Electronic Supplementary Information (ESI)

Highly-photoluminescent ZnSe nanocrystals via non-injection-based approach with precursor reactivity elevated by secondary phosphine

Kui Yu,*[a] Amy Hrdina,[a] Xinguo Zhang,[a,c] Jianying Ouyang,[a]
Donald M. Leek,[a] Xiaohua Wu,[b] Menglian Gong,[c]
Diana Wilkinson[d] and Chunsheng Li[e]

[a] Steacie Institute for Molecular Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada. *Fax: +1613-954-5242; Tel:+1-613-990-5836; E-mail: Kui.Yu@nrc-cnrc.gc.ca*

[b] Institute for Microstructural Sciences, National Research Council of Canada, Ottawa, Ontario, K1A 0R6, Canada.

[c] State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen Univeristy, Guangzhou, 510275, China.

[d] Defence Research and Development Canada, 3701 Carling Avenue, Ottawa, Ontario, K1A 0Z4, Canada.

[e] Healthy Environment and Consumer Safety Branch, Health Canada, Ottawa, Ontario, K1A 1C1, Canada.

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Scheme S2B. ^{31}P NMR spectra at different temperature of Figure 1 Batch left-bottom TOPSe stock solution made with a feed molar ratio of 1Se-1TOP 90%. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm) was detected in the stock solution, but some DOP (δ -68.9 ppm), together with TOPSe (δ 36.8 ppm) and TOP (δ -31.5 ppm). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected.

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Scheme S2C. ^{31}P NMR spectra at different temperature of Figure 1 Batch left-bottom TOPSe stock solution made with a feed molar ratio of 1Se-1TOP 90%, and with the addition of 3DPP. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm) nor DPPSe (δ 7.5 ppm) was detected, but some DOP (δ -68.9 ppm), together with TOPSe (δ 36.8 ppm), TOP (δ -31.5 ppm), and DPP (δ -39.5 ppm). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected.

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Figure S4B. Investigation on the amount of OLA affecting the ZnSe NC formation with SeDPP as a Se precursor.

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Experimental Section.

All chemicals used were obtained from commercial providers and used as received. They were oleic acid (OA, tech. 90%), 1-octadecene (ODE, tech. 90%), hexadecylamine (HDA, tech. 90%), octadecylamine (ODA, 97%), oleylamine (OLA, tech. 70%), n-trioctylphosphine (TOP, tech. 90%) and diphenylphosphine (DPP, 98%), which were purchased from Sigma-Aldrich. n-trioctylphosphine (TOP, 97%) was from Strem chemical company, zinc oxide powder (ZnO, 99.24%) from J.T. Baker Chemical Co. (Philipsburg, NJ, USA), and selenium powder (Se ~200 mesh, 99.999%) from Alfa Aeser. Solvents used for optical characterization and purification included toluene (99.5%, ACS reagent, ACP in Montreal), hexane (98.5%, GR ACS, EMD in USA), methanol (absolute, ACP in Montreal), and acetone (99.5%, ACS reagent).

To prepare a 0.658 mmol/g $Zn(oleate)_2$ stock solution, 1.18 g (14.4 mmol) ZnO, 8.95 g (31.68 mmol) OA, and 12.0 g ODE were loaded in a 3-necked 100-mL round bottom flask equipped with an air condenser and a thermocouple. For the reactions carried out in flasks, standard air-free techniques were used. The reaction mixture was degassed under vacuum at 100 °C until no vigorous bubbling. The mixture was then heated to 300 °C under N_2 and a clear solution was observed. Afterwards, the mixture was cooled down to ~110 °C and was degassed (~50 mtorr) again for 1 h. Under N_2 protection, the mixture was finally cooled down to room temperature.

To prepare the TOPSe stock solutions with a feed molar ratio of 1Se-to-1TOP (TOP 97%) and 1Se-to-1TOP (TOP 90%), Se powder and TOP were loaded into single-necked 25-mL flasks in a glovebox filled with N_2. For the former, 0.8520 g (10.793 mmol) Se powder was mixed with 4.1101 g TOP 97 % (11.090 mmol without the consideration of 97% purity and 10.758 mmol with) in 1.5288 g ODE. For the latter, 0.8550 g (10.831 mmol) Se powder was mixted with 4.1574 g TOP 90% (11.217 mmol without the consideration of 90% purity and 10.095 mmol with) in 1.6544 g ODE. The mixtures were stirred overnight at room temperature and then were gently heated for a few minutes. Clear solutions were obtained with a tiny amount of Se powder remained. Note that these two stock solutions were used for the syntheses and for NMR.

To prepare the DPPSe stock solution with a feed molar ratio of 1Se-to-1DPP, 0.12 g (1.5 mmol) elemental Se was dissolved in 0.26 mL (1.5 mmol) DPP in the glovebox. Heat was applied and a clear yellow solution was generated. The solution was allowed to cool to room temperature and a white solid appeared. The DPPSe white solid was heated to become liquid and diluted with 10 mL of toluene. All the TOPSe and DPPSe stock solutions were kept in the glovebox until further use.

For the typical synthesis of ZnSe NCs via our one-pot noninjection-based approach in a ~5 g reaction medium, the Zn-to-Se feed molar ratio was 4-to-1 with [Se] of ~60 mmol/Kg. For example, 1.84 g (1.2 mmol) Zn(oleate)$_2$ stock solution and 3.1 g ODE were loaded in a 3-necked 50-mL round bottom flask equipped with an air-condenser and a thermocouple. The flask was heated to ~100 °C under vacuum for ~1 hour. Meanwhile, the mixture was stirred continuously and the flask was purged with N_2 periodically. Afterwards, the flask temperature was changed to so-called addition temperature, 80°C (or otherwise specified). 2.0 mL of 0.15 mmol/mL (0.30 mmol) DPPSe stock solution was added to the flask. The flask was evacuated under vacuum for 45 min to remove toluene. Under the flow of purified nitrogen, the reaction mixture was heated up, stepwise, at a rate of ~ 10°C/min.

Temporal evolution of absorption was monitored. Usually, 11 samples (~100 μL each) were obtained with their growth periods/temperature of 45 min/80 °C (Sample 1), 15 min/100 °C (Sample 2), 15 min/120 °C (Sample 3), 15 min/140 °C (Sample 4), 15 min/160 °C (Sample 5), 15 min/180 °C (Sample 6), 15 min/200 °C (Sample 7), 15 min/220 °C (Sample 8), 15 min/240 °C (Sample 9), 15 min/260 °C (Sample 10), and 15 min/280 °C (Sample 11). The as-synthesized nanocrystal samples were cooled to room temperature and dispersed in toluene. The optical spectra were collected with a concentration of 10 μL crude sample dispersed in 3mL toluene.

Ultraviolet-visible (UV-Vis) absorption spectra were collected with a Lambda 45 Perkin-Elmer spectrophotometer using a 1-nm data interval. PL emission spectra were collected with a HORIBA JOBIN YVON FluoroMax-3 spectrofluorometer equipped with a Xenon arc lamp. The fluorescence spectra were collected with the increment of 1 nm. The PL QY was estimated by comparing the sample emission intensity with that of quinine sulfate dye in 0.05 M H_2SO_4 (lit. QY ~ 0.546); the optical density at 350 nm of the dye and QD solutions were controlled to be ~0.1, while the excitation wavelength was 350 nm. Corrections were made for the difference of the refractive index of the two solvents.

Purification was conducted for characterization with X-ray diffraction (XRD) and transmission electron microscopy (TEM). Briefly, crude nanocrystals were mixed with toluene and methanol with a 1:1:1 volume ratio. White solid was collected with 10-minute centrifugation, and was dispersed into a mixture of toluene and methanol (with a 1:2 volume ratio). Mixing and centrifugation were repeated, and the resulting solid was dispersed in hexane (with a 1solid : 2solvent volume ratio). With acetone as a precipitating solvent, the supernatant was removed, and the remaining solid was experienced, again, the purification procedure with hexane and acetone. Each step of the purification process was monitored by Ultraviolet-visible (UV-vis) absorption.

For powder XRD, the purified nanocrystals were deposited onto a low-background quartz plate. The XRD pattern was recorded at room temperature on a Bruker AXS D8 X-ray diffractometer using Cu Kα radiation in a θ-θ mode. The generator was operated at 40 kV and 40 mA, and data were collected between 15° and 80° (2θ), with a step size of 0.1° and counting time of 5 second per step.

For TEM, the sample was prepared by depositing a drop of a purified nanocrystals dispersion (diluted in toluene) onto a 400-mesh thin carbon-coated TEM copper grid and allowed to air dry. TEM images were obtained on a JOEL JEM-2100F transmission electron microscope operating at 200 kV and equipped with a Gatan UltraScan 1000 CCD camera. The NC size and standard deviation were obtained by analyzing ~50 individual NCs with the Gatan Digital Micrograph built-in statistics function.

High-resolution Nuclear Magnetic Resonance (NMR) was conducted. ^{31}P NMR with ^{1}H decoupling was performed on a Bruker AV-III 400 operating at 161.98 MHz. An external standard 85% H_3PO_4 was used.

Table S1. Summary of the experimental details for the batches presented in this study.

	feed molar ratios, feed concentration	**Se precursor/addition T (°C)**	**DPP added**	**Samples**
Fig 1 Batch SeTOP97%	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1TOP 97% / 80°C	no	11 samples, 80°C-280°C
Fig 1 Batch SeTOP90%	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1TOP 90% / 80°C	no	11 samples, 80°C-280°C
Fig 1 Batch SeTOP90%-DPP	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1TOP 90% / 80°C	4DPP after SeTOP	11 samples, 80°C-280°C
Fig 1 Batch SeDPP	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S1A = 1				
Fig S1B Batch SeTOP90%-DPP	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1TOP 90% / 80°C	4DPP after SeTOP	11 samples, 80°C-280°C
Fig S1B Batch SeTOP90%-DPP	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1TOP 90% / 80°C	4DPP before SeTOP	11 samples, 80°C-280°C
Fig S2A Batch 0DPP	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S2A Batch 4DPP after	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	4DPP after SeDPP	11 samples, 80°C-280°C
Fig S2A Batch 4DPP before	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	4DPP beforer SeDPP	11 samples, 80°C-280°C
Fig S2A Batch 4DPP with	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	4DPP with SeDPP	11 samples, 80°C-280°C
Fig S2B = S2A				
Fig 2-left	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 280°C	no	4 samples, 280°C-280°C
Fig 2-right-XRD	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	4DPP after SeDPP	UV PP 383 nm; PL PP 394 nm
Fig 2-right-TEM	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	UV PP 396 nm; PL PP 402 nm
Fig S2C-top = Fig 2-left				
Fig S2C-bottom Batch 1	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 200°C	no	200°C-280°C, 30min/280°C
Fig S2C-bottom Batch 2	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 240°C	no	240°C-280°C, 30min/280°C
Fig S2C-bottom Batch 3	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 280°C	no	280°C-280°C, 30min/280°C
Fig S2D-2Zn	2Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S2D-4Zn	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S2D-6Zn	6Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S3-XRD = Fig 2-right-XRD				3.06 nm (avg 111 and 311)
Fig S3-TEM = Fig 2-right-TEM				~ 3 nm
Fig S4A Batch ODE	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4A Batch 1ODE-1HDA	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4A Batch 1ODE-1HDA	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4A Batch 1ODE-1HDA	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4B Batch (1) ODE	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4B Batch (2) 17OLA-83ODE	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4B Batch (3) 25OLA-75ODE	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C
Fig S4B Batch (4) 50OLA-50ODE	4Zn-1Se, [Se] 60 mmol/Kg	1Se-1DPP / 80°C	no	11 samples, 80°C-280°C

$$\text{(A)}\ \ (\text{oleate})_2\text{Zn} \xrightarrow{\text{TOPSe}} \text{Zn – Se complex} \longrightarrow \text{ZnSe monomer}$$

(Direct, nucleation/growth 260 – 280 °C)

$$\text{(B)}\ \ (\text{oleate})_2\text{Zn} \xrightarrow{\text{DOP}} \text{Zn – P complex} \xrightarrow{\text{TOPSe}} \text{ZnSe monomer}$$

(Indirect, nucleation/growth 240 – 260 °C)

$$\text{(C)}\ \ (\text{oleate})_2\text{Zn} \xrightarrow{\text{DPP}} \text{Zn – P complex} \xrightarrow{\text{TOPSe}} \text{ZnSe monomer}$$

(Indirect, nucleation/growth 140 – 160 °C)

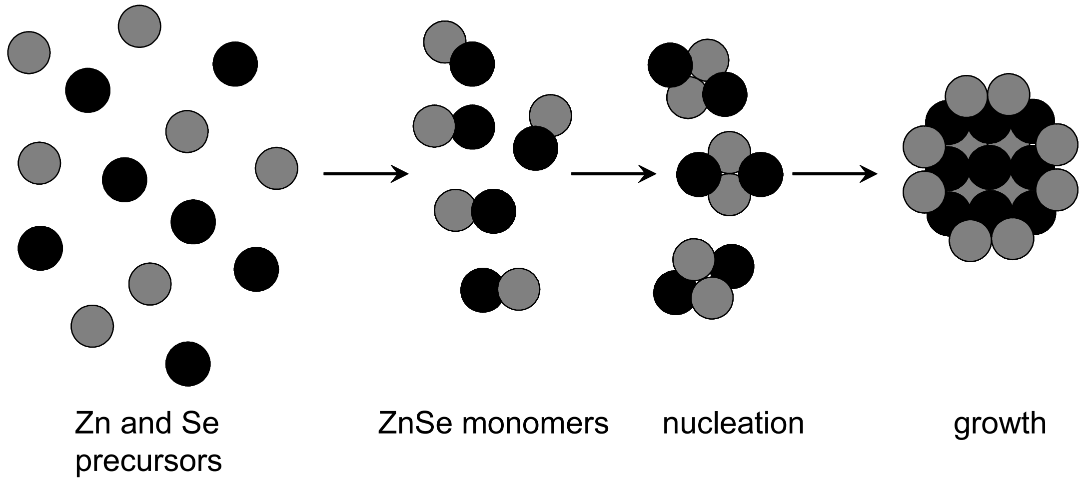
$$\text{(D)}\ \ (\text{oleate})_2\text{Zn} \xrightarrow{\text{DPPSe}} \text{Zn – Se complex} \longrightarrow \text{ZnSe monomer}$$

(Direct, nucleation/growth 100 – 120 °C)

$$\text{(E)}\ \ (\text{oleate})_2\text{Zn} \xrightarrow{\text{DPP}} \text{Zn – P complex} \xrightarrow{\text{DPPSe}} \text{ZnSe monomer}$$

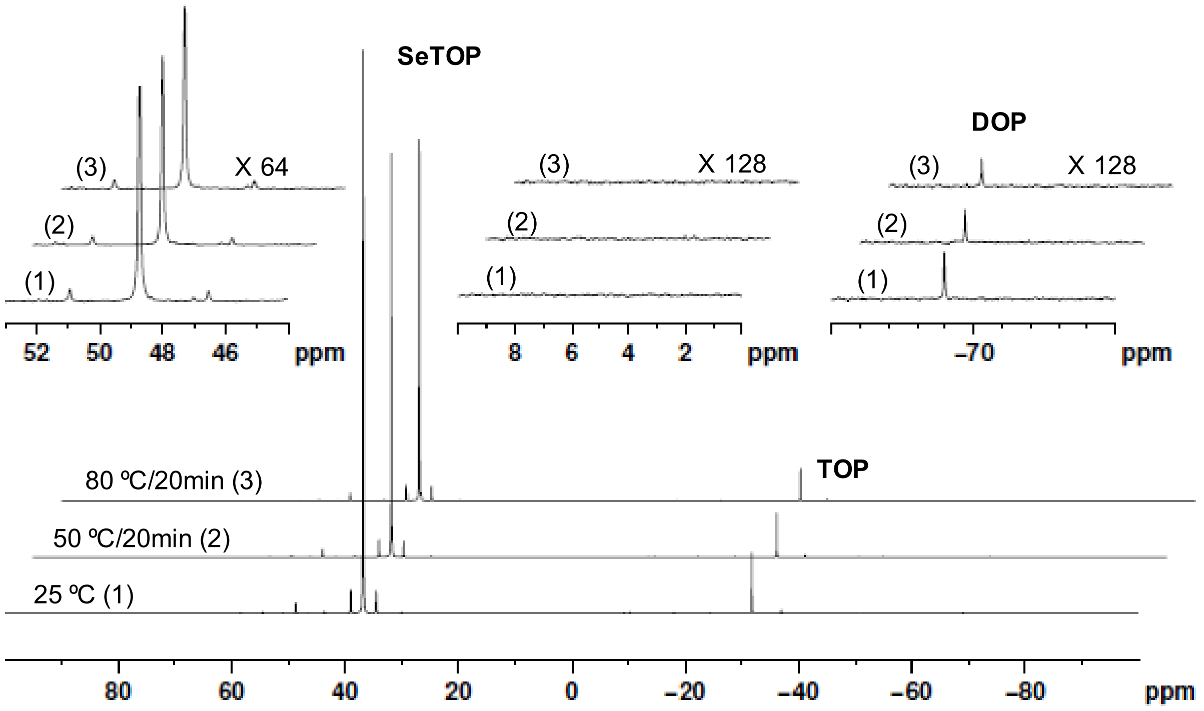
(Indirect, nucleation/growth 80 – 120 °C)

Scheme S1A. A detailed description of the reactions leading to the formation of ZnSe monomers in the different conditions explored. (A) SeTOP 97% as a Se precursor (Figure 1 left-top), (B) SeTOP 90% as a Se precursor (and DOP as a Zn activating agent) (Figure 1 left-bottom), (C) SeTOP 90% as a Se precursor and DPP as a Zn activating agent (Figure 1 right-top), (D) SeDPP as a Se precursor (Figure 1 right- bottom), and (E) SeDPP as a Se precursor and DPP as the Zn activating agent (Figure S2).



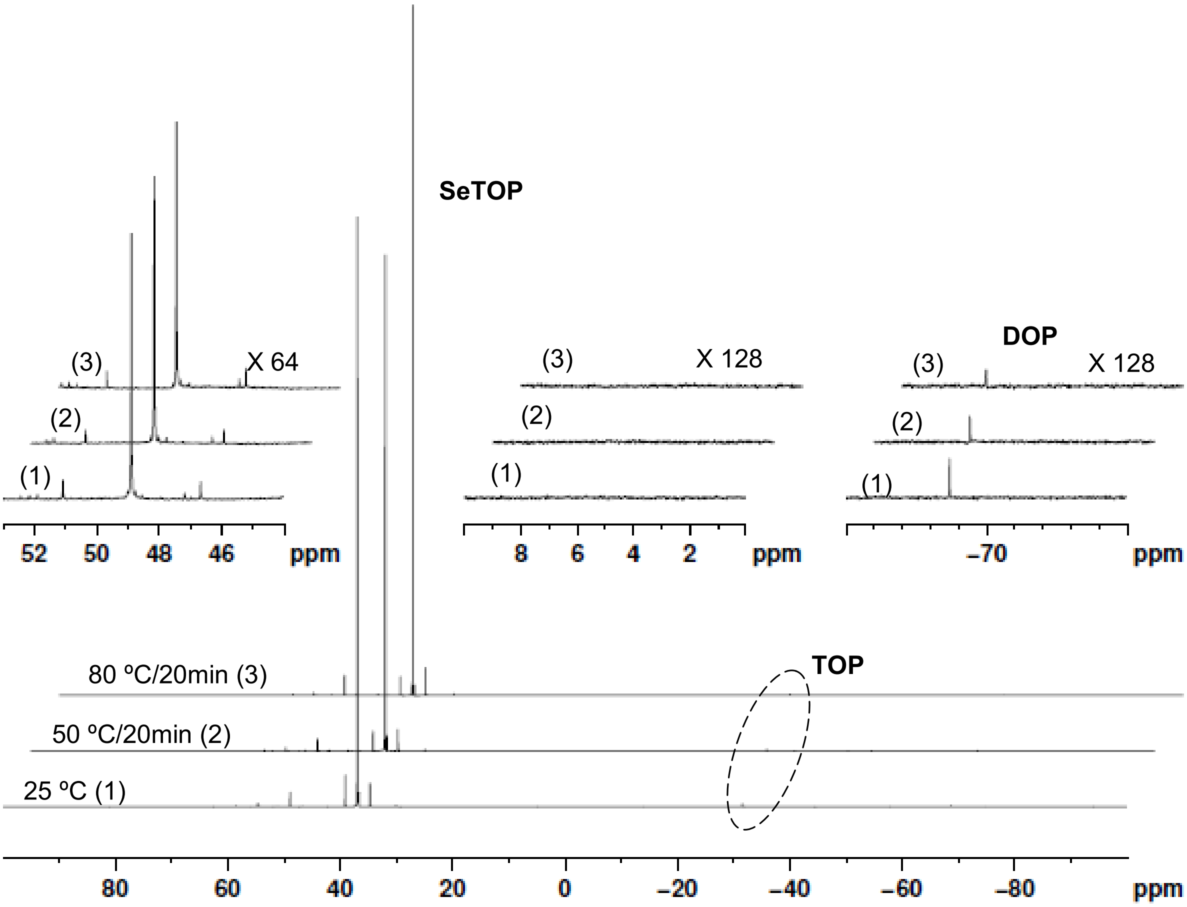
Scheme S1B. A schematic drawing of the combination of the ZnSe monomer leads to nucleation/growth of ZnSe NCs.

^{31}P NMR with ^{1}H decoupling; the 1Se-1TOP 97% stock solution.



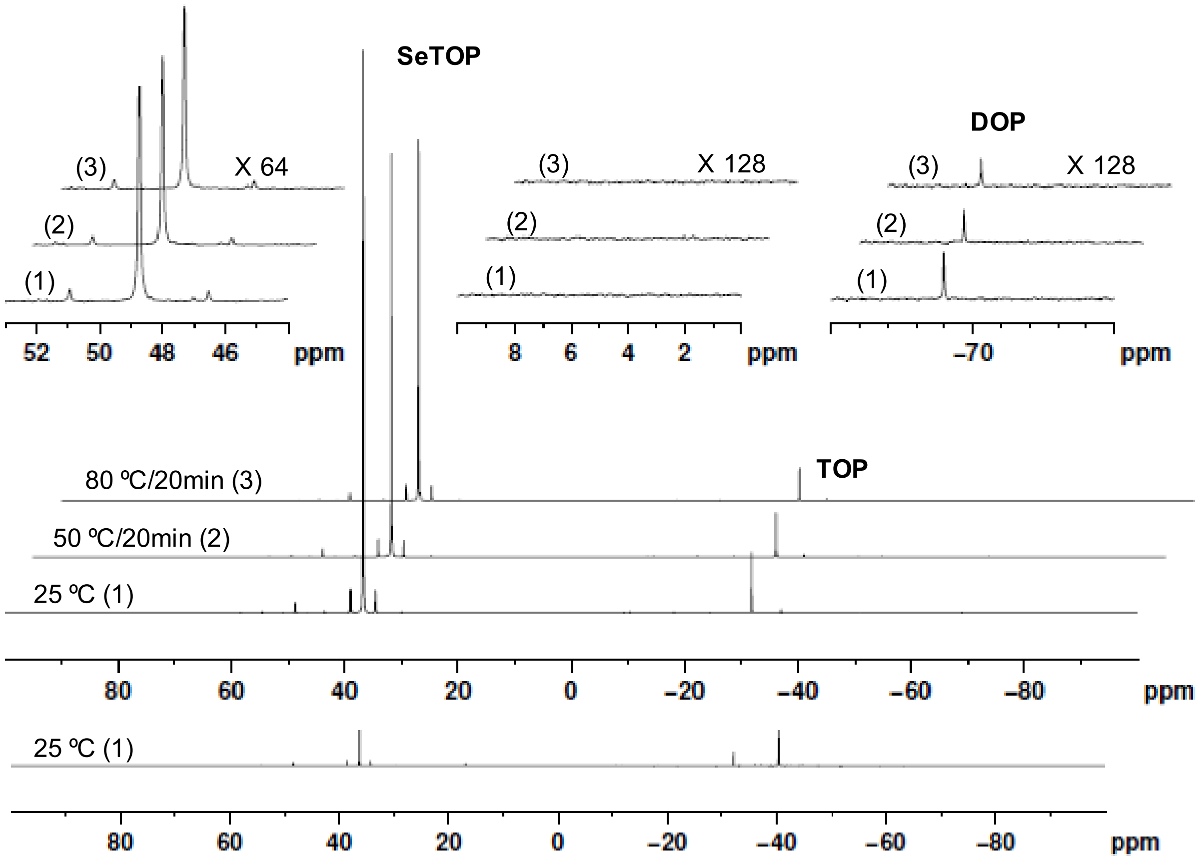
Scheme S2A. ^{31}P NMR spectra at different temperature of Figure 1 Batch left-top TOPSe stock solution made with a feed molar ratio of 1Se-1TOP 97%. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm) was detected in the stock solution, but some DOP (δ -68.9 ppm), together with TOPSe (δ 36.8 ppm) and TOP (δ -31.5 ppm). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected.

^{31}P NMR with ^{1}H decoupling; the 1Se-1TOP 90% stock solution.



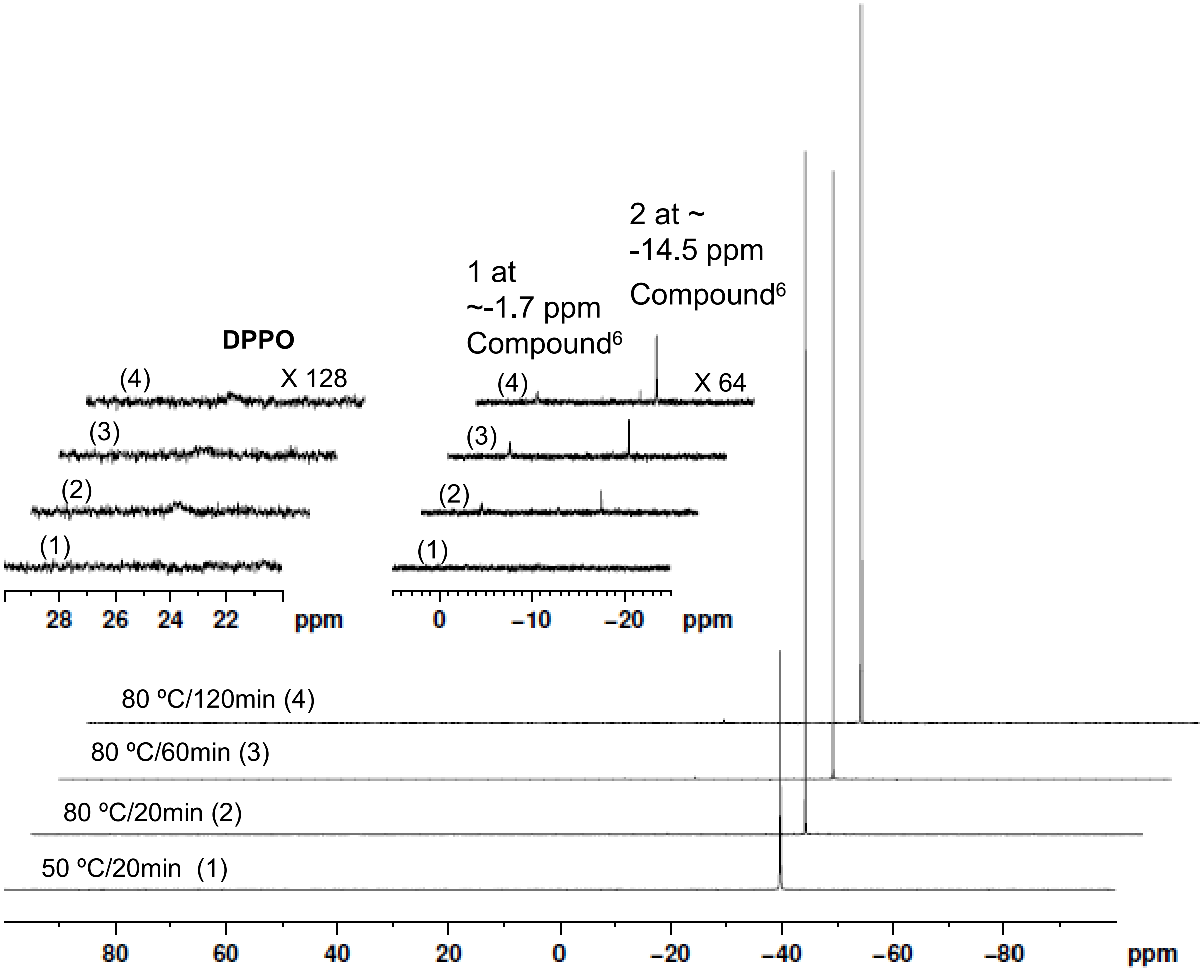
Scheme S2B. ^{31}P NMR spectra at different temperature of Figure 1 Batch left-bottom TOPSe stock solution made with a feed molar ratio of 1Se-1TOP 90%. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm) was detected in the stock solution, but some DOP (δ -68.9 ppm), together with TOPSe (δ 36.8 ppm) and TOP (δ -31.5 ppm). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected.

^{31}P NMR with ^{1}H decoupling; the 1Se-1TOP 90% solution with the presence of 3DPP.



Scheme S2C. ^{31}P NMR spectra at different temperature of Figure 1 Batch left-bottom TOPSe stock solution made with a feed molar ratio of 1Se-1TOP 90%, and with the addition of 3DPP. 85% H_3PO_4 was used as an external standard. No DOPSe (δ 4.7 ppm) nor DPPSe (δ 7.5 ppm) was detected, but some DOP (δ -68.9 ppm), together with TOPSe (δ 36.8 ppm), TOP (δ -31.5 ppm), and DPP (δ -39.5 ppm). It is worthy of notice that another Se-containing species (δ 48.4 ppm) was detected.

^{31}P NMR with ^{1}H decoupling; a mixture of $ZnOA_2$ and $PHPh_2$



Scheme S3. ^{31}P NMR spectra collected from a mixture of zinc oleate in ODE and DPP (with a feed molar ratio of 1Zn-to-1DPP)). The NMR sample was prepared in a glovebox and was loaded in a NMR tube and properly sealed. The peak 1 at -1.7 ppm might be a Zn-P intermediate, OA-Zn-PPh_2 or Ph_2P-Zn-PPh_2.[6] The peak 2 at -14.5 ppm might be Ph_2P-PPh_2.[6] The formation of the Zn-P intermediate at 80 °C is worthy of notice, supporting the observed results that the order of the DPP and SeTOP addition to a $ZnOA_2$ solution in ODE at 80 °C did not affect the resulting nucleation/growth of ZnSe NCs (Figure S1B).

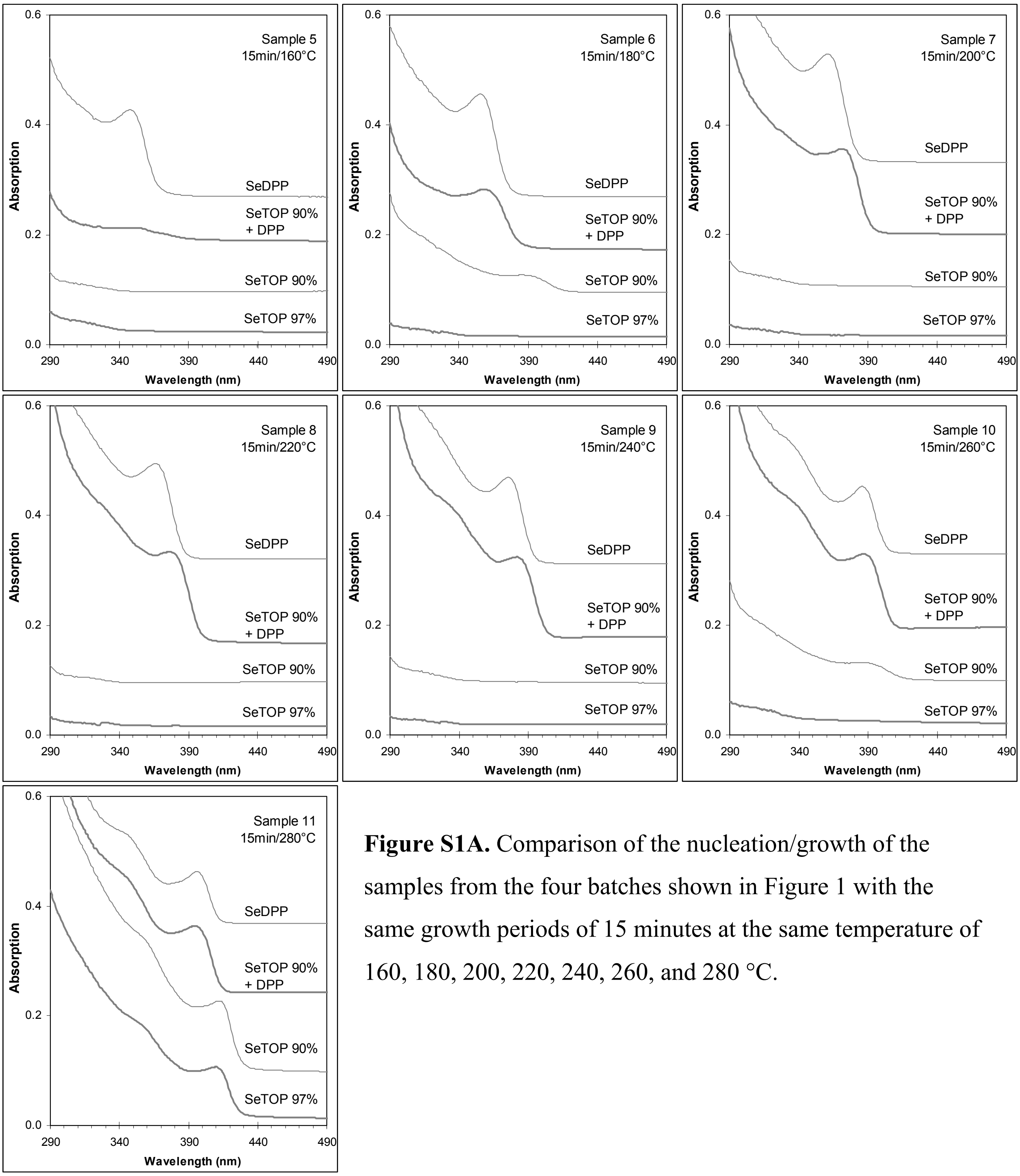


Figure S1A. Comparison of the nucleation/growth of the samples from the four batches shown in Figure 1 with the same growth periods of 15 minutes at the same temperature of 160, 180, 200, 220, 240, 260, and 280 °C.

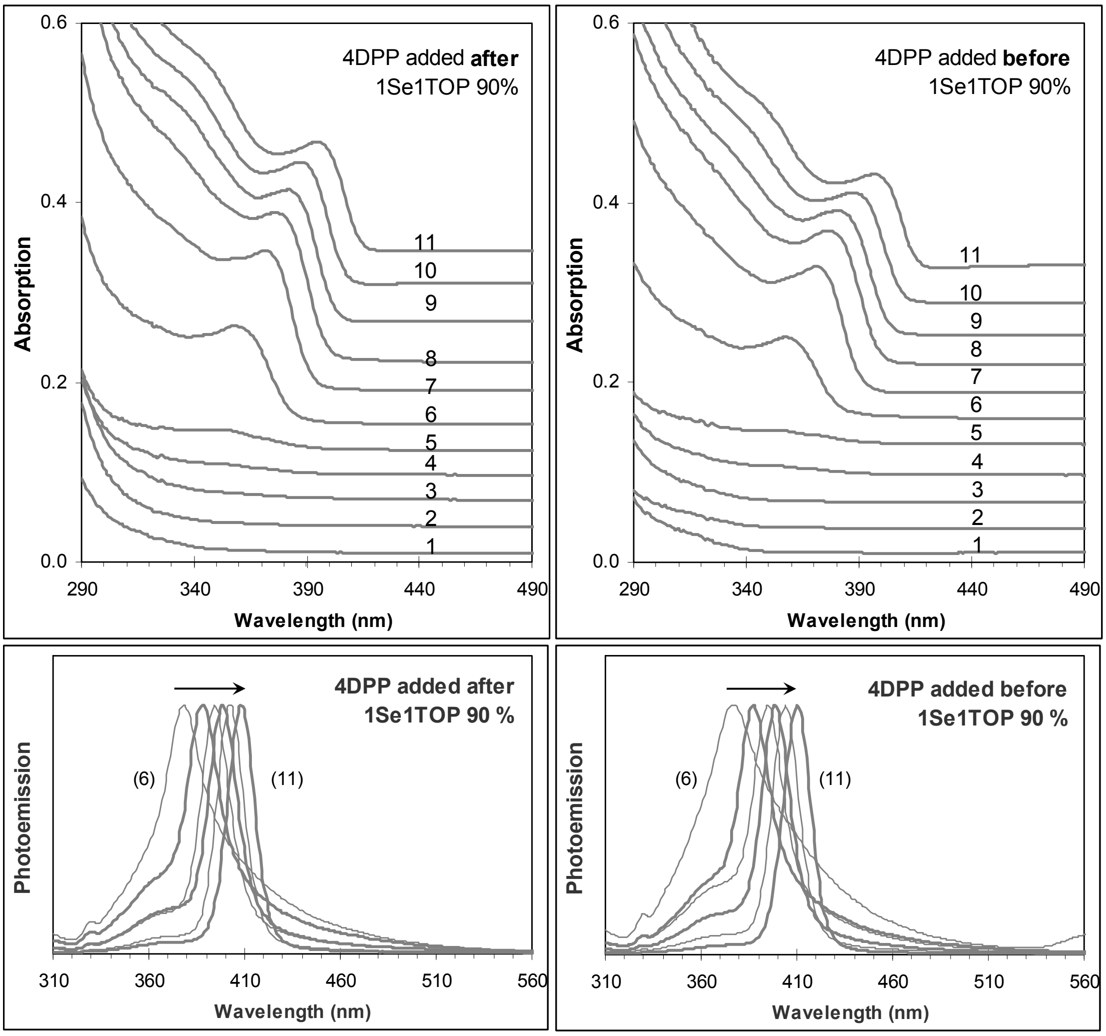


Figure S1B. Investigation on the order of the addition of DPP, before or after the addition of SeTOP, to two $ZnOA_2$ solutions in ODE at 80 °C, affecting the nucleation/growth of ZnSe NCs.

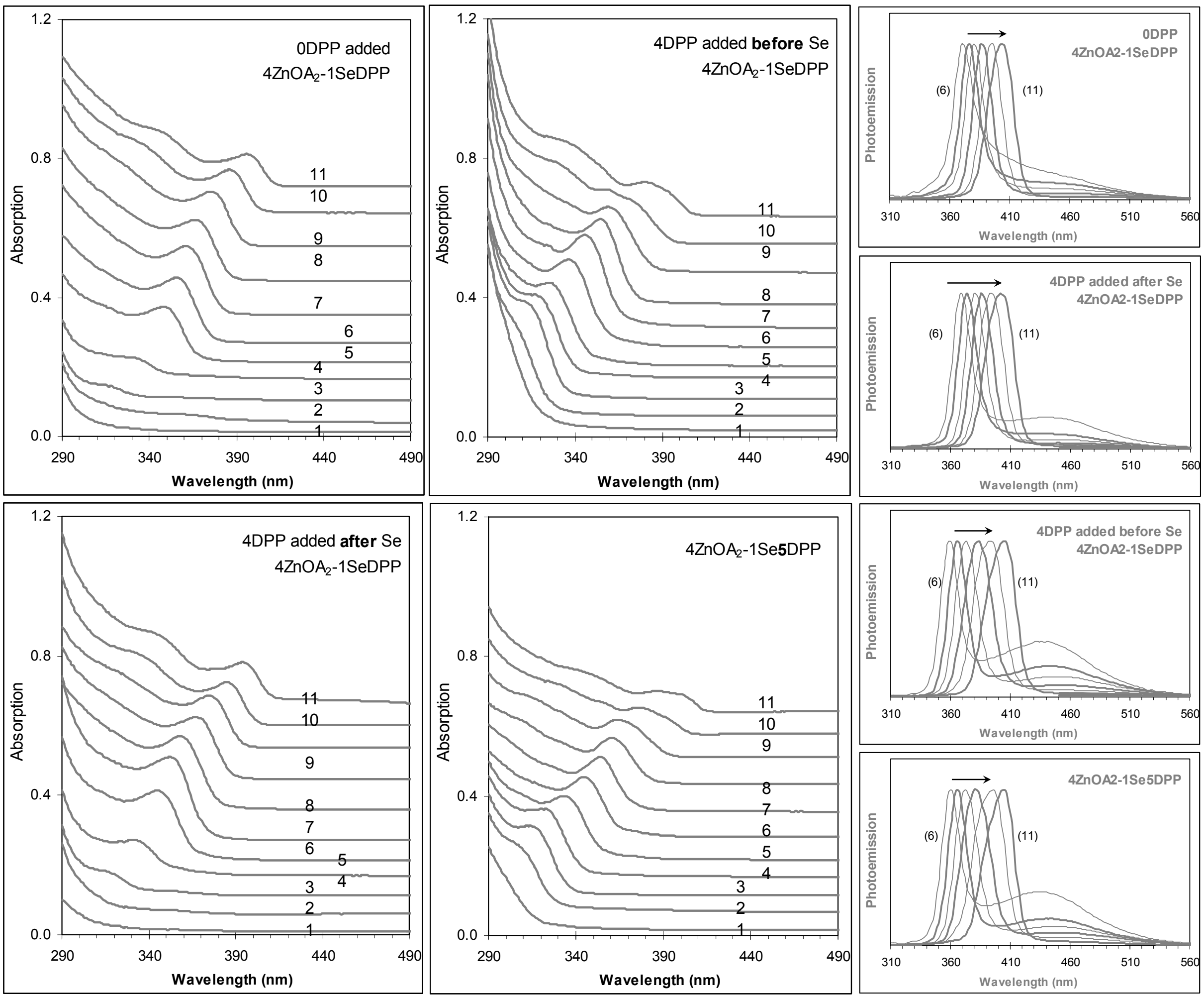


Figure S2A. Investigation on the order of the addition of DPP and SeDPP to four $ZnOA_2$ solutions in ODE at 80 °C affecting the nucleation/growth of ZnSe NCs. Temporal evolution of absorption of the NCs from the four batches without DPP addition (left-top), with 4DPP addition after (left-bottom), before (middle-top), and with (middle-bottom) the addition of SeDPP. (right) The temporal evolution of corresponding emission (normalized) from right top to bottom.

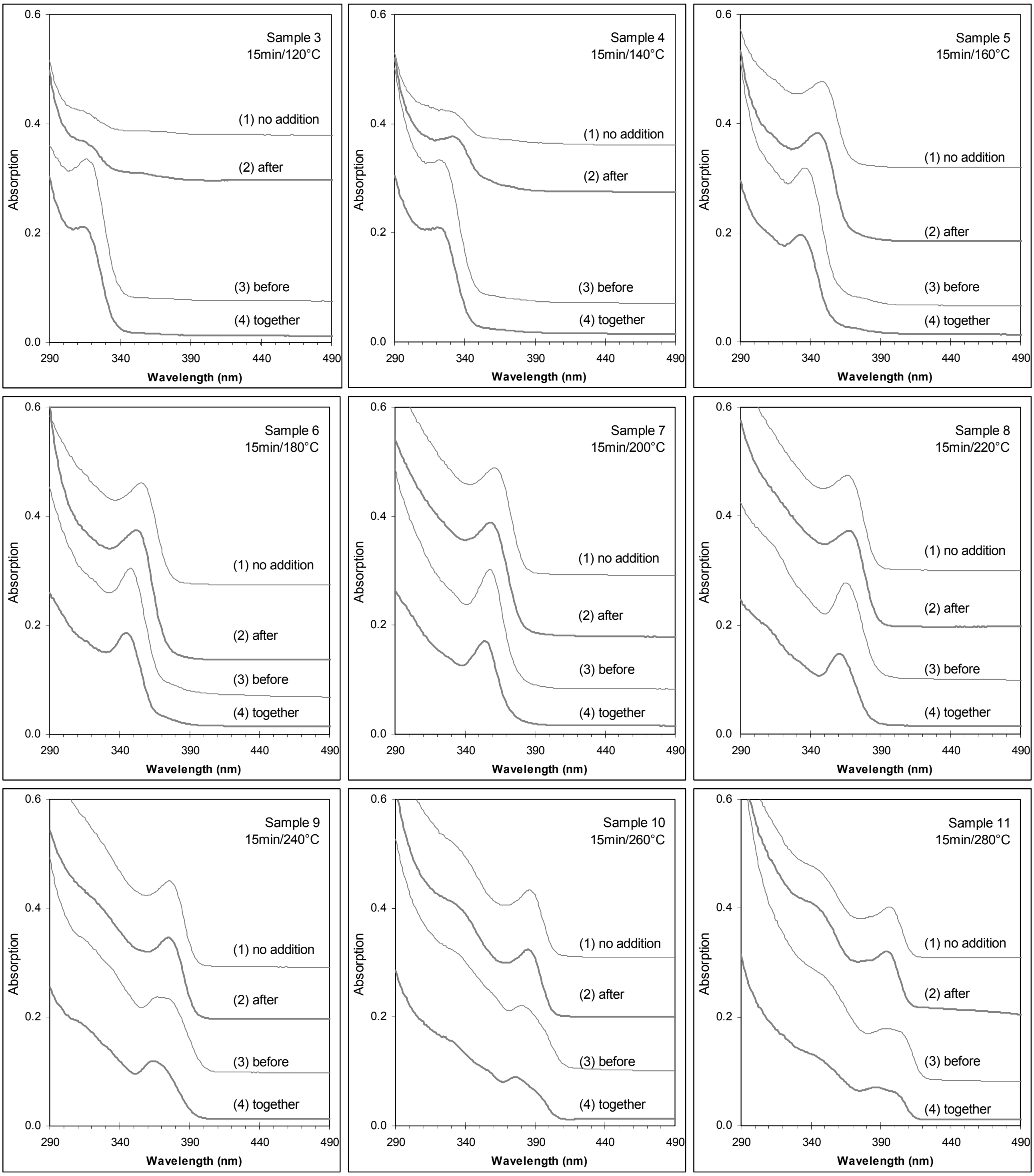


Figure S2B. Comparison of the nucleation/growth of the samples from the four batches shown in Figure S2A with the same growth periods of 15 minutes at the same temperature of 120, 140, 160, 180, 200, 220, 240, 260, and 280 °C.

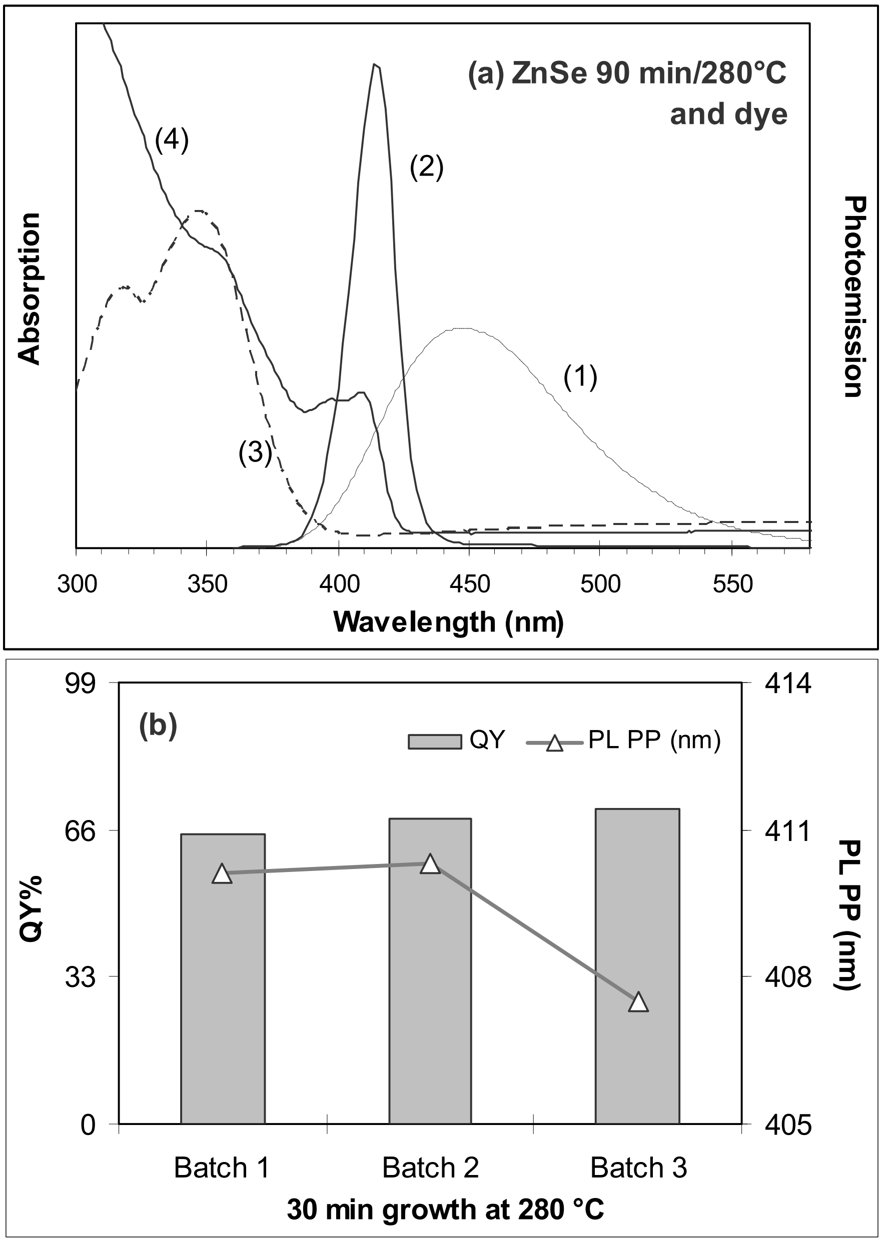


Figure S2C. (A) QY estimation of Figure 2 90-min growth ensemble to be 72 % (based on quinine sulfate in 0.05 M H_2SO_4 (lit. QY ~0.546). Curves (1) and (2) are emission (excitation 350 nm) from the dye and the QD ensemble, respectively, while Curves (3) and (4) are corresponding absorption. (B) The highly-synthetic reproducibility of our non-injection approach demonstrated with three batches. The addition of SeDPP was at 200 °C (Batch 1), 240 °C (Batch 2), and 280 °C (Batch 3). The three ensembles from the three batches with the growth at 280 °C for 30 min exhibited similar emission peak positions and PL QY.

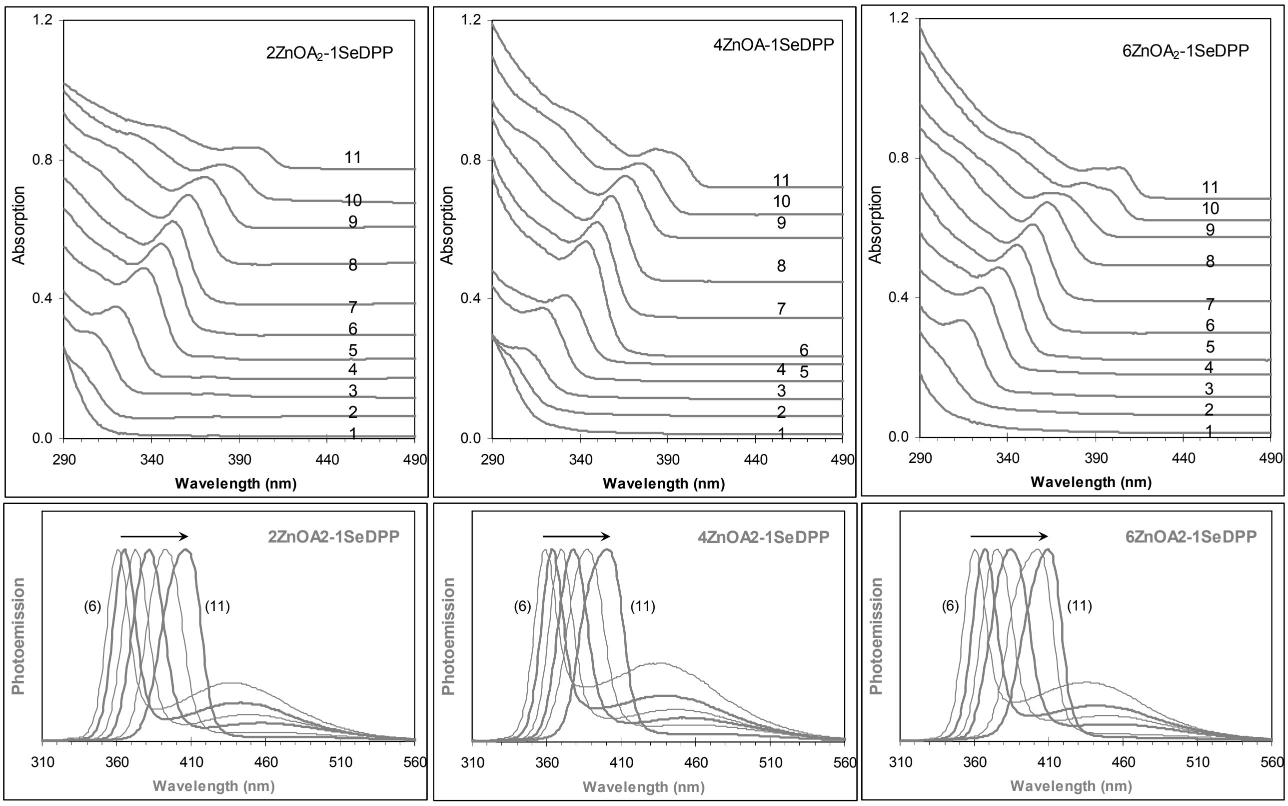


Figure S2D. Investigation on feed Zn-to-SeDPP molar ratios affecting the formation of ZnSe NCs. Temporal evolution of absorption (offset, top) and emission (normalized, bottom) of the ZnSe NCs sampled from the three non-injection-based batches in ODE, with the feed molar ratios of 2 (left), 4 (middle), and 6ZnOA$_2$-to-1SeDPP (right) and [Se] of 60 mmol/Kg. No DPP was added to these three batches. The 4Zn-to-1Se feed molar ratio was used for the rest of the batches in the present study.

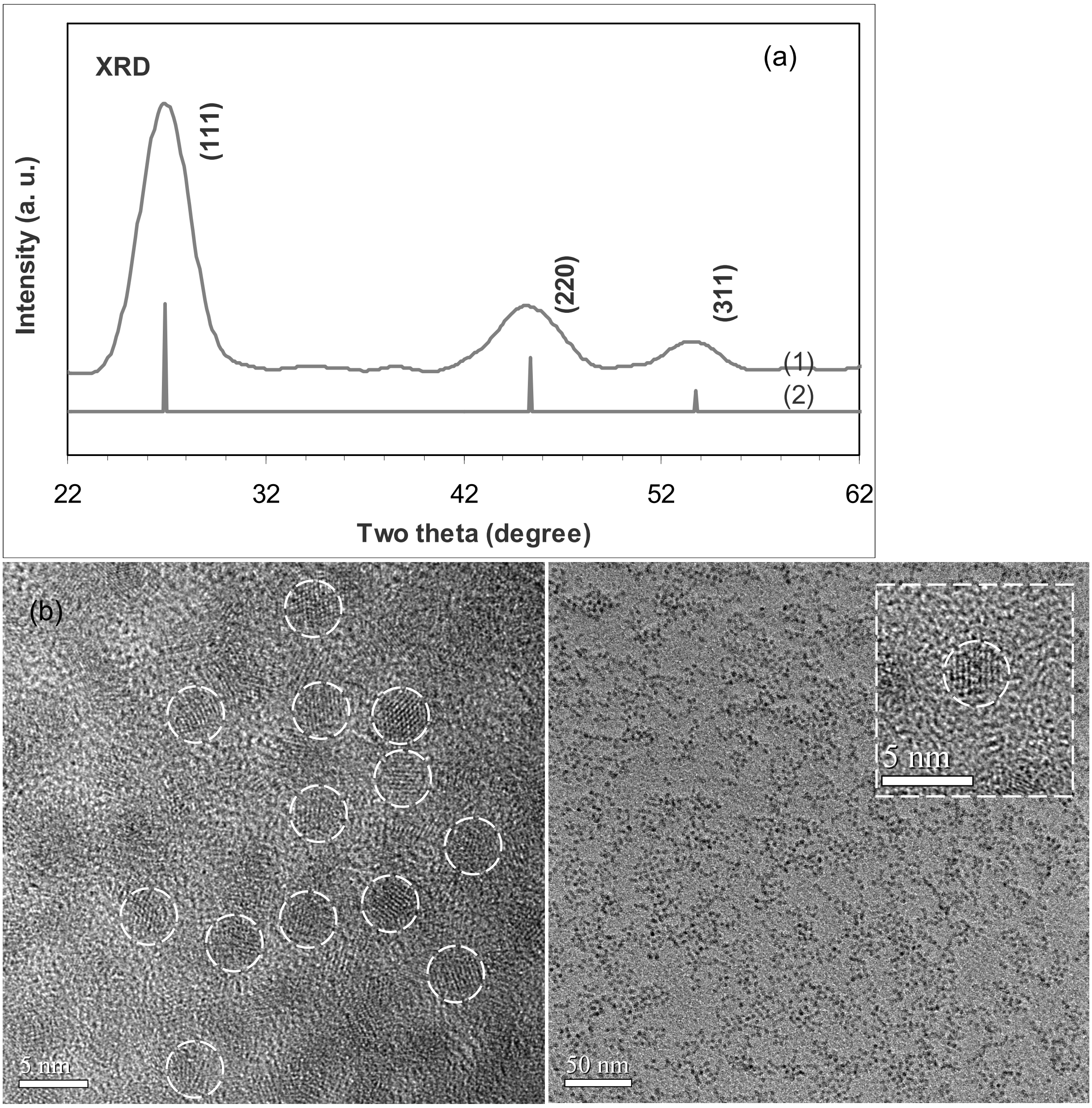


Figure S3. X-ray diffraction patterns (XRD) (a) and TEM images (b). The two purified ZnSe ensembles were from two batches with SeDPP as a Se precursor, the growth temperature of 280 °C, but with (a) and without (b) the addition of DPP, exhibiting absorption peaking at 394 nm (a1) and 402 nm (b). For the TEM sample, the size is estimated to be ~3.1 nm and size distribution ~9%.

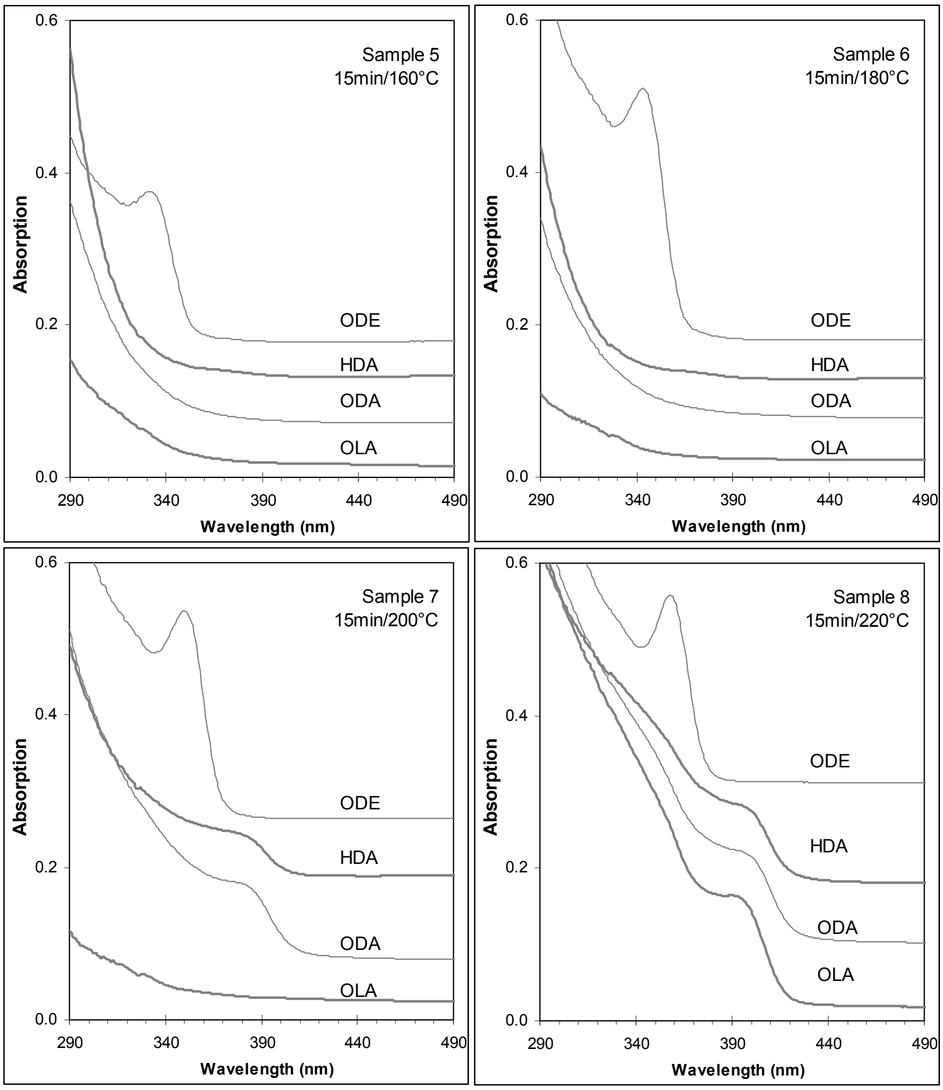


Figure S4A. Investigation on the effect of alkylamines on the formation of ZnSe nanocrystals with DPPSe as a Se precursor. The absorption spectra (offset) of the ZnSe NCs sampled from four non-injection-based batches, one in ODE, and the other in three mixtures of 1ODE-to-1amine (by weight). The three amines were hexadecylamine (HDA), octadecylamine (ODA), and oleylamine (OLA). Samples with growth periods/temperature of 15 min/160 °C (Sample 5), 15 min/180 °C (Sample 6), 15 min/200 °C (Sample 7), and 15 min/220 °C (Sample 8) are compared. The presence of the amine delayed nucleation leading to the formation of larger particles.

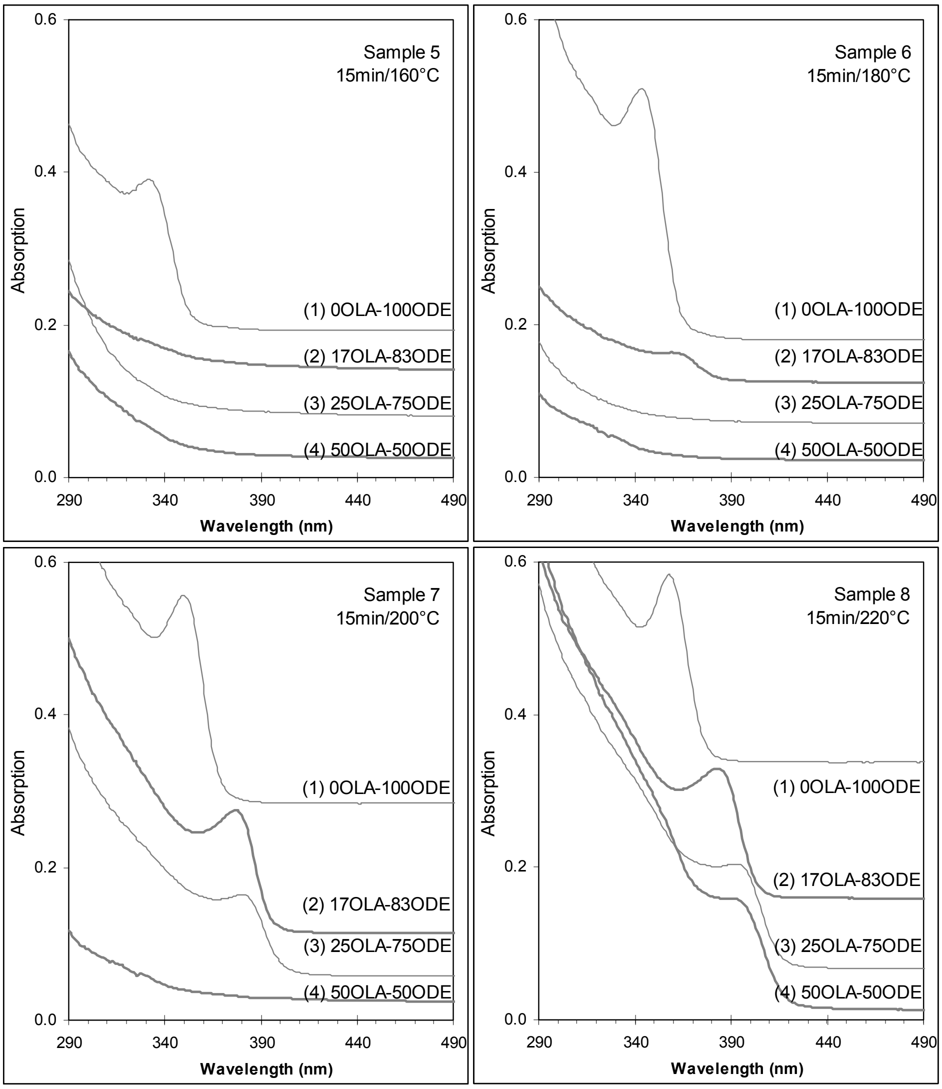


Figure S4B. Investigation on the amount of OLA affecting the ZnSe NC formation with SeDPP as a Se precursor.