

## Supporting Information

### Two-Step Nucleation of CdS Magic-Size Nanocluster MSC–311

Tingting Zhu<sup>†#</sup>, Baowei Zhang<sup>†#</sup>, Jing Zhang<sup>†</sup>, Jiao Lu<sup>‡</sup>, Hongsong Fan<sup>‡</sup>,  
Nelson Rowell<sup>§</sup>, John A. Ripmeester,<sup>§</sup> Shuo Han<sup>\*†</sup>, Kui Yu<sup>\*†‡δ</sup>

<sup>†</sup>Institute of Atomic and Molecular Physics, Sichuan University, Chengdu, 610065, P. R. China

<sup>‡</sup>Engineering Research Center in Biomaterials, Sichuan University, Chengdu, 610065, P. R. China

<sup>§</sup>National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

<sup>δ</sup>School of Chemical Engineering, Sichuan University, Chengdu, 610065, P. R. China

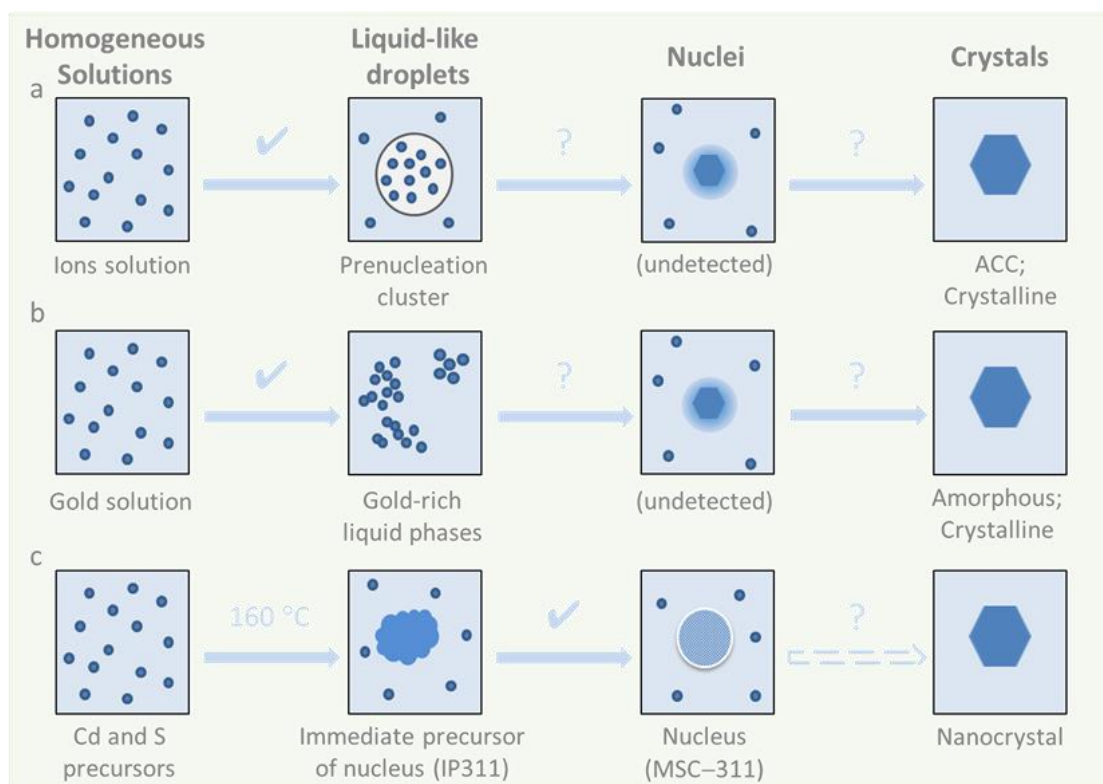
<sup>#</sup>These authors contributed equally to this work.

\*Corresponding author. (S.H.) E-mail: [shuohan@scu.edu.cn](mailto:shuohan@scu.edu.cn).

(K.Y.) E-mail: [kuiyu@scu.edu.cn](mailto:kuiyu@scu.edu.cn).

## Table of contents

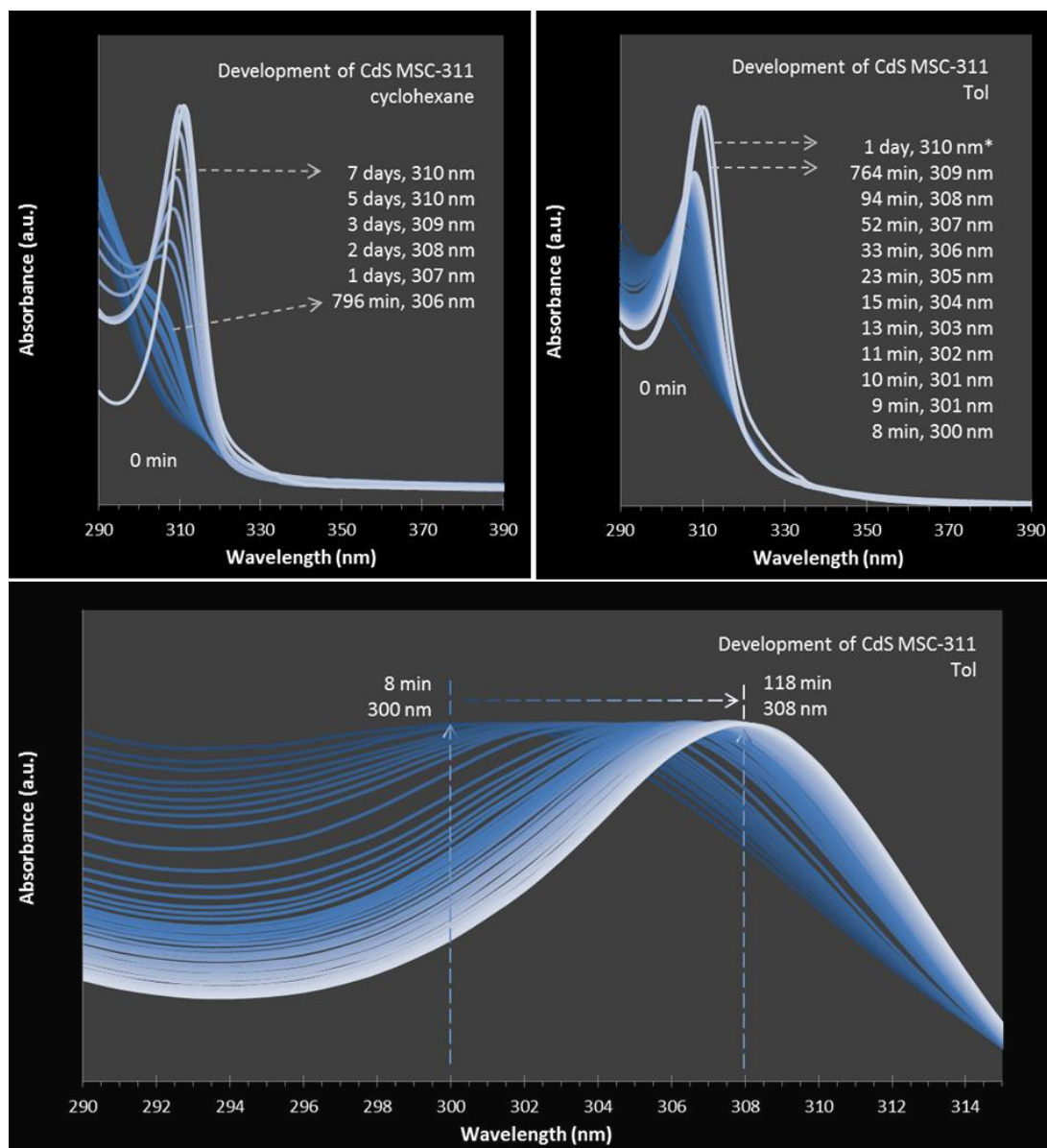
<b>Scheme S1.</b> Schematic drawing to elucidate the two-step nucleation model	S2
<b>Figure S1-1.</b> Absorption spectra collected in situ from our two preheated samples dispersed in two different solvents at room temperature	S4
<b>Figure S1-2.</b> Schematic drawing for our proposed model IP311 → MSC-311 (a) and our assumption upon the addition of Cd-S pairs (b)	S5
<b>Figure S2-1.</b> Dilution experiments of well-developed MSC-311 in toluene and in cyclohexane	S7
<b>Figure S2-2.</b> Absorption spectra collected in situ from the five identical samples of the five different amounts dispersed in 3 mL of toluene	S8
<b>Figure S2-3.</b> Reproducibility of the kinetics study of IP311 → MSC-311 via the in situ UV-vis spectroscopy, with three identical samples of the same amount in 3 mL of cyclohexane	S9
<b>Figure S3-1.</b> Absorption spectra collected with the presence of MeOH (less than 5 $\mu$ L) to accelerate the evolution of CdS MSC-311 in toluene	S10
<b>Figure S3-2.</b> Absorption spectra collected without and with the presence of MeOH (5 $\mu$ L up to 100 $\mu$ L)	S11
<b>Figure S3-3.</b> Comparison of the absorption spectra collected from Figure S3-2	S12
<b>Figure S4-1.</b> IP311 and MSC-311 stability test at different lasing powers used in the MALDI-TOF MS	S13
<b>Figure S4-2.</b> Nucleation process from IP311 to MSC-311 monitored by MALDI-TOF MS	S13
<b>Figure S4-3.</b> X-ray photoelectron spectroscopy (XPS) study of MSC-311	S14
<b>Figure S4-4.</b> X-ray powder diffraction (XRD) pattern of MSC-311	S14
<b>Figure S4-5.</b> TEM images of MSC-311 after once and twice purifications	S15
<b>Figure S5-1.</b> MALDI-TOF MS study of our preheated samples (with corresponding absorption spectra collected) at different reaction temperatures	S16
<b>Figure S5-2.</b> Comparison of the MALDI-TOF mass spectra obtained from the 120 °C and 180 °C samples in the $m/z$ range of 1800 to 3000 Da and of 4000 to 6000 Da	S17
<b>Figure S5-3.</b> Comparison of the absorption spectra collected from the as-synthesized sample dispersions and after their three-day storage	S18



**Scheme S1.** Schematic drawing to elucidate the two-step nucleation model proposed (a and b), which is compared with the present two-step nucleation pathway illustrated (c). (a) In the case of calcium carbonate,<sup>1</sup> the prenucleation cluster which is liquid-like was formed before and after supersaturation. Then, the prenucleation cluster transfers to solid amorphous calcium carbonate (ACC). The crucial nuclei were not detected; subsequent rapid crystallization shielded the detail of the nucleation process. (b) In the case of noble metal gold, gold-rich domains, which are liquid, were visualized by TEM to develop from a homogeneous gold solution in a few seconds. In the next couple of seconds, amorphous solid and crystalline gold grew from the gold-rich domains. Again, nucleation was too rapid to identify. (c) For the present system, liquid-like IP311 started to develop upon the formation of Cd–S bonds at ~160 °C. IP311 exhibits little absorption at 311 nm and could be stored for future experimental studies. Via intramolecular reorganization at lower temperatures, a single IP311 transferred to a single nucleus MSC–311. The resulting MSCs have little size variation, with a similar mass as that of IP311. The phase transformation, namely nucleation, took place in a lengthy period of time, such as days, and could be accelerated by a tiny amount of MeOH. We believe that a similar

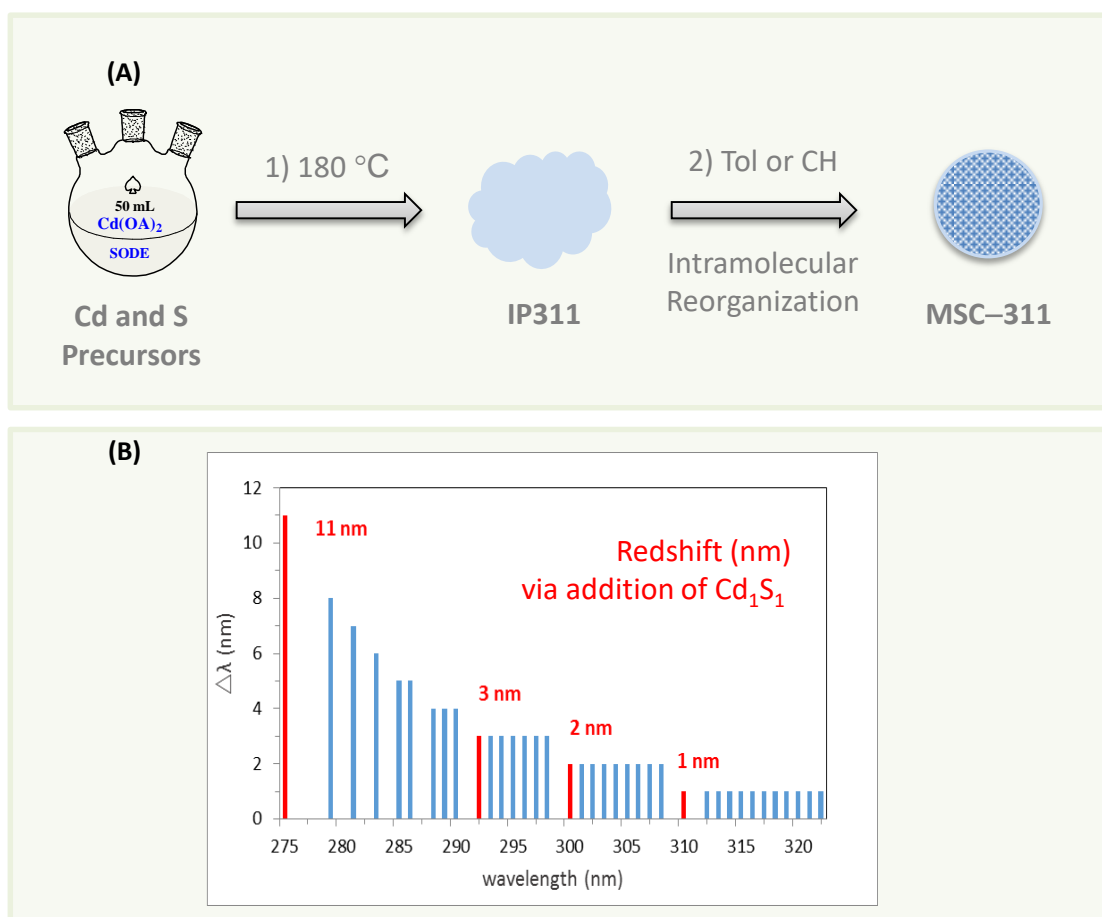
proton-mediate ligand loss mechanism<sup>3</sup> is the cause of the intramolecular reorganization of IP311 to MSC-311, the nucleation process of which exhibits first order kinetics and is not followed by growth. Thus, the nuclei MSC-311 have a long lifetime. The IP311 to MSC-311 nucleation process is separated from the subsequent crystallization growth phase, and is also decoupled from the stage of the formation of IP311.

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**Figure S1-1.** Absorption spectra in situ collected for our two samples dispersed in 3 mL of cyclohexane (25  $\mu$ L as synthesized sample, top - left with the y axis of 1.0) and 3 mL of toluene (4.2 mg after 10 days of storage under liquid  $N_2$  temperature, top - right with the y axis of 2.7) at room temperature. The two samples were from two identical batches; the reaction mixtures were both remained at 190  $^{\circ}$ C for about 5 minutes (min). The time-resolved spectra are presented with the color change from blue (0 min) to white (days). At 0 min, the sample exhibited little absorption at 311 nm. The dispersion period is indicated. It is worthy of noticing

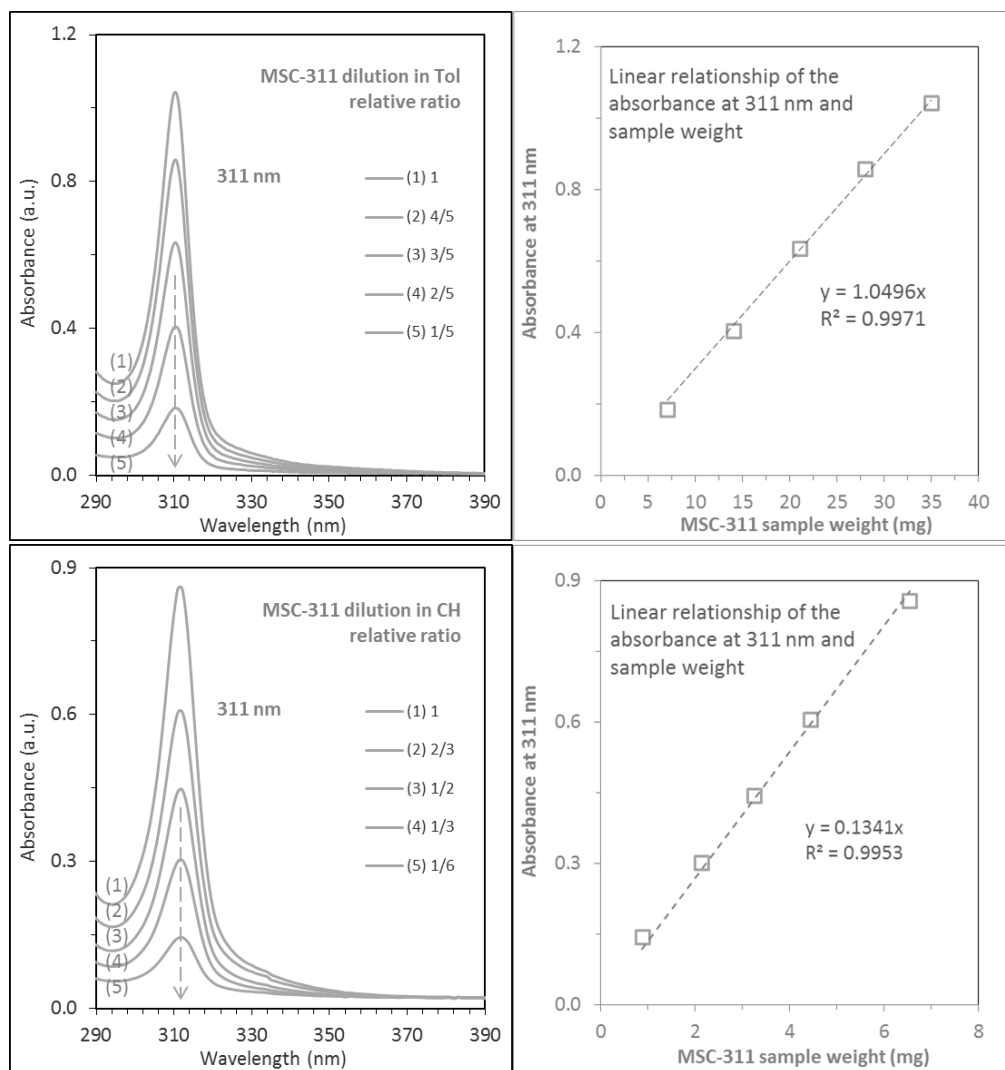
that the development pattern of MSC–311 does not seem to be affected by the sample storage conditions and the disperse solvents (cyclohexane (left) or toluene (right)). Fascinatingly, the left spectra were collected with a 1-min time interval up to 15 min, a 3 min time interval up to 70 min, and a 5 min time interval up to 100 min. Thus, there are 45 spectra collected in the first 100 min; the incremental of the redshift of 0.5 nm was monitored (bottom, limited by the instrument resolution of 0.5 nm). The bottom spectra are those from top-right collected between the disperse period of 8 and 118 min. The increase of the absorbance at 311 nm with the continuous redshift and is worthy of noticing.



**Figure S1-2.** (A) A schematic drawing presenting our model proposed for the development of MSC–311 from its immediate precursor IP311 which exhibits little absorption at wavelengths longer than 310 nm. Such a nucleation process is not in agreement with the classic nucleation

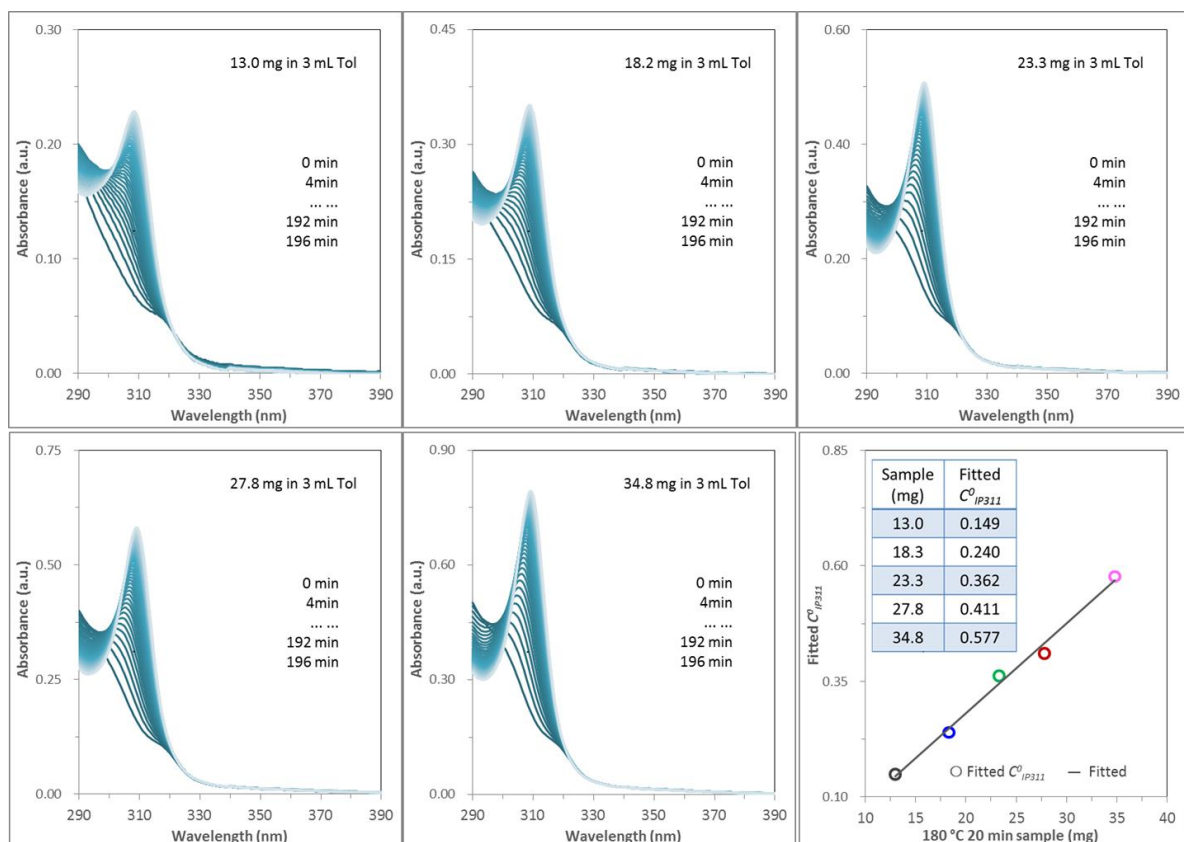
theory (CNT),<sup>1-3</sup> but share some similarities with the two-step nucleation mechanism proposed for a bio-mineralization process.<sup>4,5</sup> (B) Estimation of the redshift of bandgap (nm, y axis) of one CdS QD with the bandgap (nm, x axis), upon the hypothetical addition of one Cd–S pair. For example, according to the calibration curve of absorbance energy (nm) verse radius (nm) for CdS RQDs,<sup>6</sup> the size of one CdS QD exhibiting the bandgap of 276 nm is estimated to be 1.30 nm. With the addition of one Cd–S pair, the size is estimated to be 1.32 nm with the bandgap refshift of 11 nm to 286 nm. And the size of one CdS QD exhibiting the bandgap of 322 nm is ~1.61 nm. With the addition of one Cd–S pair, the size is estimated to be 1.62 nm with the bandgap redshift of 1 nm to 323 nm. Therefore, the addition of one Cd–S pair would lead to the redshift ranging from 1 to 11 nm, which should be diagnostic as a discrete instead of a continuous pattern.

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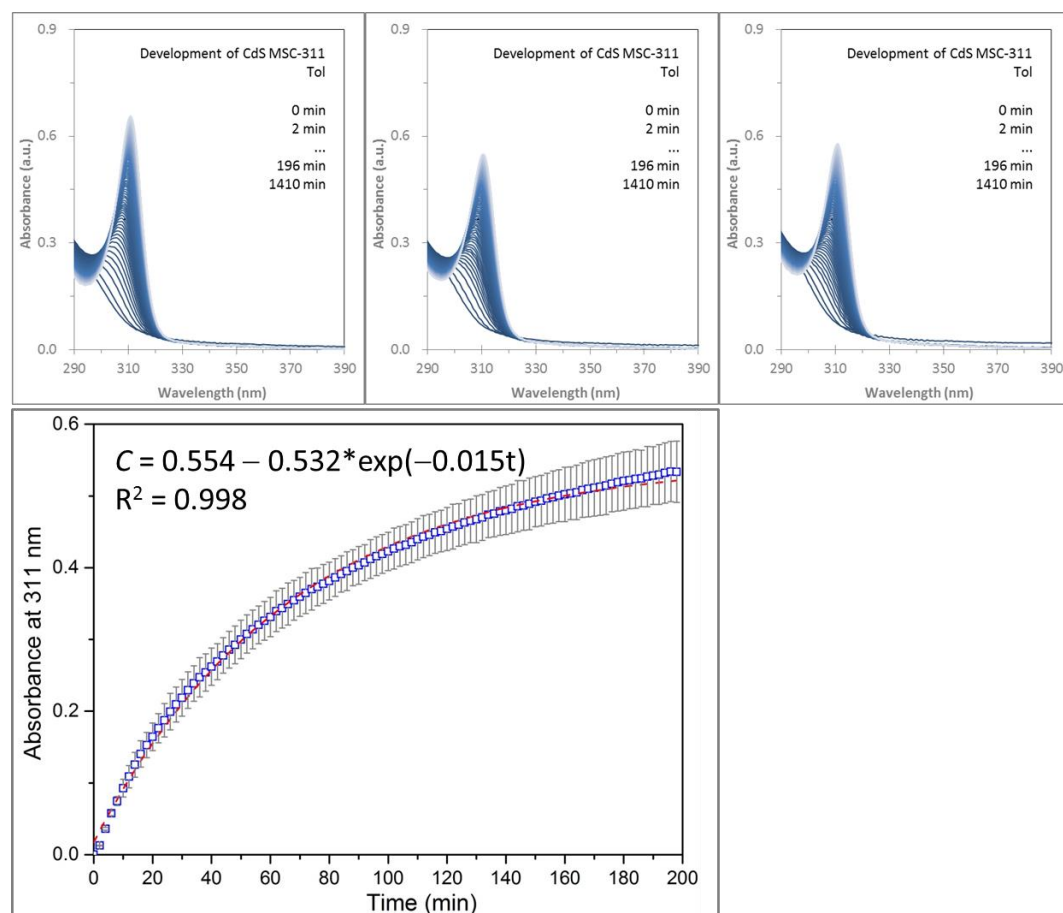


**Figure S2-1.** Concentration-dependent absorption of one MSC–311 dispersion in toluene (top) and in cyclohexane (bottom). The sample was preheated at 180°C for 20 min (top) and for 30 min (bottom). A dilution experiment was performed on Dispersion (1). The degree of dilution is indicated. (Left) The absorption spectra collected from the five toluene or cyclohexane dispersions (3 mL). (Right) The plot of the absorbance at 311 nm as a function of the concentration (in term of sample weight in mg upon dilution). Clearly, a linear relationship is obtained; thus, in the concentration range studied (as indicated by the absorbance at 311 nm), MSC–311 is stable and does not decompose, with a constant extinction coefficient.

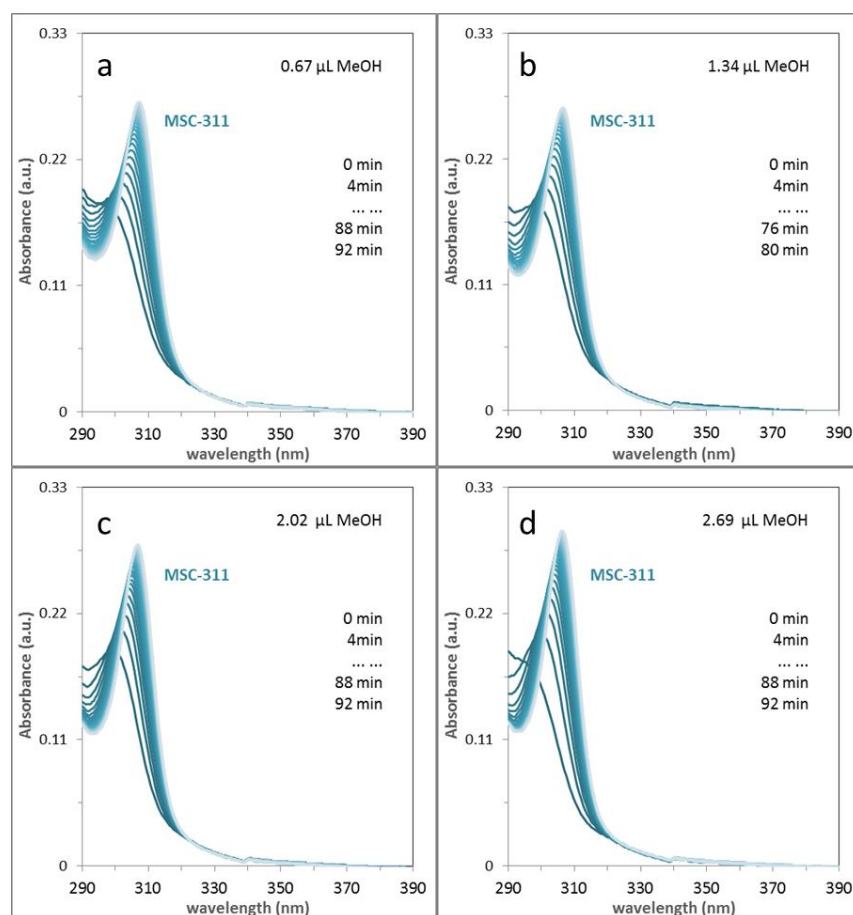




**Figure S2-2.** In situ UV-vis spectroscopy study of the five dispersions made from the same sample but different amounts in 3 mL of toluene. The weight of the sample used is 13.0 mg, 18.3 mg, 23.3 mg, 27.8 mg and 34.8 mg. The time-resolved absorption spectra are presented with the color change from dark cyan (0 min) to light cyan (196 min). After the sample dispersion, the spectra were collected with a 4 min time interval up to 196 min. (Bottom-right) The plot of the fitted  $C_{IP311}^0$  values (y axis), as a function of the sample amounts of 13.0 mg, 18.3 mg, 23.3 mg, 27.8 mg and 34.8 mg (x axis), represented by open circle symbols, suggests an linear correlation. Thus, the IP311  $\rightarrow$  MSC-311 is quite first order. And our hypothesis that one IP311 results in one MSC-311 is reasonable.



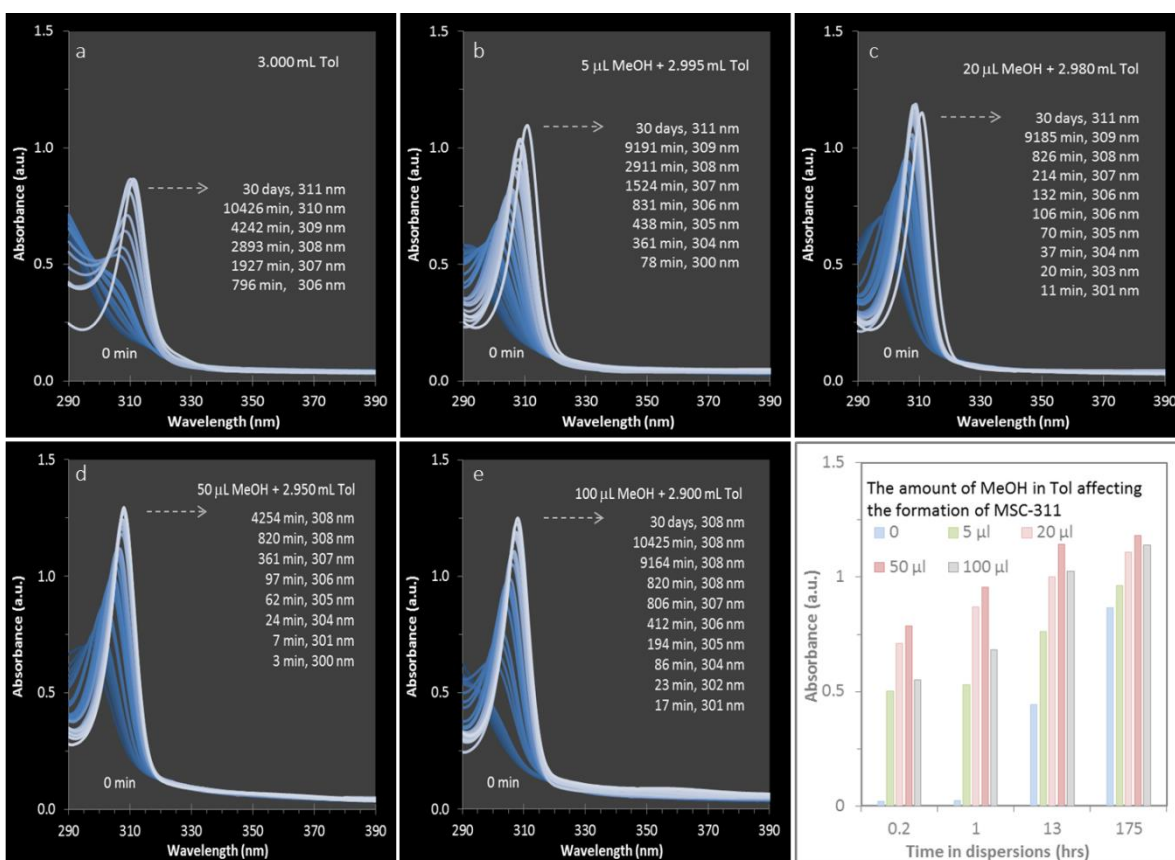
**Figure S2-3.** Reproducibility of the kinetic study. The absorption spectra collected in situ from three identical IP311 samples (20  $\mu\text{L}$  dispersed in 3 mL of cyclohexane), with a 2 min time interval up to 198 min (top panel). The IP311 sample was from a different synthetic batch but with the same experimental condition as that used for Figure 1, with the same storage period at liquid  $\text{N}_2$  temperature as Figure 2. The time-dependent absorbance at 311 nm (y axis, averaged from the three IP311 samples, empty symbols), together with the error bars (vertical lines) and the fitted first order reaction equation (red dashed line) are presented (bottom). The error is about 9%. The nucleation rate constant is about  $0.015 \text{ min}^{-1}$ . The first order reaction equation fitted supports our hypothetical model of  $\text{IP311} \rightarrow \text{MSC-311}$  proposed.



**Figure S3-1.** In situ UV-vis spectroscopy study of the four dispersions (3 mL). The time-resolved absorption spectra are presented with the color change from dark cyan (0 min) to light cyan (~90 min), with the 4 min interval up to ~90 min. 20  $\mu\text{L}$  sample (preheated at 180  $^{\circ}\text{C}$  for 20 min and stored at the liquid  $\text{N}_2$  temperature for a couple of days) was dispersed in the 3 mL of solvent mixture of toluene and MeOH prepared. The amount of MeOH is indicated. The solvent mixture was prepared as follow. 15  $\mu\text{L}$  of MeOH and 4.45 mL of toluene were mixed first; then, 0.8 mL, 0.6 mL, 0.4 mL, and 0.2 mL mixture was added into toluene to reach the total volume of 3 mL. The presence of MeOH accelerates the evolution of CdS MSC-311. It is worthy of noticing that the surface ligand exchange partially with MeOH was proposed before.<sup>1</sup> Accordingly, we propose eq S1 for the effect of MeOH in the present study.

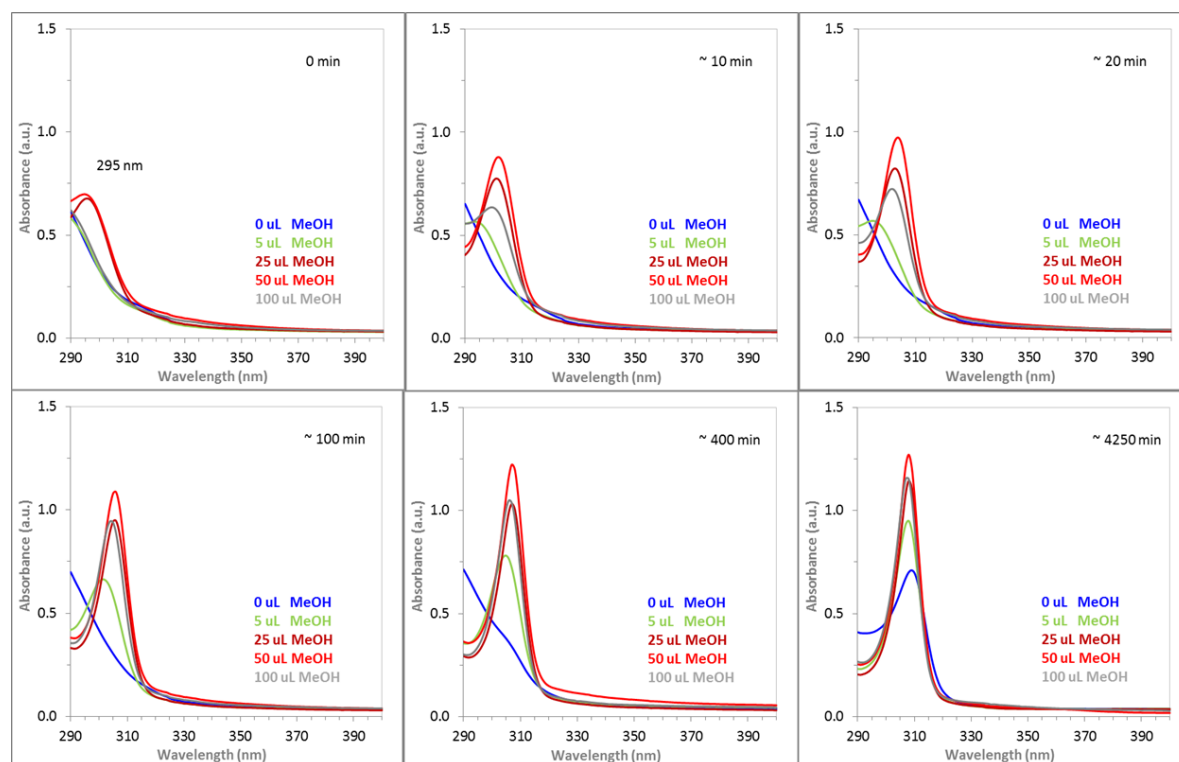


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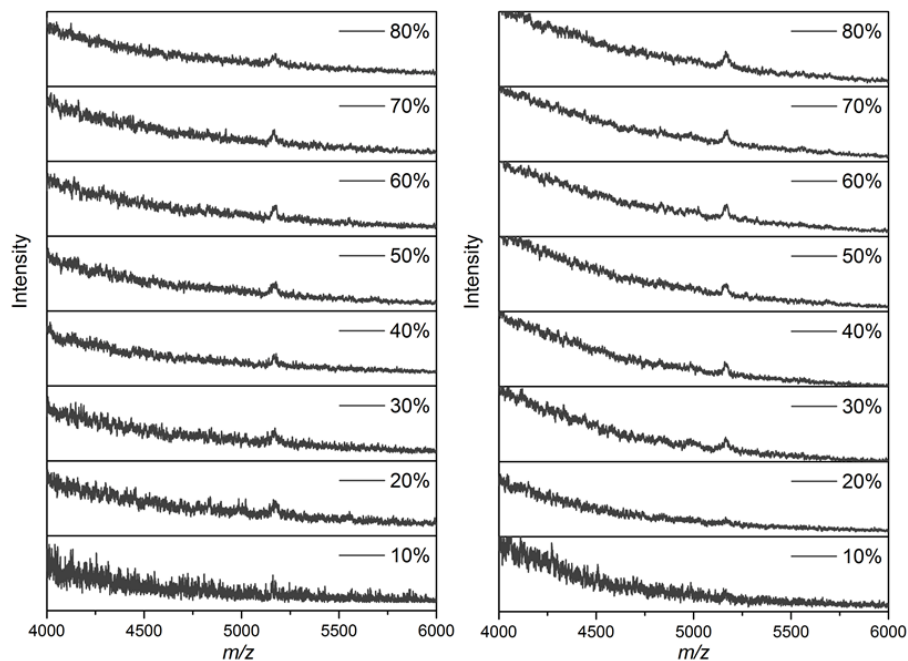


**Figure S3-2.** The time-resolved absorption spectra are presented with the color change from blue (0 min) to white (days) for (a) to (e). With 25  $\mu$ L sample (prepared under the same experimental condition used for **Figure 1**, except at 190  $^{\circ}$ C for 5 min) in the total solvent volume of 3 mL, the amount of methanol added to toluene is indicated. 3 mL of dispersion solvent mixture was prepared as follows; for example, 3 mL of toluene was sampled first followed by 5  $\mu$ L was taken away; then, 5  $\mu$ L MeOH was added. The bar graph (bottom right) summarizes the absorbance developed at 0.2, 1, 13 and 175 hrs for the five dispersions with the amount of MeOH of 0  $\mu$ L (a, blue), 5  $\mu$ L (b, green), 20  $\mu$ L (c, pink), 50  $\mu$ L (d, red), and 100  $\mu$ L (e, gray). The presence of MeOH accelerates the evolution of CdS MSC–311 in toluene. The formation rate of MSC–311 increased with the amount of methanol up to 50  $\mu$ L. With 100  $\mu$ L methanol, the growth rate slowed down but was still faster than that without MeOH; the relatively large amount of methanol (100  $\mu$ L) might have a dual effect on the

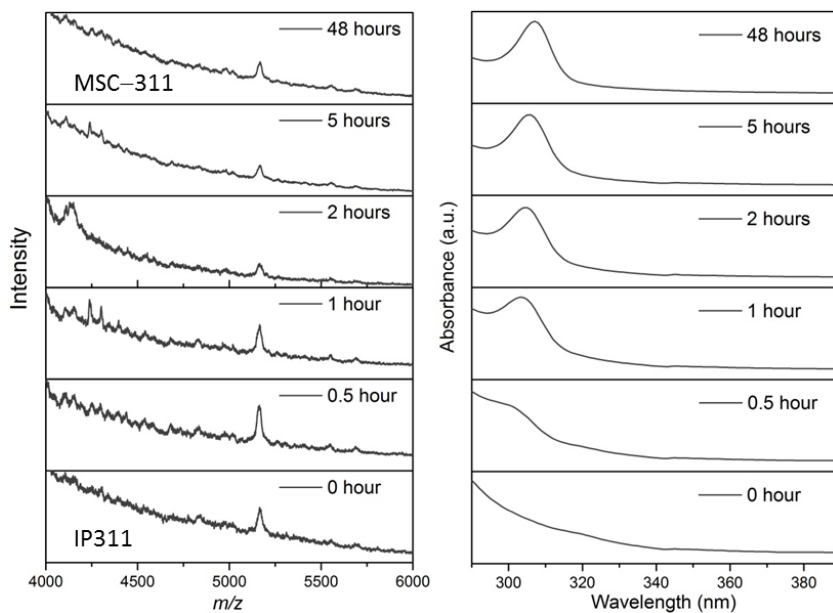
development of CdS MSC–311. The redshift of the absorption peak stopped at 308 nm (b-e, with MeOH) rather than at 311 nm (a, without MeOH). The direct comparison of absorption spectra collected from the five dispersions with or without MeOH is shown by **Figure S3-3** for the six periods of 0 min, 10 min, and up to 4250 min.



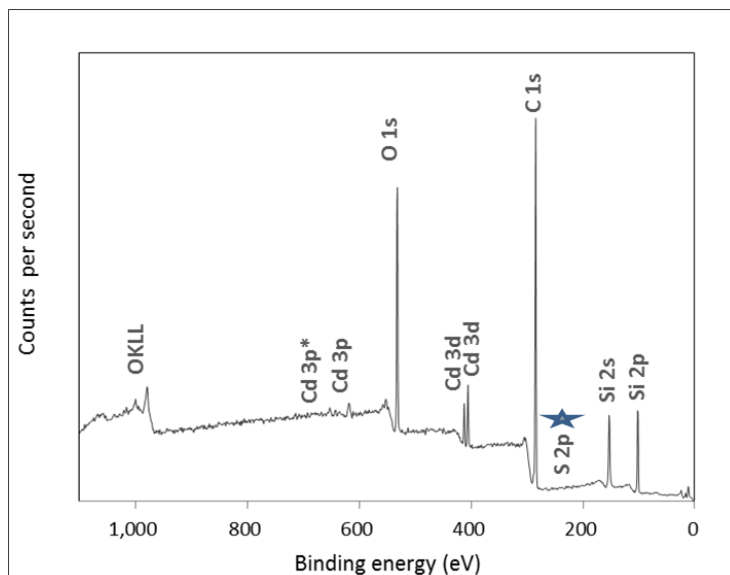
**Figure S3-3.** Comparison of the absorption spectra of IP311 → CdS MSC–311 with different amounts of MeOH added. The dispersion period is indicated as 0 min, 10 min, 20 min, 100 min, 400 min, and 4250 min. A careful examination suggests that the absorption peak position is detected to be ~295 nm (with the presence of MeOH, 5  $\mu$ L at ~10 min and 25  $\mu$ L at ~0 min) and ~306 nm (without MeOH at ~400 min). At ~10 min, the absorbance at 290 nm for the dispersions with MeOH is smaller than that of the dispersion without MeOH. Evidently, the MeOH additive effectively accelerates the early stage of the development of MSC–311 from IP311.



**Figure S4-1.** IP311 (left) and MSC-311 (right) stability test at different lasing powers (LP) setting in the MALDI-TOF instrument.

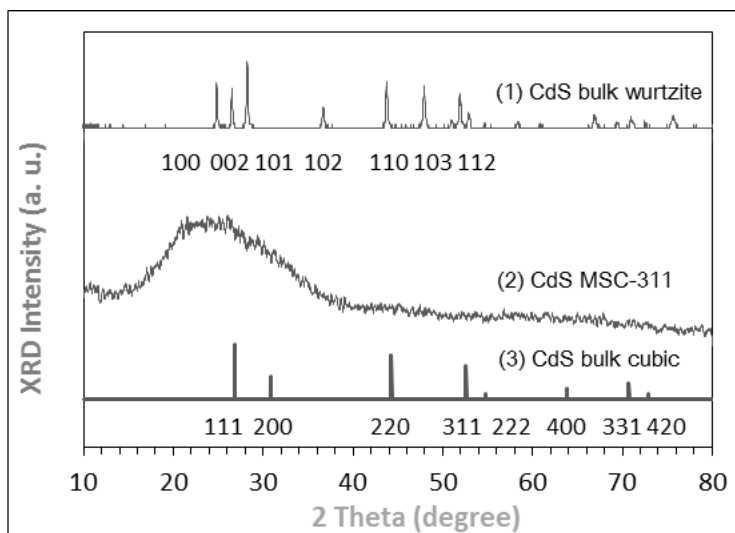


**Figure S4-2.** The evolution of MSC-311 from IP311 up to 48 hours was investigated by both by MALDI-TOF MS (left) and absorption spectroscopy (right).

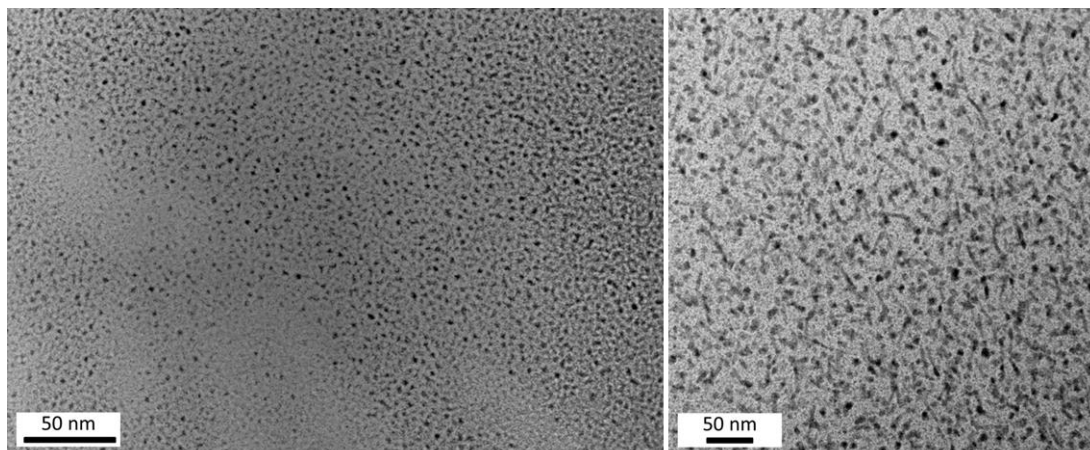


**Figure S4-3.** X-ray photoelectron spectroscopy (XPS) study (survey 1253.6 eV) of CdS MSC-311. The Cd 3d and 3p species are indicated, the Cd 3p species (left) is provided by the instrument software. The S 2p species with an asterisk might be extremely weak, which is labeled according to the literature reported before.<sup>1</sup>

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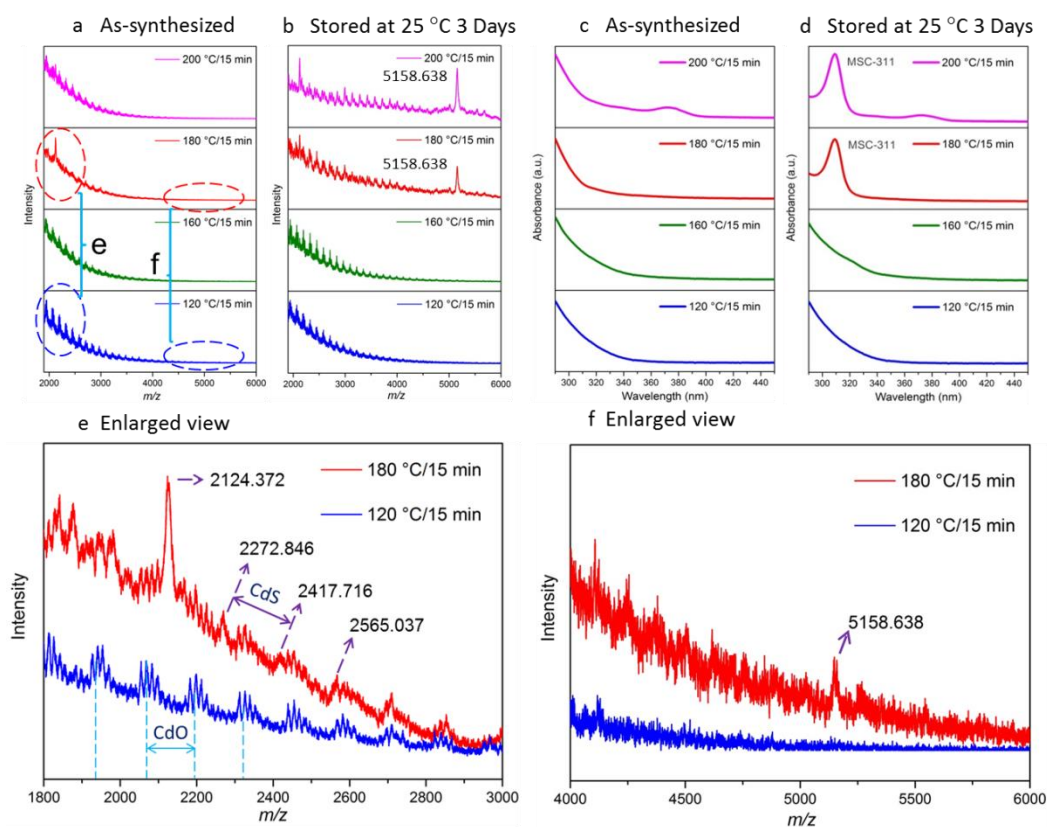


**Figure S4-4.** X-ray powder diffraction (XRD) pattern of CdS MSC-311. MSC-311 might have a mixed crystal structure of cubic and wurtzite patterns.



**Figure S4-5.** TEM images of purified MSC-311, after once purification (left) and twice purifications (right). We noticed that TEM visualization results are sensitive to purification, which leads to aggregation to exhibit a rod-like structure (such as shown in the right TEM image). The quantitative effect of purification on the aggregation is not addressed in the present study.





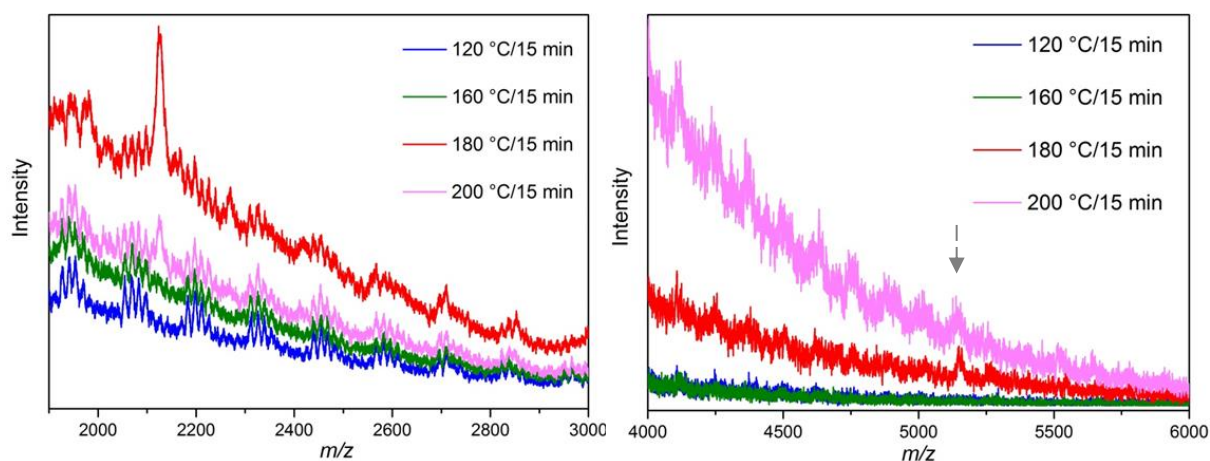
**Figure S5-1.** The MALDI-TOF mass spectrometry study of the four as-synthesized samples from one synthetic batch sampled at 120 °C/15 min (blue), 160 °C/15 min (green), 180 °C/15 min (red) and 200 °C/15 min (magenta) (a), together with the sample dispersions in toluene after three day of storage at room temperature (b). The experimental condition is similar to that used for Figure 5. The corresponding absorption spectra of the four as-synthesized samples in toluene measured (c) and after 3 days of storage (d). Two enlarged views of the mass spectra in the  $m/z$  range from 1800 Da to 3000 Da (e) and from 4000 Da to 6000 Da (f) for the two as synthesized 120 °C (blue) and 180 °C (red) samples in toluene. Here, we mixed DCTB<sup>1,2</sup> and toluene with our as-synthesized IP311 dispersion sample before and after storage. The IP311–DCTB–toluene mixture or MSC–311–DCTB–toluene mixture was then spotted and dried on a MALDI plate at an ambient atmosphere.

Undoubtedly, Figure S5-1e demonstrates that the 120 °C sample exhibits a periodic pattern with the mass of  $\sim 128$  Da (which is that the fragment of  $\text{Cd}_1\text{O}_1$  related to the Cd precursor used). The 180 °C sample also displays a periodic pattern, as indicated by at least four distinguishable

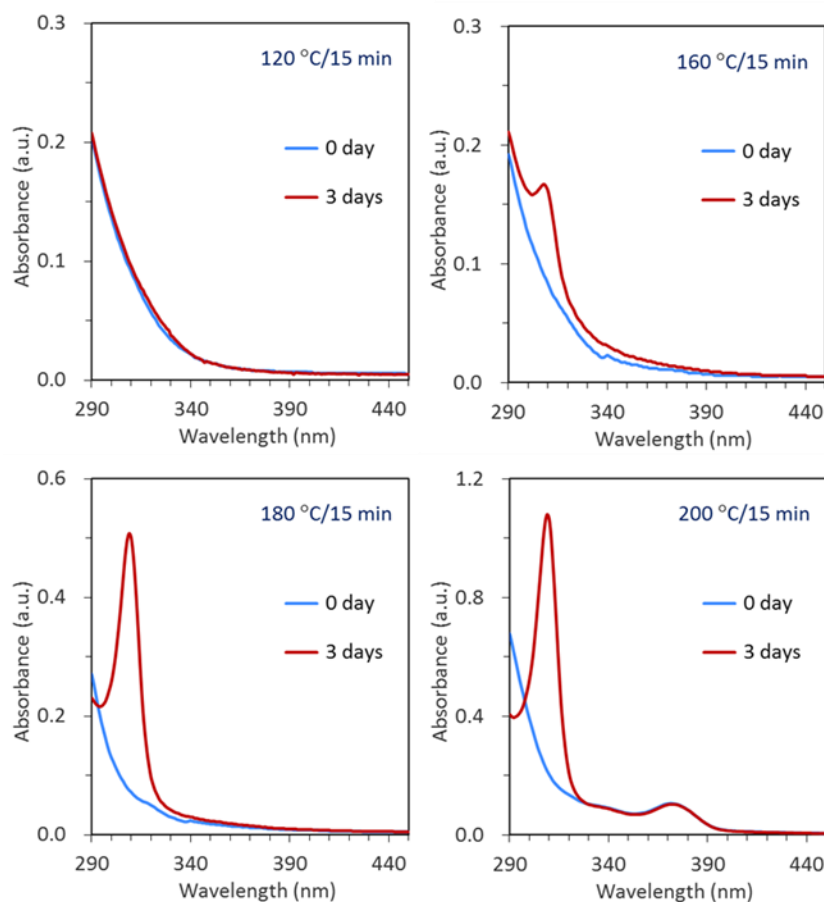
peaks with the mass of  $\sim 145$  Da (which is that of the fragment of  $\text{Cd}_1\text{S}_1$ ). Obviously, there are Cd–S bonds at  $180^\circ\text{C}$ . Figure S5-1f evidently illustrates that the  $180^\circ\text{C}$  sample reveals a peak at  $\sim 5158$  Da, while the  $120^\circ\text{C}$  sample does not. The detection of this peak becomes much more readily after the storage (b, as for both the  $180^\circ\text{C}$  and  $200^\circ\text{C}$  samples); this peak in f and in b should be associated to the presence of IP311 and MSC–311, respectively.

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**Figure S5-2.** Two enlarged views of the mass spectra in the  $m/z$  range from 1800 Da to 3000 Da (left) and from 4000 Da to 6000 Da (right) for the four as synthesized  $120^\circ\text{C}$  (blue),  $160^\circ\text{C}$  (green),  $180^\circ\text{C}$  (red) and  $200^\circ\text{C}$  (magenta) samples in toluene of Figure S5-1. The molecular ion peak around 5158 Da (as indicated by the dashed arrow) is weak for both the  $180^\circ\text{C}$  and  $200^\circ\text{C}$  samples.



**Figure S5-3.** Comparison of the absorption of the four as-synthesized samples (from 120 °C to 200 °C, blue) and after 3 day storage at 25 °C (red) of Figure S5-1. The nucleation of MSC–311 (red) from IP311 (blue) takes place for the induction period samples and for the sample with nucleation and growth of RQDs. Our two-step approach to CdS MSC–311 exhibits highly synthetic reproducibility. The development of the absorption peak at 311 nm here is consistent with that presented in Figure 5.