

Supporting Information

Colloidal CdSe 0-Dimension Nanocrystals and Their Self-Assembled 2-Dimension Structures

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Methods

Chemicals. All chemicals, including tri-*n*-octylphosphine (TOP, 90.0%, Aldrich), selenium powder (Se, 99.99%, Alfa Aesar), 1-octadecene (ODE, 90.0%, Aldrich), cadmium oxide (CdO, Aldrich), acetic acid (HAc, 99.5%, Chendu Kelong), myristic acid (MA, 99.0%, Aldrich), octylamine (OTA, 99.0%, Aldrich), oleylamine (OLA, 70.0%, Aldrich), hexadecylamine (HDA, 90.0%, Aldrich), cadmium chloride ($\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$, 99.0%, Chendu Kelong), manganese(II) chloride (MnCl_2 , 99.995%, Bai Ling Wei), acetonitrile (CH_3CN , 99.8%, Aldrich), poly(4-methyl-1-pentene, TPX, Aladdin), p-xylene (1,4-dimethylbenzene, 99.0%, DAMAO), ethanol (EtOH, 95%, Chendu Kelong), n-hexane (C_6H_{14} , 95.0%, Rgent), chloroform (CHCl_3 , 99.0%, Chendu Kelong), toluene (Tol, 99.5%, Chendu Kelong), are commercially available and were used as received.

Synthesis and Purification. To prepare $\text{Cd}(\text{MA})_2$ stock solution, cadmium oxide (0.5136 g, 4.00 mmol), myristic acid (MA, $\text{C}_{13}\text{H}_{27}\text{COOH}$, 2.0097 g, 8.80 mmol), and 1-octadecene (ODE, 17.4767 g) were added to a 50 mL three-necked round-bottom flask, which was equipped with a condenser. The mixture was degassed three times and was vacuumed under stirring at room temperature for 30 min until no bubbles were observed. Then, under N_2 , the reaction temperature was increased to 240 °C. CdO dissolved completely and a clear solution was obtained. The mixture was then cooled down to 110 °C and switched to vacuum for two hours. Under N_2 , the mixture was cooled to room temperature.

To synthesize carboxylate ligand passivated CdSe NCs which exhibit an absorption doublet at 432/460 nm, $\text{Cd}(\text{MA})_2$ stock solution (3.000 g, Cd = 0.60 mmol), Se (0.0118 g, 0.15 mmol) and ODE (0.9882 g) with a total weight of 4.000 g were added to a 50 mL three-necked round-bottom flask, which was equipped with a condenser. The mixture was degassed for three times and vacuumed under stirring at room temperature (RT) for 30 min till no bubbles were observed. Under N_2 , the reaction mixture temperature was increased to 120 °C and the reaction mixture was kept under vacuum for 2 hours. Under N_2 , a mixture of 0.300 g (5.00 mmol) acetic acid and 0.700 g ODE was dropwise added. And the temperature was increased to 220 °C with a rate of 2 °C/min; after 15 min, the reaction was stopped.

For the purification of carboxylate ligand passivated CdSe NCs, typically, 10 μL of CdSe as-synthesized materials was dispersed in 2.0 mL of toluene, then 1.0 mL of EtOH or CH_3CN was added dropwise. Centrifugation was then performed (9000 rpm, 2 min on Shuke Centrifuge

TG-16S). The supernatant was removed, and the precipitate was subjected to the same process twice. The third-time precipitate was dispersed in toluene for either 1 minute or longer periods.

Optical and 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. For the amine and carboxylate ligand passivated CdSe NCs measured, the full width half maximum (fwhm) of their static absorption and emission spectra has been estimated to be as small as ~10 nm.

For a dispersion sonication, it was carried out on the instrument KH5200E at room temperature with the frequency/power of the sonication to be 40 Hz/200 W.

For polarized emission in toluene dispersions, the measurement was performed at Beijing Horiba headquarter, with a Fluorolog-3-2 equipped with an ultrafast 405 nm laser (Figure S5-3a). About 15 μ L as-synthesized or 7.000 mg purified NCs were dispersed in toluene (3.0 mL). For the purification of the as-synthesized sample (3.0 mL), a mixture (15.0 mL) of 2Tol – 1EtOH (volume ratio) was used for three times.

For polarized emission in a polymer film, measurements were carried out at Beijing Key Laboratory of Nano-photonics and Ultrafine Optoelectronic Systems, Beijing Institute of Technology. A 405 nm laser was used as an excitation source (Figure S5-3b). The fabrication of NC embedded polymeric films followed the procedure which could be found elsewhere (*Angew. Chem. Int. Ed.* **2017**, *56*, 1780–1783 which was cited as Ref 61 in the main text). Firstly, poly (4-methyl-1-pentene) (1.000 g) and p-xylene (10.0 mL) were mixed and stirred at 100 °C for 10 min; only 1.0 mL solution was used each time. NCs (passivated by carboxylate ligands) (50 μ L) were dispersed into Tol (0.3 mL). This dispersion was then added into the polymer solution (1.0 mL) at 90 °C to form a NC–polymer dispersion. This dispersion was placed quickly onto a glass substrate, which was air dried in a fumehood for 20 min. The composite film formed was exfoliated from the glass substrate. For the purified NCs used, 50 μ L of the as-synthesized NCs was used and purified with a mixture of 2Tol – 1EtOH (three times) or 2Tol – 1CH₃CN (once). Each of the purified samples was dispersed in Tol (0.3 mL) and then mixed with the polymeric solution.

TEM images were taken on FEI Tecnai G2 F20 S-TWIN (Sichuan Univ), FE-TEM (South Sci & Tech Univ), and JEM-2100F (Southwest Jiaotong Univ and Fudan Univ). For TEM grid preparation, a drop

of one NC dispersion was placed on a TEM grid, which was then put in a fume-hood for 30 min to accelerate solvent evaporation. Under TEM, we noticed that TEM electron beam could possibly induce in situ structural and morphological changes; thus, we tried to avoid such changes via to take one image quickly in one area and to move quickly to another area. For our samples with and without post-treatment, Table S4 summarizes optical absorption spectra collected and corresponding TEM images.

Powder X-ray diffraction (XRD) measurements were performed with a generator functioning at 40 kV and 40 mA as well as Cu K α ($\lambda = 1.5418 \text{ \AA}$) radiation in a θ - θ mode on a Shimadzu X-ray diffractometer 6100.

Points for consideration on the theoretical calculations in Ref. 31 and 35. When considering a unit analysis of the following equation

$$\hbar\omega = E_g + E_{hhn} + E_{en} = E_g + \hbar^2 n^2 \pi^2 2m_{hh}^* d^2 + \hbar^2 n^2 \pi^2 / 2m_e^* d^2,$$

in Ref. 31, it becomes apparent that the equation should read as

$$\hbar\omega = E_g + E_{hhn} + E_{en} = E_g + \frac{\hbar^2 n^2 \pi^2}{2m_{hh}^* d^2} + \hbar^2 n^2 \pi^2 / 2m_e^* d^2 .$$

When repeating the calculation in Ref. 35, it becomes evident that the externally referenced equation in the right column on Page 938 has some inconsistencies. The original form of the equation from Ref. 64 should read as

$$\frac{1}{m_c} = \frac{1}{m_0} \left(\alpha + \frac{E_p}{3} \left[\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right] \right),$$

which can be derived as

$$m_e = m_0 / \{ \alpha + (E_p/3) [\frac{2}{E_g} + 1/(E_g + \Delta)] \},$$

rather than

$$m_e = m_0 / \{ 1 + \alpha + (E_p/3) [\frac{1}{E_g} + 1/(E_g + \Delta)] \}$$

in Ref 35. Note that m_c (Ref 61) = m_e (Ref 35).

The third point for consideration is related to the values of α , γ_1 and γ_2 presented in Ref. 35 Table S1. They were listed as -1.54 , -0.18 and -0.65 , respectively. However, solving the following simultaneous equations

$$\frac{1}{m_e} = \frac{1}{m_0} \left(\alpha + \frac{E_p}{3} \left[\frac{2}{E_g} + \frac{1}{E_g + \Delta} \right] \right)$$

$$m_{lh} = \frac{m_0}{\gamma_1 + 2\gamma_2 + \frac{2E_p}{3E_g}}$$

$$m_{lh} = \frac{m_0}{\gamma_1 - 2\gamma_2}$$

given the known parameters m_e/m_0 , E_p , E_g , Δ , m_{lh}/m_0 , m_{hh}/m_0 , leads to the values of -1.62 , -0.13 and -0.62 , respectively.

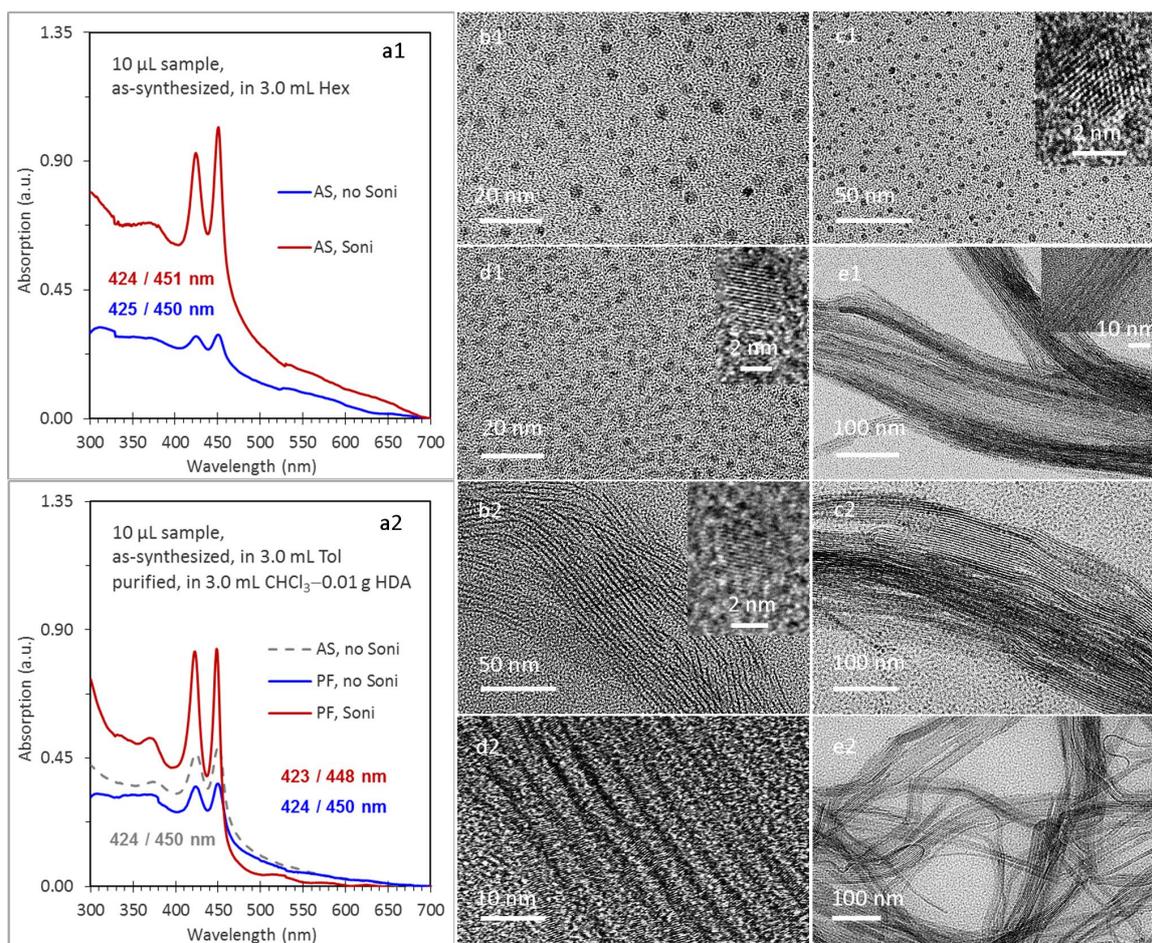


Figure S1-1. Characterization of as-synthesized (AS) NCs (top panel, a1 to e1) and purified (PF) NCs (bottom panel, a2 to e2 mainly), the synthetic approach of which followed Ref 29 (as summarized in Table S1). For the as-synthesized CdSe NCs (10 μ L), absorption spectra were collected from one 3.0 mL hexane dispersion (a1) before (blue trace) and after 30-min (red trace) sonication (Soni). The TEM images were from one sample dispersed in 3.0 mL of hexane before (b1, c1) and after 30 min sonication (d1, e1). For the purified NCs (10 μ L), absorption spectra were collected from one 3.0 mL CHCl_3 -0.010 g HDA dispersion (a2) before (blue trace) and after 30-min (red trace) sonication. The sample was purified with 3.0 mL EtOH – 0.100 g TOP for 3 times; for comparison, the unpurified sample in toluene is represented by a grey dashed trace. The TEM images were from one purified sample dispersed in the CHCl_3 -HDA mixture before (b2, c2) and after 30-min sonication (d2, e2).

Table S1-1. Summary of the experimental conditions of the literature and present approaches to amine-passivated CdSe NCs.

Method	Cd concentration (mmol/15mL OTA)	Se concentration (mmol/15mL OTA)	Reaction temperature and periods (°C/min)
Ref. 29*	1.50	4.50	70 °C/NA
Present study Fig S1-1	1.50	4.50	70 °C/360 min
Present study (Figs 1 and S1-2 to S1-7)	4.80	1.50	120 °C/90 min

*Ref. 29 (in the main text from Hyeon's group) introduces the synthetic method for the amine-passivated CdSe NCs; the growth period at 70 °C was not provided. We repeated the Ref 29 synthesis, see Figure S1-1.

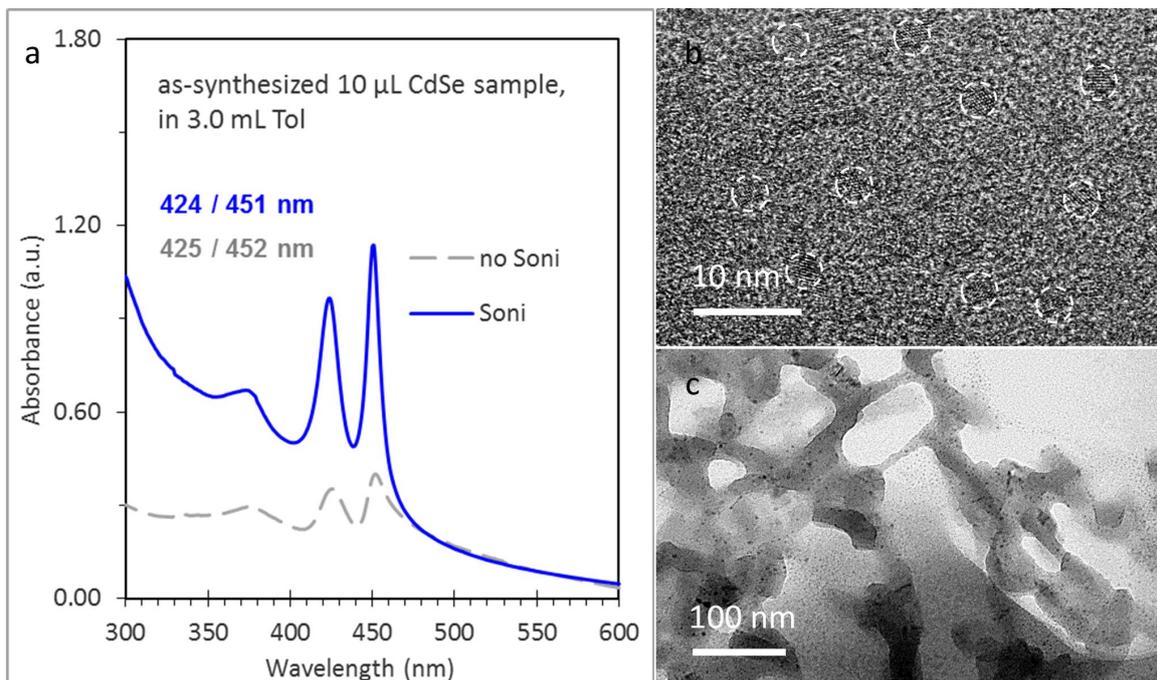


Figure S1-2. Absorption spectra (a) of our as-synthesized CdSe NCs dispersed in toluene before (dashed grey line) and after (solid blue line) 30 min of sonication (Soni). Clearly, sonication assisted the dispersity in toluene with slightly blue shift of the absorption. The sample used here was from one synthetic batch with the identical experimental conditions shown in Table S1. For the as-synthesized CdSe NCs dispersed in toluene without sonication, various structures can be seen under TEM (as demonstrated by b right-top and c right-bottom). By a side note, only representative TEM images are shown in the present study.

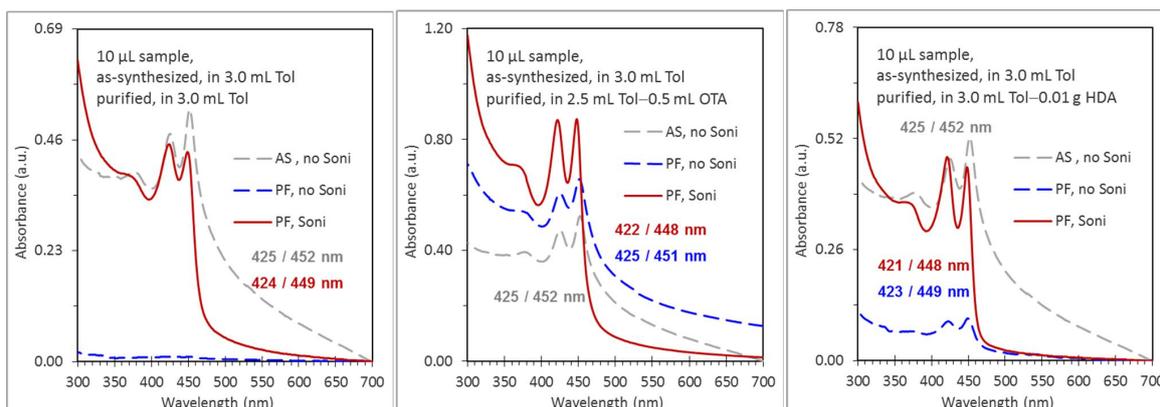


Figure S1-3. Absorption spectra of the CdSe NCs dispersed in 3.0 mL of Tol (left), 2.5 mL Tol – 0.5 mL OTA (middle), and 3.0 mL Tol – 0.010 g HDA (right). The grey spectrum was collected from the as-synthesized (AS) sample dispersed in Tol without sonication (Soni). The blue and red spectra were collected from purified (PF) samples, before and after 30 min sonication. 2.0 mL Tol – 1.0 mL EtOH was used 3 times to purify the three 10 μ L samples. The absorption doublet peak positions are indicated. Purification led to slightly blue shift. For purified samples, obviously, the dispersity in toluene alone is the lowest.

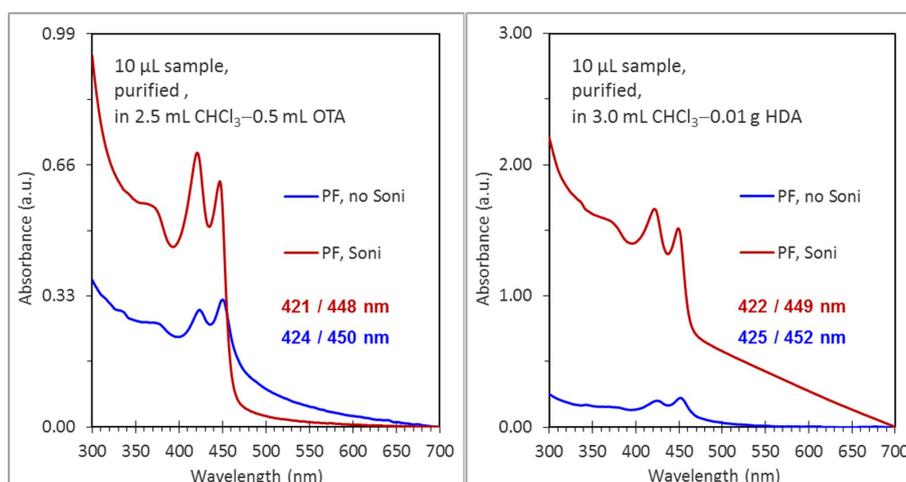


Figure S1-4. Absorption spectra of the purified (PF) CdSe NCs dispersed in 2.5 mL CHCl₃–0.5 mL OTA (left), and 3.0 mL CHCl₃ – 0.010 g HDA (right). The blue and red spectra were collected before and after 30 min sonication (Soni). 2.0 mL Tol – 1.0 mL EtOH was used 3 times to purify the two 10 μL samples. Obviously, sonication enhanced sample dispersity in both CHCl₃ – OTA and CHCl₃ – HDA solvent. The larger scattering observed after sonication (right, red trace) is in agreement with the formation of 2D structures.

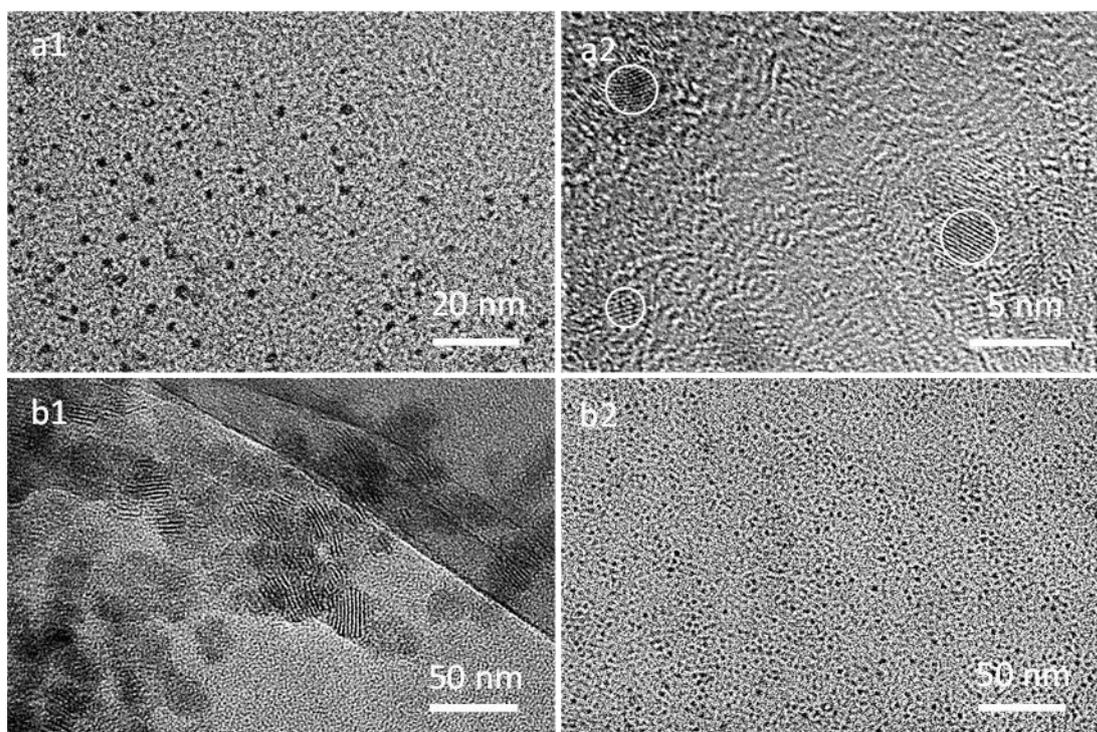


Figure S1-5. Additional TEM images of the as-synthesized CdSe NCs

dispersed in hexane before sonication (a1 and a2) and after 30 min-sonication (b1 and b2). The sonication process induced the assembly of 0D NCs.

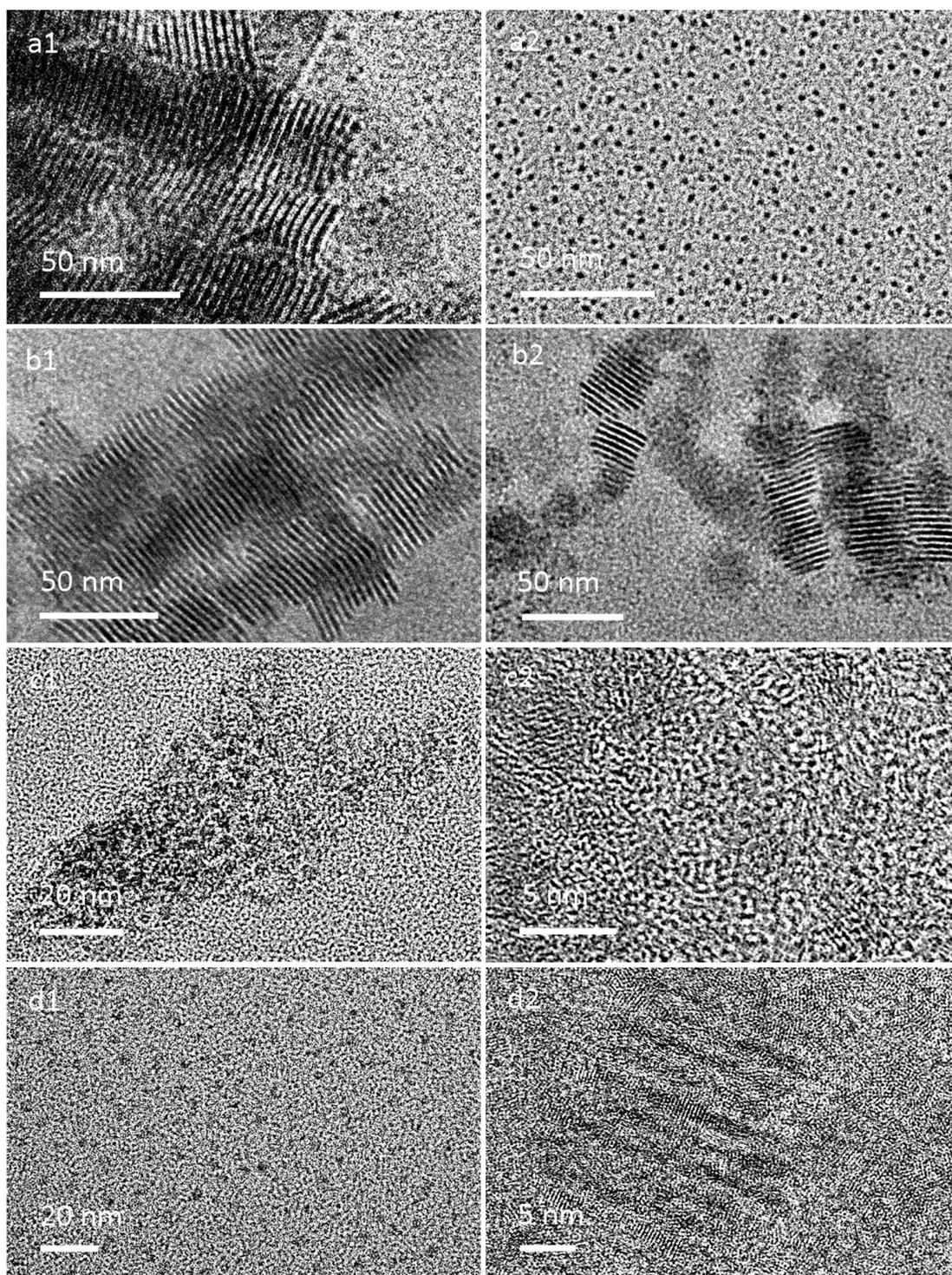


Figure S1-6. TEM images of our purified CdSe NCs (10 μ L of as-synthesized NCs purified by EtOH 3 times; each time 3.0 mL of EtOH was used) dispersed in different dispersions, 3.0 mL CHCl₃ – 0.010 g HDA (a1 and a2) before sonication and (b1 and b2) after 30 min-sonication, 2.5 mL CHCl₃ – 0.5 mL OTA (c1 and c2) before sonication and (d1 and d2) after 30 min-sonication.

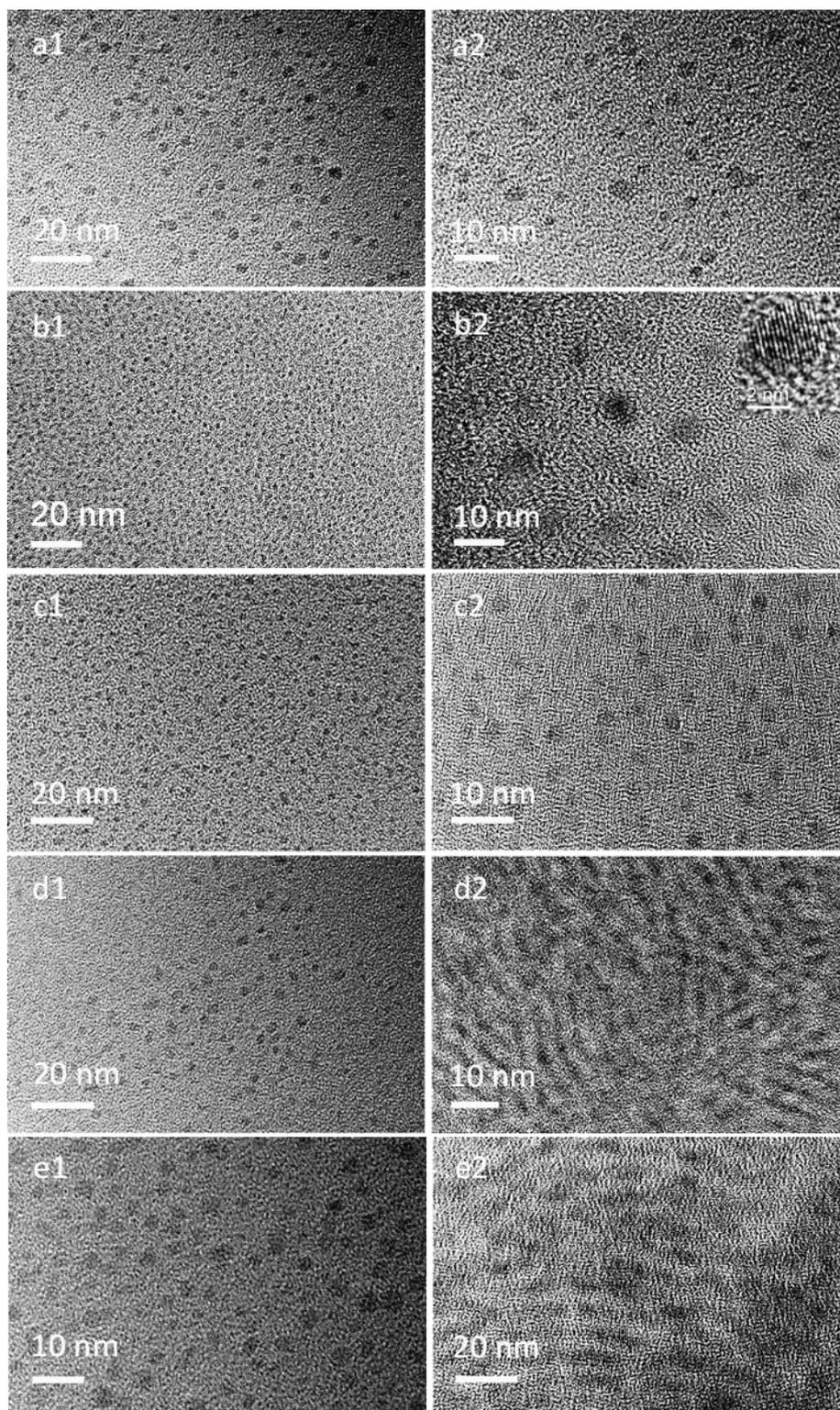


Figure S1-7. TEM images of our purified CdSe NCs dispersed in different dispersion mixtures. Each of the five samples was about 10 μ L and was purified with 2.0 mL Tol – 1.0 mL EtOH for 3

times. The dispersion mixtures used were 3.0 mL toluene (a1 and a2), 2.5 mL Tol–0.5 mL OTA (b1 and b2), 2.5 mL CHCl₃ – 0.5 mL OTA (c1 and c3), 3.0 mL Tol – 0.010 g HDA (d1 and d2), and 3.0 mL CHCl₃ – 0.010 g HDA (e1 and e2). For the toluene dispersion (a), OD NCs dominated (with a tiny amount of 2D wells seen at very thick sample places on the TEM grid (not shown)). With the presence of OTA in the dispersions (b and c), OD NCs still dominated. With the presence of HDA in the toluene (d) and CHCl₃ dispersions (e), the coexistence of OD NCs and 2D wells was observed with the former and latter dominating, respectively. The observation with Dispersions c and e is similar to that with Figure S1-6 Dispersions c and a, respectively. It is worthy of notice that the experiments for the Figure S1-6c and S1-7c images as well as for the Figure S1-6a and S1-7e images were repeated with the same sample batch, but the two dispersions for Figure S1-6 were prepared at one time and the two dispersions for Figure S1-7 were prepared after 6 months. Clearly, for the amine-passivated CdSe NCs, the presence of HDA in dispersion, together with sonication played an important role in the observation of the self-assembled wells by TEM.

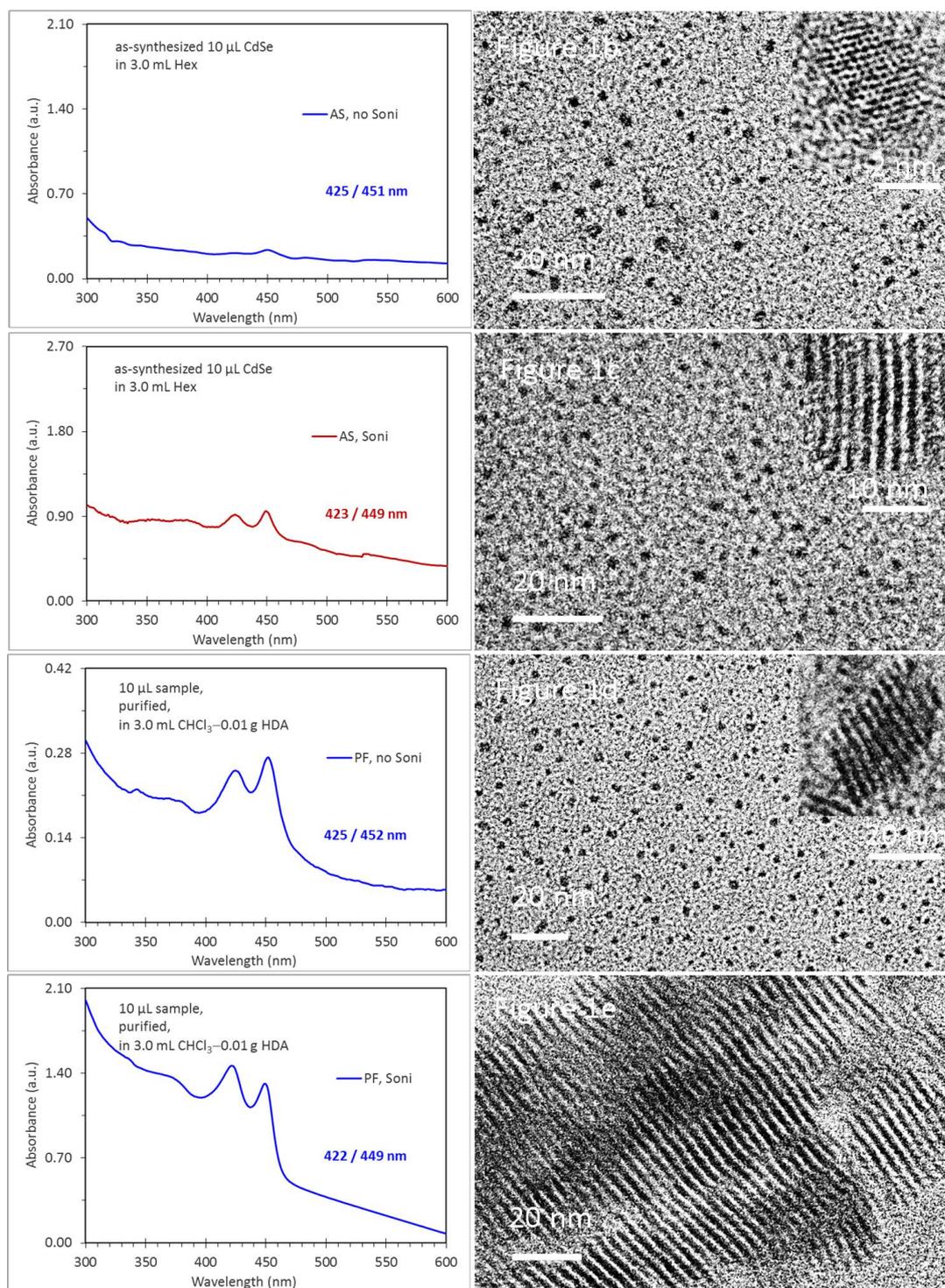


Figure S1-8. Corresponding UV spectra (left) of the TEM samples (right) in Fig. 1.

Table S1-2. TEM sample treatment and results regarding the amine-passivated CdSe NC samples^a.

Figure ^b	Purification ^c	Dispersion	Sonication	OD NCs ^d	2D QWs ^e
1b, S1-5a	None	3.0 mL Hexane	None	> 85%	< 50%
1c, S1-5b	None	3.0 mL Hexane	30min	50 – 85%	< 50%
1d, S1-6a	EtOH	3.0mL CHCl ₃ – 0.010g HDA	None	~ 50%	~ 50%
1e, S1-6b	EtOH	3.0mL CHCl ₃ – 0.010g HDA	30min	< 50%	> 85%
S1-6c	EtOH	2.5mL CHCl ₃ – 0.5mL OTA	None	> 85%	< 50%
S1-6d	EtOH	2.5mL CHCl ₃ – 0.5mL OTA	30min	> 85%	< 50%
S1-7a	1mL EtOH – 2mL Tol	3.0 mL Tol	None	> 85%	< 50%
S1-7b	1mL EtOH – 2mL Tol	2.5mL Tol – 0.5mL OTA	None	> 85%	< 50%
S1-7c	1mL EtOH – 2mL Tol	2.5mL CHCl ₃ – 0.5mL OTA	None	> 85%	< 50%
S1-7d	1mL EtOH – 2mL Tol	3.0mL Tol – 0.010g HDA	None	< 50%	> 85%
S1-7e	1mL EtOH – 2mL Tol	3.0mL CHCl ₃ – 0.010g HDA	None	< 50%	> 85%

^a Samples used for post-process in this work is 10 μ L. ^b Corresponding figures in the main text and supporting information. ^c When purification was applied, the sample is purified 3 time in 3.0 mL of corresponding solvent as noted. ^{d,e} The OD and 2D NC TEM population estimated.

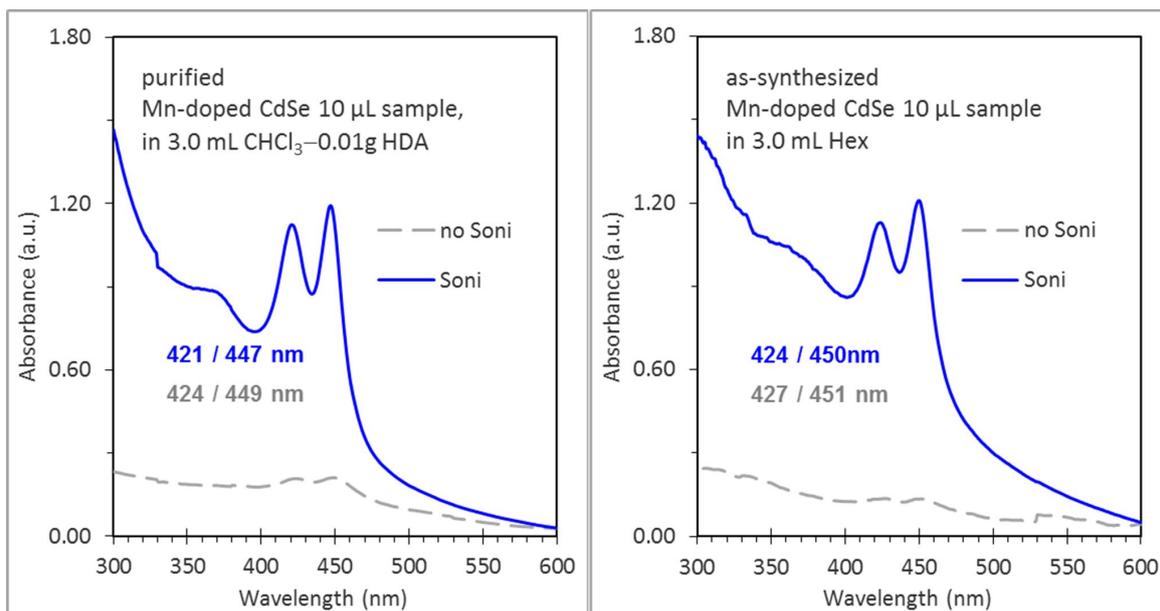


Figure S2-1. Absorption spectra of the purified (left) and the as-synthesized (right) Mn^{2+} doped CdSe NCs dispersed in 3.0 mL CHCl_3 – 0.010 g HDA, before (grey dashed line) and after (blue solid line) 30 min sonication (Soni).

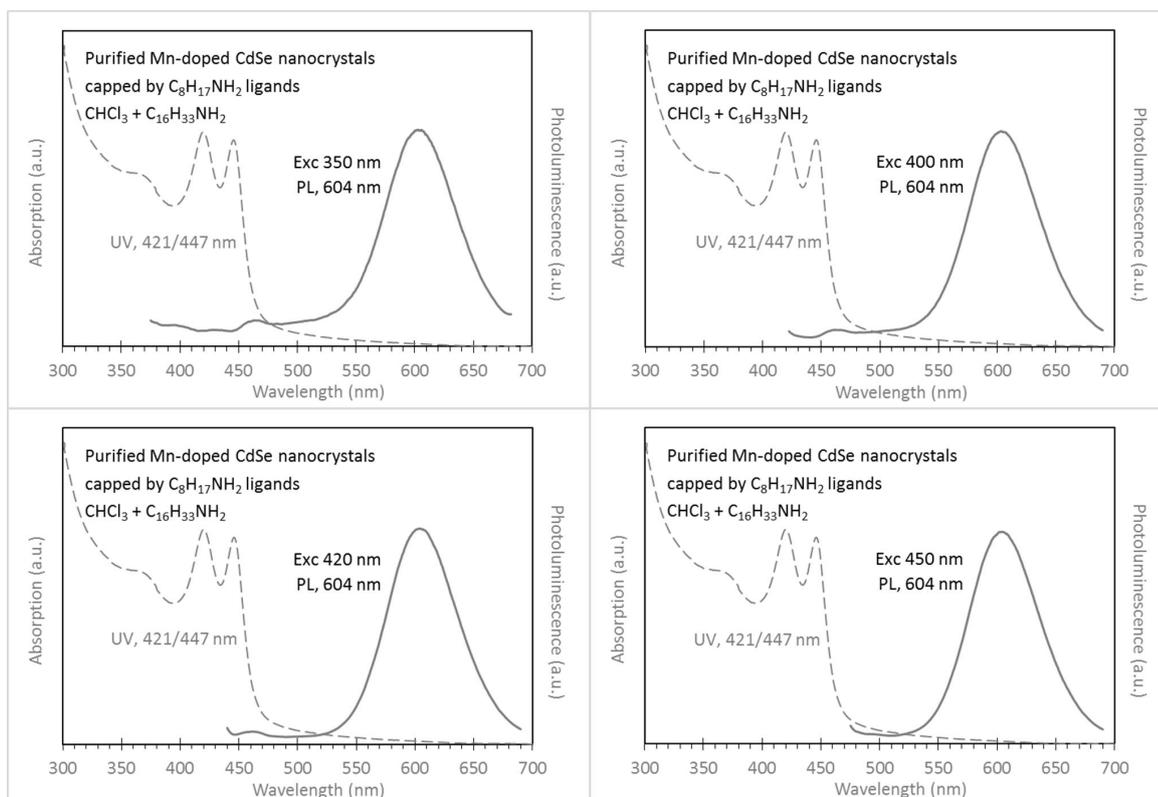


Figure S2-2. Normalized absorption (dashed lines) and photoluminescence (solid lines, excited at 350, 400, 420 and 450 nm as indicated) spectra of our purified Mn²⁺ doped CdSe NCs dispersed in 3.0 mL CHCl₃ – 0.010 g HDA after 30 min of sonication.

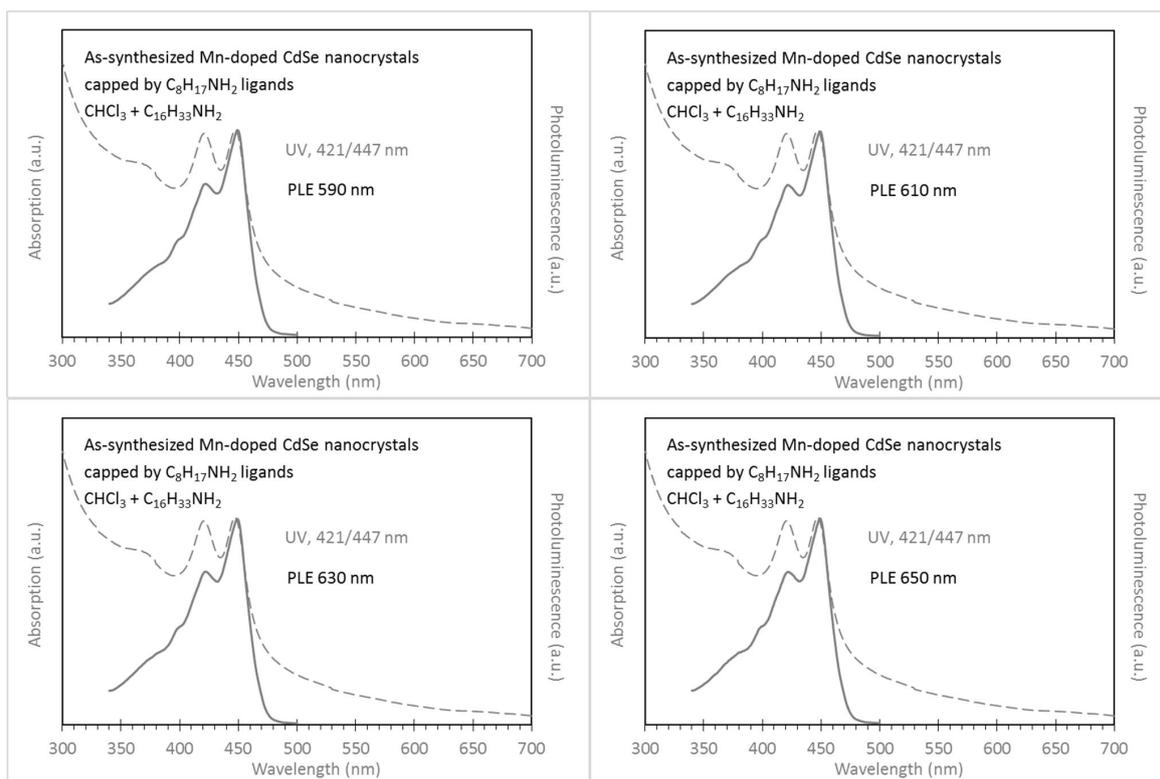


Figure S2-3. Normalized absorption (dashed lines) and photo-luminescence excitation (PLE) (solid lines, emission at 590, 610, 630 and 650 nm as indicated) spectra of the purified Mn²⁺ doped CdSe NCs dispersed in 3.0 mL CHCl₃ – 0.010 g HDA with sonication.

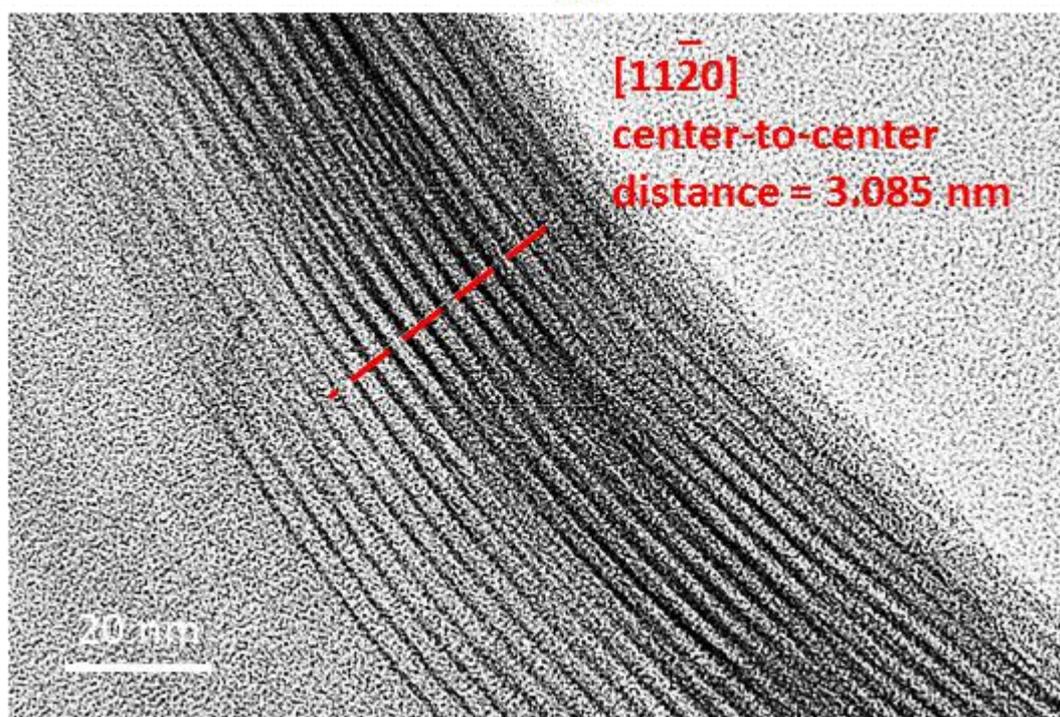
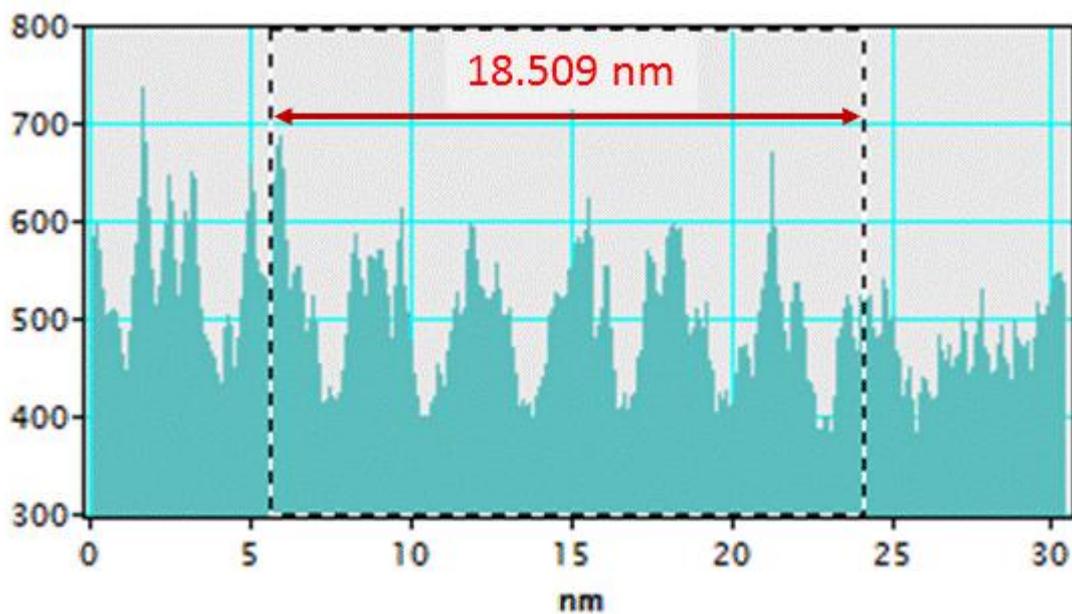


Figure S2-4. TEM study of our purified Mn^{2+} doped CdSe NCs dispersed in 3.0 mL CHCl_3 – 0.010 g HDA with 30 min of sonication. The center to center distance along the direction of $[11\bar{2}0]$ indicated is calculated to be 3.085 nm using the measurement shown in the top panel. The TEM image is very much similar to that of Ref 29 Figure 1b; and we followed Refs 29 and 54 assignments for the $[11\bar{2}0]$ direction assignment.

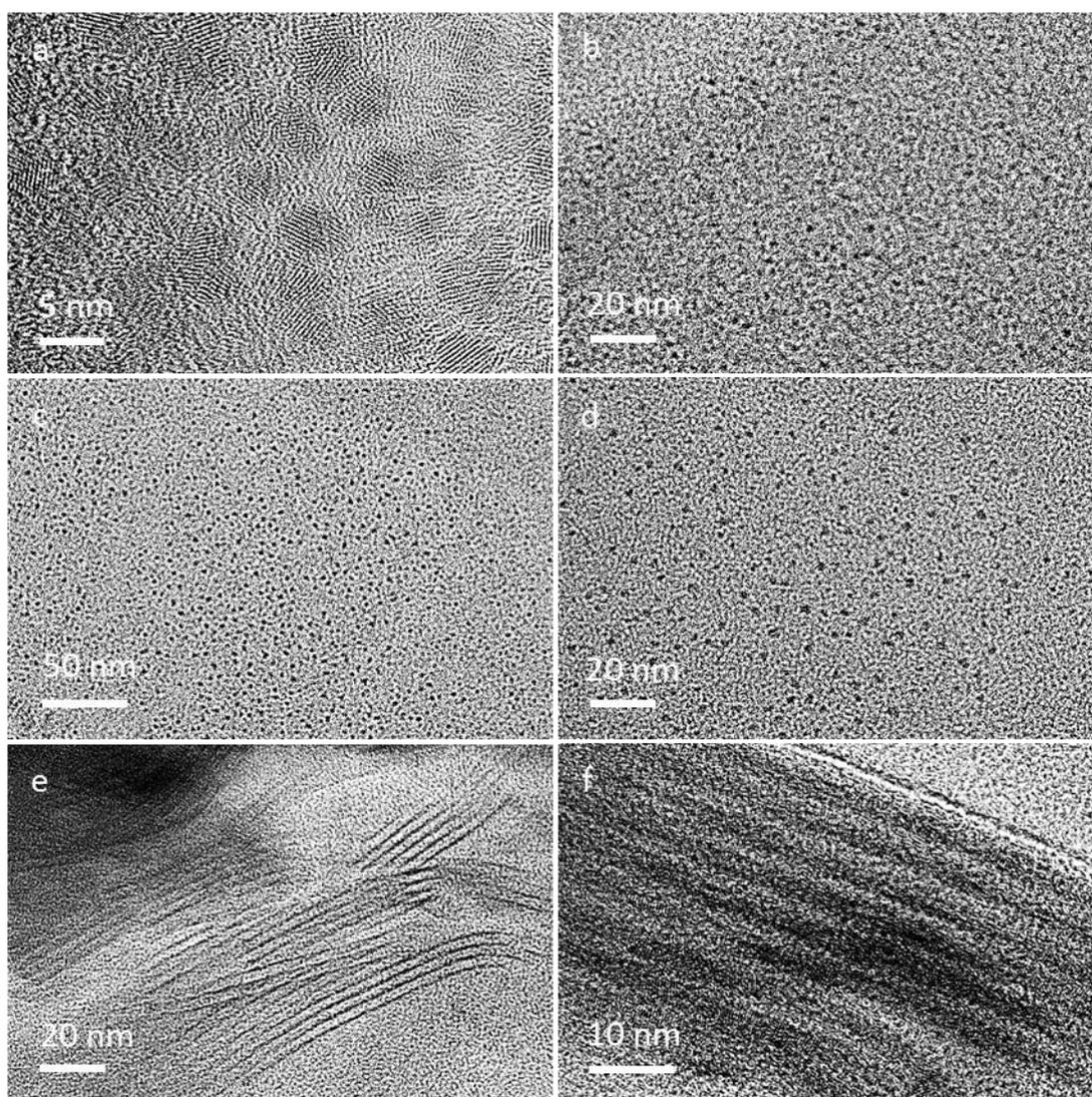


Figure S2-5. Additional TEM images of our Mn²⁺ doped CdSe NCs (shown by Figure 2), without purification and dispersed in hexane before (a) after 30 min of sonication (b), and with purification and dispersed in 3.0 mL CHCl₃ – 0.010 g HDA before (c and d) and after 30 min of sonication (e and f).

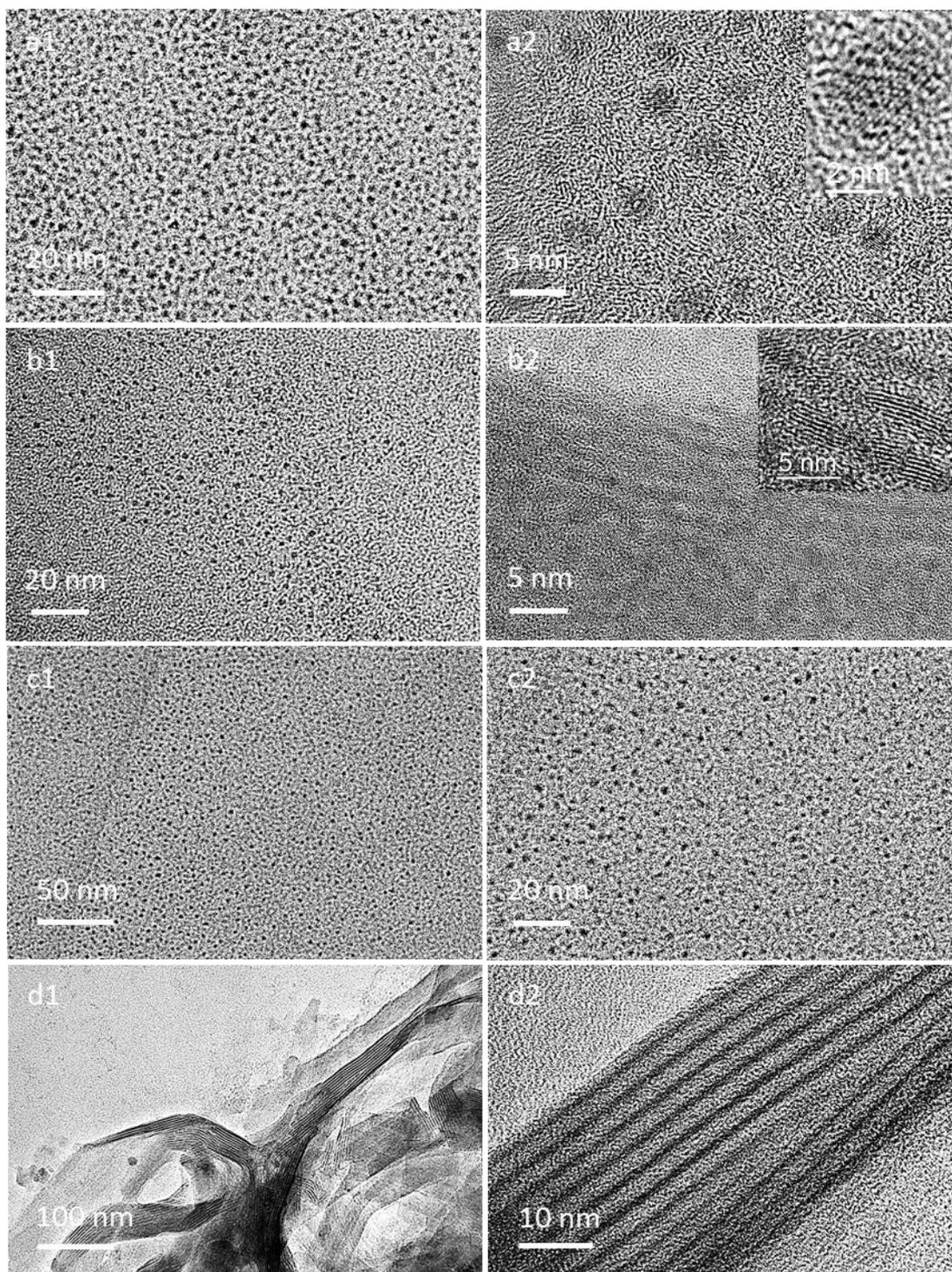


Figure S2-6. The effect of OTA, OLA, and HDA on the TEM morphologies of the purified Mn²⁺ doped CdSe NCs (without sonication). The dispersion was 2.5 mL Tol – 0.5 mL OTA (a1 and a2,

purified with 1.0 mL EtOH – 2.0 mL Tol–0.100 g TOP 3 times) and (b1 and b2, purified with 1.0 mL EtOH – 1.5 mL Tol – 0.5 mL OTA – 0.100 g TOP 3 times), 2.5 mL Tol – 0.5 mL OLA (c1 and c2, purified with 1.0 mL EtOH – 1.5 mL Tol – 0.5 mL OLA – 0.100 g TOP 3 times) and 3.0 mL Tol – 0.010 g HDA (d1 and d2, purified 1.0 mL EtOH – 2.0 mL Tol – 0.010 g HAD – 0.100 g TOP 3 times).

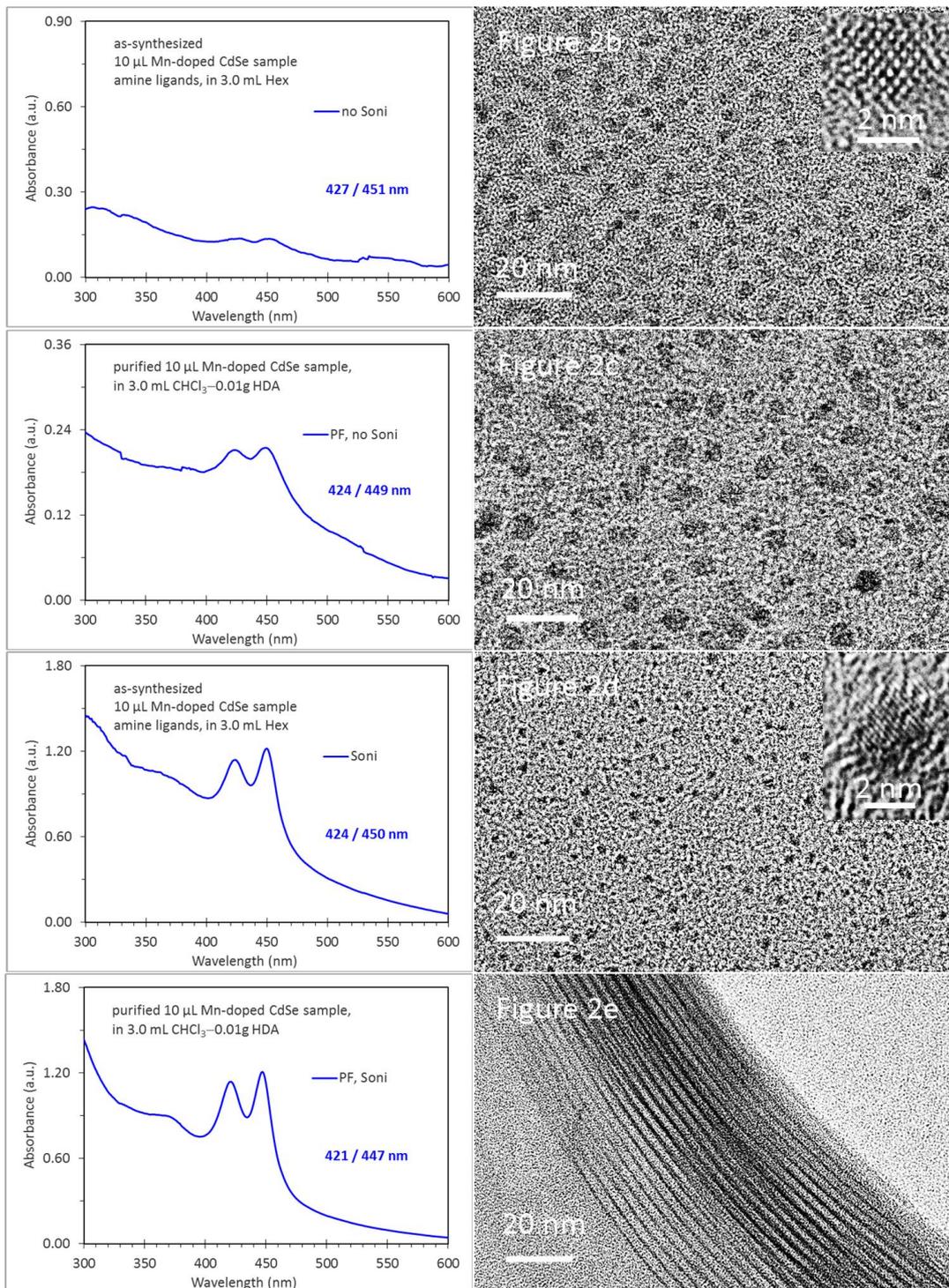


Figure S2-7. Corresponding UV spectra (left) of the TEM samples (right) in Fig. 2.

Table S2. TEM sample treatment and results for the Mn²⁺ doped CdSe NC samples^a.

Figure ^b	Purification ^c	Dispersion	Sonication	0D NCs ^d	2D QWs ^e
2b, S2-5a	None	3.0mL Hexane	None	> 85%	< 50%
2c, S2-5b	None	3.0mL Hexane	30min	50 – 85%	< 50%
2d, S2-5c S2-5d	3.0mL EtOH – 0.100 g TOP	3.0mL CHCl ₃ – 0.010g HDA	None	~ 50%	~ 50%
2e, S2-4, S2-5e S2-5f	3.0mL EtOH – 0.100 g TOP	3.0mL CHCl ₃ – 0.010g HDA	30min	< 50%	> 85%
S2-6a	1.0mL EtOH – 0.100g TOP – 2.0mL Tol	2.5mL Tol – 0.5mL OTA	None	> 85%	< 50%
S2-6b	1.0mL EtOH – 0.100g TOP – 1.5mL Tol – 0.5mL OTA	2.5mL Tol – 0.5mL OTA	None	> 85%	< 50%
S2-6c	1.0mL EtOH – 0.100g TOP – 1.5mL Tol – 0.5mL OLA	2.5mL Tol – 0.5mL OLA	None	> 85%	< 50%
S2-6d	1.0mL EtOH – 0.100g TOP – 2.0mL Tol – 0.010g HDA	3.0mL Tol – 0.010g HDA	None	> 85%	< 50%

^a Samples used for post-process in this work is 10 μ L. ^b Corresponding figures in the main text and supporting information. ^c When purification was applied, the sample is purified 3 time in 3.0 mL of corresponding solvent as noted. ^{d,e} The 0D and 2D NC TEM population estimated.

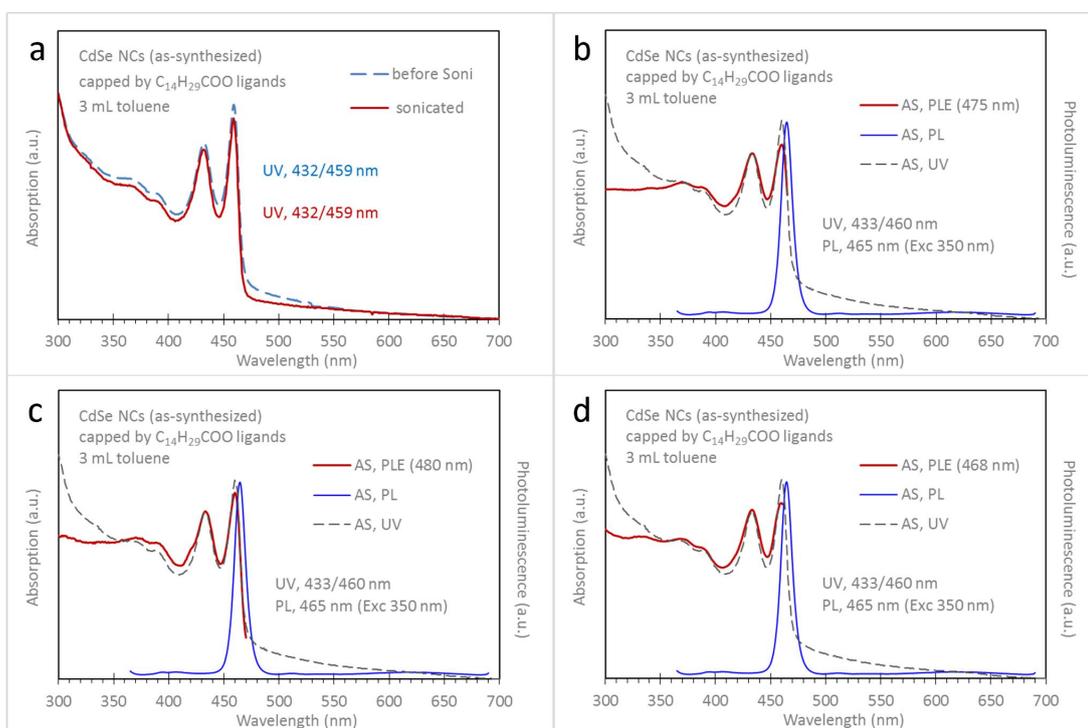


Figure S3-1. Absorption spectra (a) collected from the unpurified as-synthesized (AS) CdSe NCs (15 μ L) dispersed in 3.0 mL of toluene before (blue dashed line) and after (red solid line) 30 min of sonication (Soni). Normalized absorption (grey dashed traces) and PL (blue solid traces) spectra, together with PLE spectra (red solid traces) of our as-synthesized (b, c and d) CdSe NCs (15 μ L, from another synthetic batch) dispersed in 3.0 mL Tol. The PLE spectra were collected with emission at 480 (c), 475 (b), and 468 nm (d) as indicated.

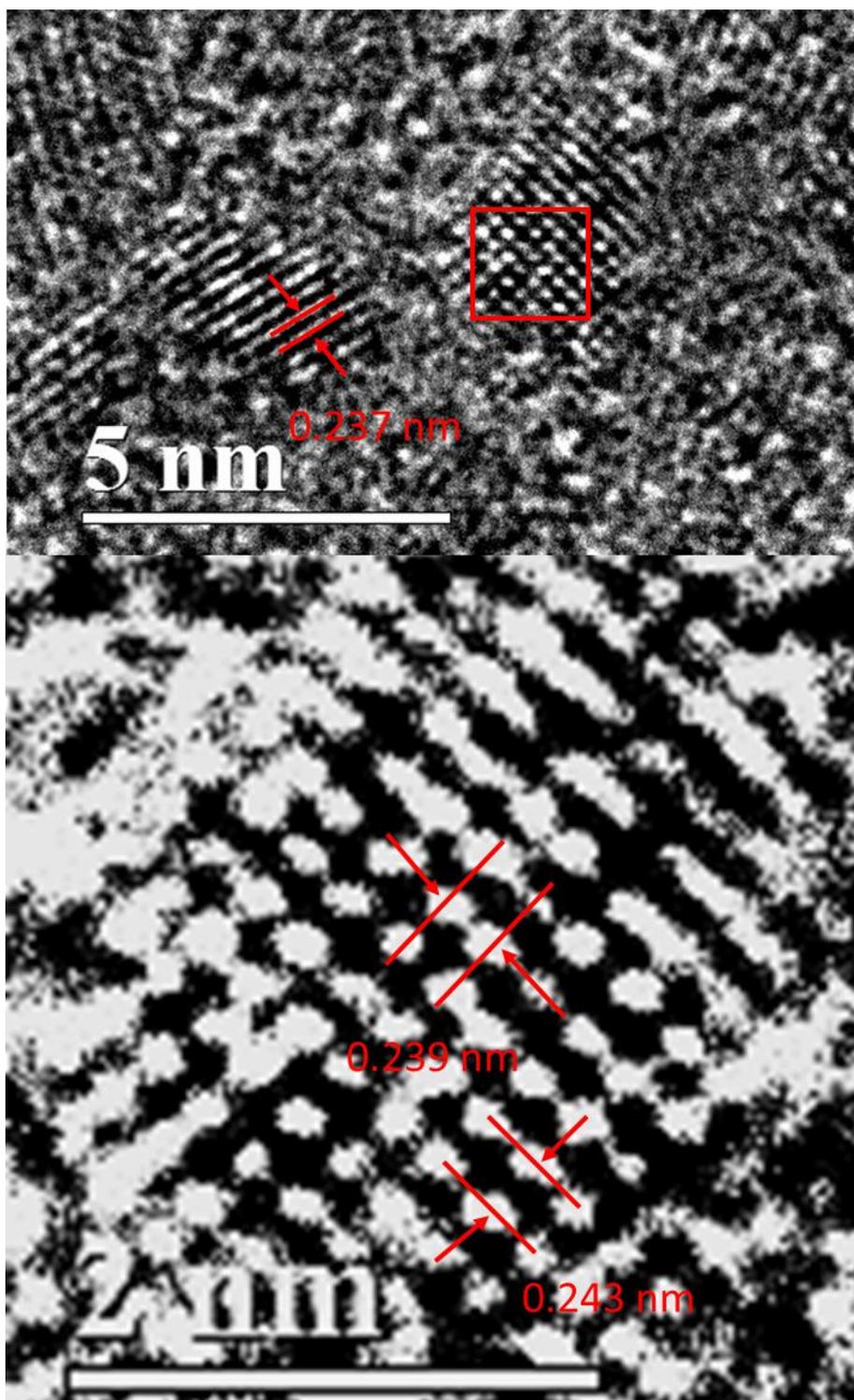


Figure S3-2. (Top) A high resolution TEM (HRTEM) image of the as-synthesized CdSe 0D NCs (10 μ L) dispersed in 3.0 mL of CHCl_3 . The scale bar is 5 nm. (Bottom) An enlarged image of the red squared area in the top image and the scale bar is 2 nm.

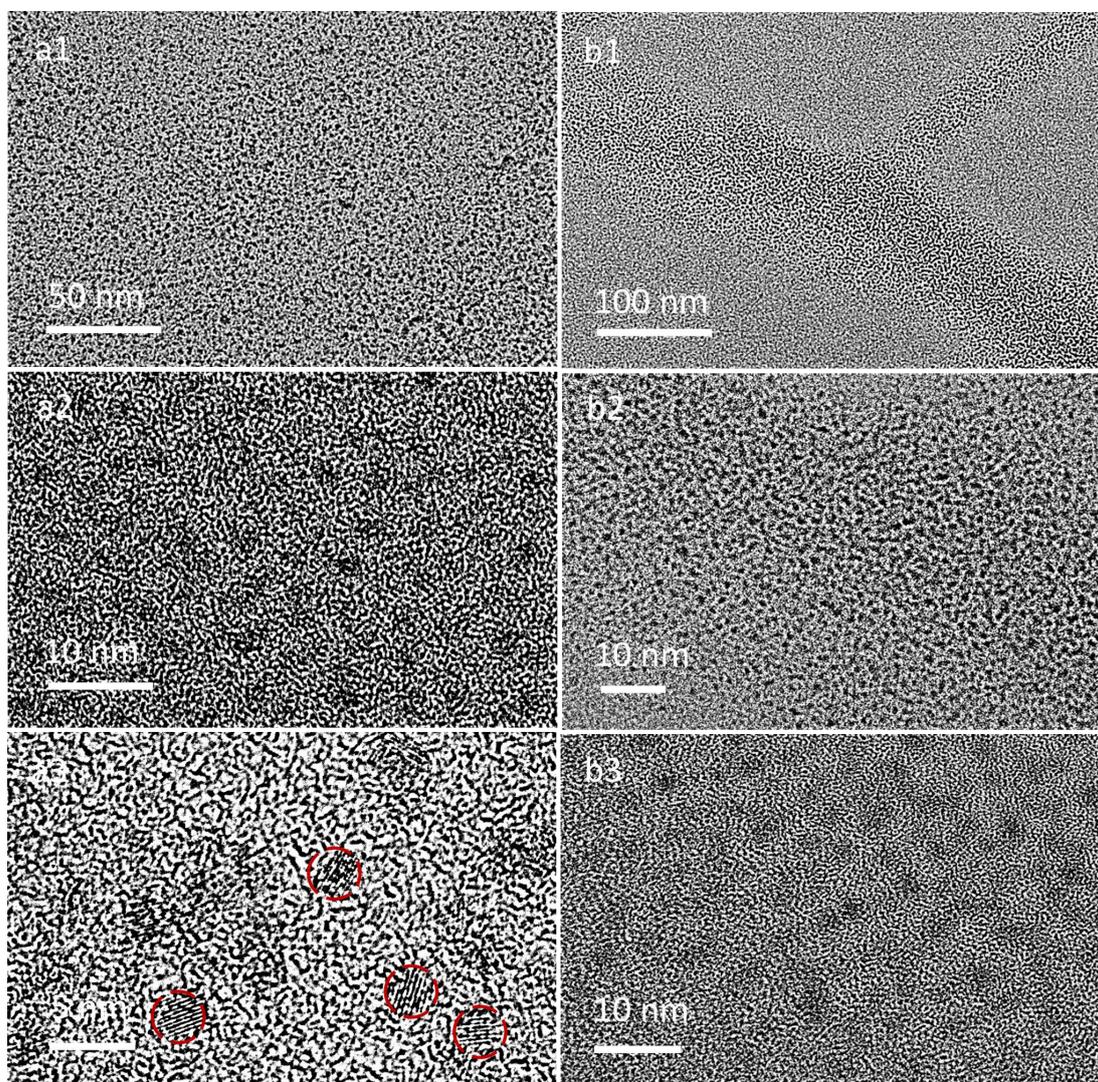


Figure S3-3. Additional TEM images of the Figure 3c in CHCl_3 dispersion (a1 to a3, left column) and of the Figure 3d in toluene dispersion (b1 to b3, right column). The scale bars for the left column from top to bottom are 50, 10, and 5 nm, respectively. The scale bars for the right column from top to bottom are 100, 10, and 10 nm, respectively.

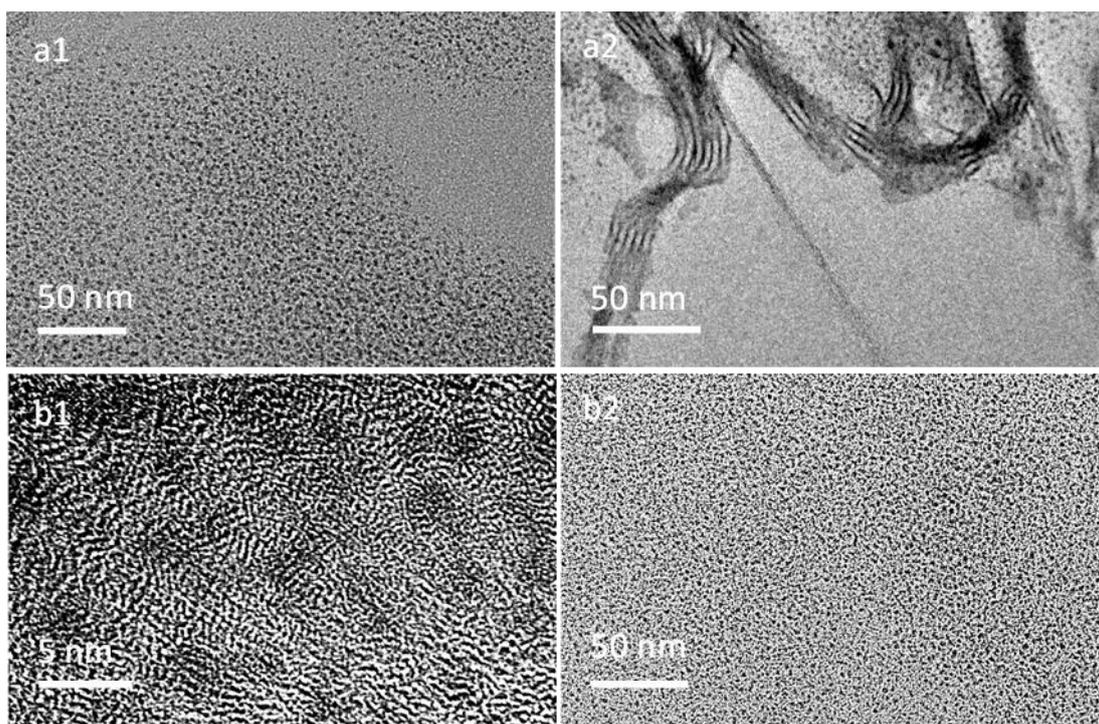


Figure S3-4. TEM images of the CdSe NCs purified with toluene for 3 times and dispersed in toluene. The two TEM grids were prepared from two dispersions without storage (a1 and a2) and with half a day storage (b1 and b2). The TEM grid b is the same as that for Figure 3f and 3g.

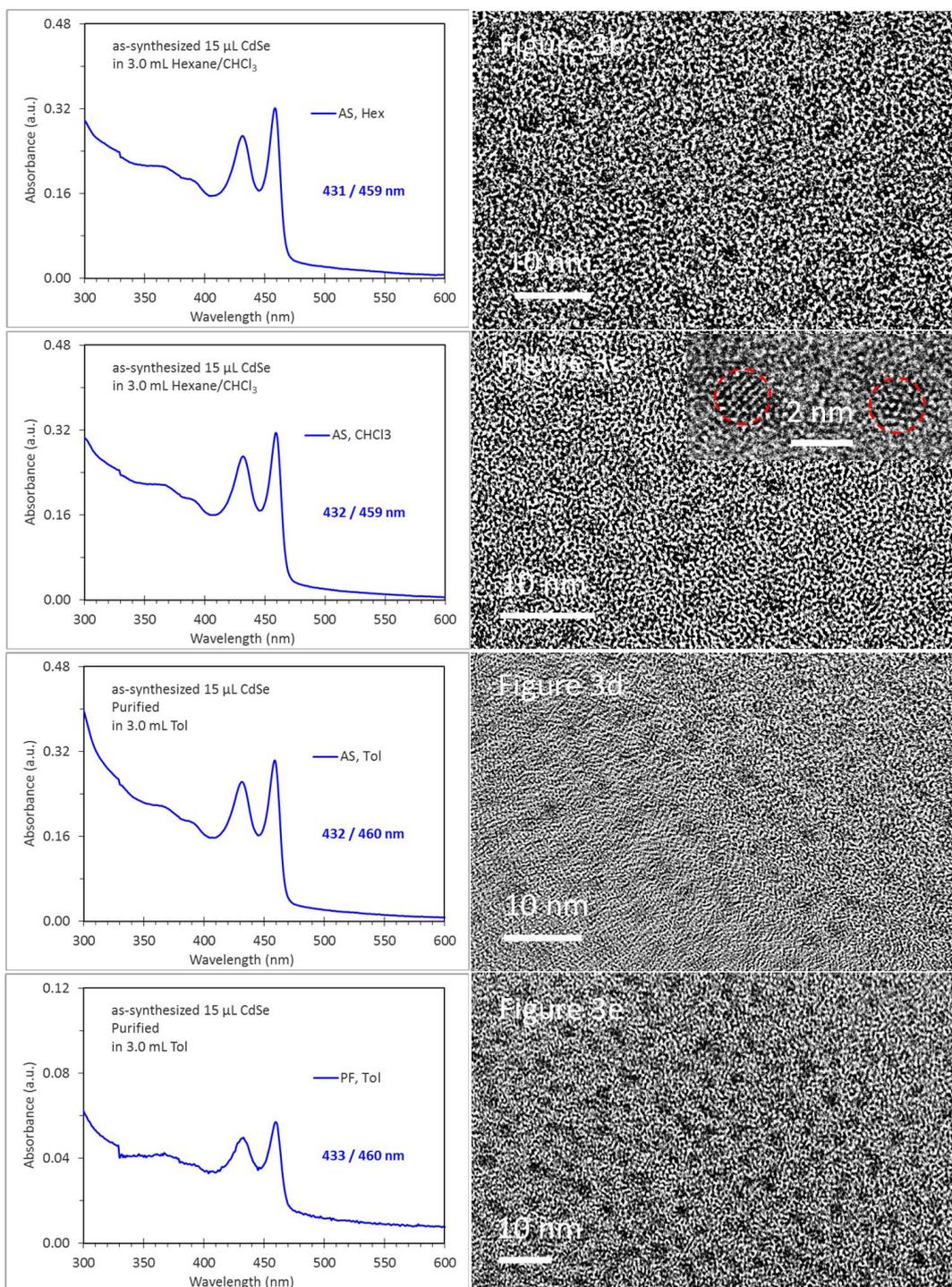


Figure S3-5. Corresponding UV spectra (left) of the TEM samples (right) of Fig. 3.

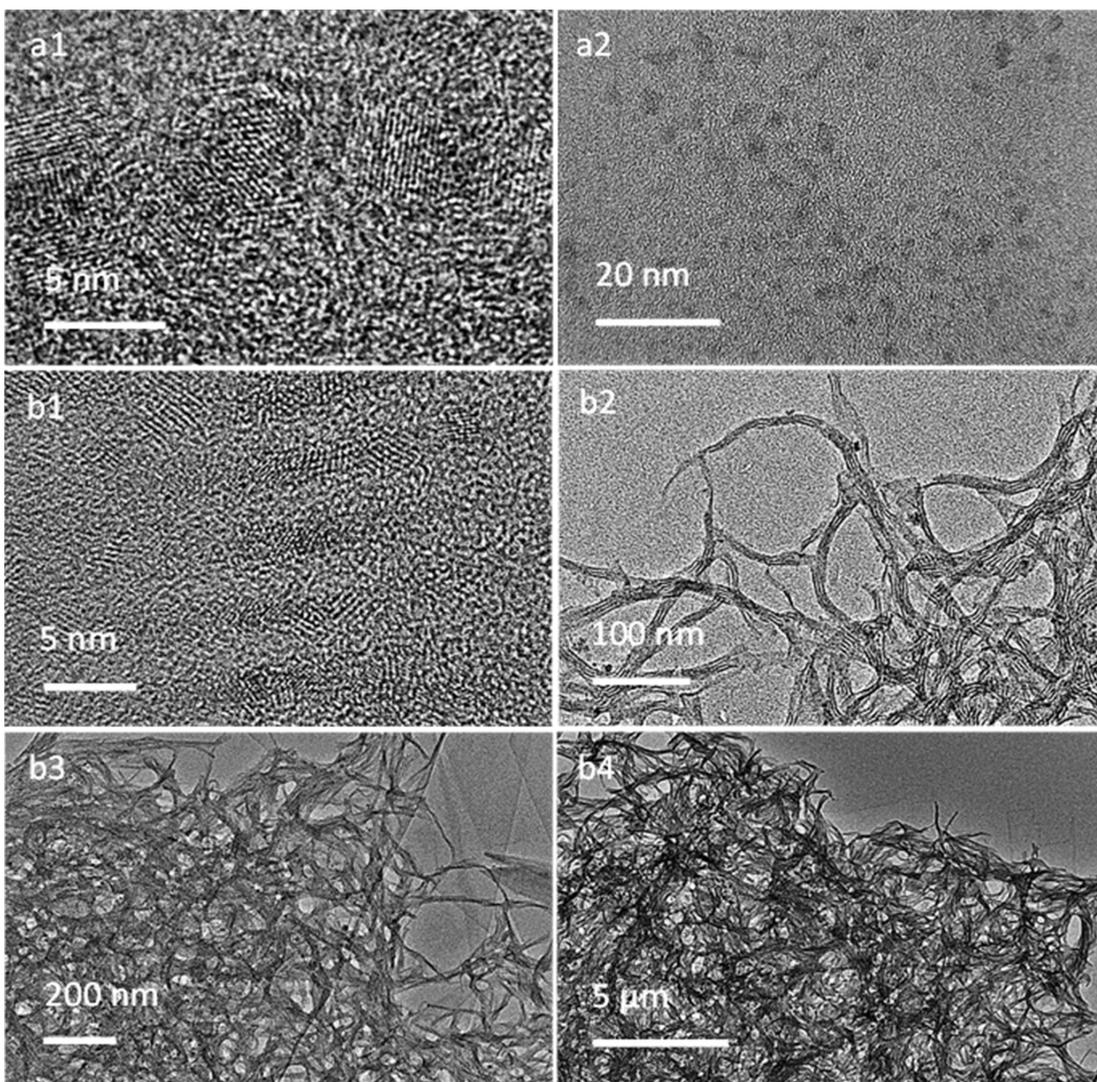


Figure S4-1. Additional TEM images of our Fig. 4 carboxylic ligand passivated CdSe NCs purified 3 times, each time with the mixture of 2.0 mL of Tol and 1.0 mL of CH₃CN then dispersed in toluene and kept for four days (a1 and a2), each time with the mixture of 2.0 mL of Tol and 1.0 mL of EtOH and then dispersed in toluene (b1 to b4).

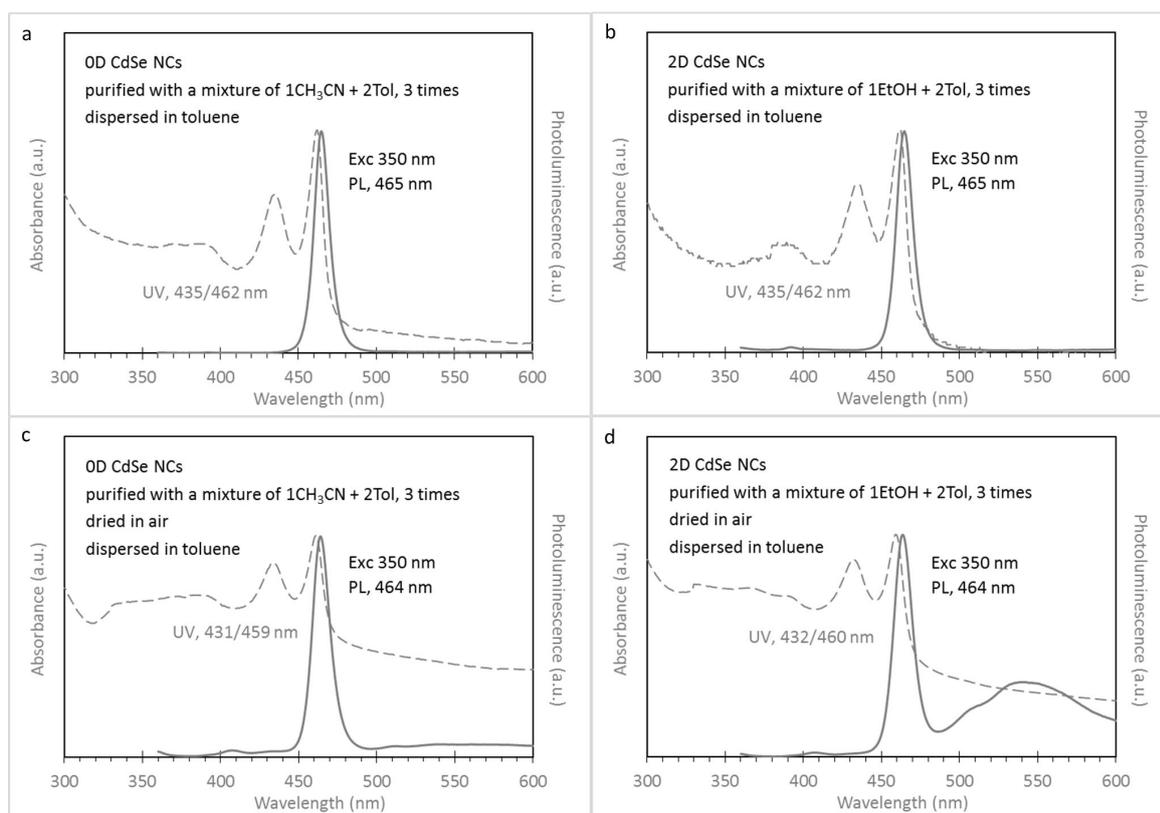


Figure S4-2. Normalized absorption (dashed line, left y axis) and emission (solid line, excited at 350 nm, right y axis) spectra of our purified CdSe NCs in toluene. The a and b samples were from one batch with the same synthetic condition as that used for Figure 3. Apparently, the CdSe NCs purified with CH_3CN (a) or EtOH (b) exhibit similar absorption doublets and bandgap emission. The c and d samples were from two identical batches with the same synthetic condition as that used for Figure 3. However, the two purified samples with CH_3CN (c) or EtOH (d) were dried in air before dispersed in toluene. The trap emission (d) could be due to the loose of surface ligands.

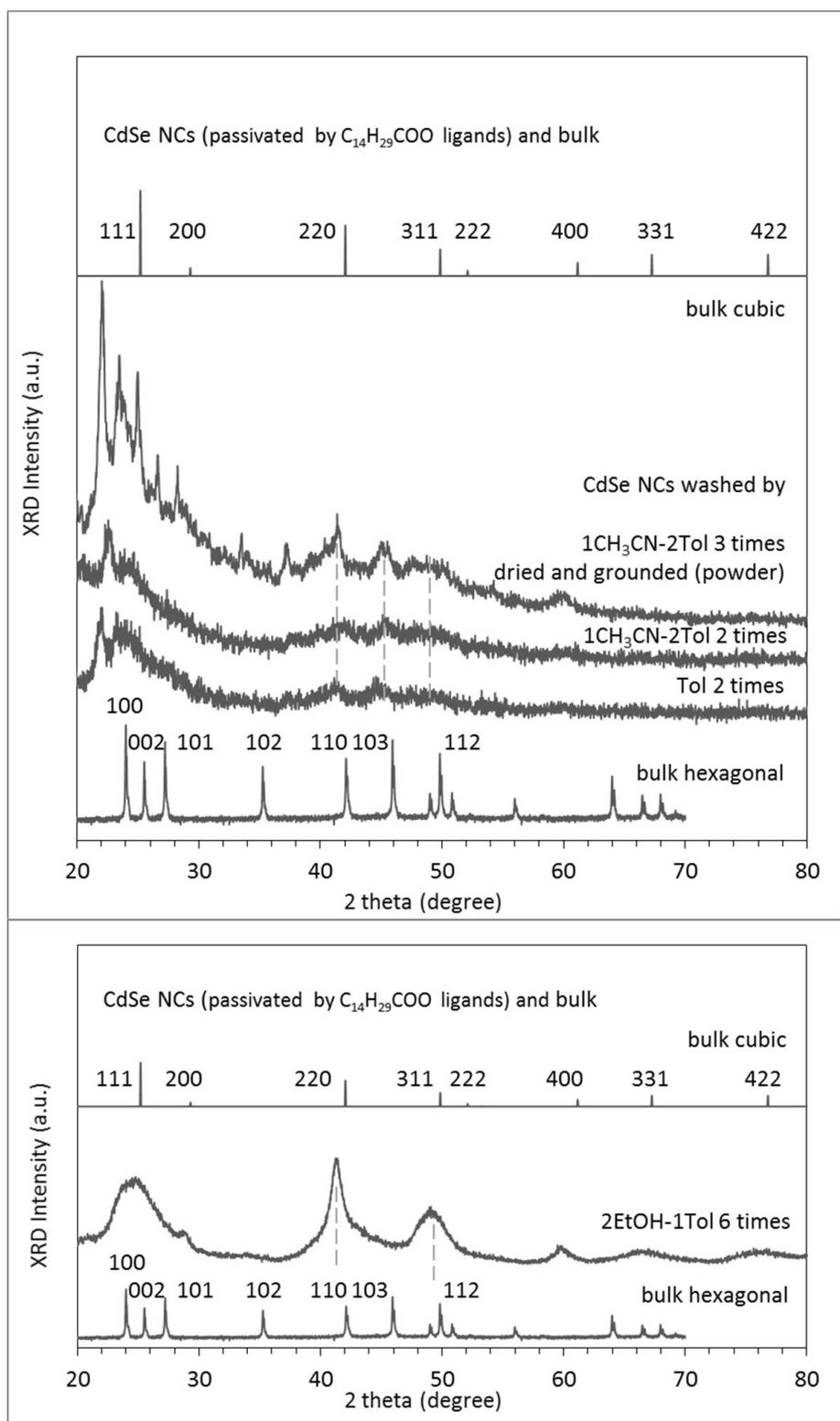


Figure S4-3. XRD study supports that the CdSe NCs were 0D after purification (top), as indicated without a protic agent. For those 2D CdSe NCs (bottom, which were purified with a

protic agent), the XRD pattern was similar to those reported, with a sharp peak near the 110 peak (bulk hexagonal, Ref 30) or 220 peak position (bulk cubic, Ref 36).

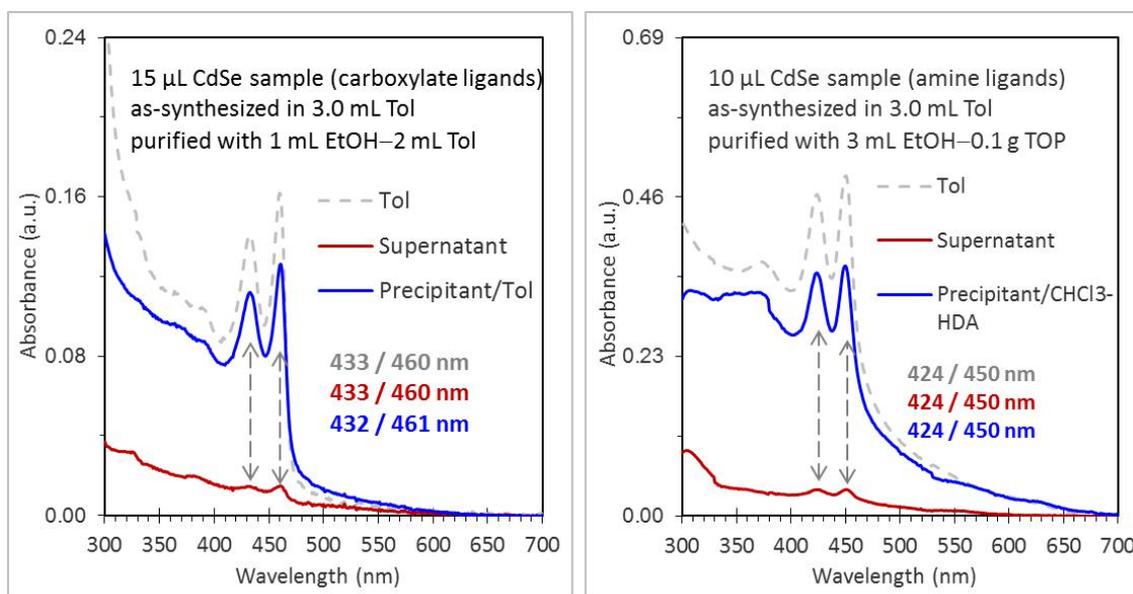


Figure S4-4. (Left) Absorption spectra of our carboxylate passivated CdSe NCs (15 μL) in 3.0 mL toluene, as-synthesized (dashed grey trace) and purified (with 1 mL EtOH – 2 mL Tol) (blue trace). (Right, for comparison) Absorption spectra of amine passivated CdSe NCs (10 μL , Batch Figure S1-1 (Ref 29)) as-synthesized in 3.0 mL of toluene (dashed grey trace) and purified (with 3 mL EtOH – 0.100 g TOP) in the mixture of CHCl_3 and HDA (blue trace). For the both types of CdSe NCs, the spectra collected from their supernatants (red traces) are presented for comparison. Clearly, the NCs left in the supernatant (red traces) exhibited a similar absorption doublet feature as the precipitant (blue traces) and the as-synthesized NCs (dashed grey traces).

Table S3. Summary of the characterization by optical absorption and TEM

Absorption spectra ^a	TEM	Purification ^b	TEM Dispersion
Fig 1a/Tol	Fig 1b (0D)	No	Hexane
Fig S1-4 (right, red T)	Fig 1e (2D)	Yes	CHCl ₃ – HDA/Soni
Fig S2-1 (right, grey T)	Fig 2b (0D)	No	Hexane
Fig 2a / S2-1 (left, blue T)	Fig 2e (2D)	Yes	CHCl ₃ – HDA/Soni
Fig 3a / S3-1 (blue T)	Fig 3b (0D)	No	Hexane
Fig S4-2 (top-left)	Fig 4a (0D)	Yes – CH ₃ CN	Toluene
Fig S4-2 (top-right)	Fig 4c (2D)	Yes – EtOH	Toluene

^a T represents trace. ^b When purification was applied, the sample is purified 3 time in 3.0 mL of corresponding solvent.

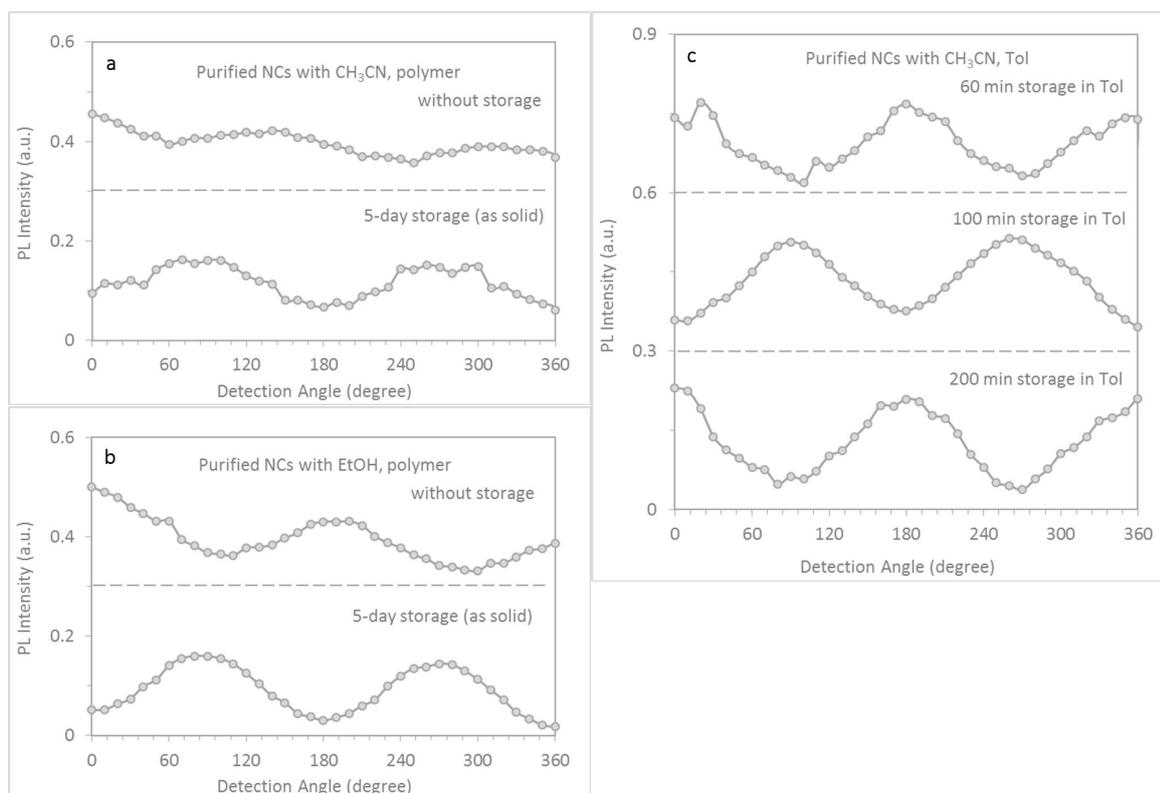


Figure S5-1. The dependence of PL intensity on detection angle (offset) of the CdSe NCs after purification with CH_3CN or EtOH and mixed with polymer, as well as after purification with CH_3CN and dispersed in toluene. The purification was carried out with either 2Tol – 1 CH_3CN (a and c) or 2Tol – 1EtOH (b). A sinusoidal function fitting suggests a polarization factor of 0.110 (a-bottom trace), 0.088 (b-top trace), and 0.142 (b-bottom trace), 0.138 (c-60 min), 0.162 (c-100 min) and 0.202 (c-200 min). The detection angle dependence increased along with storage for both the polymer films (a and b) and for the Dispersion c. For the present study, the self-assembly process leading to our TEM observed self-assembled NCs has been mainly taking place in dispersion. We do not address the possible evaporation-induced self-assembly process (during TEM sample preparation), with our TEM grid preparation carried out in a fume-hood for accelerated solvent evaporation.

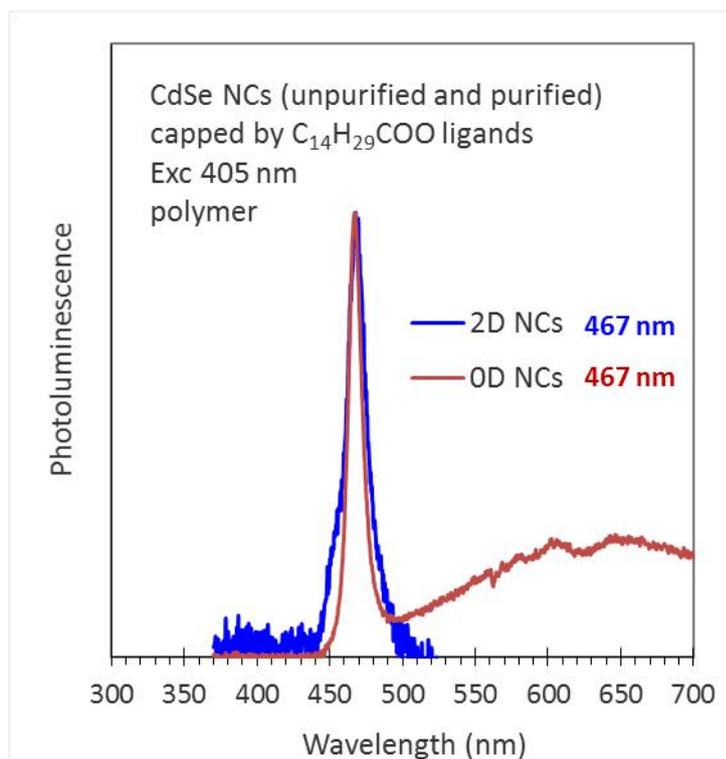


Figure S5-2. The raw data for Figure 5 (right).

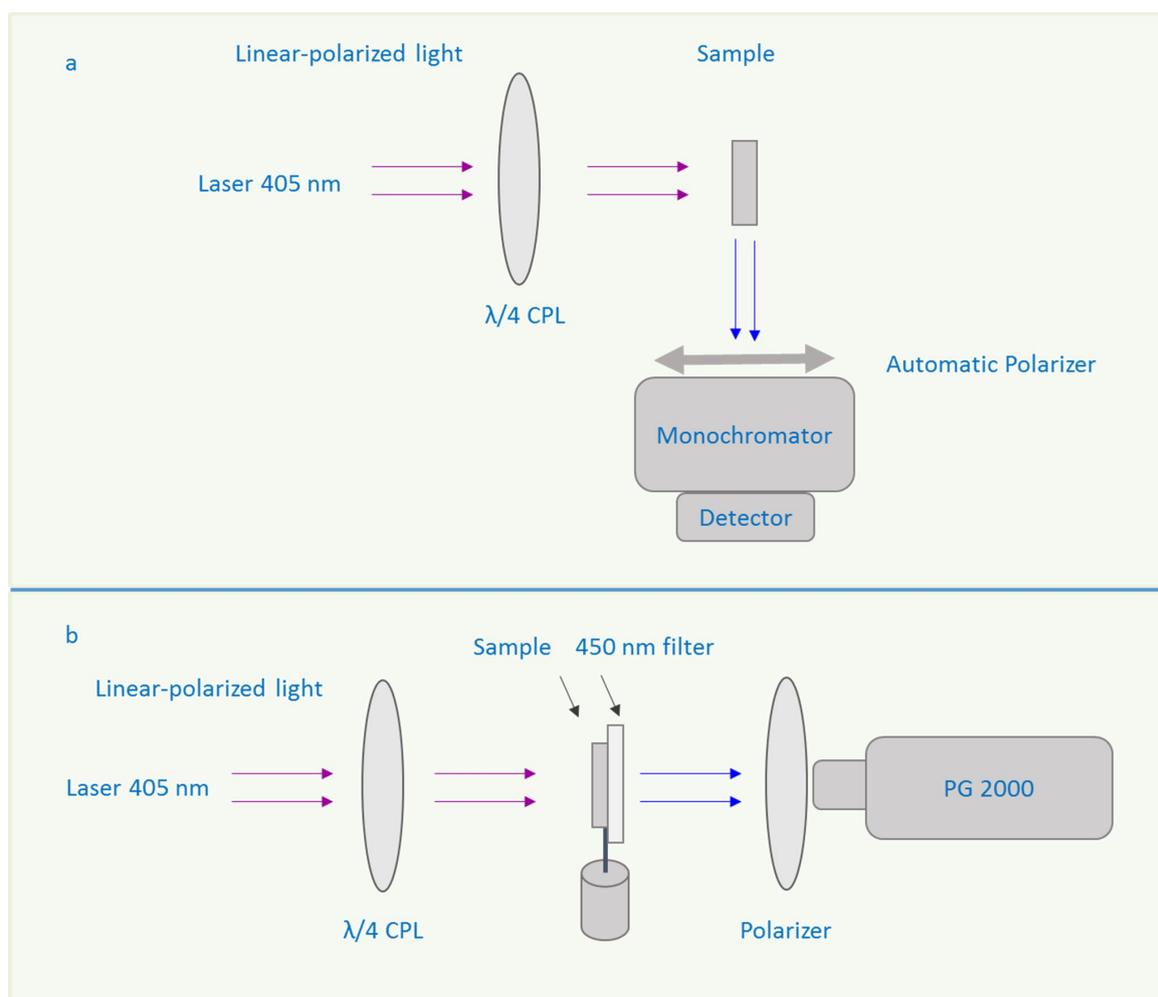


Figure S5-3. A $\lambda/4$ circular polarization lens (CPL) was placed between the excitation laser and the sample holder. (a) After the sample, an automatic polarizer was located before a monochromator (R928). The detector was used to collect the polarized emission, by control the automatic polarizer in the angle range of 0° to 360° . (b) A 450 nm highpass filter (which allows longer wavelength light through) was placed after the sample holder, followed by a polarizer which was able to rotate from 0° to 360° . The detector was a spectrometer (PG 2000).