Electronic supporting information for: Ternary synthesis of colloidal Zn₃P₂ quantum dots

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Experimental:

Sodium (dry stick, ACS reagent), potassium (in mineral oil, 98%), red phosphorus (99.999%), myristic acid (\geq 99), Rhodamine 6G, tetrabutylammonium hexafluorophosphate (for electrochemical analysis, >99%), and hexanes (a mixture of isomers, CHROMASOLV) were purchased from Sigma-Aldrich Chemical Company and used without further purification. Omni Trace nitric acid was purchased from EMD Millipore and used without further purification. 18.2 MΩ water was collected from an EMD Millipore water purification system. Acetonitrile was purchased from Burdick and Jackson® (<5ppm low-water brand) and stored in an argon pressurized stainless steel drum plumbed directly into a glove-box. Celite 545 and zinc acetate (99.99%) were purchased from Sigma-Aldrich Chemical Company and heated at 150 °C under vacuum overnight and stored in a nitrogen filled inert glove box prior to use. Oleic acid (90%) was purchased from Sigma-Aldrich Chemical Company and stirred over sieves overnight prior to being freeze-pump-thawed three times and stored in a nitrogen filled inert glove box prior to use. ZnEt₂ (95%) was purchased from Strem Chemicals and stored in a -35 °C freezer in a nitrogen filled inert atmosphere glove box. All solvents, including 1-octadecene (295%), 1,2dimethoxyethane (99%), and pentane were purchased from Sigma-Aldrich Chemical Company, dried by stirring overnight with CaH₂, distilled, and stored over 4 Å molecular sieves. C₆D₆ and was purchased from Cambridge Isotope Labs and was similarly dried and stored. ¹H (Field: 300 MHz) and ³¹P{H} (Field: 121 MHz) NMR spectra were collected on a 300 MHz Bruker Avance spectrometer. UV-Vis spectra were collected on a Cary 5000 spectrophotometer from Agilent. Fluorescence measurements were taken on a Horiba FL3-21tau Fluorescence Spectrophotometer. Powder XRD spectra were collected on a Bruker D8 Discover with GADDS 2-D XRD system. ICP-OES was performed using a Perkin Elmer Optima 8300. TEM images were collected on an FEI Tecnai G2 F20 microscope. TEM analysis was performed using manual analysis with the help of the ImageJ software package.¹ HRTEM analysis was performed using the Fei True Image software package. TGA data was collected on a TA Instruments TGA. SEM images were collected on a FEI Sirion SEM. P(SiMe₃)₃ was prepared following a literature procedure.²

Synthesis of $Zn(O_2C(CH_2)_{12}CH_3)_2$: 8.78 grams (38.4 mmol) of myristic acid was added to a 250 mL Schlenk flask and transferred into a nitrogen filled glove box. 100 to 150 mL of pentane was added to the flask to dissolve the acid. The flask was sealed with a septum and was transferred onto a Schlenk line. In the nitrogen filled glove box, 2.25 grams (18.2 mmol) of diethyl zinc was weighed out and mixed with 2 milliliters of pentane and drawn into a syringe outfitted with a needle. The needle was then capped with a septum. *Warning, the next step is very dangerous and should be performed under supervision with extreme care.* The diethyl zinc solution was added drop-wise slowly to the myristic acid solution in an ice bath and under nitrogen. After addition, the solution was removed from the ice bath and left to stir overnight. The solution was transferred into a nitrogen filled glove box and the white solid was collected in a frit. The white solid was washed with copious amounts of pentane to remove any excess myristic acid prior to being dried. The yield was 8.78 grams. The average percent yield was 88% (average of two runs).

Synthesis of $Zn(O_2C(CH_2)_7HC=CH(CH_2)_7CH_3)_2$: 8.99 grams (31.8 mmol) of oleic acid was added to a 250 mL Schlenk flask in a nitrogen filled glove box. 100 to 150 mL of pentane was added to the flask. This open port was sealed with a septum. This flask was transferred onto a Schlenk line. In the nitrogen filled glove box, 2.17 grams (17.6 mmol) of diethyl zinc was weighed out and mixed with 10 milliliters of pentane and drawn into a syringe outfitted with a needle. The needle was then capped with a septum. Warning, the next step is very dangerous and should be performed under supervision with extreme care. The diethyl zinc solution was added drop-wise slowly to the oleic acid solution over ice and under nitrogen. After addition, the solution was removed from the ice bath and left to stir overnight. The solution was transferred into a nitrogen filled glove box and the white solid was collected in a frit. The white solid was washed with copious amounts of pentane to remove any excess oleic acid prior to being dried. The yield was 7.89 grams. The average percent yield was 80% (average of two runs).

Synthesis of zinc phosphide quantum dots: 0.312 grams (0.6 mmol) of Zn(MA)₂ is dispersed in 5 grams of 1-octadecene in a nitrogen filled glove box and pulled into a syringe and stoppered with a septum. The slurry was injected into a 25 mL 3-neck flask outfitted with a reflux condenser, septum, and thermowell under nitrogen. A temperature controller with a probe inside the thermowell was used to control the temperature. The flask was degassed overnight at 100 °C under vacuum. The flask was put under nitrogen and heated to 101 °C. In a nitrogen filled glove box, 30.75 µL (0.3 mmol) of diethyl zinc and 58 µL (0.2 mmol) of P(SiMe₃)₃ were added to 3 grams of 1-octadecene and drawn into a syringe and its needle was capped with a septum. In the reaction where there is a delay in $P(SiMe_3)_3$ addition, both reagents were injected into the zinc carboxylate solution in 1.5 grams 1-ODE. The heating was turned off. At 100.2 °C the temperature controller was turned on to its highest volume setting (>2L) and set at 315 °C. At 100.0 °C, the zinc/phosphorus solution was rapidly injected into the flask. The solution was allowed to heat up and run for 60 minutes. Aliquots of 50 µL were taken out and injected into 6 mL of hexanes for UV-Vis monitoring. Alternatively, the desired amount of zinc myristate can be made by degassing the desired amount of myristic acid and injecting diethyl zinc into the flask to provide Zn(MA)₂ in situ. Additionally, analogous particles can be made with zinc oleate by weighing out the same mmol of zinc oleate into a reaction flask prior to putting the reaction vessel under nitrogen on a Schlenk line. 74.5 mg of particles were collected after work-up when using 0.6 mmol of zinc oleate. Using the TGA model of the mass % coming from the zinc phosphide core (28.46%) the 74.5 mg of particles is an 82% yield.

Zinc phosphide quantum dot work-up procedure: All work up was done under nitrogen using dry solvents. To halt particle formation, the reaction flask was removed from the heating mantle and placed in a RT oil bath. The reaction mixture was cannula transferred to a 25 mL Schlenk flask and the solvent was distilled off. The flask was brought into a nitrogen filled glove box and the QDs were dissolved in pentane. The solution was centrifuged to remove any insoluble byproducts. To the pentane solution 15 mL of ethyl acetate and 7 mL of acetonitrile were added to crash out the dots. The heterogeneous solution was centrifuged and the solution was decanted off. This was repeated until mostly solid was collecting at the bottom (usually 3 to 4 iterations). Next, toluene was used to dissolve the particles and they were crashed out with minimal acetonitrile. This was repeated once or twice. The clean particles could be stored in either pentane or toluene.

NMR experiments: In a nitrogen filled glove box, 0.0795 grams (0.15 mmol) of $Zn(MA)_2$ was added to a J-Young NMR tube. C_6D_6 was added to the solid. The NMR tube was put in a freezer overnight. While the solvent was still frozen, 14.5 µL (0.05 mmol) of P(TMS)₃ was added via syringe. This was put back in the freezer. Next, 7.75 µL (0.075 mmol) of ZnEt₂ was added and the tube was sealed. The ³¹P{H} nmr data was monitored on a 121 MHz spectrometer taking 256 scans with one minute of shaking in between spectra. This was also performed with 0.0275 (0.15 mmol) grams of Zn(Ac)₂ instead of Zn(MA)₂. For this reaction, ZnEt₂ and P(SiMe₃)₃ were pre-mixed with C_6D_6 . For the monitoring reactions, an internal standard of PPh₃ in Dowtherm® or C_6D_6 within a sealed capillary was used for referencing. If not, the phosphorus spectra were externally calibrated with a H₃PO₄ solution.

Photoresponse: A FTO coated glass slide $(5 \times 1 \text{ cm})$ with *nano*ITO deposited on one end $(1.5 \times 1 \text{ cm})$ was used as a conductive substrate.³ Electrophoretic deposition was used to deposit oleate capped particles onto the *nano*ITO. Particles were in a toluene/acetonitrile solution. The desired substrate was situated roughly 1 cm from a counter *nano*ITO electrode. A 45 V potential was applied across the two electrodes with a DC power source and was held for roughly 5 minutes. The film was annealed at 350 °C for one hour under vacuum. Chopped light controlled potential electrolysis was performed using a BASi Epsilon EC potentiostat. A 3 electrode set-up was used with the quantum dot film was the working electrode, a platinum wire was the auxiliary electrode, and a silver wire was used as the reference electrode. A 0 V bias versus the silver wire was used as the electrolyte. A white light source was used as the chopped light source. The light was manually blocked and unblocked for ten second increments.

Sample preparation for characterization: TEM: A 50/50 solution by volume of pentane and toluene was used as the solvent. A few drops of the QD solution was added to this. The TEM grid (Ultrathin carbon on holey carbon support film, 400 mesh Ted Pella; Graphene support on Lacey Carbon, 300 mesh Ted Pella; Ultra-thin carbon with removable Formvar, 400 mesh Ted Pella) was suspended and 1-2 drops was added and left to dry. The grid was put under vacuum overnight to remove any residual solvent. XRD: Particles were worked-up and dried into a paste. This paste was placed on the center of a silicon <100> single crystal wafer. A syringe was used to draw a square of Apiezon H grease around the sample and a piece of Kapton film was placed down and sealed with the grease. ICP-OES: A small pipette tip of worked up particle solution was crashed out. The solvent was removed. Enough concentrated high purity nitric acid was added to dissolve the particles so the final solution could be diluted with 18.2 M Ω water in a volumetric flask. TGA: worked-up particles were dried overnight and brought to the instrument room under nitrogen and scraped onto a TGA platinum boat.



Figure S1. 60 minute trace for a 0.2 mmol P(SiMe₃)₃ reaction where ZnEt₂ was not used.



Figure S2. Final temperature effect on LEET for particles synthesized by injecting 1.5 equivalents of $ZnEt_2$ and 1 equivalent of $P(SiMe_3)_3$ into 3 equivalents of $Zn(MA)_2$ and heating up to 315 °C. Each synthesis used 0.2 mmol of $P(SiMe_3)_3$ and was repeated three times for the standard deviation.



Figure S3. Absorbance and Fluorescence of particles grown to 255 °C showing highly red shifted fluorescence. Gaussian fit of fluorescence plotted for clarity.



Figure S4. Concentration effect on absorption of particles grown to 315 °C, determined by altering the amount of reagents and keeping the total volume (8 grams 1-ODE) the same in order to preserve ramp rate.



Figure S5. ¹H NMR control mixing 1.5 ZnEt₂ and 1 P(SiMe₃)₃ showing no reaction between these two species in C₆D₆ at room temperature or even 80 °C. The triplet at 1.19 and quartet at 0.19 ppm are from ZnEt₂ and the doublet at 0.29 is from P(SiMe₃)₃.



Figure S6. ¹H and ³¹P{¹H} NMR control mixing showing 3 $Zn(Ac)_2$ and 1 P(SiMe₃)₃ reacting very slowly over the course of hours. The half-life was determined to be around 5 hours.



Figure S7. ¹H NMR data showing the formation of $[Zn_5(Ac)_6(Et)_4]$ by mixing 3 ZnAc₂ and 1.5 ZnEt₂ in C₆D₆.



Figure S8. ¹H and ³¹P{¹H} NMR showing the very fast reaction (half-life < 5 minutes) between $[Zn_5(Ac)_6(Et)_4]$ and $P(SiMe_3)_3$.



-241 -243 -245 -247 -249 -251 -253 -255 -257 -259 -261 -263 -265 -267 -269 -271 -273 -275 -277 -279 -281 -283 -285 -287 -289 -291 f1 (ppm)

Figure S9. ${}^{31}P{}^{1}H$ NMR data showing the reaction between 3 Zn(MA)₂, 1.5 ZnEt₂, and P(SiMe₃)₃.



Figure S10. Fitting of the 125 minute time trace of the ¹H NMR data of the reaction between $3 \text{ Zn}(\text{Ac})_2$, 1.5 ZnEt₂, and P(SiMe₃)₃. These integrations show the formation of our proposed intermediate.



Figure S11. ${}^{31}P{}^{1}H$ NMR spectrum of a 30 second aliquot showing that the only molecular species present is the intermediate at -276 ppm. The inset is a close-up of the peak showing it is the only molecular species present.



Figure S12. ${}^{31}P{}^{1}H$ data for a typical QD reaction performed in a J-Young NMR tube left at the labeled temperatures for 1 minute each. This data shows the formation of the molecular

intermediate at -276 ppm followed by its disappearance without any other molecular phosphorus containing species forming.



Figure S13. UV-VIS data of aliquots taken during a reaction where the 3 precursors were premixed in 3 grams of 1-ODE for 8 hours to fully form the molecular intermediate prior to injection into 5 grams of 1-ODE and heated up to 315 °C.



Figure S14. UV-Vis data showing there is no difference in adding $P(SiMe_3)_3$ and $ZnEt_2$ simultaneously versus pre-forming the pentanuclear zinc cluster $[Zn_5(Ac)_6(Et)_4]$ prior to injecting $P(SiMe_3)_3$.





Figure S15. Size distribution of particles grown to 315 $^{\circ}$ C in a synthesis using 0.2 mmol of P(SiMe₃)₃, which were found to have an average size of 2.9 ± 0.6 nm. 300 particles were measured.



Figure S16. TEM and size distribution of particles grown to 255 °C in a synthesis using 0.2 mmol $P(SiMe_3)_3$, which were found to have an average size of 2.6 ± 0.5 nm. 300 particles were measured. The image contrast was increased in Photoshop.



Figure S17. TEM and size distribution of particles synthesized with 0.6 mmol $Zn(OA)_2$ and 0.2 mmol $P(SiMe_3)_3$. The average diameter was determined to be 2.6 ± 0.5 nm. 300 particles were measured.



Figure S18. Air-free XRD data collected from a dried sample of particles synthesized using 0.4 mmol of $P(SiMe_3)_3$ and sealed under a Kapton film. The data was collected for four hours and the signal from the Kapton film was subtracted off. The data is compared to Zn_3P_2 , ZnO, Zn, and P (COD 1010287, 1011258, 9012345, and 4307698).



Figure S19. Sample used for XRD was left out in air for several weeks and was re-analyzed showing air oxidization had occurred.



Figure S20. Air-free XRD of particles synthesized with 0.6 mmol $Zn(OA)_2$ and 0.2 mmol $P(SiMe_3)_3$.



Figure S21. TEM and size distribution of particles grown to 315 $^\circ\text{C}$ in a synthesis using 0.4 mmol P(SiMe_3)_3 , which were found to have an average size of 3.0 \pm 0.5 nm. 300 particles were measured.



Figure S22. ¹H NMR taken on a 300 MHz spectrometer in C_6D_6 of worked up QDs showing only oleate ligands.



Figure S23. TGA data and derivative of zinc phosphide particles synthesized with zinc oleate and grown at 315 $^{\circ}$ C using a ramp rate of 10 $^{\circ}$ C/min.

TGA model

Assumptions:

- Particles have a diameter of 2.9 nm
- Zn:P ratio is 2.5:1
- Possible zinc oxide shell thickness 0.116 nm (less than a monolayer)
- Surface ligands are Zn(OA)₂
- Zn(OA)₂ converts to ZnO upon thermal decomposition

Inorganic core mass:

$$mass = density \times volume = density \times \frac{4}{3}\pi r^{3}$$
$$mass = (4.55 \ g \ cm^{-3}) \times \left(\frac{4}{3}\pi \left(\left(\frac{2.9}{2} - 0.116\right) \times 10^{-7}\right)^{3}\right) = 4.524 \ \times 10^{-20} \ grams$$

Moles of zinc and phosphorus

moles of zinc:
$$3 \times \frac{4.524 \times 10^{-20} \text{ grams}}{258.12 \text{ gram mol}^{-1}} = 5.259 \times 10^{-22} \text{ moles}$$

moles of phosphorus: $2 \times \frac{4.524 \times 10^{-20} \text{ grams}}{258.12 \text{ gram mol}^{-1}} = 3.506 \times 10^{-22} \text{ moles}$

ZnO layer

volume of layer
$$=\frac{4}{3}\pi r^3 - Zn_3P_2$$
 volume
volume $=\frac{4}{3}\pi \left(\frac{2.9}{2}\right)^3 - \frac{4}{3}\pi \left(\frac{2.9}{2} - 0.116\right)^3 = 2.826 \text{ nm}^3 = 2.826 \times 10^{-21} \text{ cm}^3$

 $mass of layer = density \times volume$

mass of layer =
$$(5.61 \ g \ cm^{-1}) \times (2.826 \times 10^{-21} \ cm^3) = 1.585 \times 10^{-20} \ grams$$

moles
$$ZnO = moles Zn = \frac{mass}{MW} = \frac{1.585 \times 10^{-20} grams}{81.41 grams mol^{-1}} = 1.948 \times 10^{-22} moles$$

Surface

The total moles of zinc can be determined using the Zn:P ratio

total moles of zinc = moles $P \times 2.5 = 3.506 \times 10^{-22} \times 2.5 = 8.764 \times 10^{-22}$ moles

remaining moles of zinc =
$$8.764 \times 10^{-22} - 1.948 \times 10^{-22} - 5.259 \times 10^{-22}$$

remaining moles of zinc =
$$1.558 \times 10^{-22}$$
 moles

 $mass of surface = moles \times MW$

mass of surface = $(1.558 \times 10^{-22} \text{ moles}) \times (628.3 \text{ grams mol}^{-1})$ = $9.790 \times 10^{-20} \text{ grams}$

mass of surface ZnO post heating = surface zinc moles $\times MW_{ZnO}$

Surface $ZnO = (1.558 \times 10^{-22} \text{ moles}) \times (81.41 \text{ grams mol}^{-1}) = 1.268 \times 10^{-20} \text{ grams}$

Inorganic mass %

Total mass = 4.524×10^{-20} grams + 1.585×10^{-20} grams + 9.790×10^{-20} grams

Total mass = 1.590×10^{-19} *grams*

Inorganic mass = core mass + ZnO layer mass + surface ZnO mass

Inorganic mass = 4.524×10^{-20} *grams* + 1.585×10^{-20} *grams* + 1.268×10^{-20} *grams*

Inorganic mass = 7.378×10^{-20} grams

Inorganic mass % = 46.4%



Figure S24. SEM images of the bare *nano*ITO substrate (left) and the film of annealed electrodeposited particles on the *nano*ITO substrate (right).



Figure S25. Controlled potential electrolysis of Zn_3P_2 nanocrystals on *nano*ITO under chopped white light illumination.

Sample calculation using the Brus equation.⁴

$$E^* = E_{bulk} + \frac{\hbar^2 \pi^2}{2R^2} \times \left(\frac{1}{m_e^*} + \frac{1}{m_h^*}\right) - \frac{1.8e^2}{4\pi\varepsilon_r\varepsilon_0 R}$$

Where E^* is the LEET, E_{bulk} is the band gap of the bulk semiconductor, R is the radius of the particle, m_e^* and m_h^* are the reduced electron and hole masses, e is the charge of an electron, ε_r is the dielectric of the bulk semiconductor, and ε_0 is the permittivity of free space.

$$3.833 \times 10^{-19} = 2.403 \times 10^{-19} + \frac{\hbar^2 \pi^2}{2R^2} \times \left(\frac{1}{0.2 \times 9.109 \times 10^{-31}} + \frac{1}{0.22 \times 9.109 \times 10^{-31}}\right) - \frac{1.8e^2}{4\pi (11)\varepsilon_0 R}$$

Mathematica was used to solve for R.

$$R = 1.905 nm$$

 $D = 3.81 nm$

Table I. Summary of Brus analysis results.

m_e^*	m_h^*	255 °C particle diameter (nm)	315 °C particle diameter (nm)
0.128 ⁵	0.255^{6}	3.4	4.2
0.2^{7}	0.22^{7}	3.0	3.8
0.35 ⁸	0.45^{8}	2.1	2.7
0.2^{7}	0.45^{8}	2.6	3.2
0.35^{8}	0.22^{7}	2.6	3.3

Sample exciton Bohr radius calculation.⁹

$$a_{ex} = a_H \times \varepsilon_r \times \frac{m_0}{\mu}$$

Where a_H is the Bohr radius is 5.2819*10⁻¹¹ meters, ε_r is the bulk dielectric constant (11), m_0 is the mass of an electron, and μ is:

$$\mu = \frac{1}{m_e^{-1} + m_h^{-1}}$$

Where m_e and m_h are the reduced electron and hole masses.

$$\mu = \frac{1}{\frac{1}{0.128m_0} + \frac{1}{0.255m_0}} = 7.763 \times 10^{-32} \, kg$$

$$a_H = (5.2819 \times 10^{-11}) \times (11) \times \frac{9.109 \times 10^{-31} kg}{7.763 \times 10^{-32} kg} = 6.84 \times 10^{-9} m = 6.84 nm$$

Table II. Summary of exciton Bohr radii.

m_e^*	m_h^*	Exciton Bohr radius (nm)
0.128 ⁵	0.255^{6}	6.84
0.2^{7}	0.22^{7}	5.56
0.35 ⁸	0.45^{8}	2.96
0.2^{7}	0.45^{8}	4.21
0.35 ⁸	0.22^{7}	4.32

Sample calculation using the Scherrer equation.¹⁰

$$L = \frac{0.9\lambda}{\Delta(2\theta)\cos(\theta_0)}$$
$$D = \frac{4}{3}L$$

Where L is Scherrer or coherence length, λ is the wavelength of the x-ray radiation (0.15418 nm), $\Delta(2\theta)$ is the full-width at half-maximum in radians, θ_0 is the angle of reflection of the peak in radians, and D is the sphere diameter in nm.



How to manually measure particle diameters

- 1. Opened TEM image in ImageJ.
- 2. Set the scale appropriately.
- 3. Zoomed in on the particles.
- 4. Used the line tool to draw a line across the particle and measure it.



5. Measured 300 unique particles from pictures taken at various magnifications and from different spots on a grid to ensure proper sampling of the particles.

References:

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