Electronic Supplementary Material (ESI) for Nanoscale.

Synthesis of luminescent core/shell α-Zn_3P_2/ZnS quantum dots

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Experimental Details

Characterization

X-ray Diffraction (XRD)

XRD characterization was performed using a Bruker AXS D8 DISCOVER GADDS Microdiffractometer with Cu Kα radiation (λ = 0.154 nm). Samples were prepared by drop casting a concentrated solution of nanoparticles in hexanes onto a 1 cm x 1 cm <100> silicon substrate inside of a nitrogen filled glovebox. XRD scans were collected using an incident angle of $\omega = 3°$. XRD peaks were indexed using GSAS-II software.[1]

Transmission Electron Microscopy (TEM)

TEM samples were prepared on 300 mesh formvar/carbon grids (Ted Pella, FCF300-Cu-UA). Bright field images were obtained using a Tecnai Spirit 120kV TEM. Superlattices of Zn_3P_2 nanoparticles were prepared according to a procedure by Sainato *et al.*[2] The particle size distribution of each sample was determined using the ImageJ software.[3]

HRTEM images were taken using a FEI Titan Themis 200 kV TEM. STEM-EELS and STEM-EDX elemental maps were acquired with a Hitachi HD2700C dedicated STEM with a probe Cs corrector at an accelerating voltage of 200 kV. For HRTEM and STEM experiments, samples were prepared by drop casting a dilute filtered solution of nanoparticles dispersed in hexanes onto a TEM grid.

Absorbance Spectra

Absorbance spectra were obtained using an Agilent Cary 5000 UV-Vis-NIR spectrophotometer. The nanoparticles were dispersed in carbon tetrachloride for measurement.

Photoluminescence (PL)

For solution samples, PL spectra were obtained using a Photon Technology International QuantaMaster 4 fluorescent spectrometer. The nanoparticles were dispersed in hexanes for measurement.

For thin film samples, PL and time-resolved photoluminescence (TRPL) measurements were performed with a home-built confocal microscopy setup. A 400 nm femtosecond laser source (Coherent Chameleon) with a repetition rate of 80MHz was used as excitation light source. An objective (NA 0.55) was used for focusing the laser into a spot with diameter ~2 μm. The emitted light was directed into a spectrograph (Andor SR500i, with a grating with 150 l/mm groove density, 1250 nm blazed wavelength). A thermal-electric cooled CCD array was used to measure the PL spectra. The TRPL measurements were done by a time-correlated single photon counting (TRSPC) module (PicoQuant TimeHarp-260) and an avalanche photodiode (MPD SPAD).

X-ray Photoelectron Spectroscopy (XPS)

XPS data was measured using a Versa Probe II XPS from Physical Electronics with Al Kα source operated at 50 W 15 kV with a 200 μm spot size. Samples were prepared by drop casting a solution of nanoparticles onto a 1 cm x 1 cm glass slide (Thin Film Devices).

Supplementary Figures

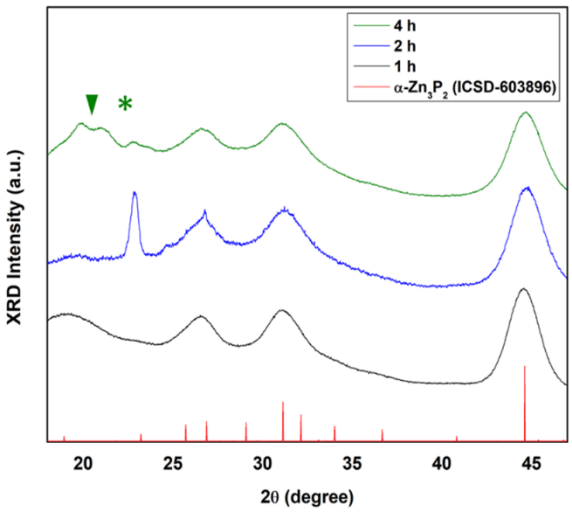

Figure S1. XRD patterns obtained for α-Zn_3P_2 (reference: ICSD-603896) nanoparticles grown for 1 hour, 2 hours, and 4 hours. Nanoparticles were grown following injection of $P(SiMe_3)$ at 220°C. In some cases, we observed the formation of a hydrated zinc phosphate tetrahydrate (triangle, reference: ICSD-34869) and zinc hydroxide (asterisk, reference: ICSD-15008).

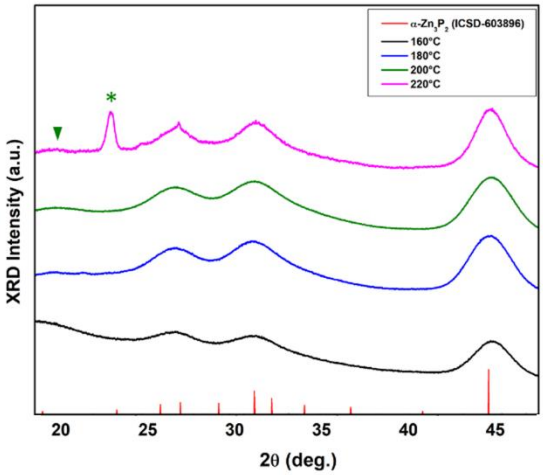

Figure S2. XRD patterns obtained for α-Zn_3P_2 nanoparticles (reference: ICSD-603896) grown at 220°C for 2 hours following injection of $P(SiMe_3)_3$ at 160°C, 180°C, 200°C, and 220°C. In some cases, we observed the formation of zinc phosphate tetrahydrate (reference: ICSD-34869) and zinc hydroxide (reference: ICSD-15008).

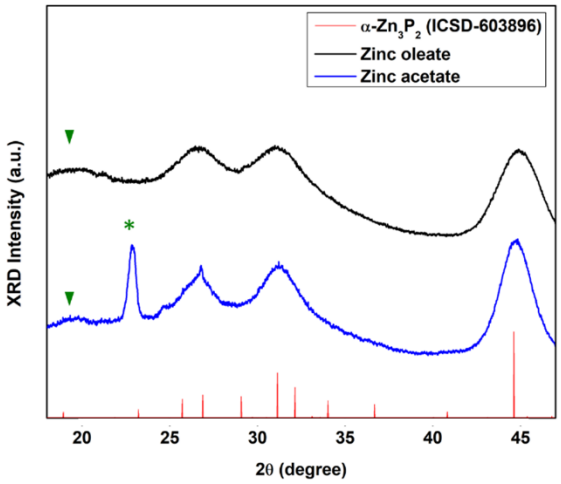

Figure S3. XRD patterns obtained for α-Zn_3P_2 nanoparticles (reference: ICSD-603896) grown for 2 hours following injection of $P(SiMe_3)_3$ at 220°C using (a) zinc acetate and (b) zinc oleate. In both cases, we observed the formation of zinc phosphate tetrahydrate (reference: ICSD-34869) or zinc hydroxide (reference: ICSD-15008).

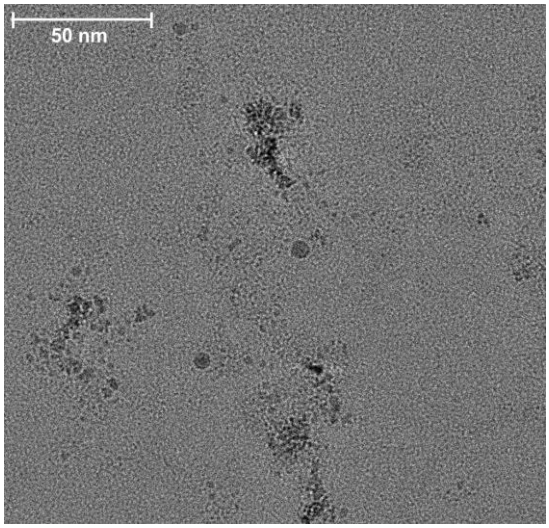

Figure S4. Bright field image for core/shell Zn_3P_2/ZnS nanocrystals synthesized from Method 1.

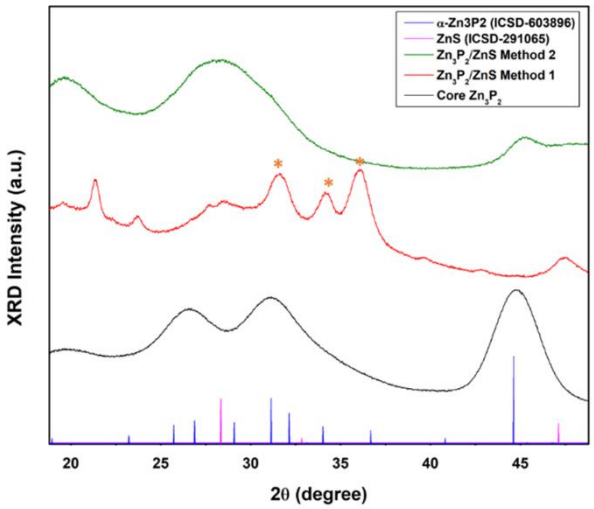

Figure S5. XRD data for Zn_3P_2/ZnS core/shell nanocrystals grown from Method 1 (red), using elemental sulfur and zinc acetate, and Method 2 (green), from zinc oleate and thioacetamide. The orange asterisks correspond to peaks for ZnO (ICSD-193696).

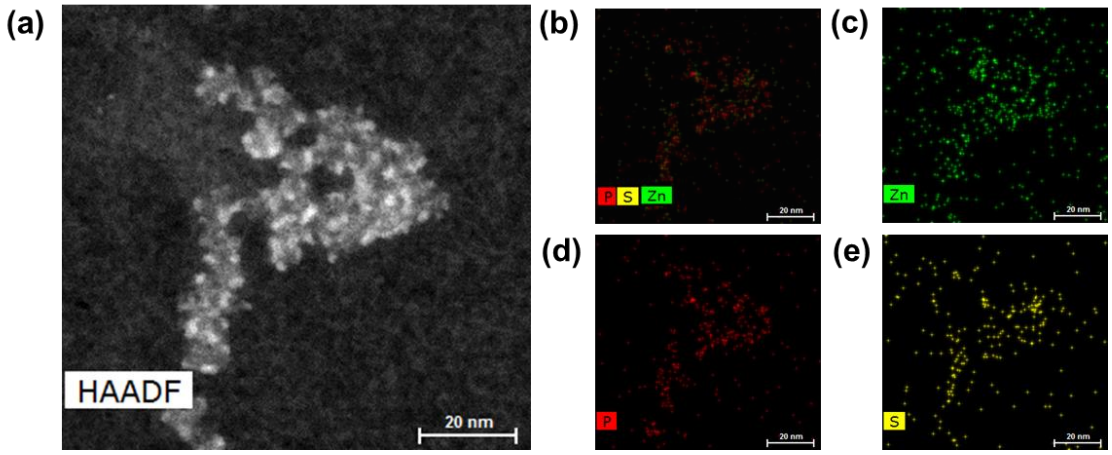

Figure S6. (a) HAADF-STEM image for a cluster of Zn_3P_2/ZnS nanocrystals. (b) Elemental mapping of the cluster of nanocrystals, with P, Zn, and S signals overlaid. (c), (d), and (e) show elemental maps for individual elements Zn, P, and S, respectively.

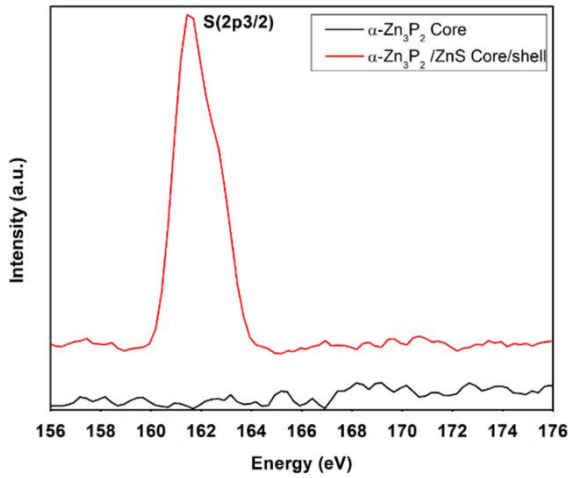

Figure S7. XPS data obtained at the sulfur (S) edge for Zn_3P_2/ZnS nanocrystals. The S(2p3/2) peak present at 162 eV that appeared following shelling of Zn_3P_2 with ZnS is characteristic of zinc sulfide.

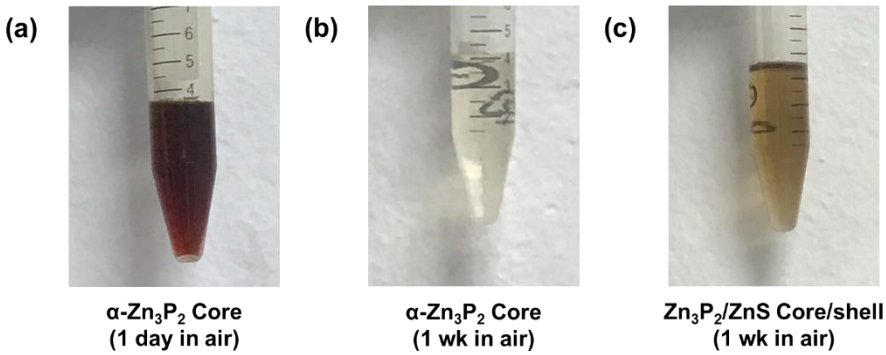

Figure S8. Photos of (a, b) core and (c) core/shell nanoparticles suspended in hexanes. Photos show samples exposed to air (a) one day after exposure and (b, c) one week after exposure. The loss of color in the core nanoparticle solution indicated oxidation of the nanocrystals, which did not occur on core/shell nanocrystals over the same length of time. The core/shell particles are dispersed at a lower concentration than the core-only particles – hence the lighter shade.

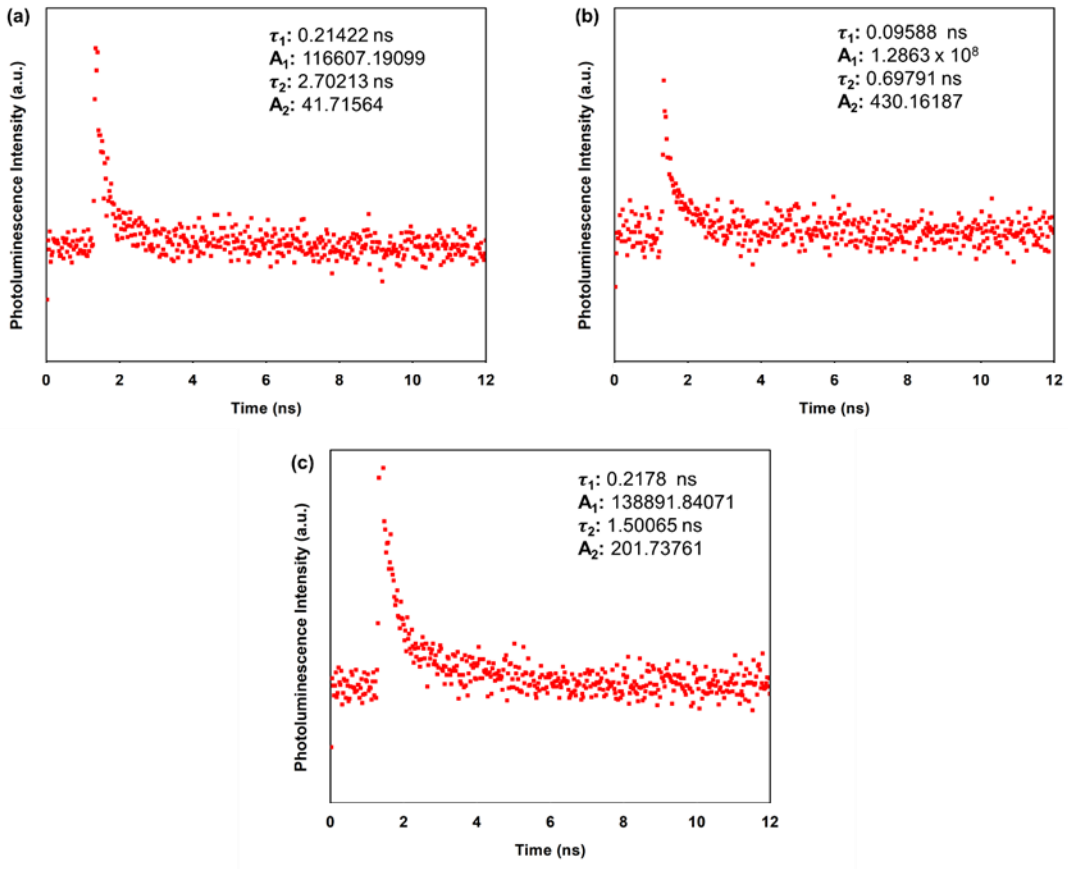

Figure S9. Time resolved photoluminescence studies performed on a thin film of Zn_3P_2/ZnS nanocrystals deposited from a dispersion of nanocrystals in toluene at 77 K. The estimated lifetime of 0.18 ± 0.08 ns was obtained from the average τ values from three measurements (a, b, c at different locations) on the same film.

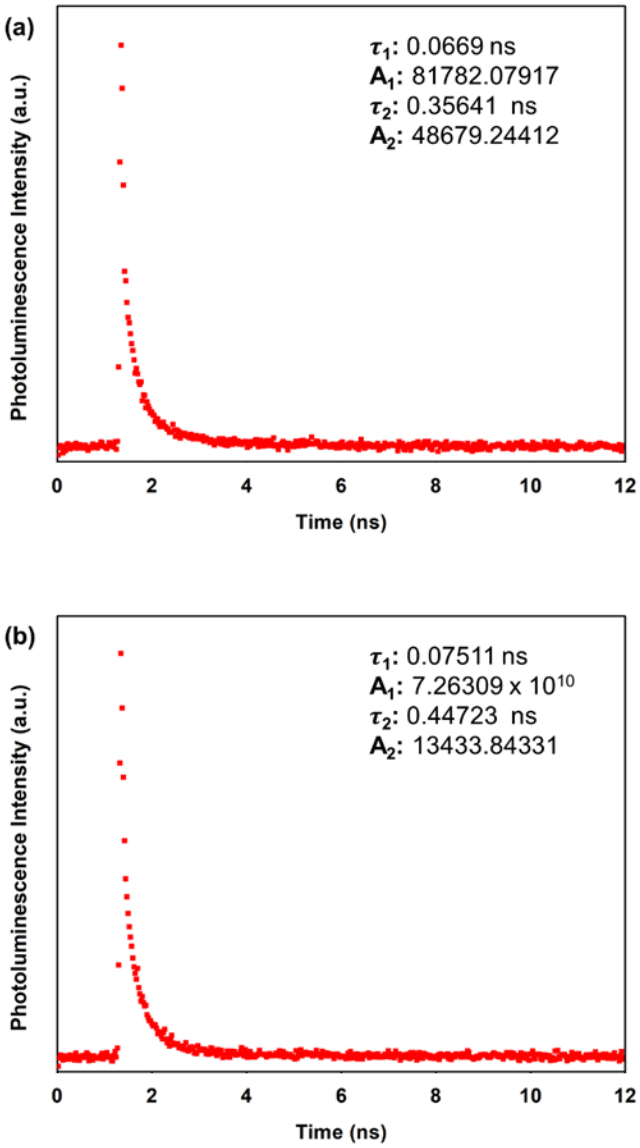

Figure S10. Time resolved photoluminescence studies performed a thin film deposited from Zn_3P_2/ZnS nanocrystals at RT. The estimated lifetime of 0.18 ± 0.15 ns was obtained from the average τ values from two measurements (a,b at different locations) on the same film.

Figure S11. Photographs of Zn_3P_2 growth within one minute of injection of tris(trimethylsilyl)phosphine. The color of the reaction solution rapidly changed from clear and colorless to dark red within one minute of injection.

Theoretical Calculations

Calculation of Bohr Radius

The Bohr radius of Zn_3P_2 is given by

$$a_{Bohr} = \varepsilon_r \left(\frac{m}{\mu}\right) a_0$$

where ε_r = 15.3 F/m for Zn_3P_2, m = mass, μ = the reduced mass (m_e = 0.09, m_h = 0.95), and a_0 = 0.053.[4] This provides a_{Bohr} = 9.87 nm for Zn_3P_2. The estimated band gap E_g can then be calculated within this range of quantum confinement is given by

$$E_g = E_{g,0} + \frac{h^2\pi^2}{2\mu R^2}$$

where $E_{g,0}$ = 1.5 eV for Zn_3P_2, h = 1.054571817 x 10^{-34} J·s, and R = the radius of the nanoparticle.

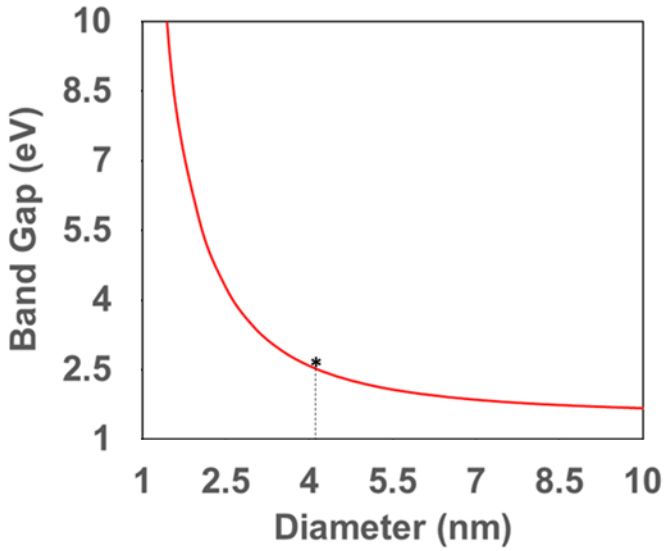

Figure S12. Predicted band gap for quantum confined Zn_3P_2. Calcuations show that Zn_3P_2 has a Bohr radius of 10 nm. The asterisk and dashed line indicate experimental data.

Table S1. Predicated Band Gap for Quantum Confined Zn_3P_2			
Diameter (nm)	Radius (nm)	Band Gap E_g (eV)	Wavelength λ (nm)
1	0.5	18.9	65.6
2	1	5.85	212
3	1.5	3.43	361
4	2	2.59	479
5	2.5	2.20	565
6	3	1.98	625
7	3.5	1.85	668
8	4	1.77	700
9	4.5	1.71	723
10	5	1.67	740
11	5.5	1.64	754
12	6	1.62	765
13	6.5	1.60	773
14	7	1.59	780
15	7.5	1.58	786
16	8	1.57	790
17	8.5	1.56	794
18	9	1.55	798
19	9.5	1.54	801
20	10	1.54	803

Calculation of Shell Precursor Volumes

The approximate amount of sulfur added per shelling experiment was determined using the following calculation.

Assumptions:

- The particles are spherical with a volume of $V = \frac{4\pi}{3} r^3$.
- The ligands take up 30% of the nanoparticles' mass.
- The bulk densities of the Zn_3P_2 (4.55 g/cm^3) and ZnS (4.09 g/cm^3) are equal to the densities of Zn_3P_2 nanoparticles and ZnS shells.
- Each monolayer of ZnS is 0.3 nm thick.

Measured Parameters

- The mass of the nanoparticles was measured following vacuum drying of the nanoparticles in a glass vial.
- The average diameter of the nanoparticles was determined from LRTEM image analysis using ImageJ.

Sample Calculation for a Single Monolayer of ZnS

The following sample calculation determines the amount of Zn and S precursors required to provide two shelling layers on 100 mg of 7 nm nanoparticles. The concentration of the Zn precursor is 0.02 M and the concentration of the S precursor is 0.04 M.

1. Determine the number of nanoparticles.

The volume of each nanoparticle is given by

$$V = \frac{4}{3}\pi\left(\frac{7}{2}\ nm\right)^3 = 179.5\ nm^3$$

Given the density of Zn_3P_2, and assuming that the ligands take up 30% of the particles' mass, the mass of one nanoparticle is equal to

$$m_{Zn_3P_2} = (179.5\ nm^3)x\ \left(4.55\frac{g}{cm^3}\right)x\ \left(\frac{1\ cm^3}{1x10^{21}nm^3}\right)x\ (100/130) = 6.29\ x\ 10^{-19}g$$

The number of nanoparticles is therefore equal to

$$n_{Zn_3P_2} = \frac{0.1\ g}{6.29\ x\ 10^{-19}g} = 1.59\ x\ 10^{17}$$

2. Determine the volume required to add one monolayer of ZnS.

Assuming that one ZnS monolayer is 0.3 nm thick, the volume of ZnS required for one nanoparticle is equal to

$$V = \frac{4}{3}\pi(3.5\ nm + 0.3\ nm)^3 - 179.5\ nm^3 = 50\ nm^3$$

For *n*, the total mass of ZnS to add is given by

$$m_{ZnS} = (50.26\ nm^3)x\ \left(\frac{4.09\ g}{cm^3}\right)x\ \left(\frac{1\ cm^3}{1\ x\ 10^{21}\ nm^3}\right)x\ (1.59\ x\ 10^{17})\ = 3.3\ x\ 10^{-2}g$$

For a 0.04 M solution of S precursor and 0.02 M solution of Zn precursor, the total volume required is therefore

$$V_{S,1} = 3.3\ x\ 10^{-2}g\ x\ \frac{1\ mol}{97.474\ g}\ x\ \left(\frac{1\ L}{0.04\ mol}\right) = 8.39\ ml\ S$$

$$V_{Zn,1} = 3.3\ x\ 10^{-2}g\ x\ \frac{1\ mol}{97.474\ g}\ x\ \left(\frac{1\ L}{0.02\ mol}\right) = 15.2\ ml\ Zn$$

Calculation of Lifetimes

We calculated the average lifetime from a biexponential fit of photoluminescence intensity *I* (a.u.) with respect to time *t* (ns):

$$I = A_1 e^{-\left(\frac{t}{\tau_1}\right)} + A_2 e^{-\frac{t}{\tau_2}}$$

where A_1 and A_2 are the preexponential factors, and τ_1 and τ_2 are the lifetimes provided by the fit.

We fitted *I* from measurements at different locations on the same film at 77 K (Figure S9) and RT (Figure S10). Results have been summarized in Table S2.

Table S2. Biexponential Fits of Time-Resolved PL Data

Conditions	A_1	τ_1 (ns)	A_2	τ_2 (ns)
RT	81782.07917	0.07511	48679.24412	0.44723
RT	7.26E+10	0.0669	13433.84331	0.35641
77 K	116607.191	0.21422	41.71564	2.70213
77K	1.29E+08	0.09588	430.16187	0.69791
77K	138891.8407	0.2178	201.73761	0.50065

From this data, we then calculated the average lifetime τ_{avg} considering from the following formula[5]:

$$\tau_{avg} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2}$$

where α is the normalized pre-exponential factor such that

$$\alpha_i = \frac{A_i}{\Sigma A_i}$$

From the data obtained from our biexponential fits, we calculated the mean τ_{avg} to be 0.18 ± 0.15 ns at RT and 0.18 ± 0.08 ns at 77 K. Results are summarized in Table S3.

Table S3. Calculations of the Average Lifetime					
Conditions	α_1	τ_1 **(ns)**	α_2	τ_2 **(ns)**	τ_{avg} **(ns)**
RT	0.6269	0.0669	0.3731	0.3561	0.2867
RT	1	0.0751	0	0.4472	0.0751
77 K	0.9996	0.2142	0.0400	2.7021	0.2254
77 K	1	0.0958	0	0.6979	0.0959
77 K	0.9985	0.2178	0.0015	1.5001	0.2305

References:

[1] B. H. Tony and R.B. Von Dreele, *J. Appl. Crystallogr.* **2013**, 46, 544.

[2] M. Sainato, B. Shevitski, A. Sahu, J.D. Forestor, S. Aloni, G. Barillaro, and J. J. Urban, *ACS Omega* **2017,** *2* (7), 3681-3690.

[3] C.A. Schneider, W.S. Rasband, and K. W. Eliceiri, *Nat. Methods*. **2012**, 9(7), 671.

[4] O.E. Madelung, U. E. Rössler, and M.E. Schulz. (Eds: W. Martienssen, O. Madelung, K. H. Hellwege. Zinc phosphide (Zn_3P_2) optical properties, dielectric constant. Springer Berlin Heidelberg: Berlin, Heidelberg, **1998**; p 1.

[5] S. K. Balakrishan and P. V. Kamat. *ACS Energy Lett.* **2017**, *2* (1), 88-93.