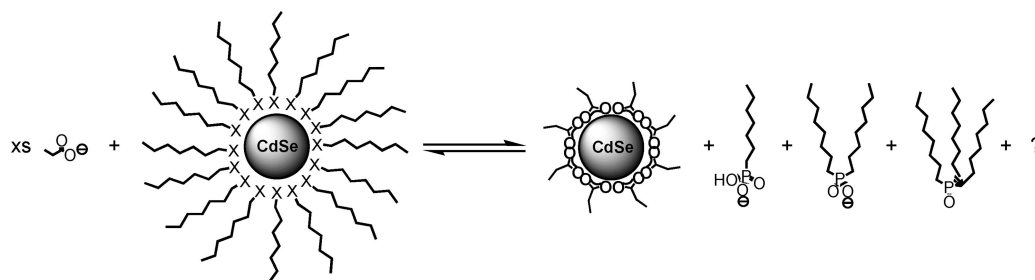
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Scheme 2



We were unable to assign the signal at 18 ppm, so we reformulated the synthetic procedure to add in known impurities systematically and to determine the corresponding surface ligand compositions. According to a general literature procedure,^{1,16} CdSe nanoparticles were synthesized using pure TOPO (99%) solvent in conjunction with OPA added as the “impurity”. In this set of syntheses, the amount of added OPA was varied from 0.30 to 3.6 mol % (20–250 mg) based on the total moles of TOPO. This concentration range was below the minimum value required for nonspherical nanocrystal formation and above the threshold point (0.30 mol %) where only dark brown suspensions of CdSe formed that could not be dispersed in THF.

The nanoparticle growth kinetics varied significantly upon changing the concentration of OPA, which can be attributed to the high stability of phosphonic acid/cadmium ion intermediates.⁷ For example, reactions involving lower amounts of OPA (~0.5 mol %) required decreased reaction temperatures and shorter reaction times to generate the target nanoparticles (we used the formation of a light red colored solution as a qualitative end point to determine when the CdSe nanoparticle diameter had reached 3.5 ± 1 nm). Conversely, reactions involving higher OPA concentrations required higher reaction temperatures and longer reaction times to reach the same end point.

The ^{31}P { ^1H } NMR spectrum of nanoparticles prepared using ~3.6 mol % of OPA (Figure 3A) exhibited at least two broad signals: a large feature centered at 25 ppm and a smaller shoulder feature centered at 33 ppm. There was a notable absence of at least one of the broad features present in the spectra of particles made using technical grade TOPO (Figure 1A), which would be consistent with the nanoparticle surface having fewer types of phosphorus ligands. A TEM image of the nanoparticles is shown in Figure 2B, with an average nanoparticle diameter of 3.3 ± 0.4 nm.

The addition of DMAP to a sample of these CdSe nanoparticles yielded a residue whose ^{31}P { ^1H } NMR spectrum contained only one sharp peak (Figure 3B, Scheme 3). A puzzling feature of this spectrum was the absence of any sharp signals corresponding to TOPO liberated from the surface. This result is notwithstanding the fact that TOPO was present during the synthesis in great excess relative to OPA. Literature studies have demonstrated that the phosphonic acid functional group adheres strongly to the CdSe surface,^{8,30,45} so the absence of any detectable TOPO from the displacement experiment might

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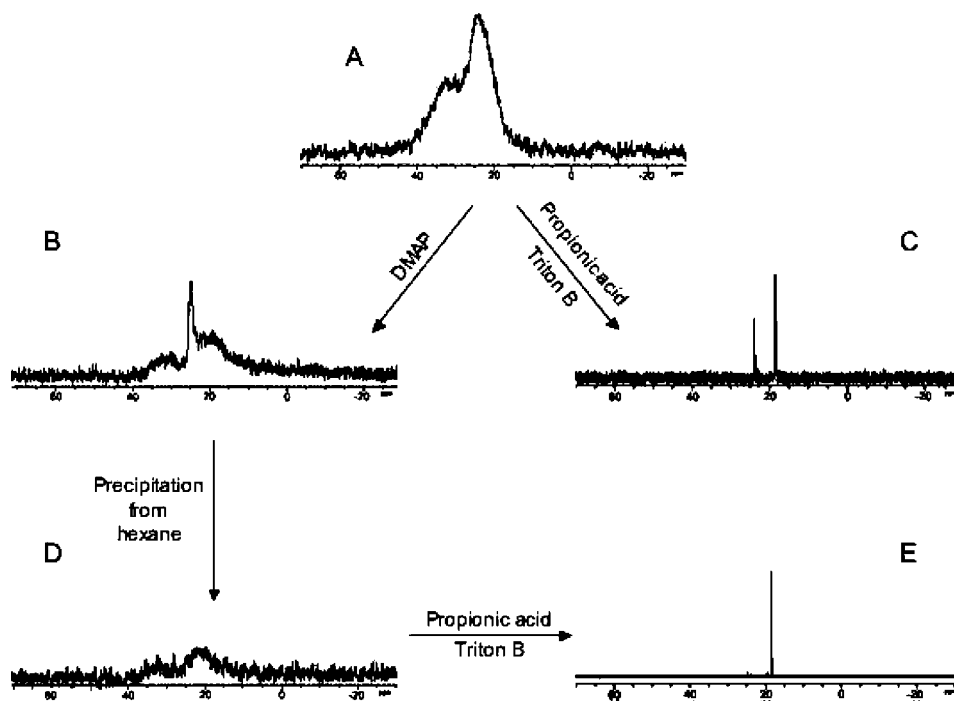
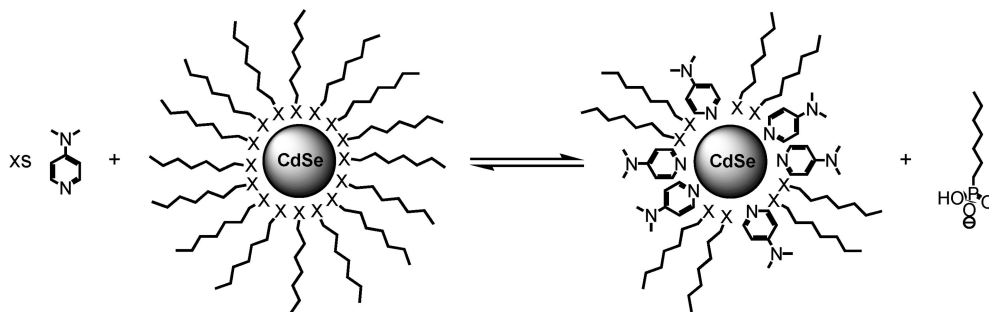
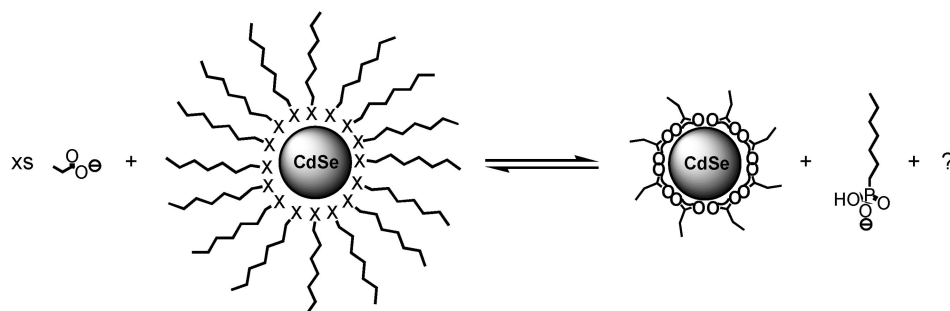


Figure 3. ^{31}P { ^1H } NMR spectra in either CDCl_3 (A–C,E) or CD_3OD (D) at 25 °C of (A) a solution of CdSe nanoparticles synthesized using high-purity TOPO and 5.6 mol % of added OPA; (B) the solution after treatment of the nanoparticles in (A) with DMAP; (C) the nanoparticles precipitated from the solution in (B); (D) the solution after treatment of the nanoparticles in (C) with propionate salt solution; and (E) the solution after treatment of the nanoparticles in (A) with propionate salt solution.

Scheme 3



Scheme 4

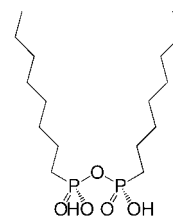


indicate that it was completely excluded from binding to the surface. Standard literature workup procedures were followed during the synthesis, so the possibility cannot be precluded that some surface TOPO was lost during the nanoparticle isolation steps. Another feature of the spectrum was the significant presence of broad signals, indicating that the nanoparticle surface still contained a significant amount of phosphorus ligands that were not displaced by DMAP.

When another portion of the nanoparticles was treated with the benzyltrimethylammonium propionate solution, the ^{31}P $\{^1\text{H}\}$ NMR spectrum of the residue exhibited two sharp signals (Figure 3C, Scheme 4). The sharp peak at 25 ppm was readily identified as *n*-octylphosphonate; however, the unassigned signal at 18 ppm was again observed. This result was unanticipated, because the synthesis was performed using pure reagents whose ^{31}P $\{^1\text{H}\}$ NMR spectra were checked beforehand to rule out the presence of further impurities. Next, we performed the ligand displacement reaction in two steps. First, a DMAP displacement reaction was performed, and the resulting nanoparticles were isolated by concentrating the THF mixture and adding hexane to precipitate the particles. After isolating the particles by centrifugation and redissolving the pellet in CD_3OD , the resulting ^{31}P $\{^1\text{H}\}$ NMR spectrum (Figure 1D) confirmed the removal of solution-phase OPA (i.e., no sharp signal at 25 ppm). The broad signal(s) indicated that surface-bound phosphorus species were still present. This material was then treated with the benzyltrimethylammonium propionate solution, and the resulting ^{31}P $\{^1\text{H}\}$ NMR spectrum exhibited a single sharp peak at 18 ppm (Figure 3E). These results are consistent with the unidentified surface-bound phosphorus species having a greater binding affinity for the nanoparticle surface than *n*-octylphosphonate.

Because the unknown species corresponding to the signal at 18 ppm was not present in the starting materials, yet was present on the nanoparticle surface, it must have formed during the synthesis. A reasonable hypothesis is that, at high reaction temperatures, two *n*-octylphosphonic acid molecules condensed

to form the corresponding pyrophosphonic acid derivative (analogous to carboxylic acid anhydride formation).⁴⁶ Liu, et al.⁴⁹ reported a mechanism for the formation of pyrophosphonates from the corresponding phosphonates in the presence of TOPSe. As a test of this idea, *P,P'*-(di-*n*-octyl) dihydrogen pyrophosphonic acid (PPA) was synthesized using reported literature methods.³² The ^{31}P $\{^1\text{H}\}$ chemical shift of PPA in CDCl_3 was 25.3 ppm, and in the presence of 1 equiv of Triton B it was 18 ppm.⁴⁷ These results confirmed the assignment of the unknown signal as PPA.



P,P'-(di-*n*-octyl) dihydrogen pyrophosphonic acid (PPA)

Another observation from conducting all the DMAP and benzyltrimethylammonium propionate displacement experiments was that CdSe nanoparticles synthesized in the presence of even small amounts of OPA (~1 mol %) had surfaces, after isolation using standard procedures, that were exclusively covered with phosphonic acid derivatives (OPA and PPA) and that TOPO and TOPSe were excluded from the surface. Estimated surface area calculations according to previous work (using bulk CdSe

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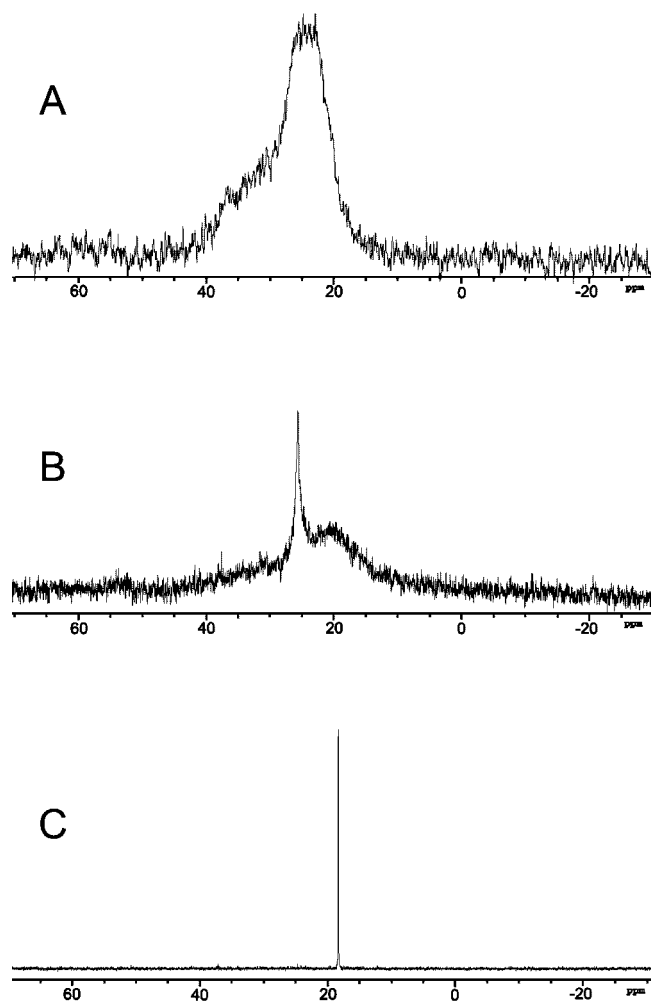


Figure 4. ^{31}P $\{^1\text{H}\}$ NMR spectra in CDCl_3 at $25\text{ }^\circ\text{C}$ of (A) a solution of CdSe nanoparticles synthesized using high-purity TOPO and 1.1 mol % of added PPA; (B) the solution after treatment with the nanoparticles in (A) with DMAP; and (C) the solution after treatment of the nanoparticles in (A) with propionate salt solution.

density and particle diameter)^{34,48} indicated that $\sim 1\%$ of impurity is more than enough to completely passivate every available Cd binding site on the nanoparticle surfaces. In addition, recent *ab initio* calculations⁴⁵ on the binding affinities of various ligands with the CdSe surface indicate that phosphonates are one of the strongest binding ligands for CdSe surfaces.

Since PPA was shown to have a greater affinity for the CdSe surface than OPA, we performed the CdSe nanoparticle syntheses again using pure TOPO solvent but with $\sim 1\%$ PPA as an additive. The ^{31}P $\{^1\text{H}\}$ NMR spectra of the resulting CdSe nanoparticles (Figure 4A) exhibited one broad feature that appeared to contain a slight shoulder similar to that observed in Figure 3A. A TEM image of the nanoparticles is shown in Figure 2C. Treatment of this material with DMAP produced a solution with a single sharp peak at 25 ppm (Figure 4B), consistent with *n*-octylphosphonate. Because OPA was never introduced as part of the synthesis, we attribute its presence here to the hydrolysis of PPA during exposure to DMAP, as no attempt was made to keep the reaction dry. The spectrum also exhibited a large broad peak most likely due to remaining surface-bound PPA. After another sample of the particles was treated with the benzyltrimethylammonium propionate solution

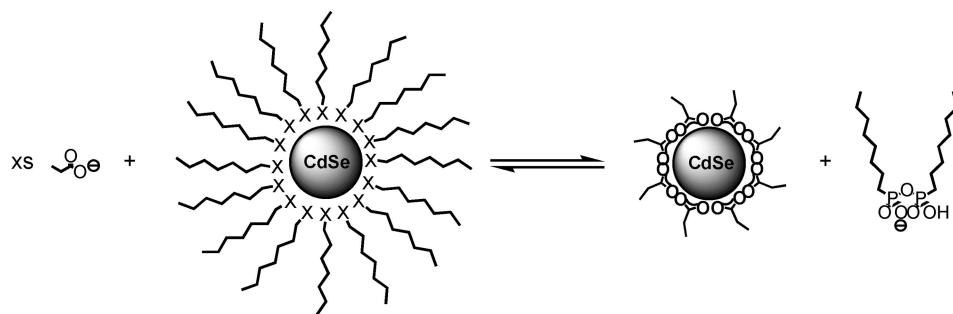
(Scheme 5), the ^{31}P $\{^1\text{H}\}$ NMR spectrum showed only a single signal at 18 ppm and no remaining broad features (Figure 4C), a result consistent with PPA as the primary ligand on the nanoparticle surface and a stronger surface binding ligand than OPA. PPA has two acidic hydroxyl groups and could chelate to the surface cadmium atoms, so in retrospect the relative strength of the surface interaction of PPA versus OPA and the other ligands is consistent with the difference in their structures.

Up to this point, the ^{31}P $\{^1\text{H}\}$ NMR data only provided a qualitative assessment of the percentage of surface ligands removed by propionate or DMAP displacement reactions. Therefore we sought to provide a more quantitative confirmation of the results. First, elemental analysis was performed on several samples of CdSe nanoparticles synthesized using TOPO and 3.6 mol % OPA. A 3.9% phosphorus content was obtained consistently, a number that was in close agreement with phosphorus content estimates calculated using the number of surface cadmium atoms in a nanocrystal of ~ 3.5 nm diameter and the stoichiometric assumption of one phosphorus ligand per surface cadmium. Subjecting a portion of this material to DMAP displacement and subsequent elemental analysis of the resulting nanoparticles yielded a residual phosphorus content of 3.04%, corresponding to the removal of only 25% of the surface phosphorus species. Observation of a finite percentage of nitrogen in the sample (1.7%) confirmed the introduction of DMAP onto the nanoparticle surface. Subjecting another portion of the nanoparticle material to benzyltrimethylammonium propionate displacement and elemental analysis of the nanoparticle residue showed a 62% yield in removal of the surface phosphorus species. The yield of ligand displacement is likely a function of the strength of the nucleophile and the position of the displacement equilibrium under the reaction conditions. Repetition of this experiment with a decanoate salt solution to see if a larger, more soluble carboxylate salt might be more effective in the displacement process yielded a somewhat worse (42%) yield of surface ligand displacement. These experiments confirmed that carboxylate salts are better at displacing surface phosphorus species on CdSe nanoparticles than DMAP and that carboxylate salts can be used to remove a significant percentage of the surface phosphorus species.

Because nanoparticle syntheses using added OPA or PPA appeared to yield samples with little or no TOPO or TOPSe, we decided to conduct experiments in which the amount of added OPA or PPA was intentionally less than stoichiometric relative to the anticipated number of surface cadmium atoms. Presumably, the weaker binding TOPO or TOPSe ligands would be found on the surfaces of the resulting nanoparticles, and their detection in these experiments would further support the conclusion that they were either not present or present in only small numbers on the surfaces of the nanoparticles prepared in the presence of OPA or PPA.

When CdSe nanoparticles were prepared using TOPO and 0.5 mol % added OPA, significantly different behavior was observed in the workup and isolation of the resulting particles as compared to nanoparticle samples prepared using higher amounts of added OPA (i.e., ~ 5 mol %). After the standard precipitation and centrifugation cycles used to purify the nanoparticles, a large majority of sample would no longer separate from methanol by centrifugation, consistent with the loss of surface ligands. The ^{31}P $\{^1\text{H}\}$ NMR spectra of particles retrieved from the workup (Figure 5A) showed weak, poorly resolved signals even after long acquisition times. The spectral features also were significantly different than those observed

Scheme 5



in spectra of nanoparticles prepared in the presence of higher amounts of OPA. The main broad signal was now centered at 35 ppm with a small shoulder at 25 ppm, and a smaller broad feature, never previously observed, was evident at 60 ppm.

When a portion of this sample was treated with the benzyltrimethylammonium propionate solution, the ^{31}P $\{^1\text{H}\}$ NMR spectrum showed signals at 18 and 25 ppm corresponding to the alkylphosphonate and dialkylpyrophosphonate species as expected (Figure 5C). However, a third signal was observed at 38 ppm consistent with the chemical shift of TOPSe. A ^{31}P $\{^1\text{H}\}$ NMR spectrum of the starting Se and tri-*n*-octylphosphine (TOP) solution similarly showed one signal with a chemical shift of 38 ppm.²¹ When another sample of these nanoparticles was treated with DMAP (Figure 5B), the signal at 25 ppm for

the weaker binding alkylphosphonate species was observed, but not the one at 18 ppm for the stronger binding dialkylpyrophosphonate, as expected. The signal for TOPSe also was not observed.

Similar experiments using 0.3 mol % of added PPA rather than OPA also produced nanoparticles whose ^{31}P $\{^1\text{H}\}$ NMR spectra exhibited the broad signal near 60 ppm (Figure 6A). Treatment of a sample of the nanoparticles with DMAP failed to produce a sufficient concentration of solution-phase ligands, because the corresponding ^{31}P $\{^1\text{H}\}$ spectra only showed the same broad signal (Figure 6B). In contrast, the ^{31}P $\{^1\text{H}\}$ spectrum of the sample treated with the benzyltrimethylammonium propionate solution showed a sharp peak at 18 ppm corresponding to PPA (Figure 6C) and a very small signal for

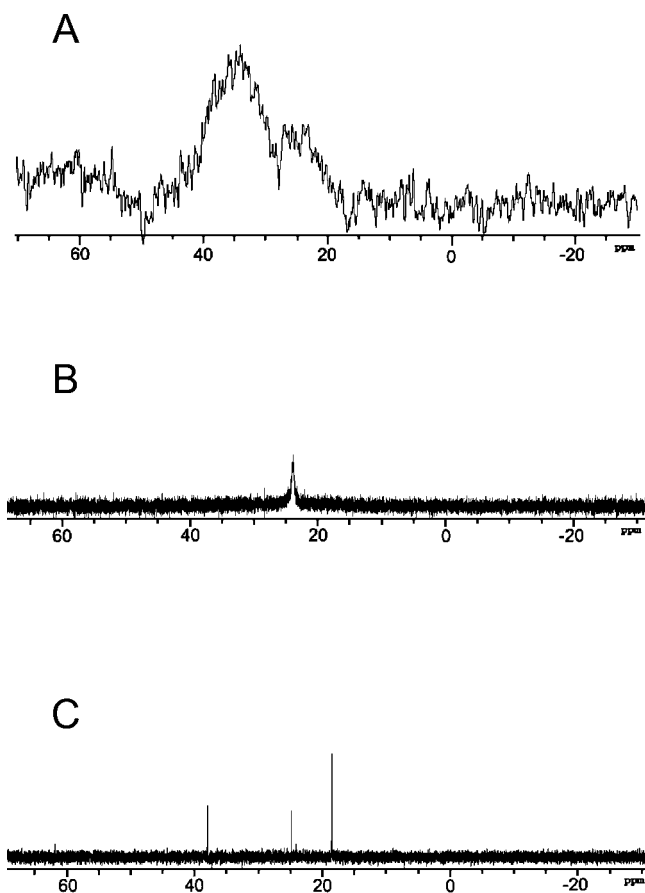


Figure 5. ^{31}P $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 25 °C of (A) a solution of CdSe nanoparticles synthesized using high-purity TOPO and 0.50 mol % of added OPA; (B) the solution after treatment with of the nanoparticles in (A) with DMAP; and (C) the solution after treatment of the nanoparticles in (A) with propionate salt solution.

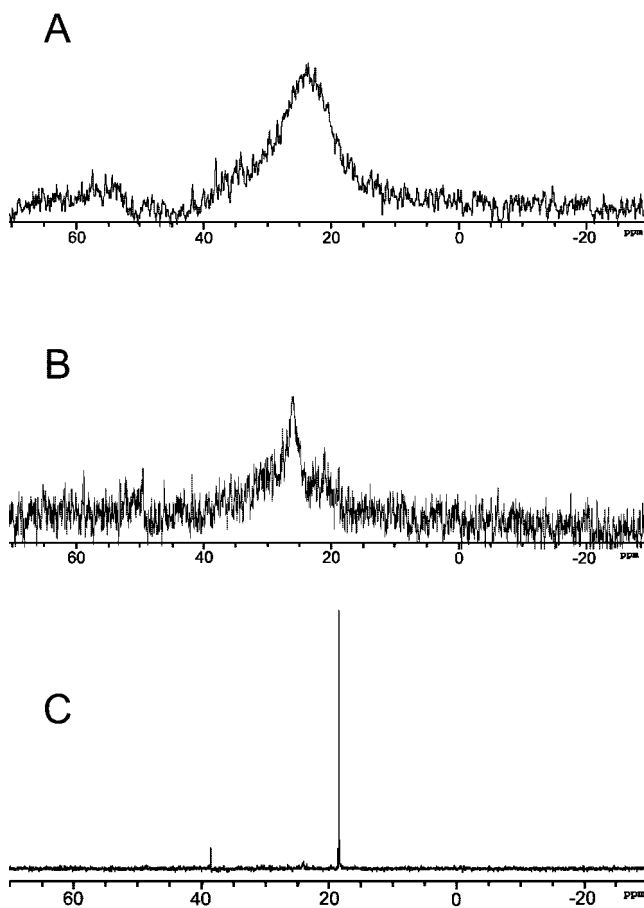


Figure 6. ^{31}P $\{^1\text{H}\}$ NMR spectra in CDCl_3 at 25 °C of (A) a solution of CdSe nanoparticles synthesized using high-purity TOPO and 0.30 mol % of added PPA; (B) the solution after treatment with of the nanoparticles in (A) with DMAP; and (C) the solution after treatment of the nanoparticles in (A) with propionate salt solution.

TOPSe at 38 ppm. TOPO, a weaker binding ligand than TOPSe, was not observed in the ^{31}P $\{^1\text{H}\}$ spectra from this series of experiments; however, the TOPO (and perhaps even some TOPSe) could have been displaced from the particle surface during purification, since the sample was difficult to isolate from methanol using centrifugation.

The presence of TOPSe and not TOPO in the ^{31}P $\{^1\text{H}\}$ spectra in this series of experiments appears to indicate a stronger or preferential binding of TOPSe to the CdSe nanoparticle surface. Phosphine selenides may exhibit stronger coordination to surface Cd sites than phosphine oxides, because selenium represents a better hard/soft base match with cadmium. Also, as proposed in other literature reports, the presence of TOPSe on the surface could be more than a simple coordination chemistry issue. Because the selenium in the nanoparticle is derived from the phosphine–selenide precursor, surface-bound TOPSe will be introduced during the growth phase of the nanoparticles when the transformation of the phosphorus center is incomplete. During the ligand displacement reactions, TOPSe is liberated rather than TOP. Literature reports also have concluded that TOPSe could account for up to 20% of the surface-bound phosphorus species,^{21,50} and as further support for this idea, there are literature observations³³ that document decreases in nanocrystal size after ligand displacement processes.

The results of the nanoparticle syntheses in the presence of significant amounts of phosphonic acids or pyrophosphonic acids were consistent with a surface composition model in which either very little or no TOPO was coordinated to the CdSe nanoparticle surfaces. Peng et al. have shown that high-quality CdSe nanoparticles may be prepared in other high-temperature solvents as long as surface coordinating ligands were present.¹⁸ Thus, to confirm the passive role of TOPO in the synthesis, we decided to test the synthesis using a non-coordinating solvent such as 1-octadecene (ODE). A nanoparticle synthesis was conducted using 3.7 mol % OPA in ODE. Similar to prior syntheses in TOPO, the final solution and resulting product were red and exhibited both good dispersibility in nonpolar solvents and a strong and narrow photoluminescence emission pattern with an emission maximum at the same wavelength within experimental error. TEM images showed that the final nanoparticles were spherical, with an average size of 2.9 ± 0.5 nm (Figure 2D), which is similar within experimental error to that of the nanoparticles prepared using OPA in TOPO.

The fact that essentially identical nanoparticles could be prepared in TOPO and a non-coordinating, high-boiling solvent indicates that the nanoparticle formation and surface stabilization can be satisfied with OPA or PPA alone. The result also suggests that the acidic phosphorus species present in technical grade TOPO or formed during the synthesis play the principal role in the growth and stabilization of CdSe nanoparticles in this solvent. One inference that can be drawn from this conclusion

is that a particular lot of technical grade TOPO, proven unsatisfactory for preparing CdSe nanoparticles, could be spiked with a few mole percent of OPA or PPA to render it useful. Another conclusion that can be made is that selective and direct surface functionalization of CdSe nanoparticles should be most effective using derivatives of OPA or PPA during the synthesis.

Conclusions

The surface ligand composition of CdSe nanoparticles prepared using technical grade TOPO was investigated using a nucleophilic ligand displacement methodology and ^{31}P $\{^1\text{H}\}$ NMR spectroscopy. DMAP and benzyltrimethylammonium propionate were added to THF solutions of the CdSe nanoparticles to displace the surface-bound ligands. DMAP was shown to be a sufficiently strong nucleophile to displace the more weakly coordinating ligands, TOPO, TOPSe, di-*n*-octylphosphinic acid, and OPA. Benzyltrimethylammonium propionate was shown to be a stronger nucleophile than DMAP and could displace the aforementioned surface-bound ligands in addition to a newly identified pyrophosphate species, PPA, which was shown to form during the synthesis via the dehydrative condensation of OPA. CdSe nanoparticle syntheses were performed using pure TOPO and added OPA, and subsequent displacement experiments showed that OPA and PPA were the predominant surface-bound ligands. CdSe nanoparticle syntheses were performed using pure TOPO and added PPA, and subsequent displacement experiments showed that PPA was the predominant surface-bound ligand. PPA was also shown to have the greatest affinity for the nanoparticle surface of all the ligands investigated.

A working qualitative model for the composition of nanoparticles prepared using technical grade TOPO can be stated as follows. The ligands OPA and PPA (formed during the synthesis) have the greatest affinity for the nanoparticle surface, and the surface content of these ligands will be a function of their concentration in the reaction mixture. If they are present in sufficiently high concentration, then the surface will be dominated by these ligands. If there is not sufficient OPA and PPA in solution to saturate the nanoparticle surface, then TOPO, TOPSe, and di-*n*-octylphosphinate will serve to fill the remaining sites on the nanoparticle surface according to their affinities to the surface cadmium atoms and their concentrations in the reaction mixture.

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Supporting Information Available: ^1H NMR spectra, as well as UV–vis spectra and photoluminescence spectra for each reaction system category. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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