

## Supporting Information

### Effect of Small Molecule Additives in the Prenucleation Stage of Semiconductor CdSe Quantum Dots

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## Experimental Methods

### 1. Chemicals

All chemicals, including cadmium acetate ( $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ , 99.99%, Aldrich), cadmium oxide ( $\text{CdO}$ , 99.99%, Aldrich), tri-*n*-octylphosphine (TOP,  $\text{C}_{24}\text{H}_{51}\text{P}$  90.0%, Aldrich), selenium powder (Se, 99.99%, Alfa Aesar), 1-octadecene (ODE,  $\text{C}_{18}\text{H}_{36}$ , 90.0%, Aldrich), acetic acid (HOAc,  $\text{CH}_3\text{COOH}$ , 99.5%, Chendu Kelong), myristic acid (HMA,  $\text{C}_{13}\text{H}_{27}\text{COOH}$ , 99.0%, Aldrich), zinc acetate ( $\text{Zn}(\text{OAc})_2$ , 99.99%, Aldrich), acetonitrile ( $\text{CH}_3\text{CN}$ , 99.8%, Aldrich), ethanol (EtOH, 95%, Chendu Kelong), n-hexane ( $\text{C}_6\text{H}_{14}$ , 95.0%, Rgent), chloroform ( $\text{CHCl}_3$ , 99.0%, Chendu Kelong), toluene (Tol, 99.5%, Chendu Kelong), toluene-d8 (Tol-d8, 99.5%, Aldrich), are commercially available and were used as received.

### 2. Stock solution preparation and the synthesis of CdSe

For our  $\text{Cd}(\text{MA})_2$  stock solution,  $\text{CdO}$  (0.5136 g, 4.00 mmol), HMA (2.0097 g, 8.80 mmol), and ODE (17.4767 g) were added to a 50 mL three-necked flask. The mixture was degassed three times and was evacuated stirring at room temperature for 30 min until no bubbles were observed. The reaction temperature was then increased to 240 °C under a  $\text{N}_2$  atmosphere (99.0%) to form a clear solution. The mixture was then cooled to 110 °C and evacuated for another two hours before it was cooled to room temperature under  $\text{N}_2$  for storage.

For our SeTOP stock solution, Se powder (0.0118 g, 0.15 mmol) and TOP (0.1223 g, 0.33 mmol) were put in a 25 mL three-necked reaction flask at room temperature. The stirred mixture was then kept at 40 °C for 30 min to achieve a clear solution under vacuum. The mixture was cooled to room temperature under  $\text{N}_2$  and kept as a stock solution.

For a typical synthesis of CdSe with  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  as a Cd source,  $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  (0.0771 g, 0.60 mmol), Se (0.0118 g, 0.15 mmol), HMA (0.3015 g, 1.32 mmol), and ODE (4.6096 g) were added to a 50 mL three-necked round-bottom flask (equipped with a condenser). The total weight of the reaction mixture was 5.00 g. The mixture was degassed and evacuated and stirred at room temperature for 30 min. The reaction mixture was then heated to 120 °C steadily ( $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$  dissolved completely at 80 °C) under vacuum/ $\text{N}_2$ , and remained at this temperature for ~2 hours under vacuum/ $\text{N}_2$  when the solution became yellowish. Details of the application of vacuum and  $\text{N}_2$  can be found in Table S1. The temperature was then increased (with a rate of ~2 °C/min), and the CdSe samples were extracted along the temperature

increase to 240 °C.

For a typical synthesis of CdSe with Cd(MA)<sub>2</sub> as a Cd precursor, Cd(MA)<sub>2</sub> stock solution (3.0000 g, with 0.60 mmol of Cd), Se (0.0118 g, 0.15 mmol) and ODE (0.9882 g) were added to a 50 mL three-necked reaction flask with a condenser. The weight of the reaction mixture was ~4.00 g. It is known that the boiling point of HOAc is about 118 °C, and the use of a condenser helps HOAc evaporated back to the flask. At the same time, it is reasonable that HOAc interacts quickly with Cd after addition. The stirred mixture was degassed and evacuated at room temperature for 30 min till no bubbles were observed. Under vacuum, the temperature was increased steadily to 120 °C and the mixture remained at this temperature for ~2 hours. Under a nitrogen atmosphere at 120 °C, various amounts of CH<sub>3</sub>COOH (0.25 to 10.00 mmol, which is mixed with 1.00 g ODE) or Zn(OAc)<sub>2</sub> (0.13 to 2.50 mmol, followed by 1.00 g ODE) were added to the mixture. The total weight of the reaction mixture was 5.00 g; based on the ODE density of 0.79 kg/L, the Se concentration of 30 mmol/kg is about 23.7 mmol/L. After 15 min at 120 °C, CdSe samples were extracted along the temperature increase to 240 °C (with a rate of ~ 2 °C/min).

Furthermore, we performed one experiment as shown in Figure S3-3 as a background experiment of the addition of HOAc (and ODE). In this batch, 1.00 g ODE was added without the presence of any HOAc.

### 3. Optical, TEM, and XRD Characterization

The UV-vis absorption spectra were collected on a Cary 5000 spectrometer with a 1 nm interval (between 300 and 700 nm). Photoluminescence spectra were collected with a 1 nm interval on a Horiba Fluoromax-4 spectrometer. The slit width for absorption was 2.5 nm and for emission was 2.5 (Figure S5-2 only) or 5.0 nm. To make a dispersion for the measurement, usually, 15 or 30 μL of one as-synthesized sample was dispersed in 3.0 mL of toluene.

Transmission electron microscope (TEM) images were taken on FEI Tecnai G2 F20 S-TWIN in Sichuan University. A drop of one NC dispersion was placed on a TEM grid; to accelerate solvent evaporation, the TEM grid was then put in a fume-hood for about 30 min.

Powder X-ray diffraction (XRD) measurements were performed with a generator functioning at 40 kV and 40 mA as well as Cu Kα (λ = 1.5418 Å) radiation in a θ-θ mode on a Shimadzu X-ray diffractometer 6100.

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**Table S1. Summary of vacuum and N<sub>2</sub> application for Figure 1 batches.**

	RT for 30 min	RT – 120 °C for 60 min	120 °C for 120 min
Batch a	Vacuum	N <sub>2</sub>	N <sub>2</sub>
Batch b	Vacuum	Vacuum	N <sub>2</sub>
Batch c	Vacuum	Vacuum	Vacuum

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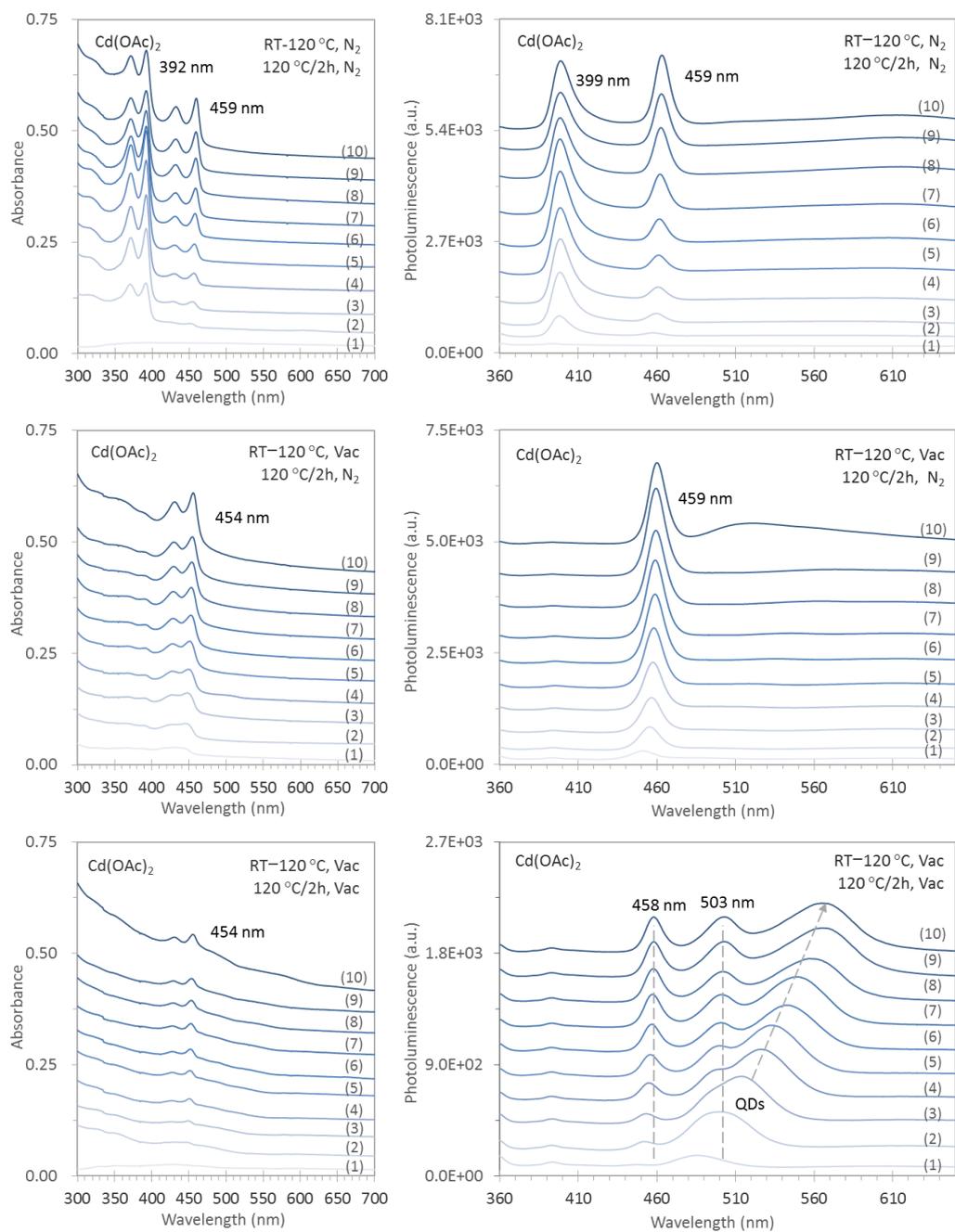


Figure S1-1. Evolution of the optical absorption (left) and emission (right, excited at 350 nm) of CdSe samples (30  $\mu\text{L}$  in 3.0 mL of toluene) extracted from Figure 1 batches a (top), b (middle) and c (bottom). Sampling was performed at (1) 140 °C/0 min, (2) 160 °C/0 min, (3) 160 °C/15 min, (4) 180 °C/0 min, (5) 180 °C/15 min, (6) 200 °C/0 min, (7) 200 °C/15 min, (8) 220 °C/0 min, (9) 220 °C/15 min and (10) 240 °C/0 min.

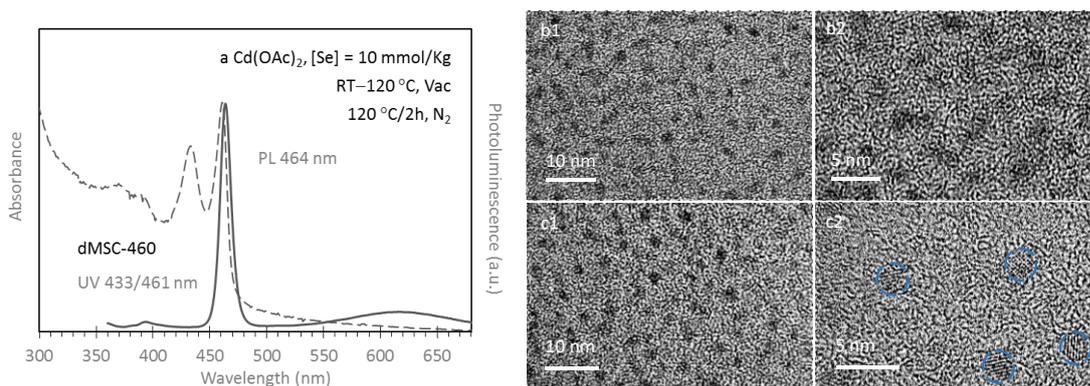


Figure S1-2. (a) Normalized absorption (dashed line, left y axis) and emission (solid line, excited at 350 nm, right y axis) spectra of the CdSe 220 °C/15 min sample obtained. For such measurements, 15  $\mu$ L of the as-synthesized sample is dispersed in 3.0 mL of toluene. The batch for a and b and c is similar to Figure 1 batch b, but with a lower Se concentration of [Se] = 10 mmol/kg instead of 30 mmol/kg. (b and c) Typical TEM images of the CdSe sample, taken from the as-synthesized sample (15  $\mu$ L unpurified) dispersed in 3.0 mL of hexane (b1 and b2) and from the purified sample (15  $\mu$ L of the as-synthesized sample, purified with 3.0 mL of 2Tol/1CH<sub>3</sub>CN) dispersed in 3.0 mL toluene (c1 and c2). dMSC-460 has a 0-dimension form with a size of  $\sim$ 2 nm.

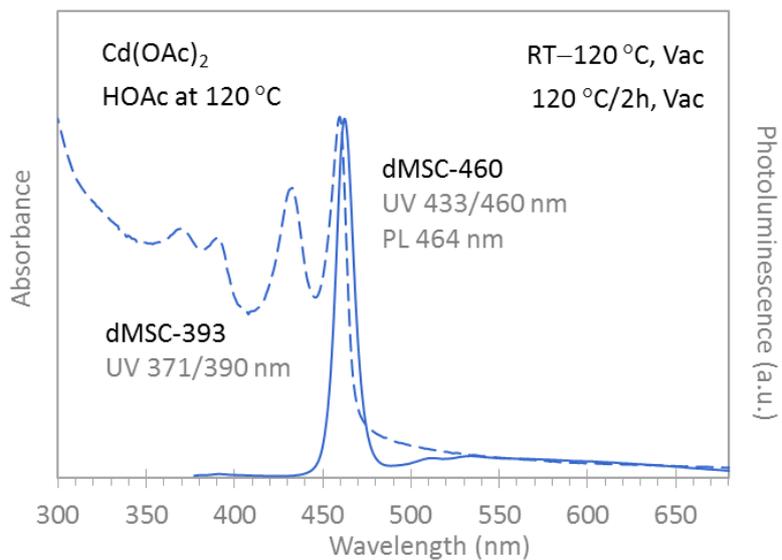


Figure S2. The absorption (dashed line) and emission (solid line, excited at 350 nm) spectra of the Figure 2 sample 9 220 °C/15 min.

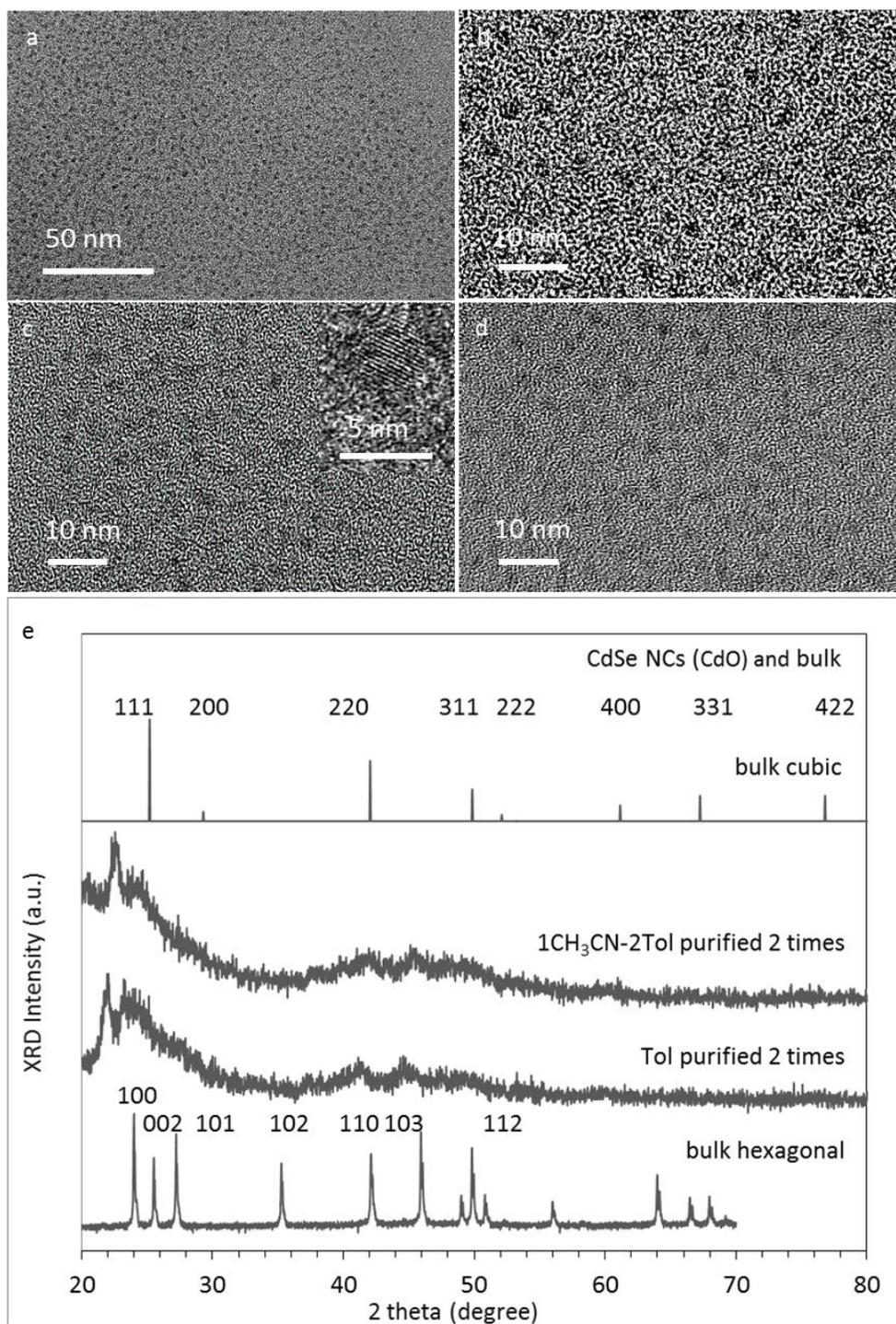


Figure S3-1. (a – d) TEM images and (e) X-ray diffraction (XRD) of the Figure 2a 220 °C/15 min sample. TEM images were taken with 15  $\mu$ L of the as-synthesized unpurified sample dispersed in 3.0 mL of hexane (a, b) and toluene (c, d). XRD data were taken on bulk

hexagonal CdSe, toluene purified and toluene/CH<sub>3</sub>CN purified samples, as indicated. The product appears to be more hexagonal-like rather than cubic-like.<sup>1</sup>

1. Soloviev, V. N.; Eichhofer, A.; Fenske, D.; Banin, U. Size-Dependent Optical Spectroscopy of a Homologous Series of CdSe Cluster Molecules, *J. Am. Chem. Soc.* **2001**, *123*, 2354–2364.

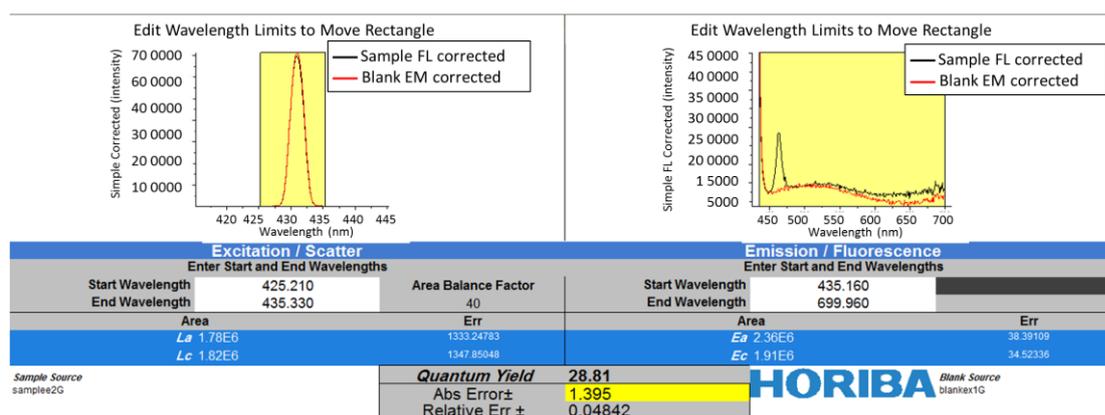


Figure S3-2. Absolute PL quantum yield (QY) characterization of the as-synthesized dMSC-460, which is Figure 3b sample 6 (220 °C/15 min) in toluene. The measurement was done on a Horiba Jobin Yvon–Edison Fluoromax-4 fluorescence spectrometer with a slit width of 3.0 nm. The PLQY of the emission peaking at ~460 nm is 28.81%. The absolute and relative errors of the measurement are +/-1.395% and +/-0.048%, respectively.

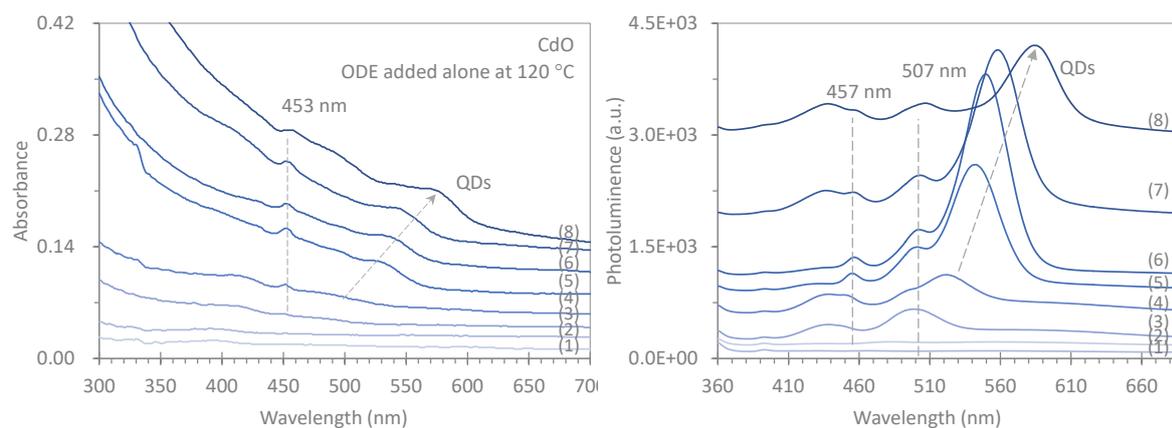


Figure S3-3. Evolution of optical absorption (left) and emission (right, excited at 350 nm) of CdSe samples (15  $\mu$ L dispersed in 3.0 mL of toluene) from the synthetic batch with a feed molar ratio of 8.8HMA (1.32 mmol)–4CdO (0.60 mmol)–1Se (0.15 mmol) and a Se concentration of 30 mmol/kg in ODE. The batch is evacuated during the temperature increase from room temperature to 120  $^{\circ}$ C and the 2-h duration at 120  $^{\circ}$ C. Afterwards, a  $N_2$  atmosphere is applied. 1.00 g ODE (without HOAc) is added and the temperature is kept at 120  $^{\circ}$ C for 15 min. After the first sample is taken at 120  $^{\circ}$ C/15 min, the reaction temperature is increased and samples are extracted. Sampling is performed at (2) 140  $^{\circ}$ C/15 min, (3) 160  $^{\circ}$ C/15 min, (4) 180  $^{\circ}$ C/15 min, (5) 200  $^{\circ}$ C/15 min, (6) 220  $^{\circ}$ C/15 min, (7) 240  $^{\circ}$ C/0 min, and (8) 240  $^{\circ}$ C/15 min.

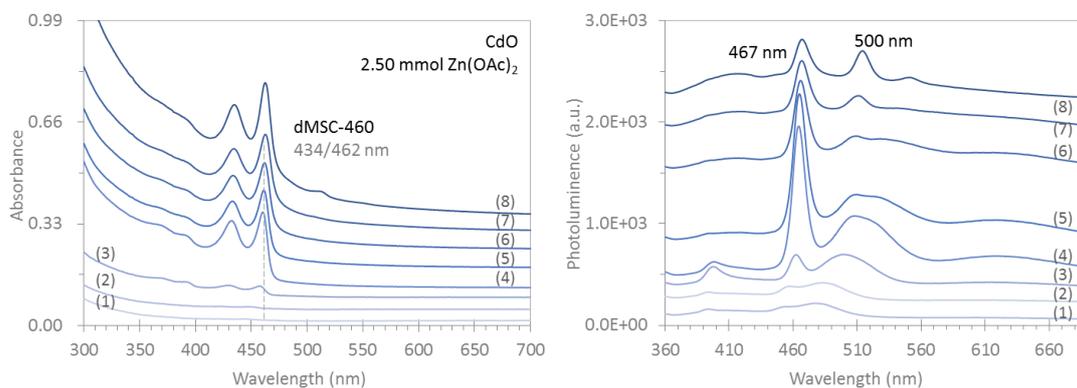


Figure S4. Evolution of optical absorption (left) and emission (right, excited at 350 nm) of CdSe samples (15  $\mu$ L dispersed in 3.0 mL of toluene) from the synthetic batches similar to those of Figure 3, with a feed molar ratio of 8.8MA (1.32 mmol)–4CdO (0.60 mmol)–1Se (0.15 mmol) and a Se concentration of 30 mmol/kg in ODE. The addition of  $\text{Zn}(\text{OAc})_2$  (2.50 mmol) is performed at 120  $^{\circ}\text{C}$ . After 15 min, the first sample is taken at 120  $^{\circ}\text{C}/15$ , and the reaction temperature is increased with sampling at (2) 140  $^{\circ}\text{C}/15$  min, (3) 160  $^{\circ}\text{C}/15$  min, (4) 180  $^{\circ}\text{C}/15$  min, (5) 200  $^{\circ}\text{C}/15$  min, (6) 220  $^{\circ}\text{C}/15$  min, (7) 240  $^{\circ}\text{C}/0$  min, and (8) 240  $^{\circ}\text{C}/15$  min.

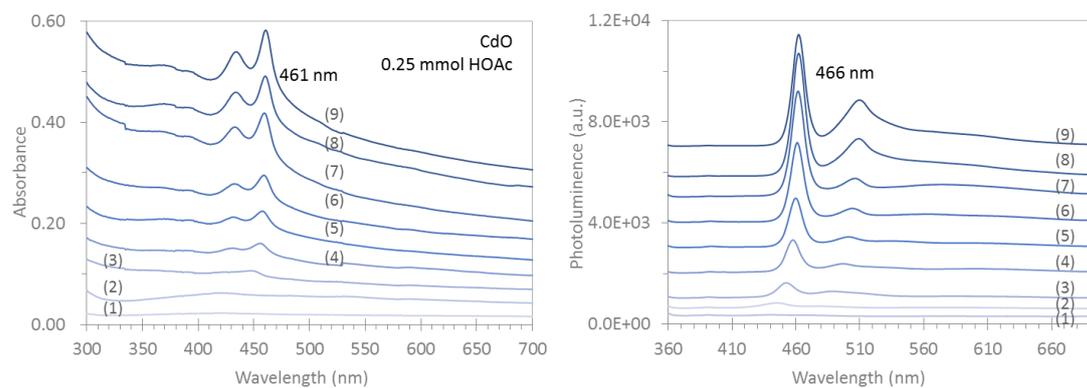


Figure S5-1. Evolution of absorption (left) and emission (right, excited at 350 nm) of the CdSe samples (15  $\mu$ L dispersed in 3.0 mL of toluene) extracted from one reaction, which is similar to Figure 3 batch b, but with the addition of HOAc of 0.25 mmol added at 120  $^{\circ}$ C.

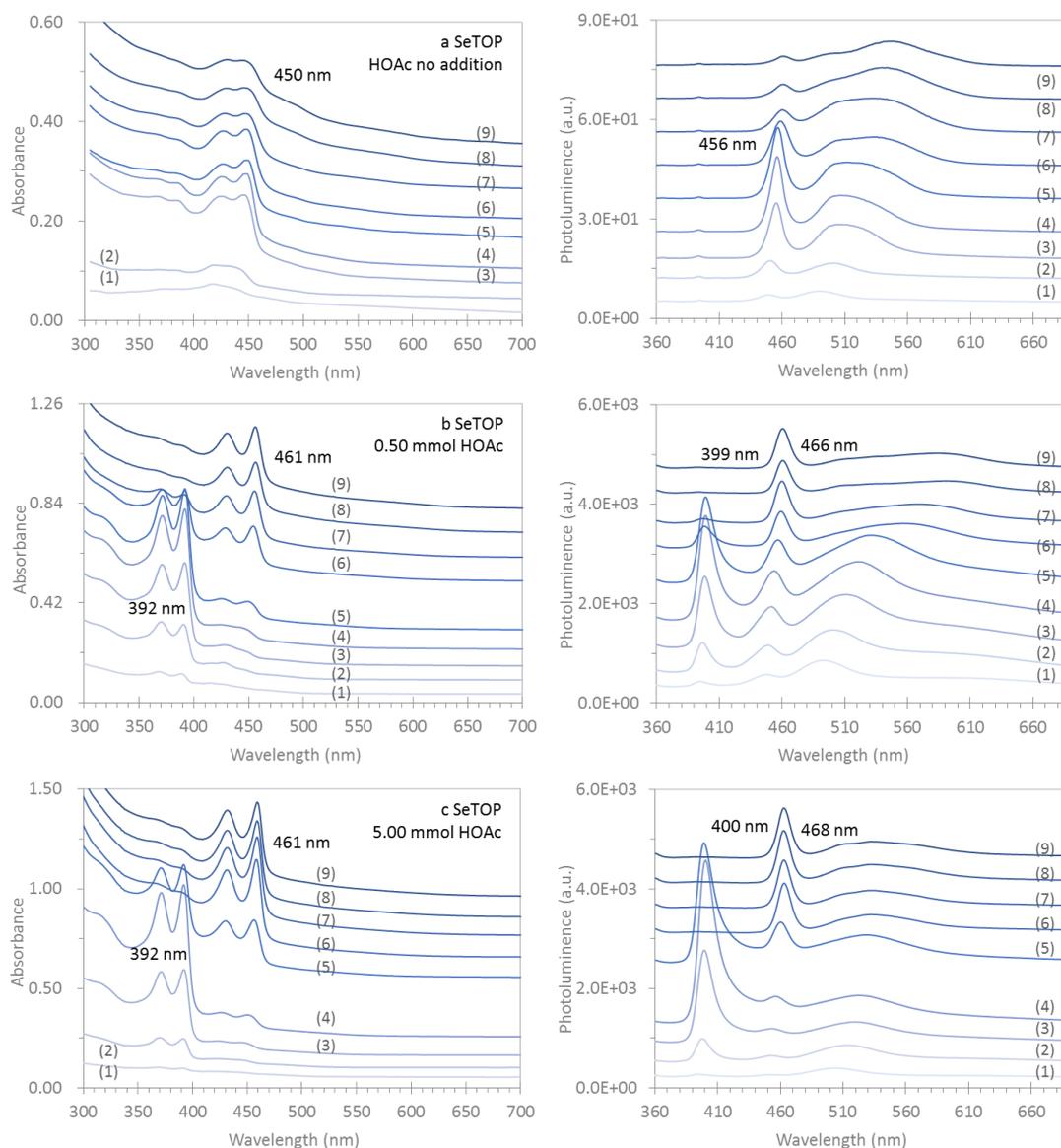


Figure S5-2. Evolution of the absorption (left) and emission (right, excited at 350 nm) of CdSe samples (15  $\mu\text{L}$  dispersed in 3 mL of toluene) taken from three batches similar to those of Figure 3, but with SeTOP as a Se precursor. The feed molar ratios are 8.8MA (1.32 mmol)–4CdO (0.60 mmol)–1TOPSe (0.15 mmol), with the Se concentration of 30 mmol/kg in ODE. No addition is performed for (a), while the addition of HOAc of 0.50 and 5.00 mmol is performed for batches b and c, respectively. Samples were taken at (1) 120  $^{\circ}\text{C}/15$  min, (2) 140  $^{\circ}\text{C}/15$  min, (3) 160  $^{\circ}\text{C}/15$  min, (4) 180  $^{\circ}\text{C}/15$  min, (5) 200  $^{\circ}\text{C}/15$  min, (6) 220  $^{\circ}\text{C}/15$  min, (7) 240  $^{\circ}\text{C}/0$  min, (8) 240  $^{\circ}\text{C}/15$  min, and (9) 240  $^{\circ}\text{C}/30$  min.

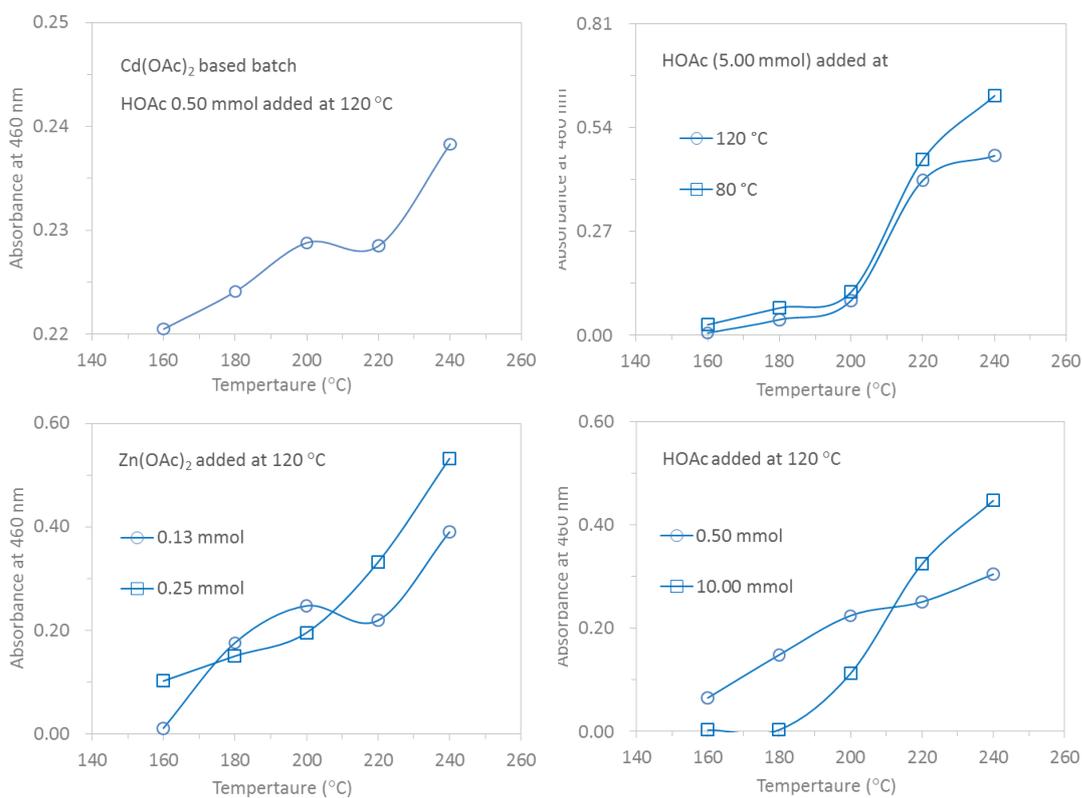


Figure S6. The optical density at 460 nm vs the reaction temperature is plotted to summarize the trend of the formation of dMSC-460 as a function of temperature, for the batches shown in Figures 2 (top-left), 3 (top-right), 4 (bottom-left), and 5 (bottom-right).