Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Sustainable Quantum Dot Chemistry: Effects of Precursor, Solvent, and Surface Chemistry on the Synthesis of Zn_3P_2 Nanocrystals

Robert A. Swain[a], Benjamin F.P. McVey[a], Héloïse Virieux[a], Fabio Ferrari[a], Yann Tison[b], Hervé Martinez[b], Bruno Chaudret[a], Céline Nayral[a*], and Fabien Delpech[a*]

[a]LPCNO, Université de Toulouse, CNRS, INSA, UPS, 135 Avenue de Rangueil, 31077 Toulouse, France

[b]Institut des Sciences Analytiques et de Physico-Chimie pour l''Environnement et les Matériaux (IPREM-ECP), Université de Pau et des Pays de l'Adour, Hélioparc, 2 Av. Président Angot, F-64053 Pau, France

Corresponding Authors: cnayral@insa-toulouse.fr, fdelpech@insa-toulouse.fr

Experimental Methods:

Materials: Acetonitrile (MeCN, 99.8%), hexadecylamine (HDA 98%), octylamine (OAm, 99%), oleylamine (OLA, 90%), and zinc acetate ($Zn(OAc)_2$, 99.99%) were purchased from Sigma-Aldrich. Tris(trimethylsilyl)phosphine ($(TMS)_3P$, >98.0%) was purchased from Strem. *Bis*(N,N'-diisopropylacetamidinato) Zinc(II) was purchased from Nanomeps. Mesitylene (RPE, analysis grade) was purchased from Carlo Erba. All reagents and solvents were dried, distilled, and degassed prior to use in synthesis. All manipulations were performed under an argon atmosphere using Schlenk line techniques, or in an argon-filled glovebox.

*Sample **1** - Zn_3P_2 Nanocrystal Synthesis from $Zn(OAc)_2(HDA)_2$:* 82.6 mg (0.450 mmol) zinc acetate and 0.900 mmol primary amine (sample **1**: HDA, 217.3 mg, Sample **1b**: OAm, 116.3 mg) were dissolved in 8 mL mesitylene in a 100 mL round-bottom flask in the glovebox. Outside the glovebox, on the Schlenk line, the system was raised to 150°C at which temperature 2 mL of a $(TMS)_3P$ solution (0.15 M in mesitylene) was injected. The reaction was stirred for two hours, during which time the solution turned from clear and colorless to light yellow, orange, and finally brick red. After cooling to room temperature, 15 mL MeCN were added in the glovebox to precipitate the particles, which were isolated by centrifugation at 20000 rpm for 15 minutes, in centrifuge tubes closed under argon. The colorless supernatant was discarded and the particles re-dispersed in 3 mL toluene, and the washing procedure was repeated a second time, after which the red solid pellet was dried for 3h under vacuum on the Schlenk line.

*Sample **2** - Zn_3P_2 Nanocrystal Synthesis from $Zn(amid)_2$ in Oleylamine:* 78.3 mg (0.225 mmol) bis(N,N'-diisopropylacetamidinato) Zinc(II) and $(TMS)_3P$ (37.1 mg (0.150 mmol) in the case of Sample **2** and 112.7 mg (0.450 mmol) in the case of Sample **2b**) were dissolved in 5 mL oleylamine in a 100 mL round-bottom flask in the glovebox. Outside the glovebox, the temperature of the vessel was raised to 230°C under argon on the Schlenk line and was allowed to react for 3 hours. The solution turned from colorless and clear to orange and finally to red-brown. After 3 hours, the system was allowed to cool to room temperature. In the glovebox, 5 mL toluene is added to facilitate miscibility between oleyalmine and MeCN, of which 15 mL were added to precipitate the particles. The particles were isolated by centrifugation at 20000 rpm for 15 minutes, in centrifuge tubes closed under argon. The colorless supernatant was discarded and the particles re-dispersed in 3 mL toluene, and the washing procedure was repeated a second time, after which the red solid pellet was dried for 3h under vacuum on the Schlenk line.

*Sample **3** - Zn_3P_2 Nanocrystal Synthesis from $Zn(amid)_2$ in Mesitylene:* 78.3 mg (0.225 mmol) bis(N,N'-diisopropylacetamidinato) Zinc(II), 380.3 mg (1.575 mmol) HDA, and 37.1 mg (0.150 mmol) $(TMS)_3P$ were dissolved in 5 mL mesitylene in a 100 mL double-walled Fischer Porter flask in the glovebox. The closed system was removed from the glovebox and raised to 200°C for a total of 18 hours, during which time the solution became dark red-brown. The system was allowed to cool to room temperature, after which 15 mL MeCN were added in the glovebox to precipitate the particles, which were isolated by centrifugation at 20000 rpm for 15 minutes, in centrifuge tubes closed under argon. The colorless supernatant was discarded and the particles re-dispersed in 3 mL toluene, and the washing procedure was repeated a second time, after which the red solid pellet (Sample **3**) was dried for 3h under vacuum on the Schlenk line.

Zn_3P_2 Seeded Particle Growth: To the crude solution of Sample **3** (described above), one-third the initial quantity of each reactant was added in the glovebox (26.1 mg (0.075 mmol) $Zn(amid)_2$, 126.8 mg (0.525 mmol) HDA, and 12.4 mg (0.05 mmol) $(TMSi)_3P$. The vials used to weigh these reactants were rinsed into the reaction vessel using the crude solution, to avoid changing the concentration by adding more solvent. The vessel was closed and removed from the glovebox, where it was raised to 200°C for 18 hours, mimicking exactly the conditions of the initial core synthesis. This process was repeated until growth appeared to stop (as monitored by a red-shift in the UV-Vis absorption peak), yielding Sample **3d**.

Sample Characterization: Inductively Coupled Plasma Mass Spectrometry (ICP-MS) data was obtained by the Mikroanalytisches Laboratorium Kolbe, in Oberhausen, Germany, with the samples being analyzed under argon to avoid air exposure. Photoluminescence (PL) spectra were acquired with a PTI Fluorescence Master System equipped with a xenon lamp ($\lambda_{excitation} = 400$ nm). Fluorescent quantum yields were calculated using the comparative method. Quartz cuvettes (10 mm pathlength) were initially cleaned with aqua regia followed by washing with toluene and ethanol. Post washing cuvettes were dried in an oven (120 °C) to remove any traces of solvent. The quantum yield standard used was rhodamine 6G (dissolved in absolute ethanol 99.5 % *Sigma-Aldrich*). All tested nanocrystals had an optical density between 0.05 - 0.17 at the excitation wavelength used (450 nm). TEM samples were prepared in the glovebox by dropping a single drop of a dilute solution of washed particles in toluene or pentane onto a carbon-covered copper grid and allowing the solvent to dry slowly. TEM analysis was performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (TEMSCAN) on a JEOL JEM 1400 electron microscope operating at 100 kV with a point resolution of 4.5 Å. The size distributions were determined by measuring at least 250 particles with Fiji (imageJ) software obtained online. Solid state NMR data were recorded by a Bruker Avance III 400 spectrometer. For each sample, approximately 50 mg was packed into a 3.2 mm zirconia rotor in the glovebox. The rotors were spun at either 16 or 20 kHz at 293 K. Small flip angles (~30°) were used with recycle delay times of 5 and 10 seconds for ^{1}H MAS and ^{13}C direct polarization (DP) analyses, respectively. ^{31}P Hahn-Echo MAS analyses were performed with a recycle delay of 60 s. ^{13}C CP-MAS and ^{31}P CP-MAS NMR spectra were obtained with a recycle delay of 3 s and contact times of 2 ms and 4 ms, respectively. UV-Visible Absorption spectra were measured with a Cary Series UV-Vis-NIR spectrometer from Agilent using cells of 2 mm. X-Ray diffraction spectra were recorded on an

MPD Pro Panalytical spectrometer using Cu K-α radiation. In almost every case, the powder was dissolved in a small amount of pentane and drop-cast on a Kapton film in the glovebox, which was covered by a second Kapton film and sealed with grease under argon to prevent exposure to air. However, this results in the appearance of a broad, intense peak at 23.1°, a second broad, pointy, but less intense peak at 37.6°, and a final small bump at 41.9° (see Figure S12 for a blank scan of the Kapton film with silicon grease). The representative X-Ray diffractogram in Figure 1, however, was obtained with no Kapton, via direct application of the powder on a silicon wafer.

Characterization of Zn_3P_2 Nanocrystals:

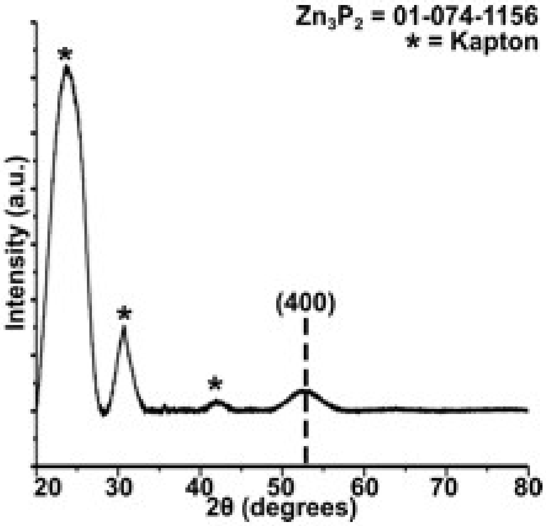

Figure S1: *XRD (b) of **Sample 1***

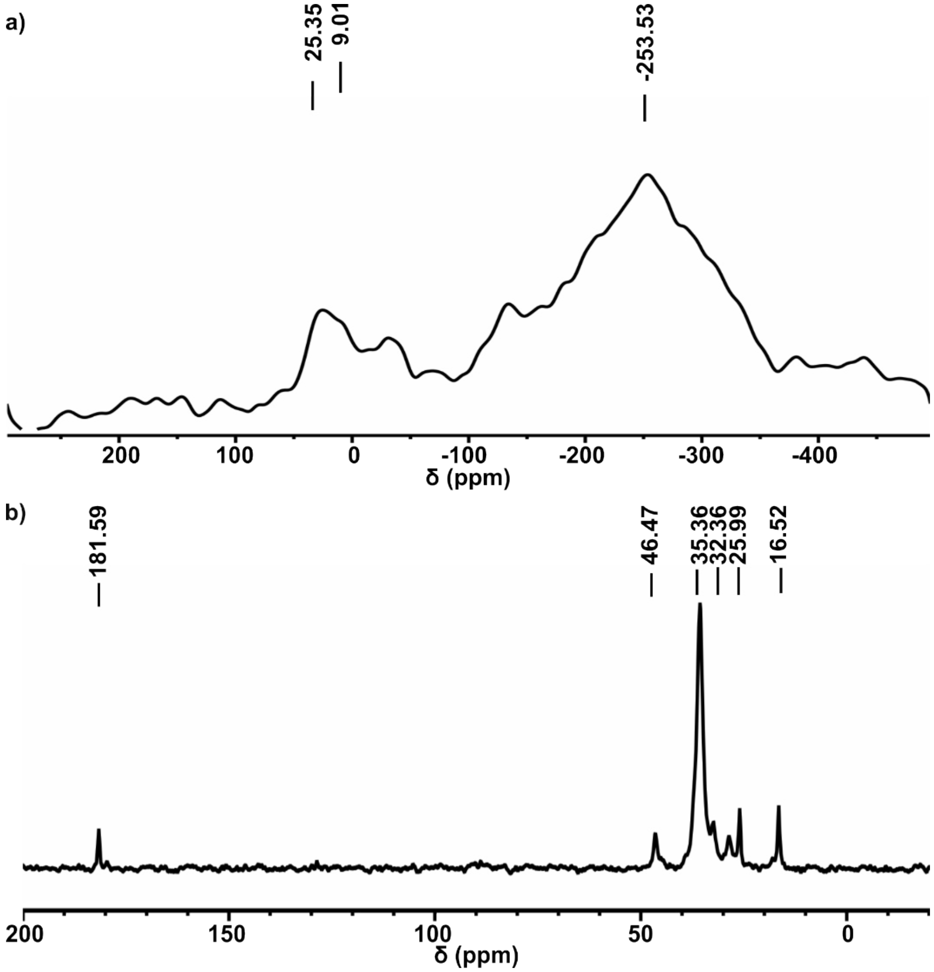

Figure S2: *$^{31}P\{^1H\}$ MAS NMR (a) and $^{13}C\{^1H\}$ CP-MAS NMR (b) of* ***Sample 1***

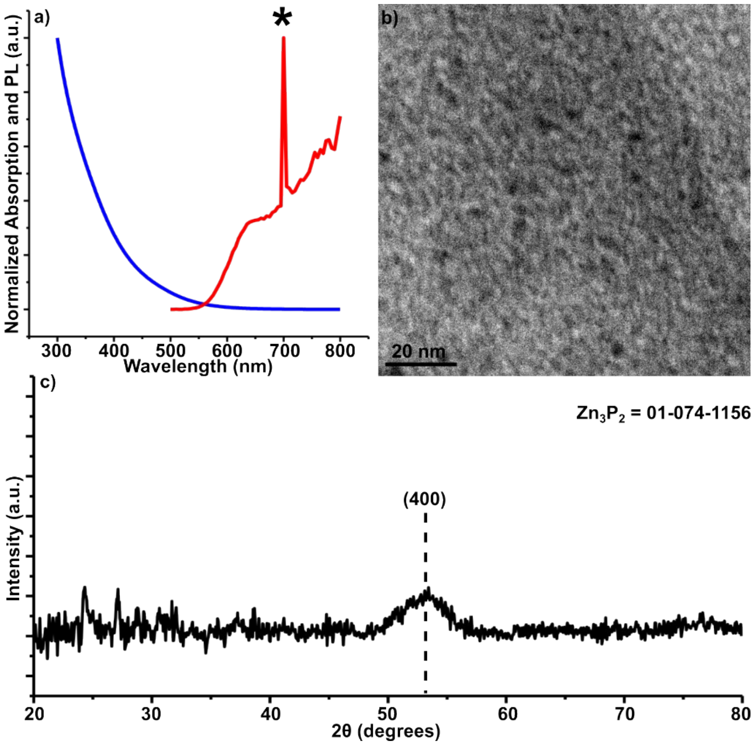

Figure S3: *Absorption (blue) and PL Emission (red, *second harmonic peak of excitation wavelength) Spectra (a), TEM image (b), and XRD (c) of* ***Sample 1b***

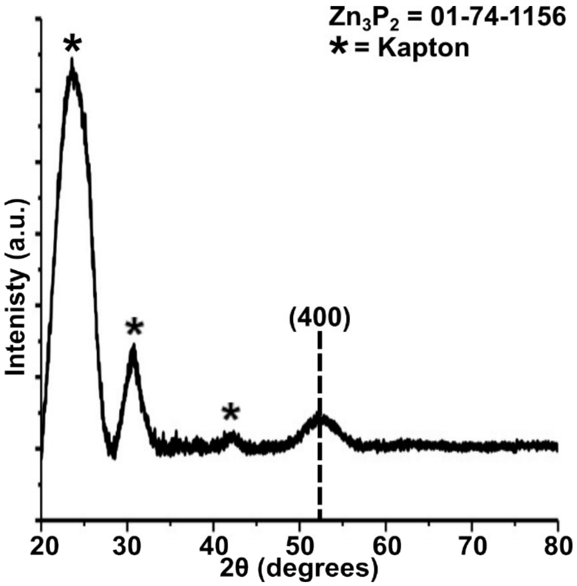

Figure S4: *X-Ray Diffractogram of Sample* ***2***

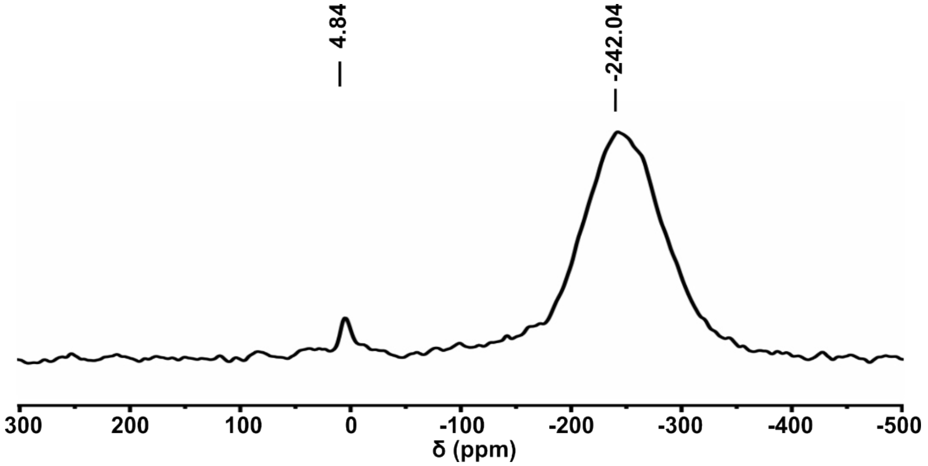

Figure S5: *$^{31}P\{^1H\}$ MAS NMR Spectrum of **Sample 2***

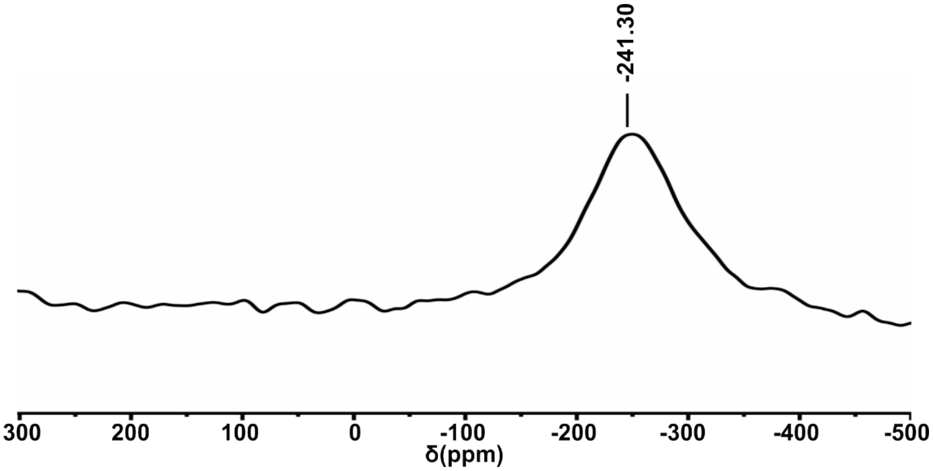

Figure S6: *$^{31}P\{^1H\}$ MAS NMR Spectrum of **Sample 3***

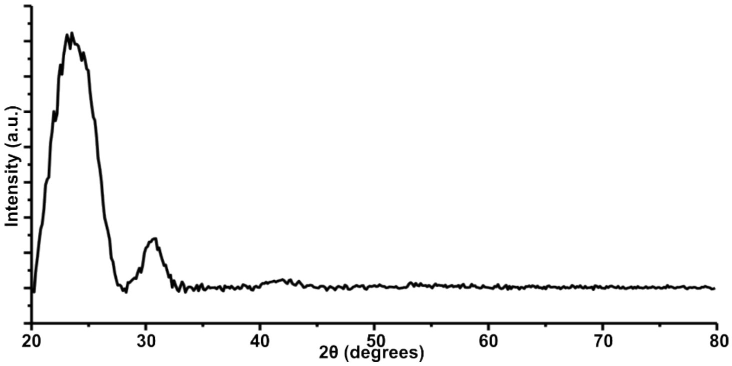

Figure S7: *Blank X-Ray Diffractogram (Kapton and Si grease)*

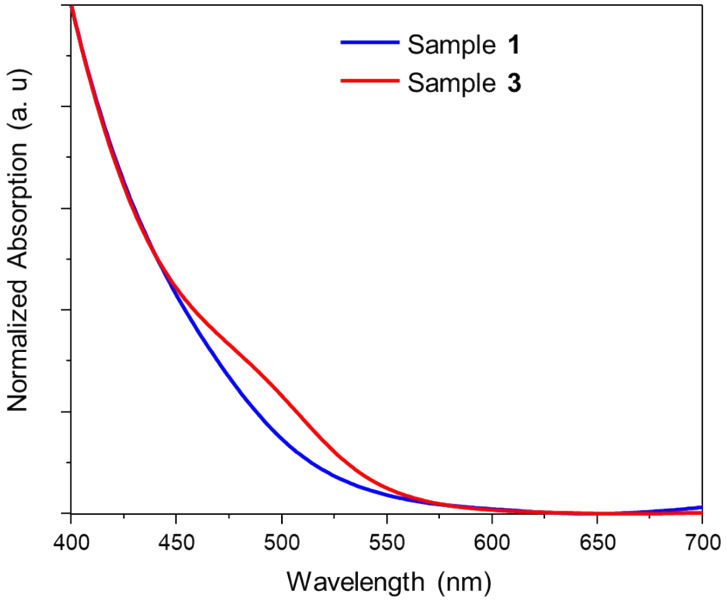

Figure S8: *Absorption Spectra of Sample **1** (blue) Sample **3** (red)*

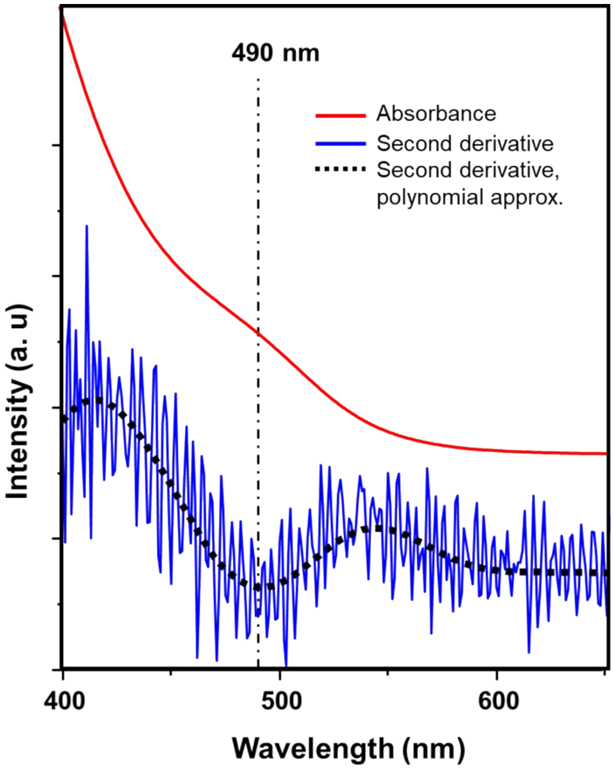

Figure S9: *Absorption Spectrum of Sample **3** (red), Second derivative (blue) and polynomial fitting of the second derivative (dashed black line)*