Journal of Visualized Experiments

Synthesis of In37P20(O2CR)51 Clusters and their Conversion to InP Quantum Dots

--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE59425R2
Full Title:	Synthesis of In37P20(O2CR)51 Clusters and their Conversion to InP Quantum Dots
Keywords:	clusters; magic-size; nanostructures; synthesis; nanocrystals; quantum dots; indium phosphide
Corresponding Author:	Brandi Cossairt University of Washington Seattle, WA UNITED STATES
Corresponding Author's Institution:	University of Washington
Corresponding Author E-Mail:	cossairt@uw.edu
Order of Authors:	Nayon Park
	Madison Monahan
	Andrew Ritchhart
	Max R. Friedfeld
	Brandi Cossairt
Additional Information:	
Question	**Response**
Please indicate whether this article will be Standard Access or Open Access.	Open Access (US$4,200)
Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Seattle, Washington, United States

TITLE:
Synthesis of $In_{37}P_{20}(O_2CR)_{51}$ Clusters and Their Conversion to InP Quantum Dots

AUTHORS:
Nayon Park[1], Madison Monahan[1], Andrew Ritchhart[1], Max R. Friedfeld[1], and Brandi M. Cossairt[1]
[1]Department of Chemistry, University of Washington, Seattle, WA, USA

Corresponding Author:
Brandi M. Cossairt (cossairt@uw.edu)

Email Addresses of Co-author:
Nayon Park (nyp28@uw.edu),
Madison Monahan (gladdm@uw.edu),
Andrew Ritchhart (ritchha2@uw.edu),
Max R. Friedfeld (maxrf@uw.edu),

KEYWORDS:
clusters, magic-size, nanostructures, synthesis, nanocrystals, quantum dots, indium phosphide

SHORT ABSTRACT:
A protocol for the synthesis of $In_{37}P_{20}(O_2C_{14}H_{27})_{51}$ clusters and their conversion to indium phosphide quantum dots is presented.

LONG ABSTRACT:
This text presents a method for the synthesis of $In_{37}P_{20}(O_2C_{14}H_{27})_{51}$ clusters and their conversion to indium phosphide quantum dots. The $In_{37}P_{20}(O_2CR)_{51}$ clusters have been observed as intermediates in the synthesis of InP quantum dots from molecular precursors ($In(O_2CR)_3$, HO_2CR, and $P(SiMe_3)_3$) and may be isolated as a pure reagent for subsequent study and use as a single-source precursor. These clusters readily convert to crystalline and relatively monodisperse samples of quasi-spherical InP quantum dots when subjected to thermolysis conditions in the absence of additional precursors above 200 °C. The optical properties, morphology, and structure of both the clusters and quantum dots are confirmed using UV-Vis spectroscopy, photoluminescence spectroscopy, transmission electron microscopy, and powder X-ray diffraction. The molecular symmetry of the clusters is additionally confirmed by solution-phase ^{31}P NMR spectroscopy. This protocol demonstrates the preparation and isolation of atomically-precise InP clusters, and their reliable and scalable conversion to InP QDs.

INTRODUCTION:
Colloidal semiconductor quantum dots have seen an acceleration in synthetic development over the previous three decades owing to their potential in a variety of optoelectronic applications including displays[1], solid-state lighting[2,3], biological imaging[4,5], catalysis[6,7], and photovoltaics[8–10]. Given their recent commercial success in the area of wide-color gamut displays, the quantum dot market is expected to exceed 16 billion dollars by 2028[11]. A significant shift in material focus from the II-VI (and IV-VI) to the III-V family has occurred in the last several years as the search for less

toxic, Cd and Pb-free alternatives for use in highly distributed electronics applications has begun. Indium phosphide in particular has been identified as a leading drop-in replacement for CdSe[12]. It has become apparent, however, that optimization of InP-based quantum dots is more difficult and does not always benefit from the same methods used for the more well-established chalcogenide materials. This is primarily because the nucleation and growth profile of InP nanoparticles follows a non-classical, two-step mechanism[13]. This mechanism is invoked due to the intermediacy of locally stable, atomically precise intermediates known as "magic-sized" clusters[14–16]. In particular, $In_{37}P_{20}(O_2CR)_{51}$ has been identified as one key, isolable intermediate in the synthesis of InP from $P(SiMe_3)_3$, indium carboxylate, and carboxylic acid[17].

The presence of this intermediate on the reaction coordinate has many tangible effects on the growth of InP nanostructures. The existence of cluster intermediates themselves invalidates classical concepts of nucleation and growth based on the La Mer model and means that optimizing reaction conditions such as concentration, temperature, and precursor may not achieve sufficiently uniform ensemble properties. Rather, it has been shown that the use of the InP cluster as a single-source precursor results in highly monodisperse quantum dots with narrow optical features[13]. Recent literature has suggested that monodispersity, however, is not the only factor limiting InP's parity with other optoelectronic materials[18]. Surface defects, oxidation, and alloying are critical factors still under intense research that will require significant innovation for optimized InP architectures[19–24]. The atomically precise nature of clusters, such as $In_{37}P_{20}(O_2CR)_{51}$, makes them ideal platforms for probing the consequences of many post-synthetic surface modifications. Normally, ensemble inhomogeneity of nanoparticles makes determining surface and compositional effects difficult, but because the cluster of InP is known to be atomically precise, both compositionally and crystallographically, it is an ideal model system.

The synthesis of the $In_{37}P_{20}(O_2CR)_{51}$ cluster is no more difficult than the synthesis of more widely used nanoparticles such as CdSe, PbS, or ZnO. It requires only standard glassware, widely available chemicals, and basic knowledge of air-free Schlenk and glovebox techniques. The procedure itself can be done on the gram scale and with yields in excess of 90%. As we will show, the successful synthesis of InP cluster is not "magic" but rather an exercise in fundamentals. Pure reagents, dry glassware, proper air-free techniques, and attention to detail are all that is required to access this atomically precise nanocluster. Moreover, we also elaborate on ideal methods for its conversion to highly crystalline InP quantum dots with narrow size distributions.

PROTOCOL:

CAUTION: Proper personal protective equipment should be worn at all times and the material safety data sheet (MSDS) should be read for each chemical prior to use. All steps should be done air-free, because exposing clusters to air and/or water will degrade clusters or prevent proper formation. Any point at which the reaction flask is open to air, N_2 should be flowing vigorously to create a protective blanket over the reagents in the flask. All N_2 used should be 99.9% or greater in purity.

1. Preparation of molecular precursors

1.1. Purification of ligand precursor

NOTE: Myristic acid can be substituted by phenylacetic, oleic, or other long-chain carboxylic acids.

1.1.1. Place a 100 mL 3-neck flask, a stir bar, a reflux condenser, a glass stopper, a thermowell, a T-adapter, and a hose adapter into a 160 °C oven overnight.

NOTE: Glassware can also be flame dried and placed in the oven for 1 h.

1.1.2. Set up the flask, condenser, and thermowell on a Schlenk line while the glassware is still warm using high temperature vacuum grease to ensure glassware remains water-free. Close the final neck of the flask with a rubber septum.

1.1.3. Place 2.65 g of myristic acid ($HO_2C_{14}H_{27}$, 11.6 mmol) into the flask and flush with N_2. Put the flask under vacuum for 2 h with mild stirring at 120 °C to remove residual water from the acid.

1.2. Preparation of indium myristate ($In(O_2C_{14}H_{27})_3$)

NOTE: Equivalent InP clusters can be prepared with trimethylindium or indium acetate.

1.2.1. Preparation via trimethylindium ($InMe_3$)

1.2.1.1. Weigh out 0.512 g of $InMe_3$ (3.2 mmol, anhydrous) and dissolve it in 10 mL of anhydrous toluene. Draw the solution into a syringe and seal with a rubber septum to keep the solution air-free during removal from the glovebox.

1.2.1.2. Add 10 mL of anhydrous toluene to myristic acid from step 1.1 via a syringe and stir at room temperature until dissolved.

1.2.1.3. Slowly add $InMe_3$ from step 1.2.1.1 via a syringe (~2 drops/s) while stirring. This step should result in rapid gas formation visible to the eye. Allow to stir for 10 min to ensure complete reaction.

1.2.2. Preparation via indium acetate ($In(OAc)_3$)

1.2.2.1. Weigh out 0.93 g of $In(OAc)_3$ (3.2 mmol) and add to the flask containing myristic acid from step 1.1 under positive N_2 flow.

1.2.2.2. Evacuate the flask and heat the flask to 100 °C while stirring. The mixture should melt. Let the solution off-gas acetic acid for 12 h (overnight) at 120 °C.

1.2.2.3. Refill the flask with N_2 and add 20 mL of anhydrous toluene via a syringe through the rubber septum.

2. Synthesis of $In_{37}P_{20}(O_2CR)_{51}$

2.1. Heat the reaction flask containing $In(O_2C_{14}H_{27})_3$ solution to 110 °C.

2.2. Add 465 µL of $P(SiMe_3)_3$ (1.6 mmol) to 10 mL of anhydrous toluene in the glovebox. Draw the solution into a syringe and insert the needle into a rubber stopper until the needle opening is completely covered. Be cautious when removing from the glovebox as $P(SiMe_3)_3$ is a pyrophoric liquid.

2.3. Rapidly inject the $P(SiMe_3)_3$ solution into the hot $In(O_2C_{14}H_{27})_3$ solution. The solution should turn yellow quickly after the addition of $P(SiMe_3)_3$. Monitor the reaction by taking 50 µL aliquots of reaction solution into 3 mL of toluene for UV-Vis analysis. The reaction is finished when no further changes are seen in the aliquot spectra.

2.4. Remove from heat to cool the flask and halt the reaction.

NOTE: The growth of InP clusters is optimal at a temperature range of 100-110 °C. The reaction proceeds at lower temperatures, including room temperature, but goes very slowly. Higher temperatures result in evolution of quantum dots of varying sizes depending on the temperature. The reaction typically requires 20-60 min to go to completion, depending on the ligands used. Failure to run the reaction to completion could result in small, unstable clusters that will quickly decompose. Running the reaction past completion will not alter the cluster composition as long as the temperature is at or below 110 °C.

3. Workup of $In_{37}P_{20}(O_2CR)_{51}$

NOTE: All solvents used in the purification steps are anhydrous and stored over 4 Å sieves in the N_2-filled glovebox.

3.1. Isolation of $In_{37}P_{20}(O_2CR)_{51}$

3.1.1. Remove the solvent from the cluster solution under reduced pressure on the Schlenk line.

3.1.2. Seal the flask under N_2 using the glass stopper and T-adapter from the oven. Fasten the flask and adapters with electrical tape and bring into the glovebox.

3.2. Purification via precipitation, centrifugation, and re-dissolution

3.2.1. Resuspend the clusters in minimal toluene (~1 mL) and centrifuge to remove solid impurities (7197 x *g,* 10 min). Decant and keep the clear, yellow supernatant and discard any solids.

3.2.2. Add 3 mL of acetonitrile (3:1, MeCN:tol) to the supernatant to precipitate the clusters (yellow precipitate) and centrifuge again under the same parameters. Discard the clear, colorless supernatant and resuspend the yellow solid pellet of clusters in minimal toluene.

3.2.3. Repeat step 3.2.2 for a total of 5 cycles.

3.3. Purification via column

3.3.1. Take the clusters dissolved in minimal toluene (~0.5 mL) and apply them in a thin band to a freshly cleaned size-exclusion, liquid column (60 cm, 25 mm) packed with permeable gel beads (see **Table of Materials**) using toluene as the solvent.

3.3.2. Allow the clusters to run through the column ensuring to keep the beads wet by adding fresh toluene as the liquid runs through the column. Collect all yellow fluid but make sure to stop collecting immediately after the yellow passes as excess ligand will come off after the cluster. Typically, the clusters take about 20 min to elute at room temperature.

NOTE: To confirm where the cluster region ends on the column, a laser pointer (405 nm) can be used to see where glowing resumes. The portion of the column containing clusters will not glow.

3.3.3. Remove solvent under reduced pressure via a vacuum pump until a waxy solid is achieved. Store dry clusters under N_2 for best stability. In a typical synthesis, 1.2 g of clusters should be isolated, representing a 90% yield.

4. Synthesis of InP quantum dots using $In_{37}P_{20}(O_2CR)_{51}$ as a single source precursor

NOTE: Indium phosphide quantum dots can be synthesized from purified InP clusters using a heat-up or hot injection method.

4.1. Heat-up method

4.1.1. Degas a 100 mL 3-neck round bottom flask equipped with a stir bar, a glass thermowell, a T-adapter, and a rubber septum. Assemble the glassware using high temperature vacuum grease.

4.1.2. Dissolve 200 mg of purified InP clusters in 20 mL of anhydrous 1-octadecene. Inject the InP cluster solution into the reaction flask via a syringe under a positive N_2 flow, followed by an additional 20 mL of anhydrous 1-octadecene. Briefly degas to ensure the reaction flask is air-free.

4.1.3. Heat the solution to 300 °C under a positive N_2 flow while stirring. The growth of QDs can be monitored by UV-Vis spectroscopy with timed aliquots. The bright yellow color persists up to around 200 °C and changes from yellow to bright orange to dark red-brown. The reaction is complete in 30-40 min.

4.1.4. Cool down the reaction flask to room temperature by removing the heating mantle. The solution after cooling displays an optically clear red color. Remove 1-octadecene by vacuum distillation at 160 °C. Replace the appropriate glassware as quickly as possible to limit air exposure.

4.1.5. Dissolve InP QDs using minimal amount (<5 mL) of anhydrous toluene in a N_2-filled glovebox. Transfer the crude solution to a centrifuge tube. Add ~40 mL of anhydrous acetonitrile and centrifuge for purification (7197 x *g*, 10 min).

4.1.6. Pour off the supernatant and re-dissolve the precipitate in approximately 5 mL of anhydrous toluene. Repeat the purification steps for a total of 3 cycles. Store the purified product dissolved in anhydrous toluene.

4.2. Hot-injection method

4.2.1. Degas a 100 mL 3-neck round bottom flask equipped with a thermowell, a Schlenk adapter, and a rubber septum. Assemble the glassware using high temperature vacuum grease.

4.2.2. Inject 35 mL of anhydrous 1-octadecene into the reaction flask. Heat the solvent to 300 °C under inert gas while stirring.

4.2.3. Dissolve 200 mg of purified InP clusters in 5 mL of anhydrous 1-octadecene and inject the cluster solution into the reaction flask. The reaction is complete in 15-20 min.

4.2.4. Cool down the solution to room temperature by removing the heating mantle. Distill off 1-octadecene and purify InP QDs as described in steps 4.1.5 to 4.1.6.

5. Characterization of $In_{37}P_{20}(O_2CR)_{51}$ and InP quantum dots

5.1. Transmission electron microscopy (TEM)

5.1.1. Prepare a dilute solution of cluster (~5 mg) or quantum dots in pentane:toluene (1:1, 2 mL total). Solution color should be barely visible.

5.1.2. Pick up a lacey carbon TEM grid (400 mesh, ultra-fine) with tweezers and place off the edge of a surface, making sure the grid is not touching anything besides the tweezers.

5.1.3. Drop-cast one large drop onto the grid and let it dry completely with no dabbing away solution (~20 min). Place the grid under vacuum and let further dry overnight.

5.1.4. Image the sample with TEM. Typical image conditions include spot size 5,200 kV electron beam, objective aperture completely open, and magnification of 350,000X.

5.1.5. In the native image format (.dm3), measure the particle size using the straight-line tool to create a line across the imaged particle (see **Table of Materials** for software). The command tool finder will give a length in nanometers corresponding to the drawn line, when the line is actively being dragged or clicked on and measure the particle diameter.

5.2. Nuclear magnetic resonance (NMR)

NOTE: ^{1}H NMR needs as little as 20 mg of clusters, but ^{31}P NMR requires at least 40 mg of clusters to resolve the cluster region.

5.2.1. Prepare cluster solution (40 mg) in deuterated benzene (C_6D_6, ~0.7 mL) in the glovebox and transfer the solution into an oven-dried J-young NMR tube. Seal the tube under N_2 and remove from the glovebox for measurements.

5.2.2. Collect ^{1}H NMR spectra on a 300 MHz or greater instrument. Common parameters include 2 dummy scans, 6 scans, and 30 s delay time.

5.2.3. Collect ^{31}P NMR spectra on a 500 MHz or greater instrument. Use a phosphoric acid standard to calibrate the instrument prior to use. Common parameters include an offset of -100 ppm, sweep width of 500 ppm, and 256 scans repeated 40 times (about 14 h of total run time to ensure a strong enough signal).

5.3. X-ray Diffraction (XRD)

5.3.1. Prepare a highly concentrated solution of clusters or quantum dots by either dissolving dried material in minimal toluene (< 1 mL) or removing toluene from a stock solution.

5.3.2. Drop-cast onto an oven-dried Si wafer and let dry for ~30 min. For consistency of drop size, use a digital micropipette with the setting at 3~5 µL. Repeat 2-3 times until a film of clusters or quantum dots has sufficiently set.

5.3.3. Collect XRD data from 10 to 70° with 0.5° intervals. Set each interval to 30 s acquisition time for a quick run or 240 s acquisition for higher resolution.

5.4. Photoluminescence (PL)

5.4.1. Transfer the solution for PL analysis into a 1 x 1 cm quartz fluorescence spectrophotometer cell.

5.4.2. Set the excitation at 450 nm and the monochromator slit widths for both entrance and exit slits at 3 nm. Set the integration time at 0.1 s/nm or 1 s/nm for higher resolution.

REPRESENTATIVE RESULTS:

InP clusters and quantum dots are characterized by UV-Vis absorption and PL spectroscopy, XRD, TEM, and NMR spectroscopy. For the InP clusters, an asymmetric absorption feature is observed, with a peak maximum at 386 nm (**Figure 1a**). Despite the true monodispersity of the sample, this lowest energy peak exhibits a broad linewidth, which narrows upon decrease in temperature. This has been attributed to a set of discrete electronic transitions that are specific to the vibrational motions of the low-symmetry nanocluster lattice[17]. No appreciable PL QY is observed for clusters at 298 K despite the lack of obvious trap states that would arise from undercoordinated indium or phosphorus ions.

The non-stoichiometric, In-rich cluster (where In is present in a 1.85:1 ratio relative to phosphorus) results in a structure that corresponds with neither the zinc blende nor the wurzite XRD patterns of bulk InP (**Figure 1b**). Instead, the InP clusters attain a low-symmetry, pseudo-C_{2v} structure that is best described by a set of intersecting polytwistane units[25]. The core diameter is in the 1-2 nm range depending on the axis from which it is viewed (**Figure 1c**). This low symmetry structure is reflected in the solution-phase ^{31}P NMR spectrum of the cluster. The ^{31}P NMR spectrum of myristate-capped InP clusters shows 11 distinct peaks (2 P atoms on the C_2 axis that each give a unique peak and the remaining 18 P each have a symmetry equivalent, resulting in an additional 9 peaks) ranging from -256 to -311 ppm (**Figure 1d**)[26]. The broadness observed in the ^{31}P NMR spectrum varies as a function of solvent and concentration, and purification method as has been recently described for related nanoscale systems[27].

The optical spectra of InP QDs synthesized from clusters using the method described here display a lowest energy excitonic transition (LEET) at 564 nm and the corresponding PL emission peak at 598 nm with a full width at half maximum of 52 nm and trap emission evident at redder wavelengths (**Figure 2a**). It is worth noting that while the two synthetic methods (heat-up and hot-injection) yield InP QDs of comparable optical quality, the hot injection method typically leads to a sample with higher monodispersity due to the rapid nucleation at elevated temperature[13]. The typically low PL quantum yields obtained directly from the synthesis without further surface treatment (shelling, F- etching, or Lewis acid coordination) are hypothesized to result from a mixture of hole and electron traps present at the surface of these nanocrystals[18,28]. The XRD pattern of the resultant InP QDs confirms the zinc blende phase (**Figure 2b**). Peak broadening in the XRD data occurs due to the finite size of the highly crystalline structures, which in the case of InP QDs is 3.1 nm +/- 0.5 nm in diameter (**Figure 2c**, a size histogram can be found in ref. 13).

FIGURE LEGENDS:

Figure 1. Representative characterization data for InP clusters. (**A**) UV-Vis spectrum of InP clusters. (**B**) XRD pattern for purified InP clusters showing deviation from the expected bulk zinc blende (black trace) and wurtzite (grey trace) InP pattern. (**C**) TEM image of isolated InP clusters. (**D**) ^{31}P NMR spectrum of InP clusters collected at 202 MHz in C_6D_6 at 298 K.

Figure 2. Representative characterization data for InP quantum dots prepared from InP clusters. (**A**) UV-Vis (solid) and PL (dotted) spectra of InP QDs prepared from myristate-capped InP clusters using the hot-injection protocol. (**B**) XRD pattern of purified InP QDs showing

agreement with the bulk zinc blende InP pattern. (**C**) TEM images of InP QDs grown from clusters using the hot-injection protocol.

Discussion:

The synthesis of InP magic-sized clusters and their conversion into quantum dots follow straightforward procedures that have been shown to consistently produce high quality samples. The ability to synthesize and isolate InP clusters as an intermediate has distinct advantages in terms of subjecting these nanostructures to modifications that can be well-characterized and consequently be incorporated in the final QDs. The atomically precise nature of the clusters and the high reproducibility provide a platform for innovative studies in surface modifications, defects, and alloying of the InP systems and open doors to a wide range of applications such as in displays, solid-state lighting, catalysis, and photovoltaics.

In the synthesis of InP clusters, it is critical that all reagents are high purity and thoroughly dried, as the success of the synthesis is contingent upon water- and air-free experimental conditions and purity of the precursors for uniform growth in high yields. Additionally, it is recommended that sufficient precautions are taken when handling $P(SiMe_3)_3$, which is light-sensitive and pyrophoric. This reagent should be stored in a light-, air-, and water-free environment and caution should be taken to prevent air and water exposure before and during the reaction. For efficient growth of the clusters, the temperature range should be 100-110 °C; at room temperature, the growth is extremely slow, and a higher temperature will result in conversion into quantum dots of varying sizes depending on the temperature. The presented protocol is also highly scalable and versatile, allowing synthetic control and modifications through a breadth of parameters. The myristic acid used as the ligands for InP clusters and subsequent QDs can be replaced by phenylacetic acid, oleic acid, or other short and long-chain carboxylic acids. Post-synthetic addition of $P(SiMe_3)_3$ to solutions of InP clusters that have slightly perturbed absorption features (red-shifted and/or broadened) has been observed to result in a size focusing effect where the consumption of excess indium myristate results in a ~3 nm blueshift in the absorption spectra[29].

The purification method of the clusters has been empirically optimized in our lab to avoid oxidation and to isolate the highest possible yields. The choice of acetonitrile as the antisolvent and its volume ratio with toluene fulfill these goals. Finally, the clusters are resuspended in minimal amount of toluene and centrifuged to remove any solid impurities that may have resulted during synthesis. Removing toluene from the final solution gives a yellow paste that can be stored for at least 36 months under air- and water-free conditions. It should also be noted in regard to preparing NMR samples for characterization of the purified product that the precise chemical shifts for the 11 distinct resonances in ^{31}P NMR spectrum vary depending on the identity of the indium precursors. Furthermore, insufficient purification and variation in cluster concentration can result in line broadening. In order to obtain a clean spectrum with sharp features, it is suggested that at least 40 mg of the cluster is dissolved in a minimal amount of anhydrous C_6D_6 (~0.7 mL).

Similarly, the synthesis of InP QDs via clusters must be performed under water- and air-free conditions. Previous studies have shown that the presence of water in indium precursors and the addition of trace amounts of water or hydroxide lead to significant changes in the growth of InP QDs and the surface chemistry of the final product[25]. When running the reaction at a different scale than described in the protocol, it should be noted that for the hot-inject method, the cluster solution for injection should be sufficiently concentrated and the volume should be smaller compared to the heated solvent in the flask. This is to minimize the abrupt decrease in temperature as the reaction temperature profile plays a nontrivial role in the synthesis. Detailed work on the conversion mechanism of InP clusters to QDs has been recently reported where the effects of the addition of different precursors (i.e., -carboxylic acid, indium carboxylate), temperatures, and concentration have been explored[30]. Through these studies, it has been revealed that thermolysis temperatures > 220 °C are required for obtaining high yields of optimal quality QDs. The purification of InP QDs follows similar logic and process as mentioned above for the clusters, except that the storage of purified QDs is recommended in solution with a solvent such as toluene. In solid form, the QDs have been observed to form aggregates over time, preventing homogeneous colloidal dispersion. One final note regarding the protocol is that removing 1-octadecene by vacuum distillation after the synthesis of InP QDs rather than by only precipitation-redissolution is a recommended first step of QD purification. This is to limit the volume of solvent required in the workup and because the residual ODE may interdigitate with the long-chain carboxylate ligand shell, causing difficulties with sample preparation for characterization and subsequent use.

We have demonstrated the synthesis and characterization of atomically-precise InP magic-size clusters, $In_{37}P_{20}(O_2CR)_{51}$, and their use as single source precursors for the synthesis of InP quantum dots using both heat-up and hot-injection methods. The reported synthesis of InP clusters is versatile and can be generalized to a wide range of alkyl carboxylate ligands. The synthesis of the InP QDs from the clusters provides a highly reproducible method for the synthesis of these challenging nanostructures with high quality in terms of size distribution and crystallinity. Opportunities abound for further elaboration of this method through post-synthetic modification of the clusters themselves and for engineering the cluster to quantum dot conversion strategy. Because of this, we believe these methods are useful and potentially technologically meaningful for the synthesis of InP and related emissive materials for display and lighting applications.

ACKNOWLEDGEMENTS:

We gratefully acknowledge support from the National Science Foundation under grant CHE-1552164 for development of the original synthesis and characterization methods presented in this manuscript. During preparation of this manuscript, we acknowledge the following agencies for support of student and postdoctoral salaries: Nayon Park (National Science Foundation, CHE-1552164), Madison Monahan (US Department of Energy, Office of Science, Office of Basic Energy Sciences, as part of the Energy Frontier Research Centers program: CSSAS--The Center for the Science of Synthesis Across Scales under Award Number DE-SC0019288), Andrew Ritchhart (National Science Foundation, CHE-1552164), Max R. Friedfeld (Washington Research Foundation).

DISCLOSURES:

The authors have nothing to disclose.

REFERENCES:

(1) Shirasaki, Y., Supran, G. J., Bawendi, M. G., Bulović, V. Emergence of Colloidal Quantum-Dot Light-Emitting Technologies. *Nature Photonics.* ***7***, 13–23 (2013). https://doi.org/10.1038/nphoton.2012.328.

(2) Shea-Rohwer, L. E., Martin, J. E., Cai, X., Kelley, D. F. Red-Emitting Quantum Dots for Solid-State Lighting. *ECS Journal of Solid State Science and Technology.* ***2***, R3112–R3118 (2013). https://doi.org/10.1149/2.015302jss.

(3) Kazlas, P. T., Linton, J. R. Quantum Dot-Based Light Sheets Useful for Solid-State Lighting. US20100283072A1, November 11, 2010.

(4) Kairdolf, B. A., Smith, A. M., Stokes, T. H., Wang, M. D., Young, A. N., Nie, S. Semiconductor Quantum Dots for Bioimaging and Biodiagnostic Applications. *Annual Review of Analytical Chemistry.* ***6***, 143–162 (2013). https://doi.org/10.1146/annurev-anchem-060908-155136.

(5) Petryayeva, E., Algar, W. R., Medintz, I. L. Quantum Dots in Bioanalysis: A Review of Applications across Various Platforms for Fluorescence Spectroscopy and Imaging. *Applied Spectroscopy* ***67***, 215–252 (2013). https://doi.org/10.1366/12-06948.

(6) Sambur, J. B., Chen, P. Approaches to Single-Nanoparticle Catalysis. *Annual Review of Physical Chemistry.* ***65***, 395–422 (2014). https://doi.org/10.1146/annurev-physchem-040513-103729.

(7) Xia, Y., Yang, H., Campbell, C. T. Nanoparticles for Catalysis. *Accounts of Chemical Research.* ***46***, 1671–1672 (2013). https://doi.org/10.1021/ar400148q.

(8) Lewis, N. S. Toward Cost-Effective Solar Energy Use. *Science.* ***315***, 798–801 (2007). https://doi.org/10.1126/science.1137014.

(9) Semonin, O. E., Luther, J. M.; Beard, M. C. Quantum Dots for Next-Generation Photovoltaics. *Materials Today.* ***15***, 508–515 (2012). https://doi.org/10.1016/S1369-7021(12)70220-1.

(10) Carey, G. H., Abdelhady, A. L., Ning, Z., Thon, S. M., Bakr, O. M., Sargent, E. H. Colloidal Quantum Dot Solar Cells. *Chemical Reviews.* ***115***, 12732–12763 (2015). https://doi.org/10.1021/acs.chemrev.5b00063.

(11) Colegrove. *Quantum Dot Technology Supply Chain and Market Forecast*; Touch Display Research; (2018).

(12) Pu, Y., Cai, F., Wang, D., Wang, J.-X., Chen, J.-F. Colloidal Synthesis of Semiconductor Quantum Dots toward Large-Scale Production: A Review. *Industrial Engineering Chemical Research.* ***57***, 1790–1802 (2018). https://doi.org/10.1021/acs.iecr.7b04836.

(13) 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. *Chemistry of Materials.* ***27***, 1432–1441 (2015). https://doi.org/10.1021/acs.chemmater.5b00286.

(14) Cossairt, B. M., Owen, J. S. CdSe Clusters: At the Interface of Small Molecules and Quantum Dots. *Chemistry of Materials.* ***23***, 3114–3119 (2011). https://doi.org/10.1021/cm2008686.

(15) Zhang, J. et al. Evolution of Self-Assembled ZnTe Magic-Sized Nanoclusters. *Journal of the American Chemical Society.* ***137***, 742–749 (2015). https://doi.org/10.1021/ja509782n.

(16) Zhu, T. et al. Two-Step Nucleation of CdS Magic-Size Nanocluster MSC–311. *Chemisty of Materials.* ***29***, 5727–5735 (2017). https://doi.org/10.1021/acs.chemmater.7b02014.

(17) Gary, D. C., Flowers, S. E., Kaminsky, W., Petrone, A., Li, X., Cossairt, B. M. Single-Crystal and Electronic Structure of a 1.3 Nm Indium Phosphide Nanocluster. *Journal of the American Chemical Society.* ***138***, 1510–1513 (2016). https://doi.org/10.1021/jacs.5b13214.

(18) Janke, E. M. et al. Origin of Broad Emission Spectra in InP Quantum Dots: Contributions from Structural and Electronic Disorder. *Journal of the American Chemical Society.* ***140***, 15791–15803 (2018). https://doi.org/10.1021/jacs.8b08753.

(19) Stein, J. L., et al. Probing Surface Defects of InP Quantum Dots Using Phosphorus Kα and Kβ X-Ray Emission Spectroscopy. *Chemistry Materials.* ***30***, 6377–6388 (2018). https://doi.org/10.1021/acs.chemmater.8b02590.

(20) Giansante, C., Infante, I. Surface Traps in Colloidal Quantum Dots: A Combined Experimental and Theoretical Perspective. *Journal of Physical Chemistry Letters.* ***8***, 5209–5215 (2017). https://doi.org/10.1021/acs.jpclett.7b02193.

(21) Tessier, M. D. et al. Interfacial Oxidation and Photoluminescence of InP-Based Core/Shell Quantum Dots. *Chemistry of Materials.* ***30***, 6877–6883 (2018). https://doi.org/10.1021/acs.chemmater.8b03117.

(22) Brown, R. P., Gallagher, M. J., Fairbrother, D. H., Rosenzweig, Z. Synthesis and Degradation of Cadmium-Free InP and InPZn/ZnS Quantum Dots in Solution. *Langmuir* ***34***, 13924–13934 (2018). https://doi.org/10.1021/acs.langmuir.8b02402.

(23) Brodu, A. et al. Exciton Fine Structure and Lattice Dynamics in InP/ZnSe Core/Shell Quantum Dots. *ACS Photonics.* ***5***, 3353–3362 (2018). https://doi.org/10.1021/acsphotonics.8b00615.

(24) Yang, J., et al. Chemical Synthesis, Doping, and Transformation of Magic-Sized Semiconductor Alloy Nanoclusters. *Journal of the American Chemical Society.* ***139***, 6761–6770 (2017). https://doi.org/10.1021/jacs.7b02953.

(25) Xie, L., Harris, D. K., Bawendi, M. G., Jensen, K. F. Effect of Trace Water on the Growth of Indium Phosphide Quantum Dots. *Chemistry of Materials.* ***27*** (14), 5058–5063 (2015). https://doi.org/10.1021/acs.chemmater.5b01626.

(26) Gary, D. C., Petrone, A., Li, X., Cossairt, B. M. Investigating the Role of Amine in InP Nanocrystal Synthesis: Destabilizing Cluster Intermediates by Z-Type Ligand Displacement. *Chemical Communications.* ***53*** (1), 161–164 (2017). https://doi.org/10.1039/C6CC07952K.

(27) De Roo, J. et al. Probing Solvent–Ligand Interactions in Colloidal Nanocrystals by the NMR Line Broadening. *Chemistry of Materials.* ***30*** (15), 5485–5492 (2018). https://doi.org/10.1021/acs.chemmater.8b02523.

(28) Kirkwood, N. et al. Finding and Fixing Traps in II–VI and III–V Colloidal Quantum Dots: The Importance of Z-Type Ligand Passivation. *Journal of the American Chemical Society.* ***140*** (46), 15712–15723 (2018). https://doi.org/10.1021/jacs.8b07783.

(29) Ritchhart, A., Cossairt, B. M. Templated Growth of InP Nanocrystals with a Polytwistane Structure. *Angewandte Chemie International Edition.* ***57*** (7), 1908–1912 (2018). https://doi.org/10.1002/anie.201711539.

(30) Friedfeld, M. R., Johnson, D. A., Cossairt, B. M. Conversion of InP Clusters to Quantum Dots. *Inorganic Chemistry.* ***58*** (1), 803–810 (2019). https://doi.org/10.1021/acs.inorgchem.8b02945.
(31) Gary, D. C., Cossairt, B. M. Role of Acid in Precursor Conversion During InP Quantum Dot Synthesis. *Chemistry of Materials*. ***25*** (12), 2463−2469 (2013). https://doi.org/10.1021/cm401289j
(32) Becker, G., et al. *Inorganic Synthesis*. **27**, 243−249 (1990).

Figure 1

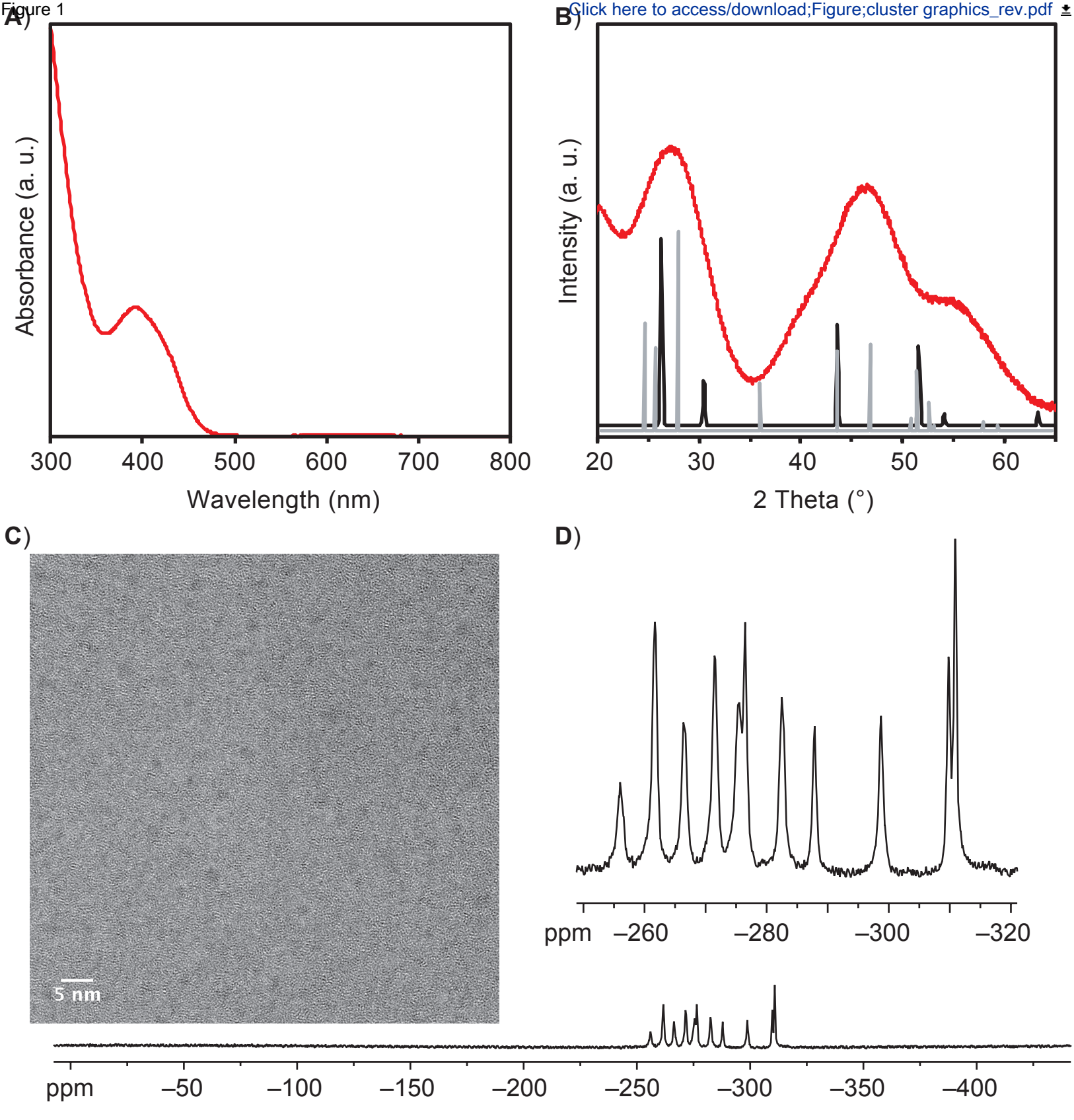
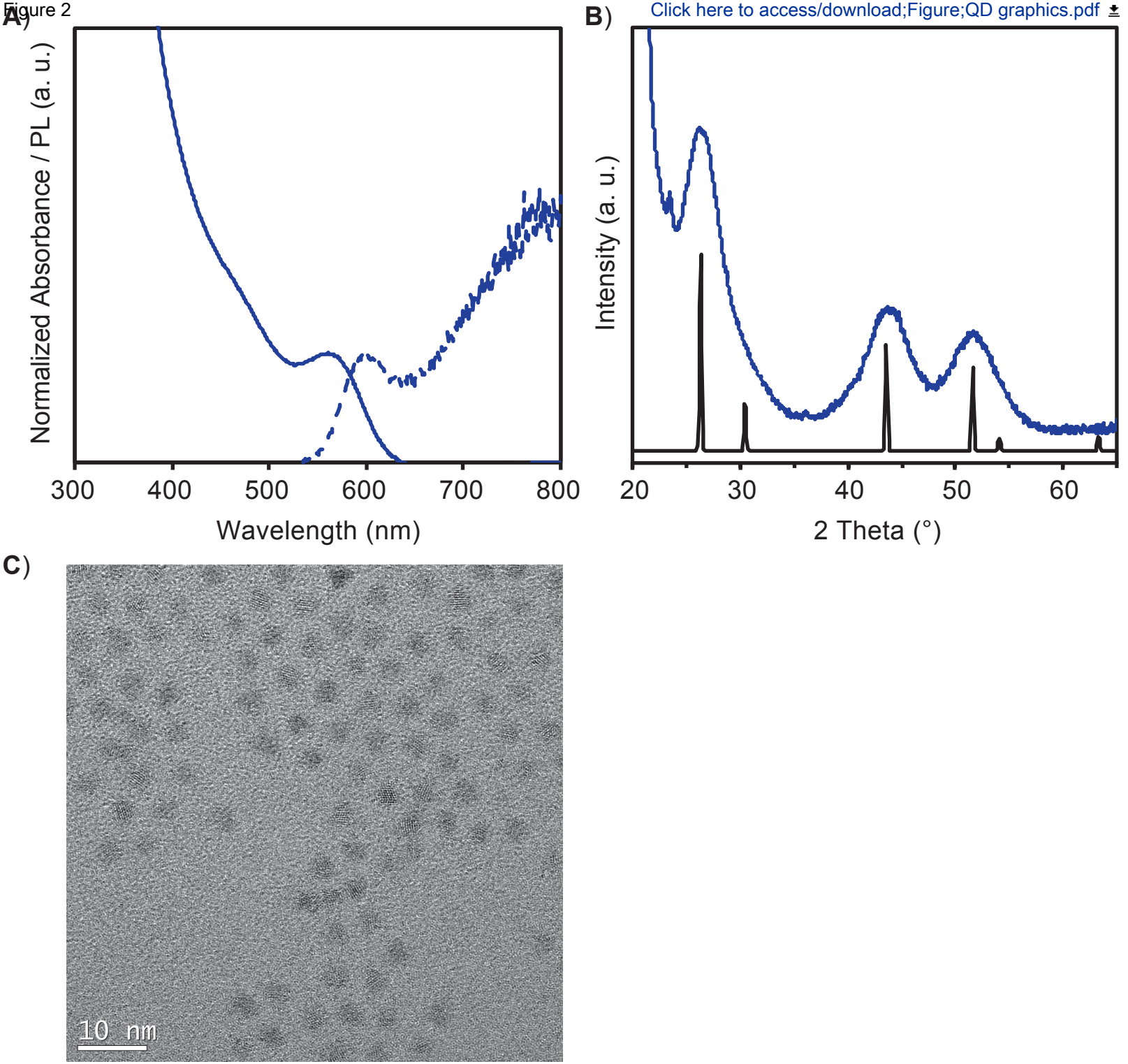


Figure 2



Name of Material/ Equipment	Company	Catalog Number	Comments/Description
Acetonitrile, anhydrous, 99.8%	Sigma Aldrich	271004	Dried over 4Å sieves
Adapter, Airfree, 14/20 Joint, 0 - 4mm Chem-Cap (T-adapter)	Chemglass Life Sciences LLC	AF-0501-01	
Adapter, Inlet, 14/20 Inner Joint	Chemglass Life Sciences LLC	CG-1014-14	
Bio-Beads S-X1, 200-400 mesh	Bio-Rad Laboratories	152-2150	
Cary 5000 UV-Vis-NIR	Agilent		
Column, Chromatography, 24/40 Outer Joint, 3/4in ID X 10in E.L., 2mm Stpk	Chemglass Life Sciences LLC	CG-1188-06	
Condenser, Liebig, 185mm, 14/20 Top Outer, 14/20 Lower Inner, 110mm Jacket Length	Chemglass Life Sciences LLC	CG-1218-A-20	
Distilling heads, short paths, jacketed	Chemglass Life Sciences LLC	CG-1240	
Eppendorf Microcentrifuge 5430	Fisher Chemical	05-100-177	
Falcon 15mL Conical Centrifuge Tubes	Fisher Chemical	14-959-49B	
Flask, Round Bottom, 50mL, Heavy Wall, 14/20 - 14/20, 3-Neck, Angled 20°	Chemglass Life Sciences LLC	CG-1524-A-05	
ImageJ	Developed at National Institutes of Health and the Laboratory for Optical and Computational Instrumentation		Open source Java image processing program
Indium acetate, 99.99%	Sigma Aldrich	510270	
Myristic acid, 99%	Sigma Aldrich	M3128	
Temperature controller	Fisher Chemical	50 401 831	
Thermometers, non-mercury, 10/18	Chemglass Life Sciences LLC	CG-3508-N	

Thermometers, non-mercury, 10/18	Chemglass Life Sciences LLC	CG-3308-N	
Thermowell, 14/20 Inner Jt, 1/2" OD above the Jt, 6mm OD Round Bottomed Tube below the Jt, for 25ml RBF	Chemglass Life Sciences LLC	UW-1205-171JS	Custom ordered
Toluene, anhydrous, 99.8%	Sigma Aldrich	244511	Dried over 4Å sieves
Trimethylindium, 98%	Strem	49-2010	Heat sensitive, moisture sensitive
Tris(trimethylsilyl)phosphine	Ref #31, 32		Pyrophoric
Ultrathin Carbon Film on Lacey Carbon Support Film, 400 mesh, Copper	Ted Pella Inc.	1824	
Vacuum gauge 1-STA 115VAC 60Hz	Fisher Chemical	11 278	
Vacuum pump 115VAC 60Hz	Fisher Chemical	01 096	
1-Octadecene (ODE), 90%	Sigma Aldrich	O806	Technical grade, distilled and dried over 4

1Å sieves

jove JOURNAL OF VISUALIZED EXPERIMENTS

1 Alewife Center #200
Cambridge, MA 02140
tel. 617.945.9051
www.jove.com

ARTICLE AND VIDEO LICENSE AGREEMENT

Title of Article: Synthesis of In37P20(O2CR)51 Clusters and their Conversion to InP Quantum Dots

Author(s): Nayon Park, Madison Monahan, Andrew Ritchhart, Max R. Friedfeld, and Brandi M. Cossairt

Item 1 (check one box): The Author elects to have the Materials be made available (as described at http://www.jove.com/author) via: ☐ Standard Access ■ Open Access

Item 2 (check one box):

■ The Author is NOT a United States government employee.

☐ The Author is a United States government employee and the Materials were prepared in the course of his or her duties as a United States government employee.

☐ The Author is a United States government employee but the Materials were NOT prepared in the course of his or her duties as a United States government employee.

ARTICLE AND VIDEO LICENSE AGREEMENT

1. Defined Terms. As used in this Article and Video License Agreement, the following terms shall have the following meanings: "**Agreement**" means this Article and Video License Agreement; "**Article**" means the article specified on the last page of this Agreement, including any associated materials such as texts, figures, tables, artwork, abstracts, or summaries contained therein; "**Author**" means the author who is a signatory to this Agreement; "**Collective Work**" means a work, such as a periodical issue, anthology or encyclopedia, in which the Materials in their entirety in unmodified form, along with a number of other contributions, constituting separate and independent works in themselves, are assembled into a collective whole; "**CRC License**" means the Creative Commons Attribution-Non Commercial-No Derivs 3.0 Unported Agreement, the terms and conditions of which can be found at: http://creativecommons.org/licenses/by-nc-nd/3.0/legalcode; "**Derivative Work**" means a work based upon the Materials or upon the Materials and other pre-existing works, such as a translation, musical arrangement, dramatization, fictionalization, motion picture version, sound recording, art reproduction, abridgment, condensation, or any other form in which the Materials may be recast, transformed, or adapted; "**Institution**" means the institution, listed on the last page of this Agreement, by which the Author was employed at the time of the creation of the Materials; "**JoVE**" means MyJove Corporation, a Massachusetts corporation and the publisher of *The Journal of Visualized Experiments;* "**Materials**" means the Article and / or the Video; "**Parties**" means the Author and JoVE; "**Video**" means any video(s) made by the Author, alone or in conjunction with any other parties, or by JoVE or its affiliates or agents, individually or in collaboration with the Author or any other parties, incorporating all or any portion of the Article, and in which the Author may or may not appear.

2. Background. The Author, who is the author of the Article, in order to ensure the dissemination and protection of the Article, desires to have the JoVE publish the Article and create and transmit videos based on the Article. In furtherance of such goals, the Parties desire to memorialize in this Agreement the respective rights of each Party in and to the Article and the Video.

3. Grant of Rights in Article. In consideration of JoVE agreeing to publish the Article, the Author hereby grants to JoVE, subject to **Sections 4** and **7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Article in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Article into other languages, create adaptations, summaries or extracts of the Article or other Derivative Works (including, without limitation, the Video) or Collective Works based on all or any portion of the Article and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. If the "Open Access" box has been checked in **Item 1** above, JoVE and the Author hereby grant to the public all such rights in the Article as provided in, but subject to all limitations and requirements set forth in, the CRC License.

4. Retention of Rights in Article. Notwithstanding the exclusive license granted to JoVE in **Section 3** above, the Author shall, with respect to the Article, retain the non-exclusive right to use all or part of the Article for the non-commercial purpose of giving lectures, presentations or teaching classes, and to post a copy of the Article on the Institution's website or the Author's personal website, in each case provided that a link to the Article on the JoVE website is provided and notice of JoVE's copyright in the Article is included. All non-copyright intellectual property rights in and to the Article, such as patent rights, shall remain with the Author.

5. Grant of Rights in Video – Standard Access. This **Section 5** applies if the "Standard Access" box has been checked in **Item 1** above or if no box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby acknowledges and agrees that, Subject to **Section 7** below, JoVE is and shall be the sole and exclusive owner of all rights of any nature, including, without limitation, all copyrights, in and to the Video. To the extent that, by law, the Author is deemed, now or at any time in the future, to have any rights of any nature in or to the Video, the Author hereby disclaims all such rights and transfers all such rights to JoVE.

6. Grant of Rights in Video – Open Access. This **Section 6** applies only if the "Open Access" box has been checked in **Item 1** above. In consideration of JoVE agreeing to produce, display or otherwise assist with the Video, the Author hereby grants to JoVE, subject to **Section 7** below, the exclusive, royalty-free, perpetual (for the full term of copyright in the Article, including any extensions thereto) license (a) to publish, reproduce, distribute, display and store the Video in all forms, formats and media whether now known or hereafter developed (including without limitation in print, digital and electronic form) throughout the world, (b) to translate the Video into other languages, create adaptations, summaries or extracts of the Video or other Derivative Works or Collective Works based on all or any portion of the Video and exercise all of the rights set forth in (a) above in such translations, adaptations, summaries, extracts, Derivative Works or Collective Works and (c) to license others to do any or all of the above. The foregoing rights may be exercised in all media and formats, whether now known or hereafter devised, and include the right to make such modifications as are technically necessary to exercise the rights in other media and formats. For any Video to which this Section 6 is applicable, JoVE and the Author hereby grant to the public all such rights in the Video as provided in, but subject to all limitations and requirements set forth in, the CRC License.

7. Government Employees. If the Author is a United States government employee and the Article was prepared in the course of his or her duties as a United States government employee, as indicated in **Item 2** above, and any of the licenses or grants granted by the Author hereunder exceed the scope of the 17 U.S.C. 403, then the rights granted hereunder shall be limited to the maximum rights permitted under such statute. In such case, all provisions contained herein that are not in conflict with such statute shall remain in full force and effect, and all provisions contained herein that do so conflict shall be deemed to be amended so as to provide to JoVE the maximum rights permissible within such statute.

8. Likeness, Privacy, Personality. The Author hereby grants JoVE the right to use the Author's name, voice, likeness, picture, photograph, image, biography and performance in any way, commercial or otherwise, in connection with the Materials and the sale, promotion and distribution thereof. The Author hereby waives any and all rights he or she may have, relating to his or her appearance in the Video or otherwise relating to the Materials, under all applicable privacy, likeness, personality or similar laws.

9. Author Warranties. The Author represents and warrants that the Article is original, that it has not been published, that the copyright interest is owned by the Author (or, if more than one author is listed at the beginning of this Agreement, by such authors collectively) and has not been assigned, licensed, or otherwise transferred to any other party. The Author represents and warrants that the author(s) listed at the top of this Agreement are the only authors of the Materials. If more than one author is listed at the top of this Agreement and if any such author has not entered into a separate Article and Video License Agreement with JoVE relating to the Materials, the Author represents and warrants that the Author has been authorized by each of the other such authors to execute this Agreement on his or her behalf and to bind him or her with respect to the terms of this Agreement as if each of them had been a party hereto as an Author. The Author warrants that the use, reproduction, distribution, public or private performance or display, and/or modification of all or any portion of the Materials does not and will not violate, infringe and/or misappropriate the patent, trademark, intellectual property or other rights of any third party. The Author represents and warrants that it has and will continue to comply with all government, institutional and other regulations, including, without limitation all institutional, laboratory, hospital, ethical, human and animal treatment, privacy, and all other rules, regulations, laws, procedures or guidelines, applicable to the Materials, and that all research involving human and animal subjects has been approved by the Author's relevant institutional review board.

10. JoVE Discretion. If the Author requests the assistance of JoVE in producing the Video in the Author's facility, the Author shall ensure that the presence of JoVE employees, agents or independent contractors is in accordance with the relevant regulations of the Author's institution. If more than one author is listed at the beginning of this Agreement, JoVE may, in its sole discretion, elect not take any action with respect to the Article until such time as it has received complete, executed Article and Video License Agreements from each such author. JoVE reserves the right, in its absolute and sole discretion and without giving any reason therefore, to accept or decline any work submitted to JoVE. JoVE and its employees, agents and independent contractors shall have

full, unfettered access to the facilities of the Author or of the Author's institution as necessary to make the Video, whether actually published or not. JoVE has sole discretion as to the method of making and publishing the Materials, including, without limitation, to all decisions regarding editing, lighting, filming, timing of publication, if any, length, quality, content and the like.

11. Indemnification. The Author agrees to indemnify JoVE and/or its successors and assigns from and against any and all claims, costs, and expenses, including attorney's fees, arising out of any breach of any warranty or other representations contained herein. The Author further agrees to indemnify and hold harmless JoVE from and against any and all claims, costs, and expenses, including attorney's fees, resulting from the breach by the Author of any representation or warranty contained herein or from allegations or instances of violation of intellectual property rights, damage to the Author's or the Author's institution's facilities, fraud, libel, defamation, research, equipment, experiments, property damage, personal injury, violations of institutional, laboratory, hospital, ethical, human and animal treatment, privacy or other rules, regulations, laws, procedures or guidelines, liabilities and other losses or damages related in any way to the submission of work to JoVE, making of videos by JoVE, or publication in *JoVE* or elsewhere by JoVE. The Author shall be responsible for, and shall hold JoVE harmless from, damages caused by lack of sterilization, lack of cleanliness or by contamination due to the making of a video by JoVE its employees, agents or independent contractors. All sterilization, cleanliness or decontamination procedures shall be solely the responsibility of the Author and shall be undertaken at the Author's expense. All indemnifications provided herein shall include JoVE's attorney's fees and costs related to said losses or damages. Such indemnification and holding harmless shall include such losses or damages incurred by, or in connection with, acts or omissions of JoVE, its employees, agents or independent contractors.

12. Fees. To cover the cost incurred for publication, JoVE must receive payment before production and publication the Materials. Payment is due in 21 days of invoice. Should the Materials not be published due to an editorial or production decision, these funds will be returned to the Author. Withdrawal by the Author of any submitted Materials after final peer review approval will result in a US$1,200 fee to cover pre-production expenses incurred by JoVE. If payment is not received by the completion of filming, production and publication of the Materials will be suspended until payment is received.

13. Transfer, Governing Law. This Agreement may be assigned by JoVE and shall inure to the benefits of any of JoVE's successors and assignees. This Agreement shall be governed and construed by the internal laws of the Commonwealth of Massachusetts without giving effect to any conflict of law provision thereunder. This Agreement may be executed in counterparts, each of which shall be deemed an original, but all of which together shall be deemed to me one and the same agreement. A signed copy of this Agreement delivered by facsimile, e-mail or other means of electronic transmission shall be deemed to have the same legal effect as delivery of an original signed copy of this Agreement.

A signed copy of this document must be sent with all new submissions. Only one Agreement required per submission.

CORRESPONDING AUTHOR:

Name:	Brandi Cossairt
Department:	Chemistry
Institution:	University of Washington
Article Title:	Synthesis of In37P20(O2CR)51 Clusters and their Conversion to InP Quantum Dots
Signature:	
Date:	11/21/2018

Please submit a signed and dated copy of this license by one of the following three methods:

1) Upload a scanned copy of the document as a pfd on the JoVE submission site;
2) Fax the document to +1.866.381.2236;
3) Mail the document to JoVE / Attn: JoVE Editorial / 1 Alewife Center #200 / Cambridge, MA 02139

For questions, please email submissions@jove.com or call +1.617.945.9051

UNIVERSITY of WASHINGTON

Brandi M. Cossairt
Associate Professor of Chemistry
University of Washington
Box 351700, Seattle, WA 98195-1700
cossairt@uw.edu
(206) 543-4643

January 14, 2019

Dear Editors at JoVE,

We believe we have addressed the requested editorial changes as delineated below.

Sincerely,

Dr. Brandi M Cossairt
Associate Professor of Chemistry
University of Washington
Seattle, WA 98195-1700

Editorial comments:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. Done.
2. For in-text referencing, please put the reference number before a period or comma. Done.
3. Please sperate Discussion and Representative Spectra into two sections: Representative Results and Discussion. Done
Representative Results: Please include at least one paragraph of text to explain the Representative Results in the context of the technique you have described, e.g., how do these results show the technique, suggestions about how to analyze the outcome, etc. The paragraph text should refer to all of the figures.
Discussion: Please revise the Discussion to explicitly cover the following in detail in 3-6 paragraphs with citations:
a) Critical steps within the protocol
b) Any modifications and troubleshooting of the technique
c) Any limitations of the technique
d) The significance with respect to existing methods
e) Any future applications of the technique
4. Please use h, min, s for time units. Done.
5. For each figure, please provide a title for the whole figure. Please bold the title in the manuscript. Done.

UNIVERSITY of WASHINGTON

Brandi M. Cossairt
Associate Professor of Chemistry
University of Washington
Box 351700, Seattle, WA 98195-1700
cossairt@uw.edu
(206) 543-4643

6. Please remove trademark (™) and registered (®) symbols from the Table of Equipment and Materials. Done.