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Supporting Information

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In-Situ Observation of Nucleation and Growth of PbSe Magic-Sized Nanoclusters and Regular Nanocrystals

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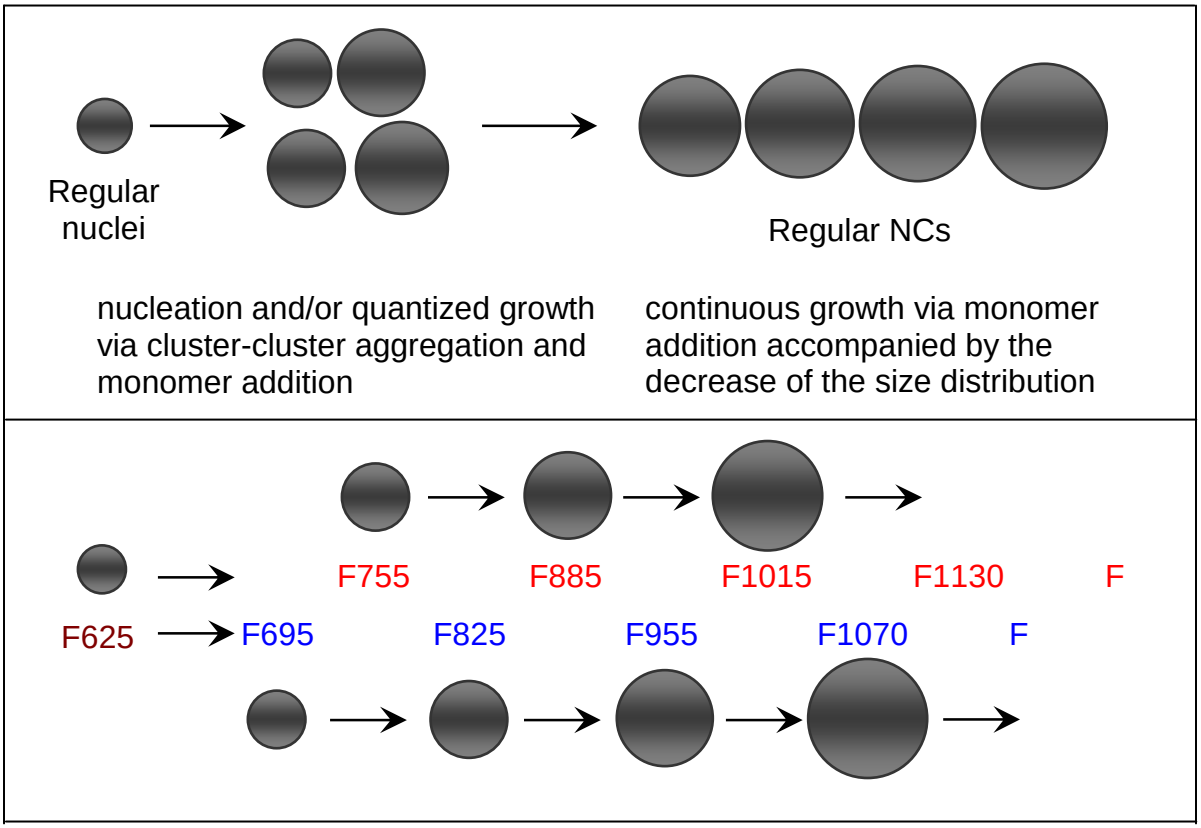
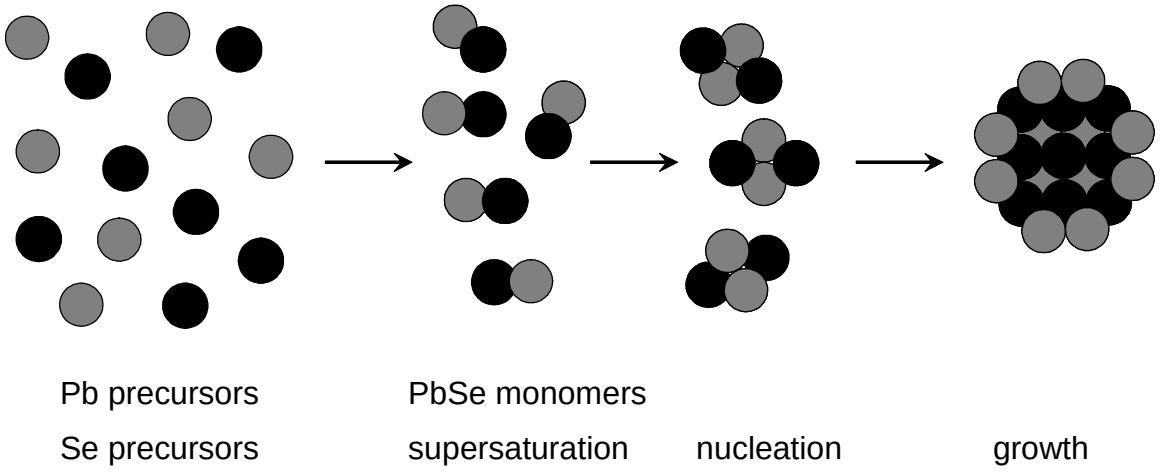
$$(oleate)_2Pb + DPP/DOP/TOP \Rightarrow Pb\text{-}P\ complex \xRightarrow{TOPSe} PbSe\ monomer$$

(Indirect reaction pathway, dominate)



Contents of Main Text

Contents of Supporting Information



Scheme S1. Schematic drawing of the progression of PbSe NCs via the formation of PbSe monomers and their combination leading to nucleation and growth.[16] The formation mechanisms proposed by Refs 16 and 18 are summarized in Figure S6, together with the one proposed in the present study.

Table S1. Summary on the preparation of the batches shown in Figures 1-5 and S2-S4, as well as in situ collection of the temporal evolution of absorption from these batches.

	Pb-Se feed molar ratios, feed concentration	SeTOP	TOP or DPP added	Segment (min)/Interval (min)
Fig 1 Batch 1 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 5.5TOP 90%	no	0-50/5; -200/10
Fig 1 Batch 2 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 2.5TOP 90%	3TOP 90%	0-50/5; -180/10
Fig 1 Batch 3 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 2.5TOP 97%	3TOP 90%	0-50/5; -200/10
Fig 1 Batch 4 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 2.5TOP 90%	no	0-50/5; -180/10
Fig 1 Batch 5 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 2.5TOP 97%	3TOP 97%	0-50/5; -200/10
Fig 1 Batch 6 50℃	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se- 2.5TOP 97%	no	0-50/5; above/10
Fig 2 S2 Batch 50℃ 0.5 uL DPP	1Pb-2.5Se, [Pb] 178 m mol/Kg	2.5Se-2.5TOP 90%	0.06DPP-1Pb-2.5Se	0-50/5; 200/10
Fig 2 S2 Batch 50℃ 5 uL DPP	1Pb-2.5Se, [Pb] 178 mmol/Kg	2.5Se-2.5TOP 90%	0.006DPP-1Pb-2.5Se	0-90/5; 220/10*
Fig S2C Batch 55℃ (0- 5) uL DPP	1Pb-2.5Se, [Pb] 52 mmol/Kg	2.5Se-5.5TOP 90%	0.25DPP-1Pb-2.5Se	0-50/5; above/10
Fig S2D Batch 65℃ (0-20) uL DPP	1Pb-2.5Se, [Pb] 25 mmol/Kg	2.5Se-5.5TOP 90%	2DPP-1Pb-2.5Se	0-25/2.5; above/5
Fig 3 Batch 45℃ 5uL DPP	1Pb-2.5Se, [Pb] 51 mmol/Kg	2 .5Se-5.5TOP 90%	0.25DPP-1Pb-2.5Se	0-50/5; -430/10
Fig 3 Batch 35℃ 5uL DPP	1Pb-2.5Se, [Pb] 102 mmol/Kg	2.5Se-5.5TOP 90%	0.13DPP-1Pb-2.5Se	0-50/5; -430/10
Fig 4 Batch 40℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 4 Batch 50℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 4 Batch 50℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -210/10;
Fig 4 Batch 65℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-25/2.5; -50/5; -160/10
Fig 4 Batch 70℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-25/2.5; -105/5
Fig 4 Batch 80℃	8Pb-1Se, [Se] 20 mmol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-25/2.5; -60/5
Fig S3 Batch 50℃ [Se] 10 mmol/Kg	8Pb-1Se, [Se] 10 m mol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig S3 Batch 50℃ [Se] 20 mmol/Kg	8Pb-1Se, [Se] 20 m mol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig S3 Batch 50℃ [Se] 36 mmol/Kg	8Pb-1Se, [Se] 36 m mol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig S3 Batch 50℃ [Se] 45 mmol/Kg	8Pb-1Se, [Se] 45 m mol/Kg	1Se-2.2TOP 90%	5 uL, 0.6DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 5 S4 Batch 50℃ 0.12DPP	8Pb-1Se, [Se] 20 mmol/K g	1Se-2.2TOP 90%	0.12DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 5 S4 Batch 50℃ 0.31DPP	8Pb-1Se, [Se] 20 mmol/K g	1Se-2.2TOP 90%	0.31DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 5 S4 Batch 50℃ 0.60DPP	8Pb-1Se, [Se] 20 mmol/K g	1Se-2.2TOP 90%	0.60DPP-8Pb-1Se	0-50/5; -300/10; -900/20
Fig 5 S4 Batch 50℃ 1.24DPP	8Pb-1Se, [Se] 20 mmol/K g	1Se-2.2TOP 90%	1.24DPP-8Pb-1Se	0-50/5; -300/10
Fig S4 Batch 50℃ 0.01DPP	8Pb-1Se, [Se] 20 mmol/Kg	1 Se-2.2TOP 90%	0.01DPP-8Pb-1Se	0-50/5; -300/10; -900/20

All the reactions started with 3.5 mL cuvettes; Se-precursor solutions were added to $PbOA_2$ solutions in ODE under stir. For example, for Figure 1 batches, the Se precursor was TOPSe made with 1Se-to-2.2TOP (90%, Batch 1) and 1Se-to-1TOP (90% for Batches 2 and 4; 97% for Batches 3, 5, and 6) feed molar ratios. Additional TOP (90%, 90%, and 97%) was added for Batches 2, 3, and 5, respectively.

The absorption spectra of Figure 1 were collected with a 5-min time interval in the first 50 min and a 10-min time interval afterwards.

For Figure 4 Batches 40 °C and 50 °C, the temporal evolution of the absorption spectra was collected with a 5-min time interval up to 50 min, a 10-min time interval up to 300 min, and a 20-min time interval afterwards up to 900 min. The red absorption spectra stand for the growth periods of 200, 400, 600, and 800 min. For Batch 60 °C, the absorption spectra were acquired

with a 5-min time interval up to 50 min and a 10-min time interval up to 210 min, with the red absorption spectra being suggestive of the growth periods of 100 and 200 min. For Batch 65 °C, the absorption spectra were collected with a 2.5-min time interval up to 25 min, a 5-min time interval up to 50 min, and a 10-min time interval afterwards up to 160 min. The red absorption spectra denote the growth period of 100 min. For Batch 70 °C, the absorption spectra were obtained with a 2.5-min time interval up to 25 min and a 5-min time interval afterwards up to 105 min. For Batch 80 °C, the absorption spectra were collected with a 2.5-min time interval up to 60 min. The red absorption lines for Batches 70 °C and 80 °C represent the growth period of 50 min. The ready observation of the PbSe MSNCs was by Batches 40 °C and 50 °C, while that of the PbSe RNCs by Batch 80 °C.

For * of Figure S2 Batch 5 uL DPP, the change of light path was carried out from 10 mm to 4 mm. See Figure S2 below.

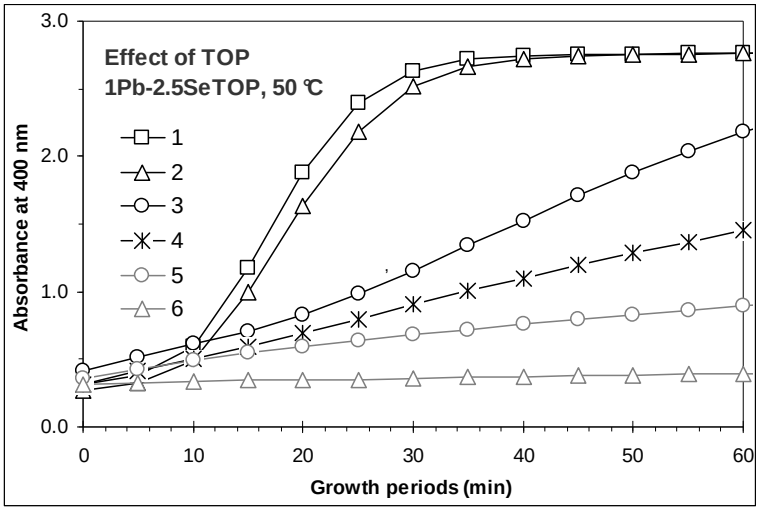


Figure S1. Investigation on the use of commercially-available TOP 90% and 97% affecting the development of the PbSe NCs, with the absorbance at 400 nm obtained from in situ observation of absorption of Batches 1 to 6 presented in Figure 1.

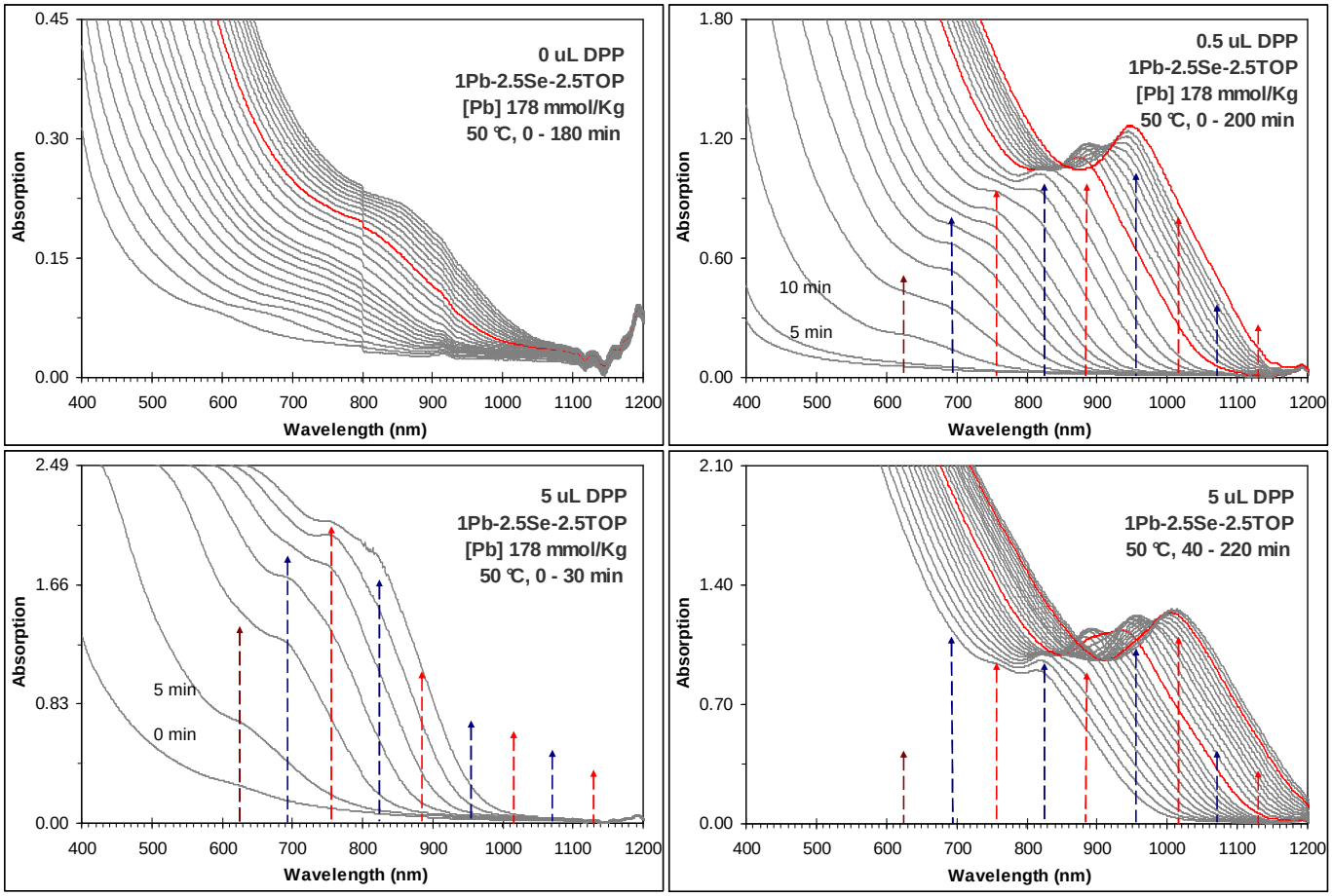


Figure S2A. (Top) Batch 0 uL DPP (top-left) is Figure 1 Batch 4. Investigation on the effect of the addition of DPP affecting the formation of PbSe MSNCs vs RNCs, via in situ observation of the temporal evolution of absorption of the NCs from three synthetic batches with the 1Pb-to-2.5SeTOP feed molar ratio and [Pb] ~178 mmol kg^{-1} at 50 °C.

For Batches 0 uL (top-left) and 0.5 uL (top-right), the temporal evolution of the absorption spectra was collected with a 5-min time interval up to 50 min, a 10-min time interval up to 300 min, and a 20-min time interval afterwards up to 900 min.

For Batch 5 uL DPP (bottom-left), the absorption spectra was collected with a 5-min time interval up to 30 min and 10 mm light path. Afterwards (bottom-right), the light path was changed to 4 mm (with 10 min for background collection), with a 10-min time interval up 220 min.

See Figure S2B for Batch 5 uL the later stage growth 230 - 920 min. Note that for a clear view, the interval is 20 min from 230-330 min, 30 min from 330-360min, and 40 min from 360-920min. The red absorption spectrum stands for the growth periods of 400 min and 800 min.

It is clear that without the addition of DPP (top-left), the formation of RNCs was preferred; with the DPP addition (the rest), MSNCs were formed with the nucleation taking place at 5 – 10 minutes (Batch 0.5 uL) and at 0 – 5 minutes (Batch 5 uL).

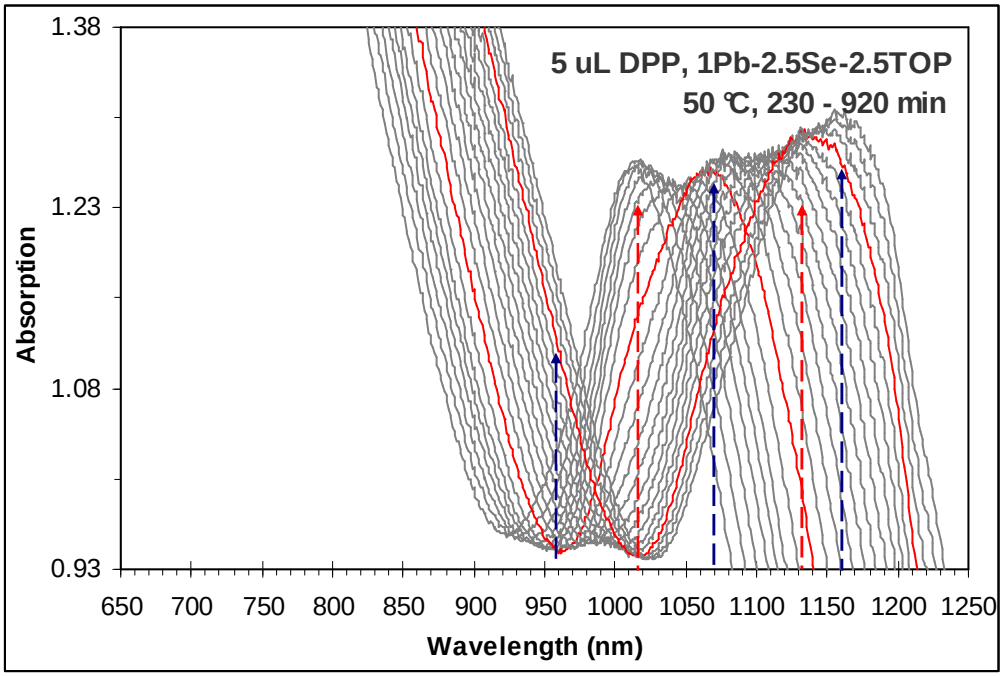


Figure S2B. Various magic-sized families are obtained, including (F625, F695, F755, F825, F885, F955,) F1015, F1070, F1130, and F(>1170).

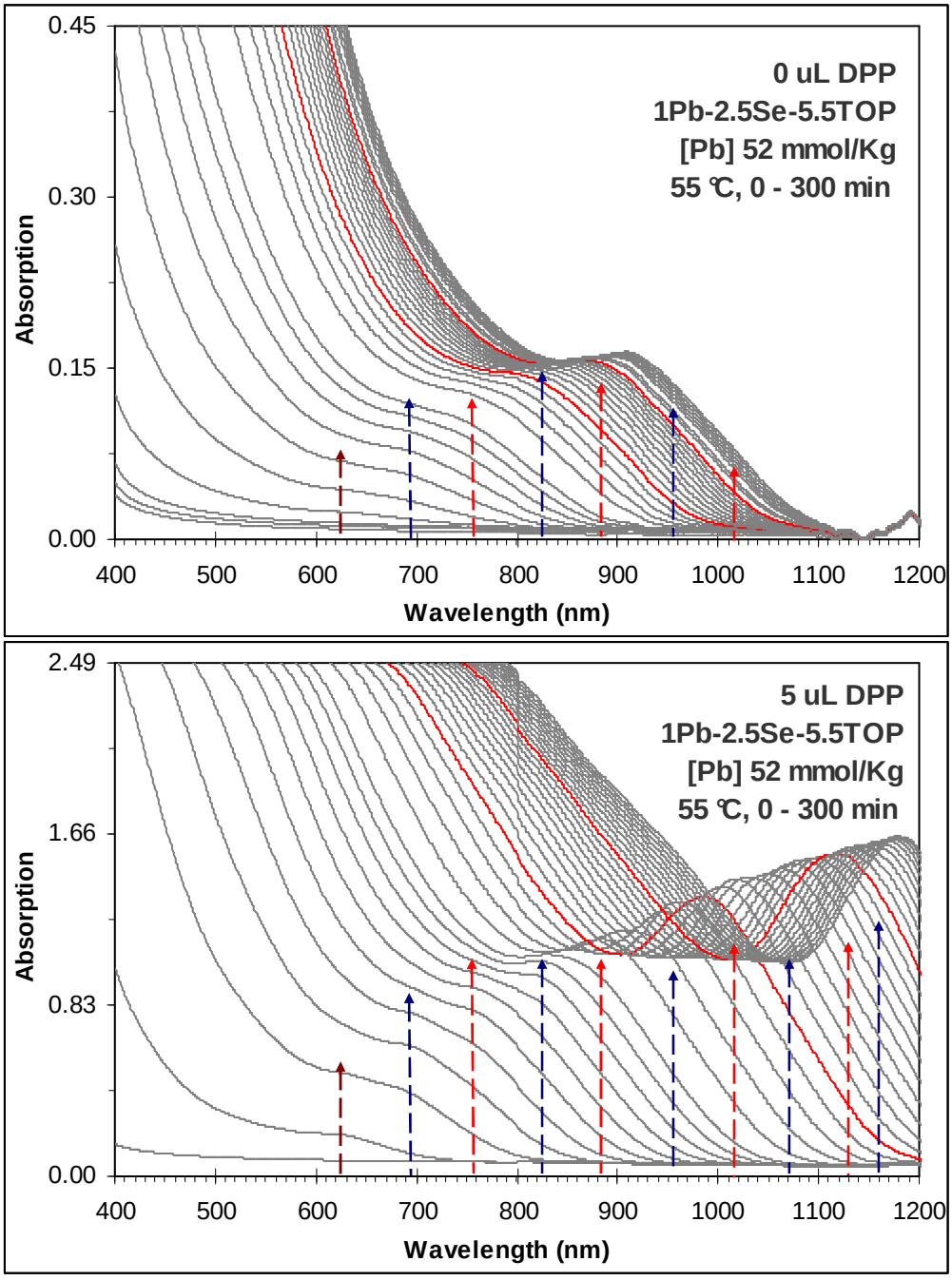


Figure S2C. Investigation on the effect of the addition of DPP affecting the formation of PbSe MSNCs vs RNCs, via in situ observation of the temporal evolution of absorption of the NCs from two synthetic batches with the 1Pb-to-2.5SeTOP feed molar ratio and [Pb] ~52 mmol kg^{-1} at 55 °C. The temporal evolution of the absorption spectra was collected with a 5-min time interval up to 50 min, and a 10-min time interval up to 300 min. The red absorption spectra stand for the growth periods of 100 and 200 min.

It is clear that without the addition of DPP (top), the formation of RNCs is preferred; with the DPP addition (bottom), MSNCs are formed.

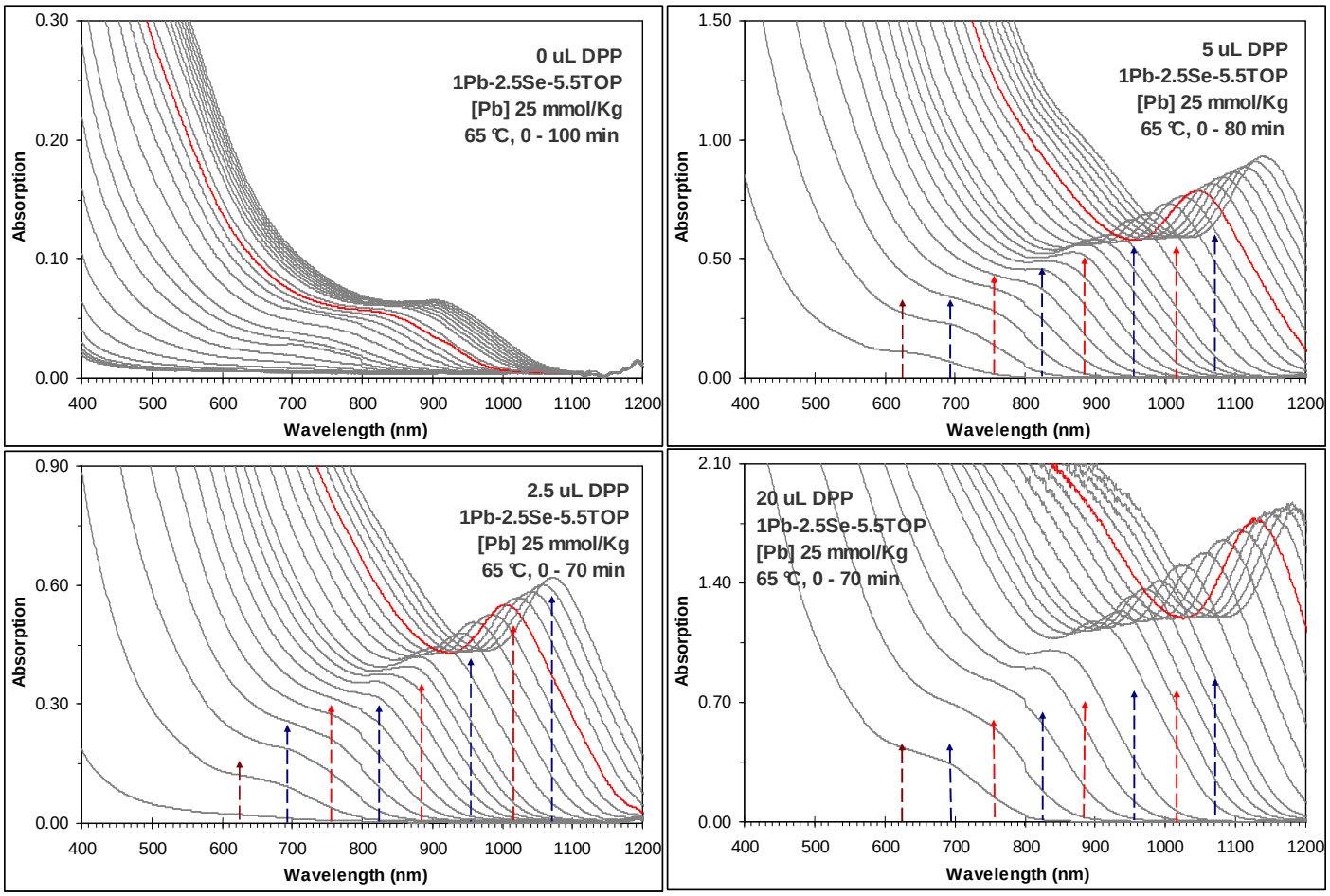


Figure S2D. Investigation on the effect of the addition of DPP affecting the formation of PbSe MSNCs vs RNCs, via in situ observation of the temporal evolution of absorption of the NCs from four synthetic batches with the 1Pb-to-2.5SeTOP feed molar ratio and [Pb] ~25 mmol kg^{-1} at 65 °C. The temporal evolution of the absorption spectra was collected with a 2.5-min time interval up to 25 min, and a 5-min time interval afterwards. The red absorption spectra stand for the growth periods of 50 min.

It is clear that without the addition of DPP (left-top), the formation of RNCs is preferred; with the DPP addition (the rest), MSNCs are formed.

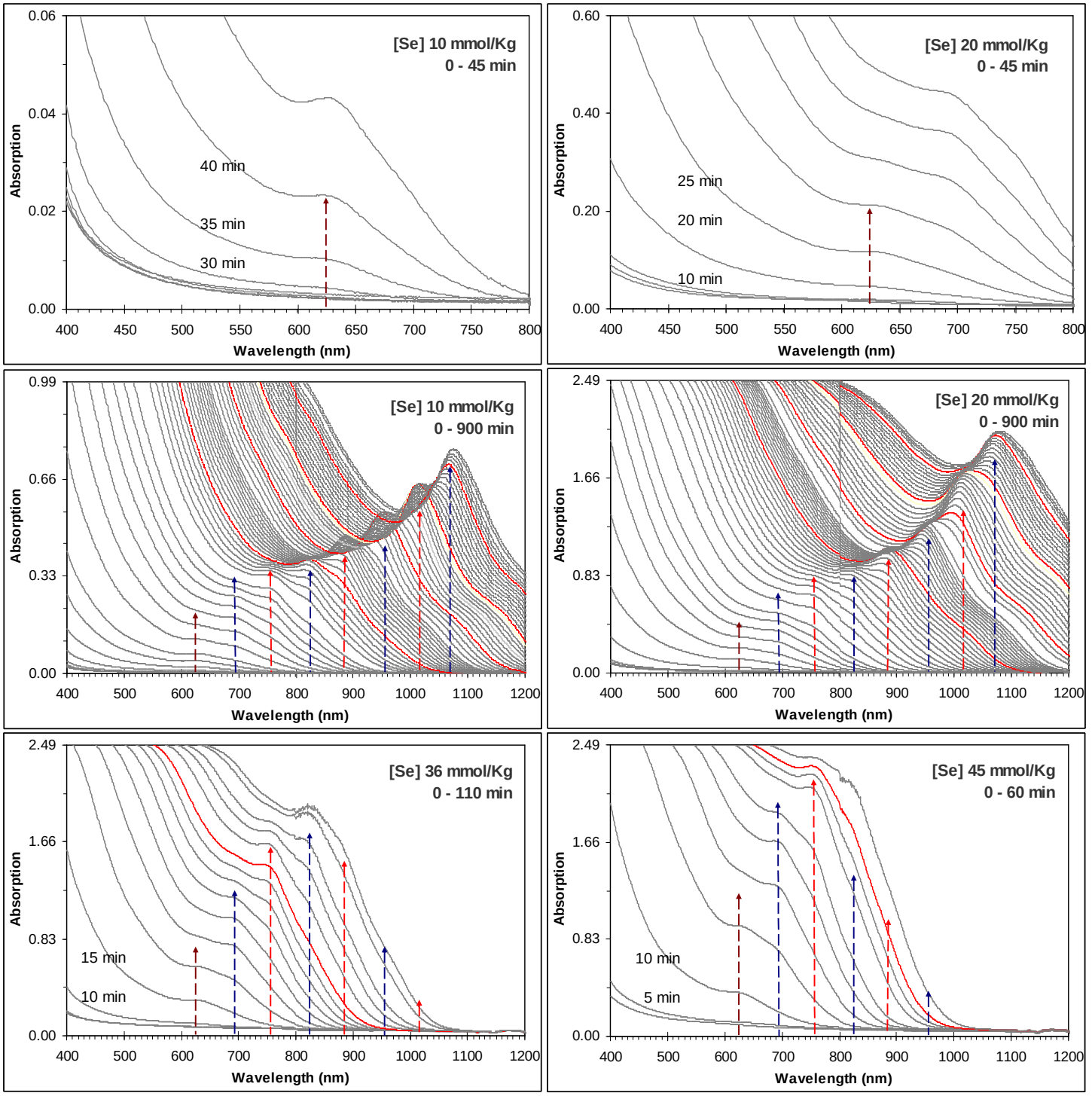


Figure S3A. Investigation on the effect of feed Se concentrations affecting the evolution of PbSe NCs, via in situ observation of the temporal evolution of absorption of the PbSe NCs from four synthetic batches with the 0.6DPP-to-8Pb-to-1SeTOP feed molar ratio and the reaction temperature of 50 °C. The feed [Se] concentrations are indicated, together with the growth periods. Here, the temporal evolution of the absorption spectra was collected with a 5-min time

interval up to 50 min, a 10-min time interval up to 300 min, and a 20-min time interval afterwards up to 900 min. The red absorption spectra stand for the growth periods of 200, 400, 600, and 800 min for Batch 10 mmol kg^{-1} and Batch 20 mmol kg^{-1}. The latter is that of Figure 4 Batch 50 °C. Also, the red absorption spectra stand for the growth periods of 50 min for Batch 36 mmol kg^{-1} and Batch 45 mmol kg^{-1}. For the first batch, see Figure S3B also for a precise observation of the growth of the MSNCs.

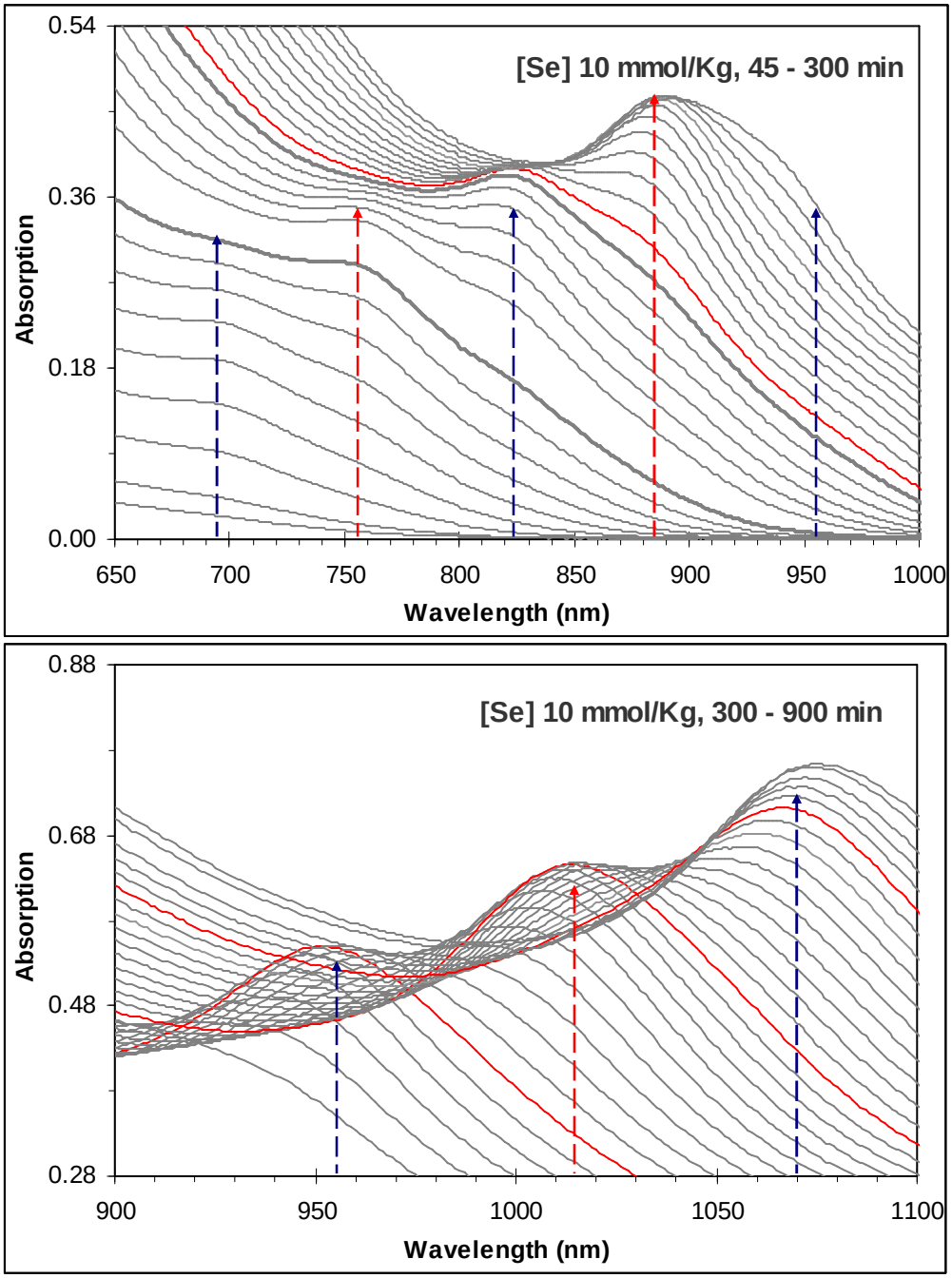


Figure S3B. A large view of Batch [Se] 10 mmol kg^{-1} for a precise observation of the growth of the PbSe MSNCs; again, the MSNC families are identified by arrowed lines. The disappearance of F695 is accompanied with the presence of F825; the disappearance of F755 is accompanied with the presence of F885.

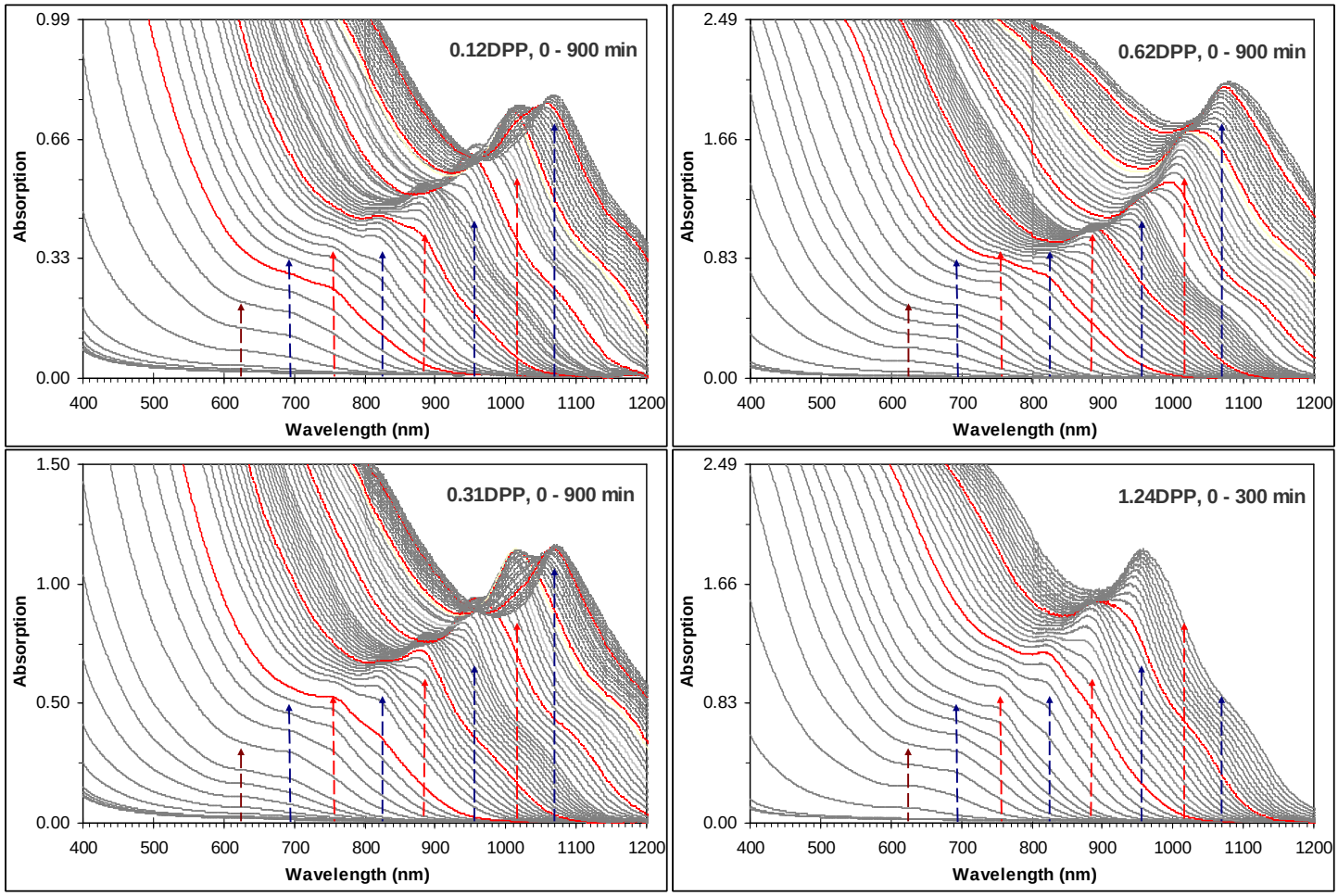
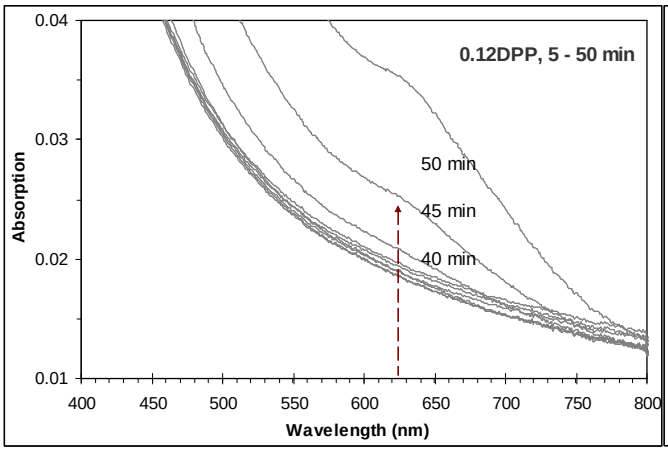
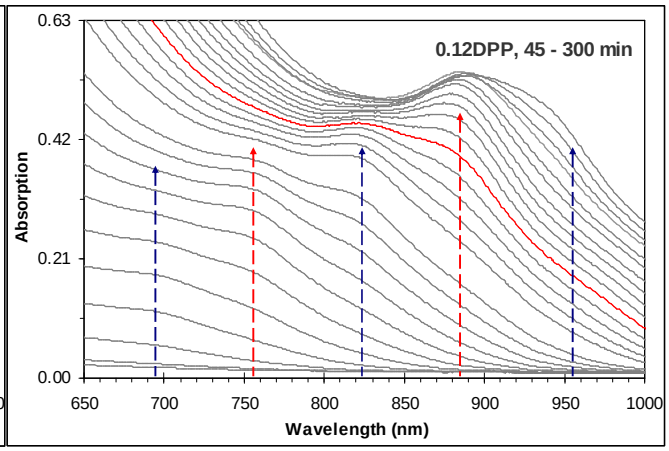
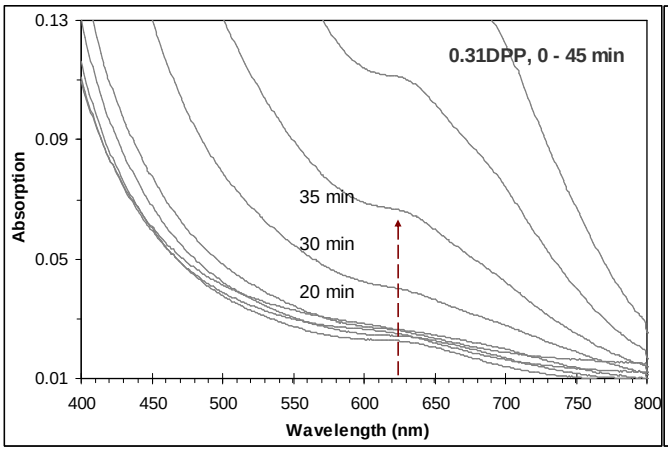


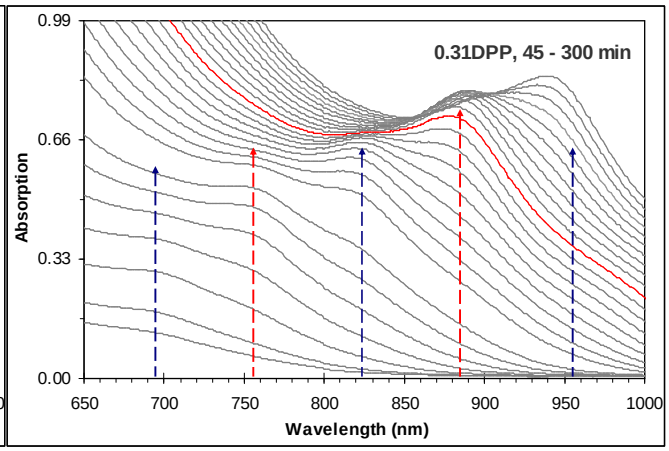
Figure S4A. Investigation on the effect of DPP amounts affecting the evolution of PbSe NCs, via in situ observation of the temporal evolution of absorption of the PbSe NCs from four synthetic batches with the 8Pb-to-1SeTOP feed molar ratio and [Se] ~20 mmol kg^{-1}. The reaction temperature was 50 °C. The DPP amounts are indicated as DPP-to-8Pb feed molar ratios. The growth periods are indicated. Here, the temporal evolution of the absorption spectra was collected with a 5-min time interval up to 50 min, a 10-min time interval up to 300 min, and a 20-min time interval afterwards up to 900 min. The red absorption spectra stand for the growth periods of 100, 200, 400, 600, and 800 min. See Figure S4B for details.

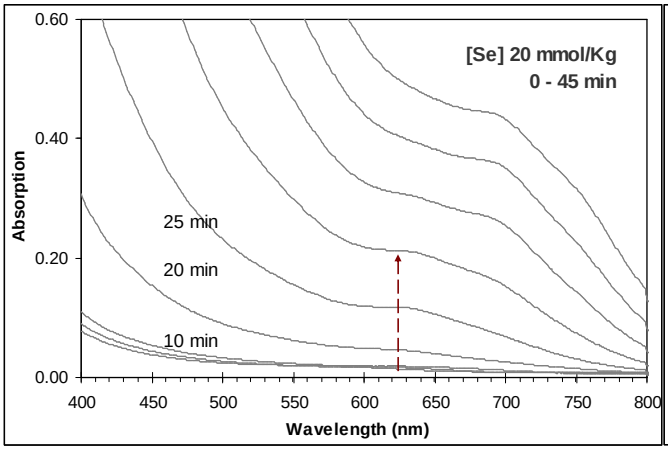
Figure S4B. The growth periods are indicated as 0-50 min or 0–45 min (left) and 45–300 min (right).

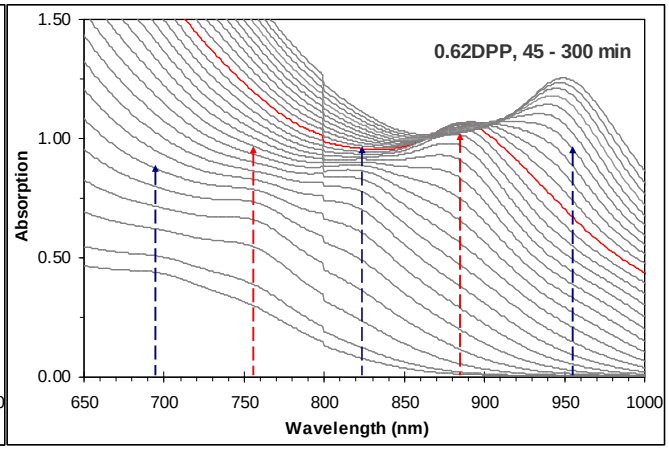

0.12DPP, 5 - 50 min
50 min
45 min
40 min
Absorption
Wavelength (nm)

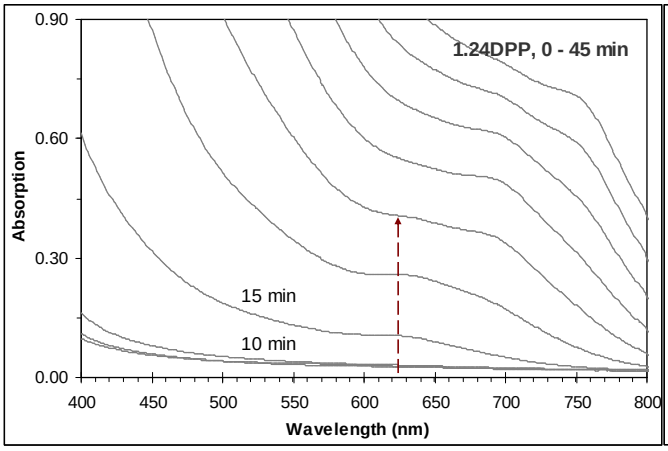

0.12DPP, 45 - 300 min
Absorption
Wavelength (nm)

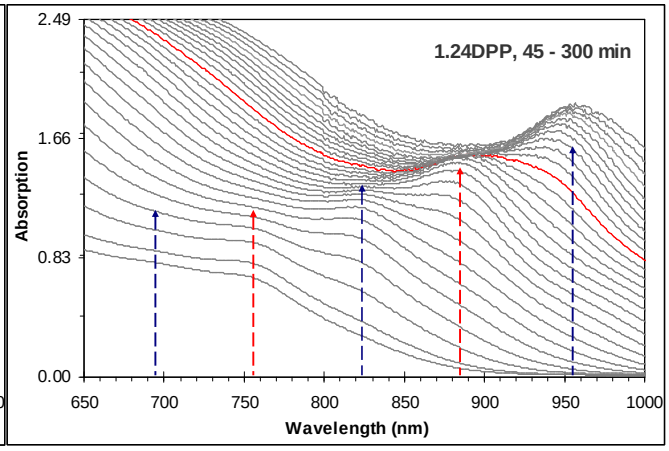

0.31DPP, 0 - 45 min
35 min
30 min
20 min
Absorption
Wavelength (nm)


0.31DPP, 45 - 300 min
Absorption
Wavelength (nm)


[Se] 20 mmol/Kg
0 - 45 min
25 min
20 min
10 min
Absorption
Wavelength (nm)


0.62DPP, 45 - 300 min
Absorption
Wavelength (nm)


1.24DPP, 0 - 45 min
15 min
10 min
Absorption
Wavelength (nm)


1.24DPP, 45 - 300 min
Absorption
Wavelength (nm)

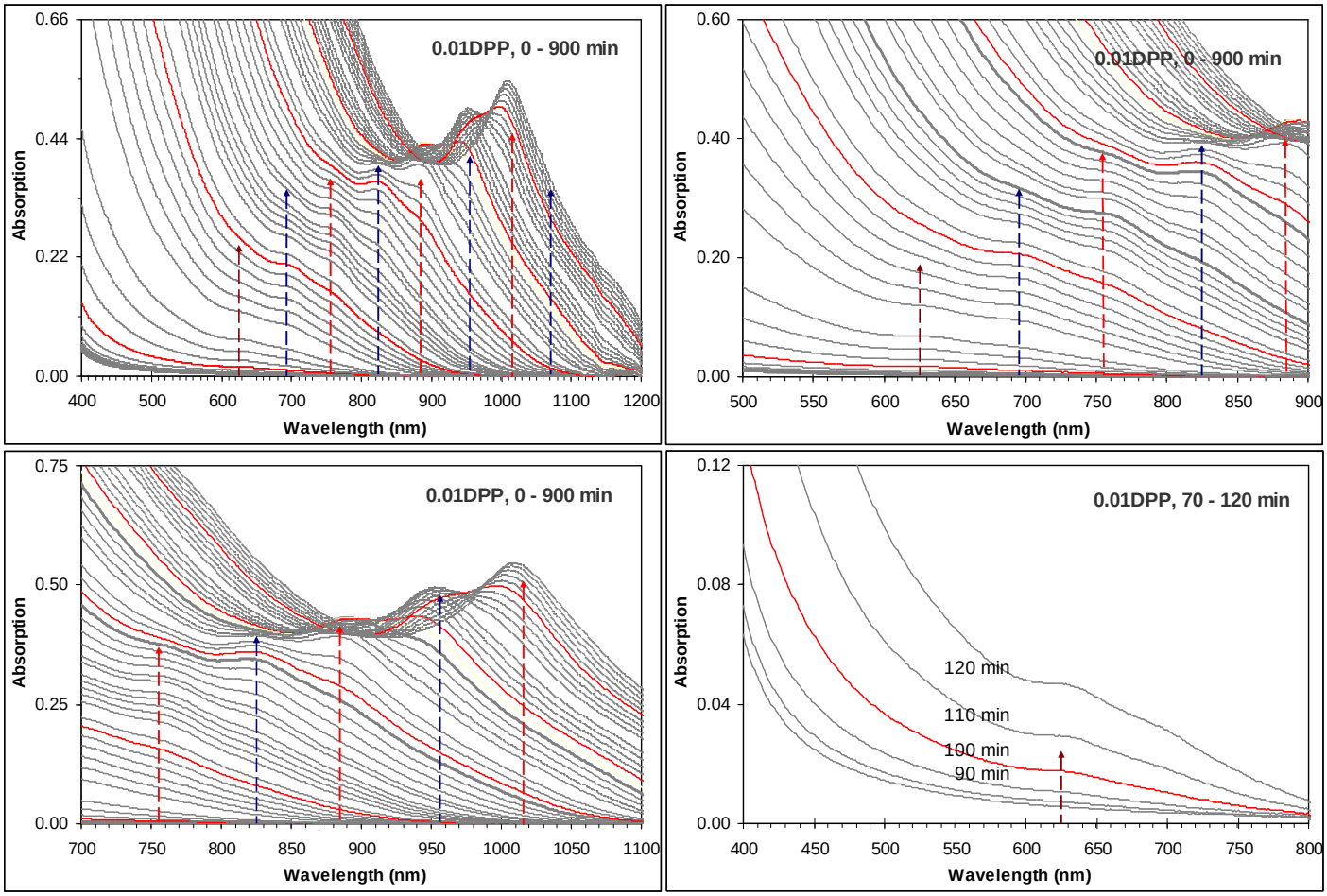


Figure S4C. Investigation on the effect of DPP amounts affecting the evolution of PbSe NCs, via in situ observation of the temporal evolution of absorption of the PbSe NCs from this synthetic batch with the 8Pb-to-1SeTOP feed molar ratio and [Se] ~20 mmol kg^{-1}. The reaction temperature was 50 °C. The DPP amount is indicated as DPP-to-8Pb feed molar ratios. The growth periods are indicated. The nucleation, the presence of F625 was monitored at 90 min, for this Batch. Here, the temporal evolution of the absorption spectra was collected with a 5-min time interval up to 50 min, a 10-min time interval up to 300 min, and a 20-min time interval afterwards up to 900 min. The red absorption spectra stand for the growth periods of 100, 200, 400, 600, and 800 min.

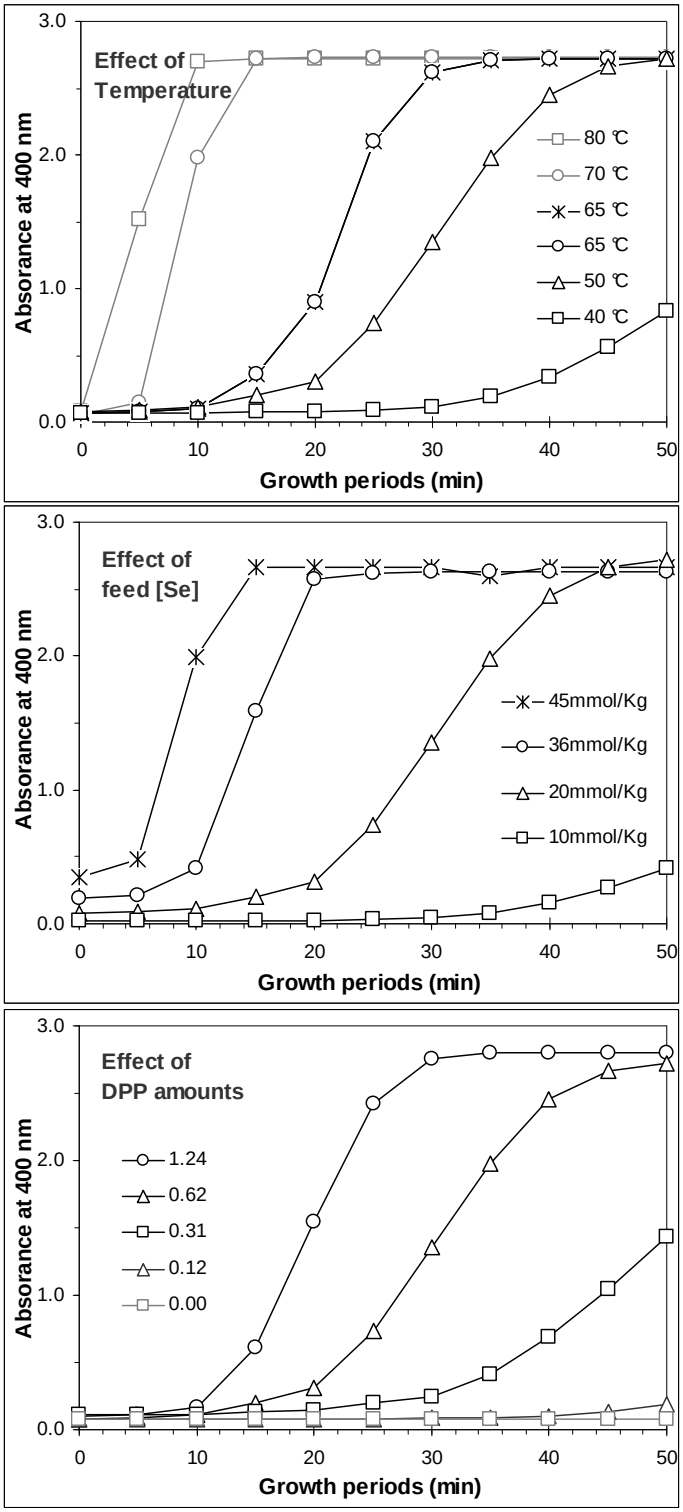


Figure S5. Investigations on the effects of growth temperature (top), feed [Se] (middle), and the amount of DPP added (bottom) affecting the evolution of the PbSe NCs, via in situ observation of the absorbance at 400 nm from the various Batches studied. With the feed molar ratio of 0.62DPP-to-8Pb-to-1TOPSe and [Se] 20 mmol kg^{-1}, the effect of the growth temperature in the range of 40─80°C is shown in the top part; these six batches are also shown in Figure 4. With the feed molar ratio of 0.62DPP-to-8Pb-to-1TOPSe and the growth temperature of 50°C, the effect of the feed [Se] is shown in the middle part; these four batches are shown in Figure S3. With the feed molar ratio of 8Pb-to-1TOPSe and [Se] 20 mmol kg^{-1} and the growth temperature of 50°C, the effect of the amount of DPP added is shown in the bottom part; these four batches are shown in Figures 4 and S4.

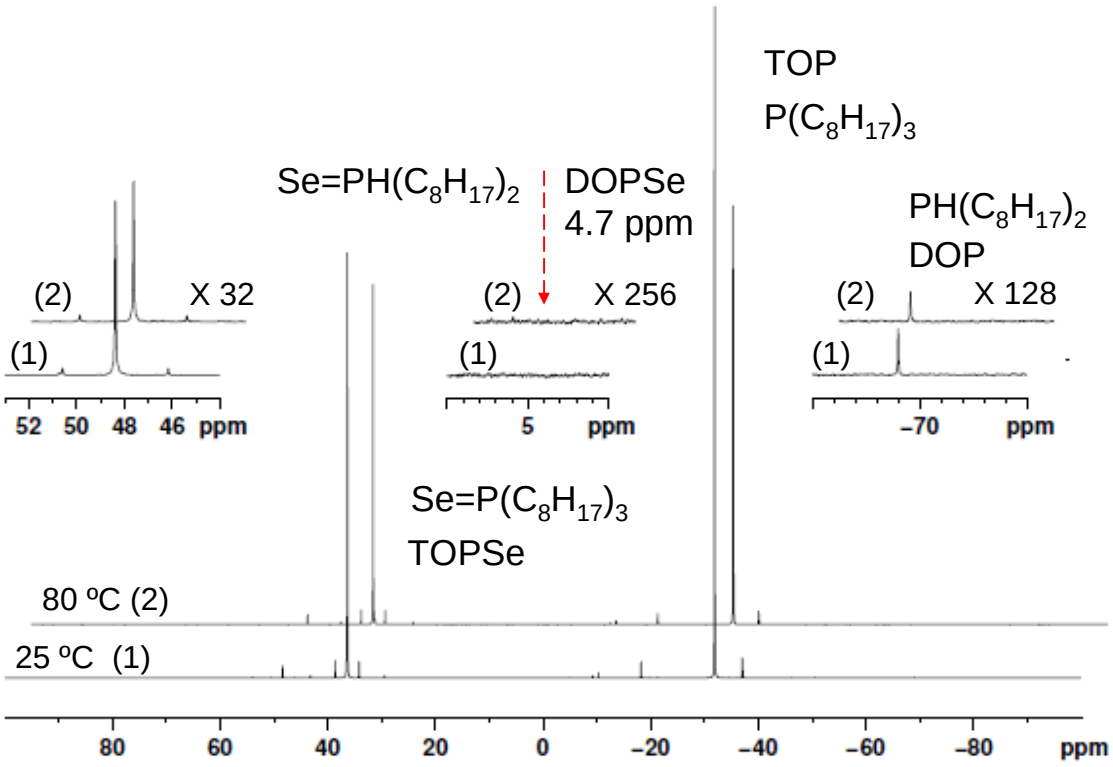


Figure S6A. ^{31}P NMR detected no DOPSe (δ 4.7 ppm[18]) but some DOP (δ -68.9 ppm[18]), together with TOPSe (δ 36.9 ppm[18]) and TOP (δ -31.7 ppm[18]) from our ~1.0 M TOPSe/TOP solution, with external standard 85% H_3PO_4. The NMR sample was prepared in a glovebox, where 12.6569 g (34.15 mmol) TOP 90% and 1.2256 g (15.52 mmol) Se were mixed. The mixture was stirred overnight at room temperature in the glovebox. The mixture was loaded in a NMR tube and properly sealed. The NMR measurements were carried out at 25 °C and 80 °C/10min. The magnification of the insets is indicated. It is noteworthy that another Se-containing species (~48.4 ppm) was detected.

^{31}P NMR, thus, suggests that DOP/TOP + Se ⇒ TOPSe (no DOPSe).

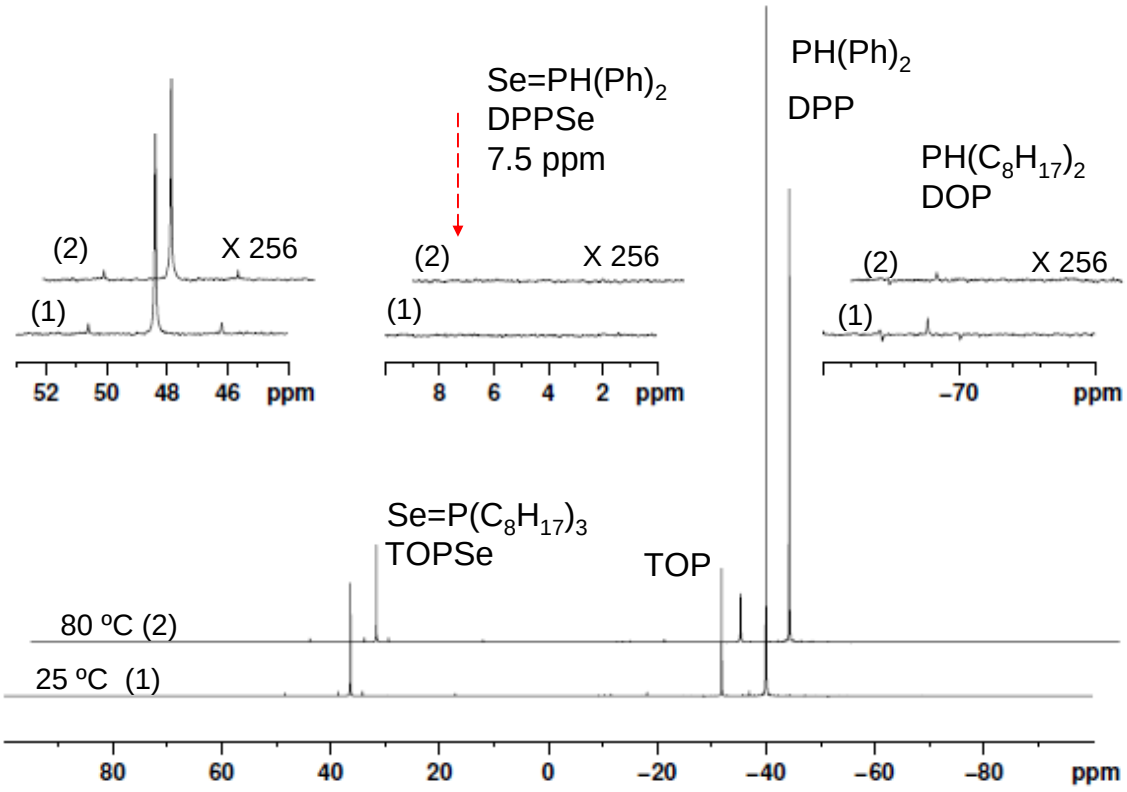


Figure S6B. ^{31}P NMR detected no DPPSe (δ 7.5 ppm[18]) with the addition of DPP (δ -39.5 ppm[18]) to the ~1.0 M TOPSe/TOP (TOPSe δ 36.9 ppm[18] and TOP δ -31.7 ppm) solution, with external standard 85% H_3PO_4. The NMR sample was prepared in a glovebox, where 0.43 mL (0.44 mmol) of the 1.0 M TOPSe stock solution was mixed with 0.31 mL (1.75 mmol) DPP. The mixture was loaded in a NMR tube and properly sealed. The NMR measurements were performed at 25 °C and 80 °C/10 min. The magnification of the insets is 256. It is noteworthy that another Se-containing species (~48.4 ppm) was detected.

^{31}P NMR, thus, suggests that TOPSe + DPP, still TOPSe and no DPPSe.

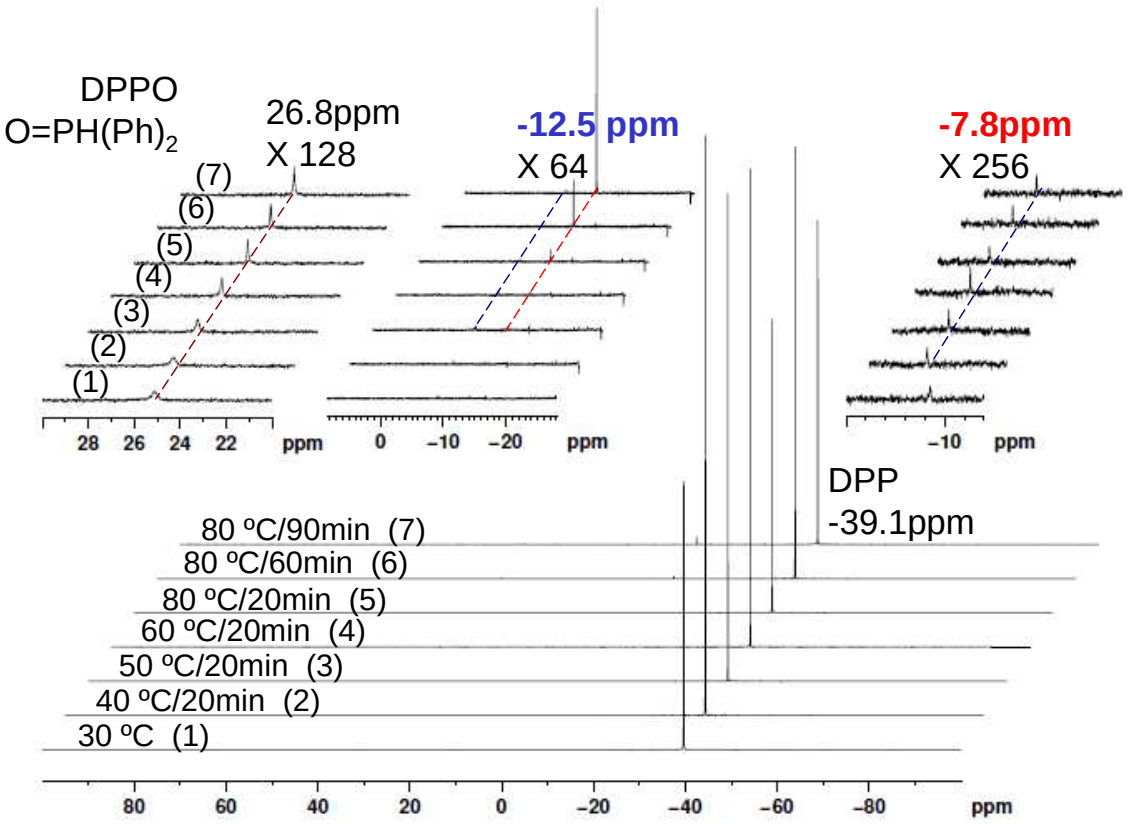


Figure S6C. ^{31}P NMR detected new peaks, such as at 26.8 ppm (DPPO[16]) and -7.8 ppm (unknown, which might be a Pb-P complex), from a reaction of 0.7986 g (0.54 mmol) of our $PbOA_2$ stock solution and 0.1 mL (0.57 mmol) DPP (δ -39.1 ppm,) with external standard 85% H_3PO_4. The NMR sample was prepared in a glovebox, and the mixture was loaded in a NMR tube and properly sealed. The NMR spectra were collected from 30 °C to 80 °C. The magnification of the inset is indicated.

	JACS 2006 (Ref 16)	JACS 2010 (Ref 18)	Present study
TOPO	54.2	53.5	54.6
TOPSe	36.9, 36.7	36.8	36.9
DPPO	24.5	27.1	26.8
DPPSe	N/A	7.5 (in tol-d8), 5.9	not detected
DOPSe	N/A	4.7, 4.3	not detected
TOP	-20.4	-31.7	-31.7
DPP	-39.9	-40.2 (in tol-d8)	-39.1/-39.5
DOP	N/A	-69.1	-68.9

Figure S6D. We summarized the chemical shifts (ppm) of the various species reported from the two ^{31}P NMR studies documented in JACS 2006 (Ref 16) and JACS 2010 (Ref 18). For the present study, an external standard 85% H_3PO_4 was used.

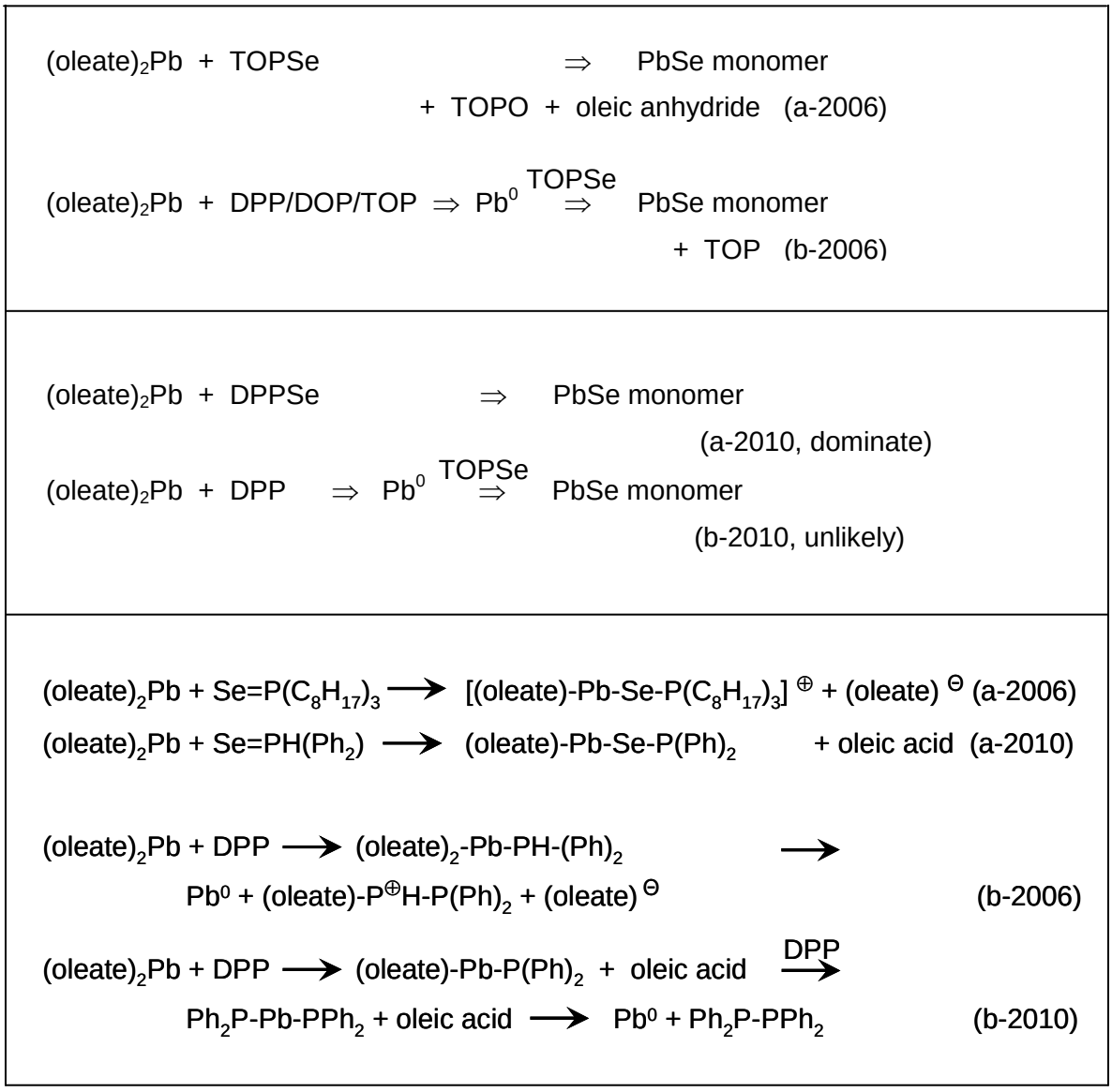


Figure S6E. We summarized the two formation mechanisms of PbSe monomers proposed in 2006 (top, Ref 16) and 2010 (middle, Ref 18), with some detail (bottom) in their difference for the two routes a and b.

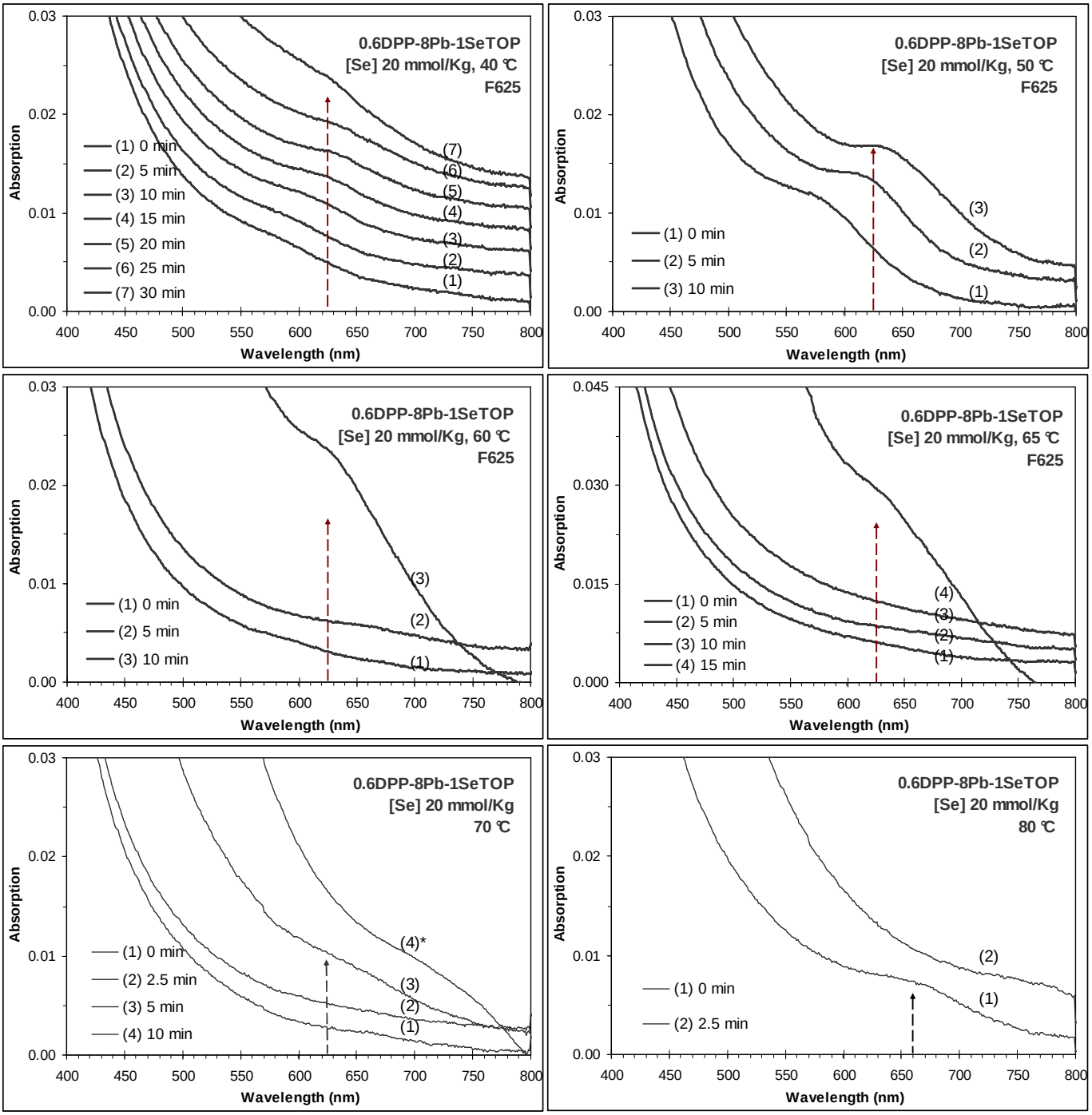


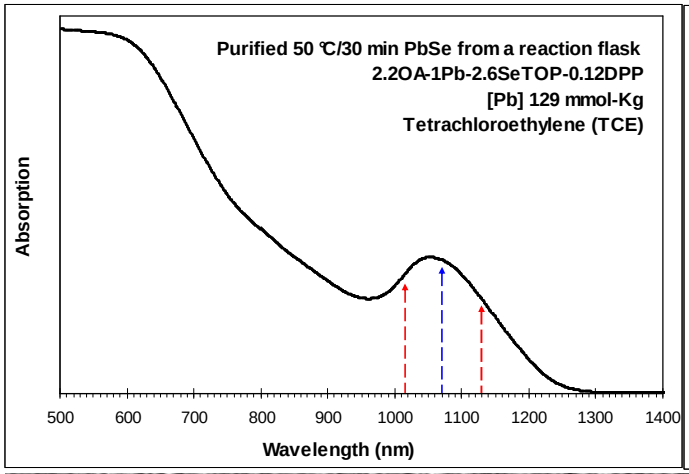
Figure S7. In situ observation of nucleation of the six Figure 4 batches, whose experimental conditions including the growth periods are indicated. For a meaningful examination, the absorption spectra are offset; and the optical density of Batch 70 °C Curve (4)* was one-tenth of its true value. For Batches 50 °C, the emergence and disappearance of the PbSe NCs peaking at

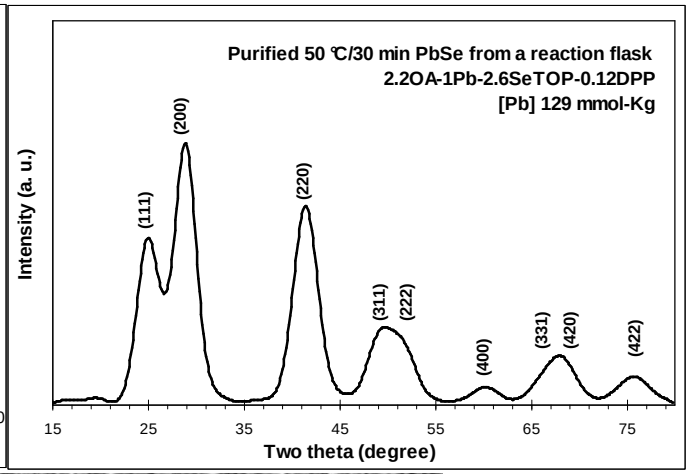
570 nm is worthy of notice, together with the development of the NCs peaking at 625 nm. The cluster peaking at 570 nm does not seem to be magic-sized according to its growth pattern monitored.[23-26] For Batch 80 °C, nucleation might take place at 0 min with the presence of one ensemble peaking at ~660 nm.

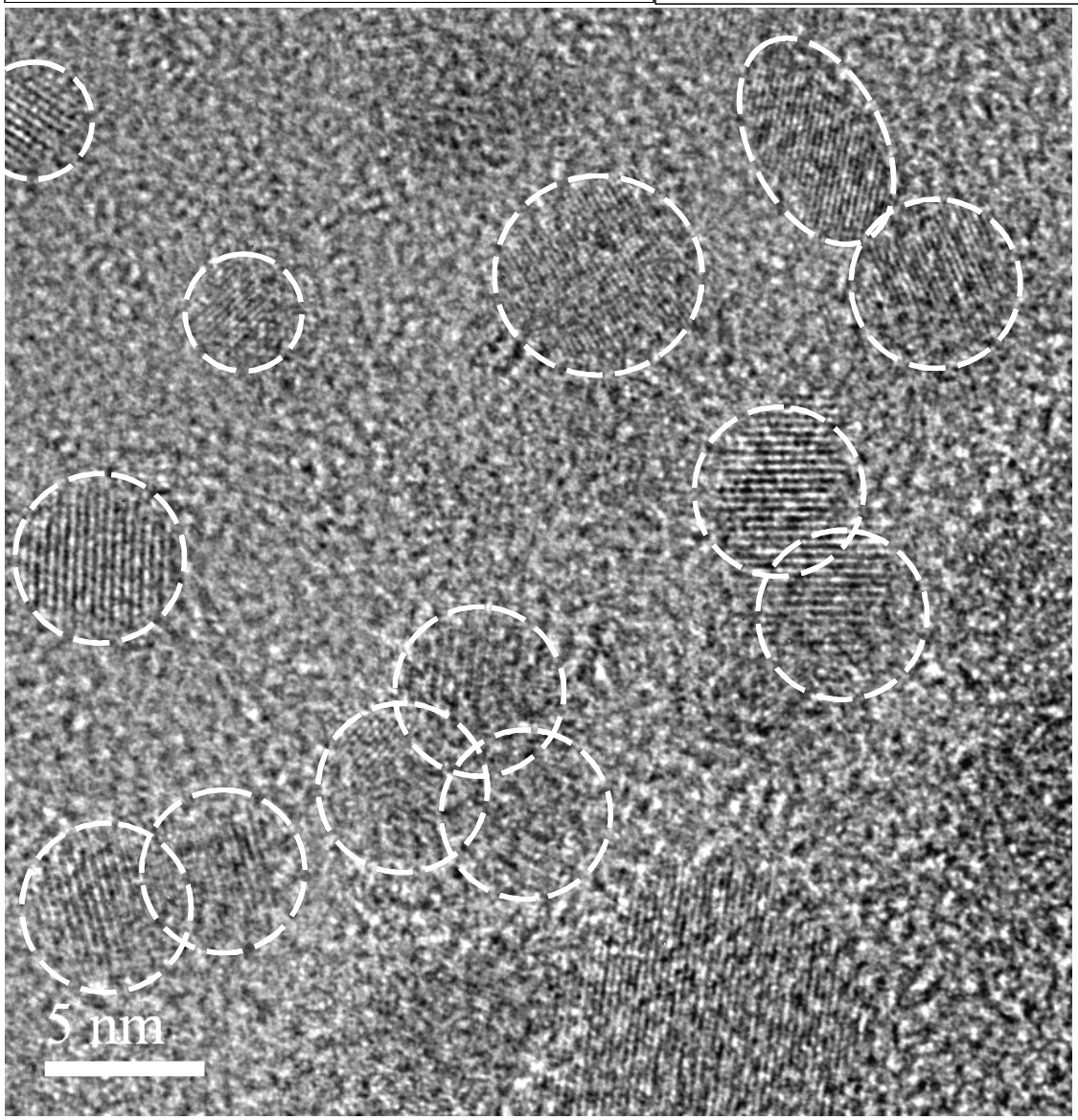
Figure S8. XRD (top-right) and TEM (bottom) study of one purified PbSe NC ensemble (whose absorption was shown (top-left)) from a reaction flask with the feed molar ratios of 2.2OA-1Pb-2.6SeTOP-0.12DPP and [Pb] 129 mmol kg^{-1}. The TOPSe solution was made with a feed molar ratio of 1Se-2.2TOP. The growth period of the ensemble was 30 min at 50 °C. The TEM image shows a certain degree of aggregation.

For the present study with the coexistence of various PbSe nanocrystals, it seems that traditional characterization tools such as XRD, TEM, elementary analysis, and XPS, for size and composition of one particular family, exhibit limitation. For our small-sized PbSe RNCs, EDX and XPS were used to study the Pb-to-Se atomic number ratios [Ref 19a].

Particularly, TEM has been widely used in the characterization of size and size distribution; however, for ~2 nm NCs, TEM has its limitation. Meanwhile, for such small NCs, the aggregation during TEM sample preparation is significant. Accordingly, it is challenging to accurately obtain the size information of each PbSe MSNC family [Ref 25] and small-sized PbSe NCs [Ref 19]. For small-sized NCs, the use of their first excitonic absorption peak positions instead of their sizes can be practical to minimize the confusion due to the discrepancy in size determination by different techniques or by the same technique but used in various research groups [Ref 13 and 19].


Purified 50 ℃/30 min PbSe from a reaction flask
2.2OA-1Pb-2.6SeTOP-0.12DPP
[Pb] 129 mmol-Kg
Tetrachloroethylene (TCE)
Absorption
500
600
700
800
900
1000
1100
1200
1300
1400
Wavelength (nm)


Purified 50 ℃/30 min PbSe from a reaction flask
2.2OA-1Pb-2.6SeTOP-0.12DPP
[Pb] 129 mmol-Kg
Intensity (a. u.)
(111)
(200)
(220)
(311)
(222)
(400)
(331)
(420)
(422)
15
25
35
45
55
65
75
Two theta (degree)


5 nm

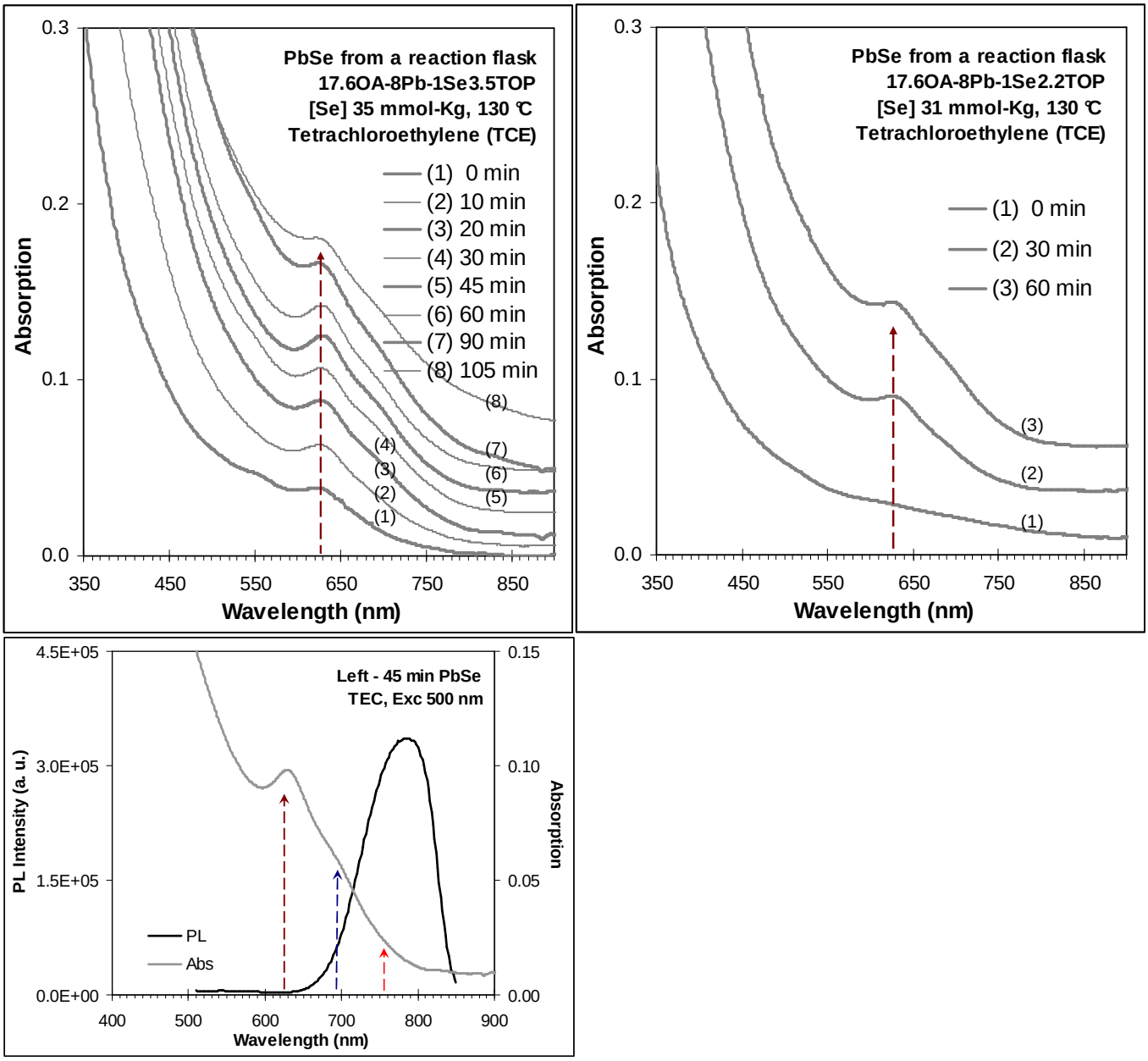


Figure S9. The temporal evolution of absorption (top, offset) from two reaction flasks (left and right) for the synthesis of PbSe F625. Highly-synthetic reproducibility was demonstrated. For the two flasks, the feed molar ratios and [Se] are indicated. The TOPSe solutions were added at 40 °C; the growth was carried out at 130 °C and the growth periods are indicated. For each spectrum, 100 uL sample was dispersed in 1 mL TCE for the measurement. (Bottom) An example of emission detected of Batch Left Sample (5) with 45 min growth.

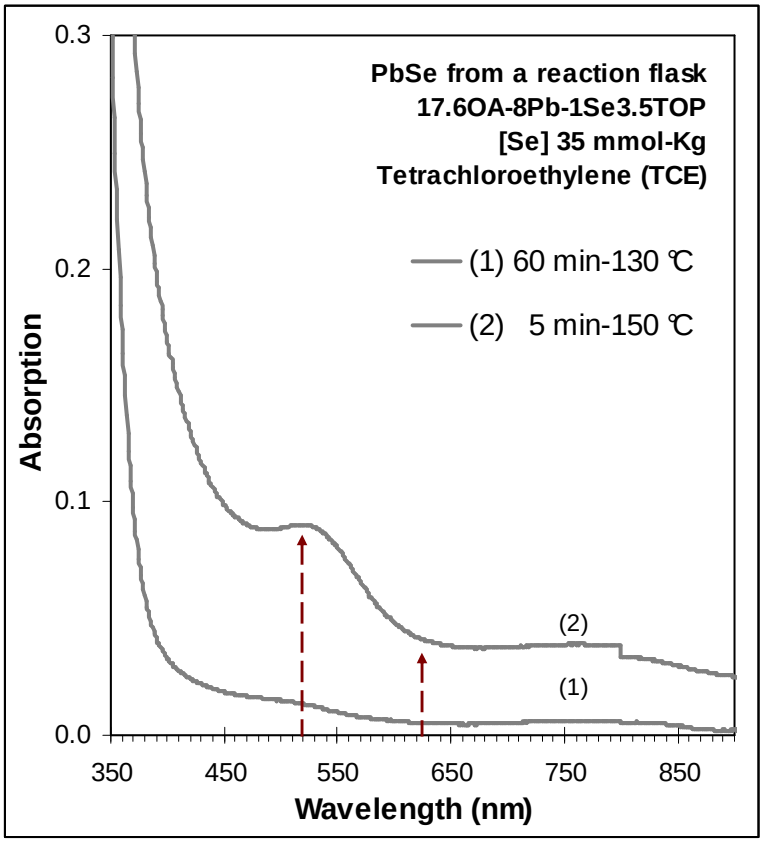


Figure S10. The temporal evolution of absorption (offset) from one reaction flask with the same recipe as that of Batch Figure S9–left but the weight of ~16 g instead of ~8 g. The TOPSe solution was added at 40 °C; the growth periods and temperature are indicated. For each spectrum, 100 uL sample was dispersed in 1 mL TCE for the measurement. The presence of the PbSe ensemble exhibiting absorption peaking at ~520 nm is worthy of notice.