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Supporting Information

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Isolation of the Magic-Size CdSe Nanoclusters $[(CdSe)_{13}(n\text{-octylamine})_{13}]$ and $[(CdSe)_{13}(\text{oleylamine})_{13}]$**

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Materials. *n*-Octylamine (*n*-OA) was obtained from Aldrich (+99%) and Alfa Aesar (99%), selenourea (99.9%, metal basis) from Alpha Aesar, $Cd(OAc)_2{\cdot}2H_2O$ from Aldrich, trioctylphosphine (TOP) from Sigma-Aldrich (97%), and oleylamine (or cis-9-octadecenylamine) from TCI (> 40.0% by GC) and Sigma-Aldrich (technical grade, 70%). All were used as received, and stored under N_2.Toluene from Sigma-Aldrich (CHROMASOLV®, for HPLC, ≥ 99.9%) was purged with dry N_2 for at least 1 h and stored under N_2 prior to use.

Analyses. Elemental analyses (C, H, N) were obtained from Galbraith Laboratories, Inc. (Knoxville, TN). The analysis by Rutherford backscattering spectrometry was provided by the Characterization Facility at the University of Minnesota (Minneapolis, MN). UV-visible spectra were obtained from a Perkin Elmer Lambda 950 UV/Vis spectrometer. IR spectra were obtained from a Perkin Elmer Spectrum BX FT-IR System. The LDI mass spectra were recorded on a Bruker UltrafleXtreme MALDI-TOF/TOF mass spectrometer. No matrix was employed in these mass-spectral analyses.

Synthesis of $[(CdSe)_{13}($*n*-octylamine$)_{13}]$.[1] All synthetic procedures were conducted under dry N_2.Cadmium acetate dihydrate $[Cd(OAc)_2{\cdot}2H_2O]$ (65 mg, 0.24mmol) was dissolved in *n*-octylamine (*n*-OA, 5.6g, 0.043mol) in a septum-capped Schlenk tube and heated in a70-°C oil bath for 1h. Selenourea (52 mg, 0.42mmol) was dissolved in *n*-OA (1.2 g, 0.0093mol) in the glove box, and then sonicated in a bench-top sonicator for dissolution.

The selenourea solution was injected into the $Cd(OAc)_2$ solutionat room temperature (20-25 ^{o}C) without stirring. During the first hour, the reaction mixture underwent a change from colorless (0 min) to a cloudy greenish-yellow. Some brown precipitate also formed. After another 5-20 h under ambient conditions, a white precipitate formed under a light-red supernatant.

The reaction mixture was subsequently heated at 70^{o}C in an oil bath for 1h. During this time, the solution turned dark red and a small amount of black or gray precipitate was mixed in with the white precipitate. The black solid and red solution were the byproduct elemental selenium, which was subsequently converted to TOP=Se by addition of TOP. TOP (0.5-1.0 mL) was injected into the reaction mixture, whereupon the red supernatant quickly turned clear and colorless, and the remaining precipitate was white.

The white precipitate was centrifuged in a bench-top centrifuge (700 *g*) for 5 min, and the supernatant was discarded. The white slush so obtained was washed with a TOP solution (10 mL, 5-10 % w/w in toluene). This purification process was repeated 5-6 times using a TOP-toluene solution. (To ensure removal of the last traces of TOP, pure toluene can be used in the last few purification cycles; however, the resulting product is less thermally stable toward nanocluster growth.) The residual solvent was removed in vacuo, leaving [$(CdSe)_{13}$(*n*-octylamine)$_{13}$] as a white slushy solid (75 mg, 0.018 mmol, 95.9%). Anal.Calcd for [$(CdSe)_{13}$(*n*-octylamine)$_{13}$]: C, 29.97; H, 5.97; N, 4.37. Found, C, 30.89; H, 5.84; N, 4.57. All values are given as percentages. UV-vis (toluene) λ_{max}, nm (logε): 312 (3.35), 335 (4.28), 350 (4.27).

The purification procedure in the paragraph above can be applied to the white precipitate before or after the heating step. To optimize the stability of [$(CdSe)_{13}$(*n*-octylamine)$_{13}$], we typically store the [$(CdSe)_{13}$(*n*-octylamine)$_{13}$],TOP, toluene mixture obtained just prior to purification, and purify aliquots of this mixture as needed.

Dissolution of[$(CdSe)_{13}$(oleylamine)$_{13}$]. This procedure was conducted under an ambient, air atmosphere. An aliquot(ca. 0.02 mL, 5.09 × 10^{-5}mmol of [$(CdSe)_{13}$(*n*-octylamine)$_{13}$]) from the as-made [$(CdSe)_{13}$(*n*-octylamine)$_{13}$], TOP, toluene mixture was diluted into toluene (3 mL) in a small vial, to which oleylamine (0.5 mL, 1.06 × 10^{-3}mmol)was added. The mixture was sonicated for at least 5 h at room temperature. The resulting clear, colorless dispersion was free [$(CdSe)_{13}$(oleylamine)$_{13}$], which was used directly for further analyses. UV-vis (toluene) λ_{max}, nm: 312, 339, 350.

Isolation of [$(CdSe)_{13}$(oleylamine)$_{13}$]from ligand exchange. This procedure was conducted in air. An aliquot (ca. 3.00 mL, 7.63× 10^{-3}mmol of [$(CdSe)_{13}$(*n*-octylamine)$_{13}$]) from the as-made[$(CdSe)_{13}$(*n*-octylamine)$_{13}$], TOP, toluene mixture was centrifuged and the supernatant discarded. The residual solid was washed 3-5 times with toluene (3 mL each) to remove TOP, and the solid was redispersed in oleylamine (6 mL) and allowed to stand at room temperature without stirring for more than one week. The vial was manually shaken (10-15 s) once each day. In the first two days, some precipitate still remained at the bottom of the vial, which was bundled [$(CdSe)_{13}$(*n*-octylamine)$_{13}$]. As ligand exchange proceeded, the precipitate gradually diminished, eventually leaving a solution with a small amount of white slush. After more than one week, the mixture was centrifuged (700 *g*, 30 min) and the supernatant discarded. The white slush so obtained was washed with toluene (3 mL), the mixture centrifuged, and the supernatant discarded. This purification process was repeated 5-7 times. The residual solvent was removed *in vacuo*, leaving [$(CdSe)_{13}$(oleylamine)$_{13}$] as a white slushy solid. Anal.Calcd for [$(CdSe)_{13}$(oleylamine)$_{13}$]:C, 47.04; H, 8.06; N, 3.05. Found, C, 47.25; H, 8.34; N, 4.60.UV-vis (toluene) λ_{max}, nm: 312, 339, 350.

Direct synthesis of [$(CdSe)_{13}$(oleylamine)$_{13}$]. All synthetic procedures were conducted under dry N_2.Cadmium acetate dihydrate [$Cd(OAc)_2\cdot 2H_2O$] (65 mg, 0.24mmol) was dissolved in oleylamine (2.0 g, 7.48 mmol) in a septum-capped Schlenk tube and heated in a70°C oil bath for 1h. Selenourea (50 mg, 0.41mmol) was dissolved in oleylamine (6.8 g, 0.025mol) in the glove box, and then sonicated in a bench-top sonicator for dissolution. The selenourea solution was injected into the $Cd(OAc)_2$ solutionat room temperature (20-25 ^{o}C) without stirring. The color changed from colorless to light yellow in one minute, and then turned to cloudy orange after 200 minutes. After one week, a white precipitate formed under a red supernatant. The purification procedure was the same as that used in the synthesis [$(CdSe)_{13}$(*n*-octylamine)$_{13}$] (see above). After washing by toluene for more than 5 times, the residual solvent was removed in vacuo, leaving [$(CdSe)_{13}$(oleylamine)$_{13}$] as a white slushy solid (97 mg, 0.016mmol, 86.6%). Anal.Calcd for [$(CdSe)_{13}$(oleylamine)$_{13}$]: C, 47.04; H, 8.06; N, 3.05.UV-vis (toluene) λ_{max}, nm: 310, 338,349.

LDI MS analysis. Using a spatula, the viscous $(CdSe)_{13}$ sample was smeared directly onto a 384-position stainless-steel MALDI plate. The sample was left to dry for several minutes and no matrix was applied. All MS experiments were performed on an UltrafleXtreme^{TM} MALDI TOF TOF (Bruker, Billerica, MA) in both the linear and reflectron modes. External calibration of the plate was done with insulin. Detailed parameters are listed in Table S1.

Measurement of [$(CdSe)_{13}$(oleylamine)$_{13}$] growth kinetics in the presence of small, polar ligands. These procedures were performed at room temperature in air. An aliquot (ca.0.10 mL, 1.70×10^{-6}mmol of[$(CdSe)_{13}$(oleylamine)$_{13}$)] from the dissolution of

$[(CdSe)_{13}(oleylamine)_{13}]$ was diluted into toluene (2 mL) in a quartz cuvette. Various quantities of MeOH, *i*-propanol, or acetone were then measured into a separate vial (0.06 mL, 0. 13 mL, 0.25 mL, and 0.5 mL for methanol; 0.50 mL, 0.75 mL, 1.00 mL for *i*-propanol or acetone), and quantitatively transferred into the cuvette. The UV-visible spectrometer was configured to record the absorbance value at 350 nm at 10-s intervals for 1800 s at room temperature. During data collection the cuvette was stirred by a small stirring bar.

The data collected at 350 nm were plotted in Figure 6 as $-\ln[(A_t-A_b)/(A_0-A_b)]$ vs. time, where A_t is the absorbance at time t, A_0 is the absorbance at t = 0 s, and A_b is the background absorbance measured at t = 1800 s. The slopes were extracted by linear least-squares fitting using Origin software (http://originlab.com/). The errors in the reported k_{obs} and $t_{1/2}$ values were propagated from the standard deviations in the slopes from individual linear least-squares fits.

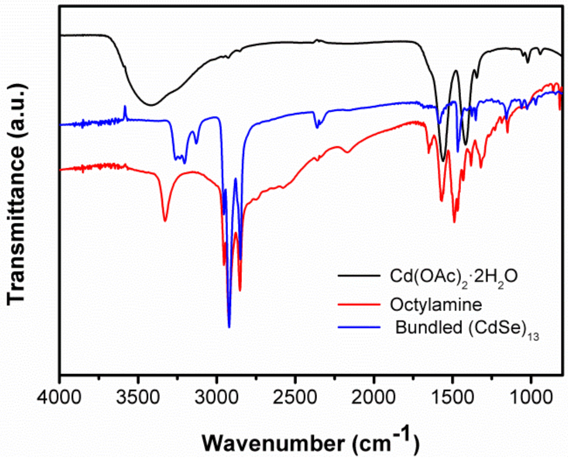

Figure S1. IR spectra from KBr pellets of the starting material Cd(OAc)$_2$·2H$_2$O (black curve), the solvent *n*-octylamine (red curve), and the bundled [(CdSe)$_{13}$(*n*-octylamine)$_{13}$] (blue curve).

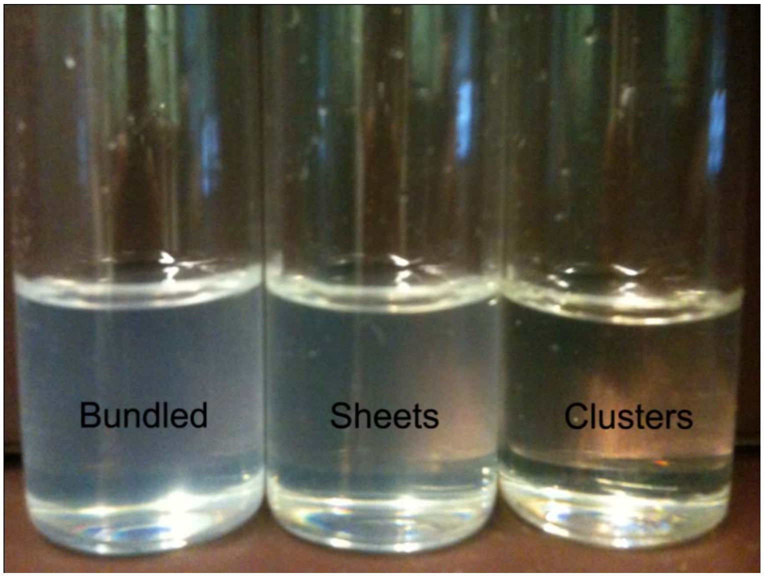

Figure S2. A photograph of a dispersion of bundled [$(CdSe)_{13}$(*n*-octylamine)$_{13}$] (left), a dispersion of [$(CdSe)_{13}$(*n*-octylamine)$_x$(oleylamine)$_{13-x}$] sheets (center), and a solution of [$(CdSe)_{13}$(oleylamine)$_{13}$] nanoclusters.

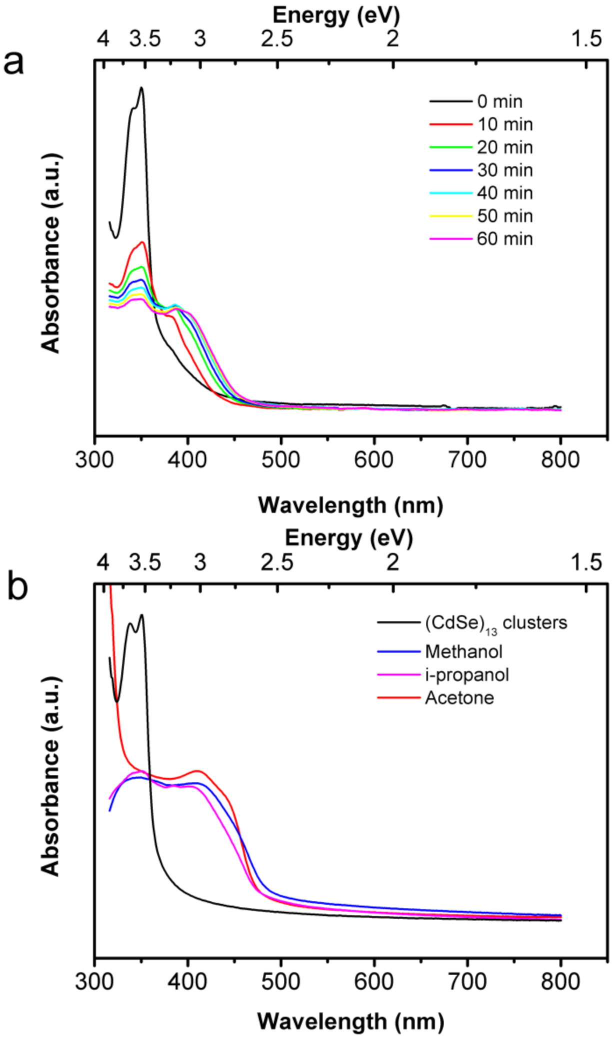

Figure S3. UV-visible spectral changes occurring during nanocluster growth. (a) Spectra as a function of time after addition of MeOH. (b) A spectrum of the starting [$(CdSe)_{13}(oleylamine)_{13}$] nanoclusters (black) and those at the conclusion of nanocluster growth induced by MeOH (blue), *i*-propanol (magenta), and acetone (red).

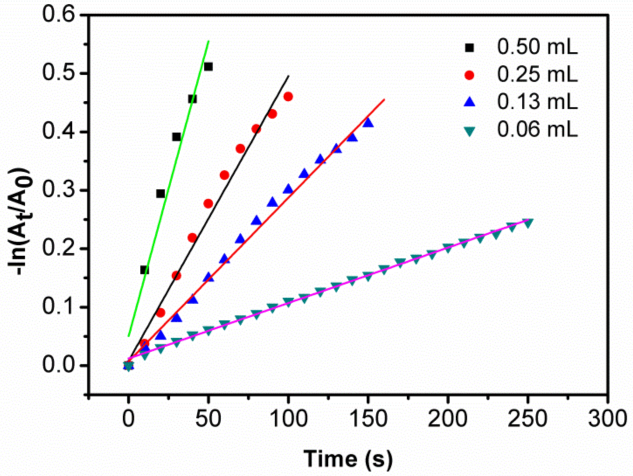

Figure S4. Initial $[(CdSe)_{13}(oleylamine)_{13}]$ nanocluster growth rates as a function of the amount of added MeOH. The slopes are 1.01×10^{-2} s^{-1} (green line, black points), 4.87×10^{-3} s^{-1} (black line, red points), 2.80×10^{-3} s^{-1} (red line, blue points), and 9.50×10^{-4} s^{-1} (magenta line, cyan points).

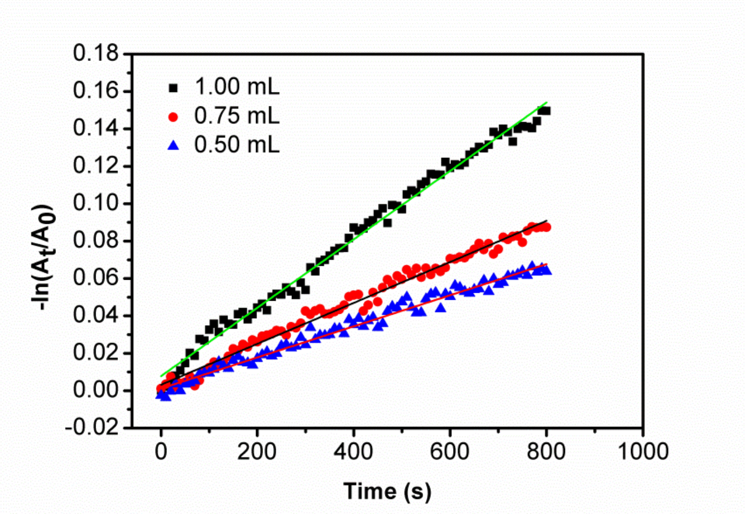

Figure S5. Initial [$(CdSe)_{13}(oleylamine)_{13}$] nanocluster growth rates as a function of the amount of added *i*-propanol. The slopes are 1.83×10^{-4} s^{-1} (green line, black points), 1.09×10^{-4} s^{-1} (black line, red points), and 8.32×10^{-5} s^{-1} (red line, blue points).

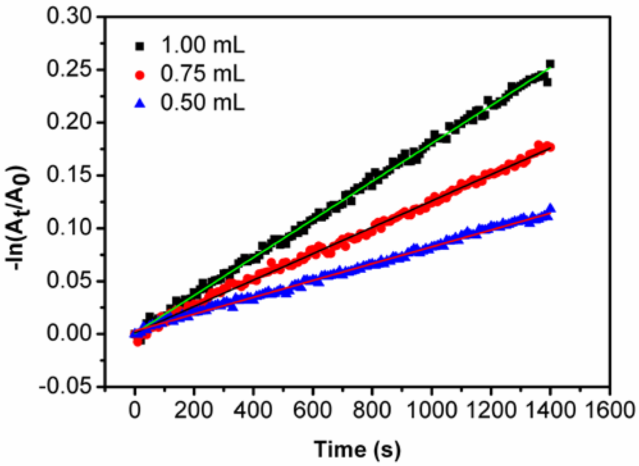

Figure S6. Initial $[(CdSe)_{13}(oleylamine)_{13}]$ nanocluster growth rates as a function of the amount of added acetone. The slopes are 1.80×10^{-4} s^{-1} (green line, black points), 1.25×10^{-4} s^{-1} (black line, red points), and 7.96×10^{-5} s^{-1} (red line, blue points).

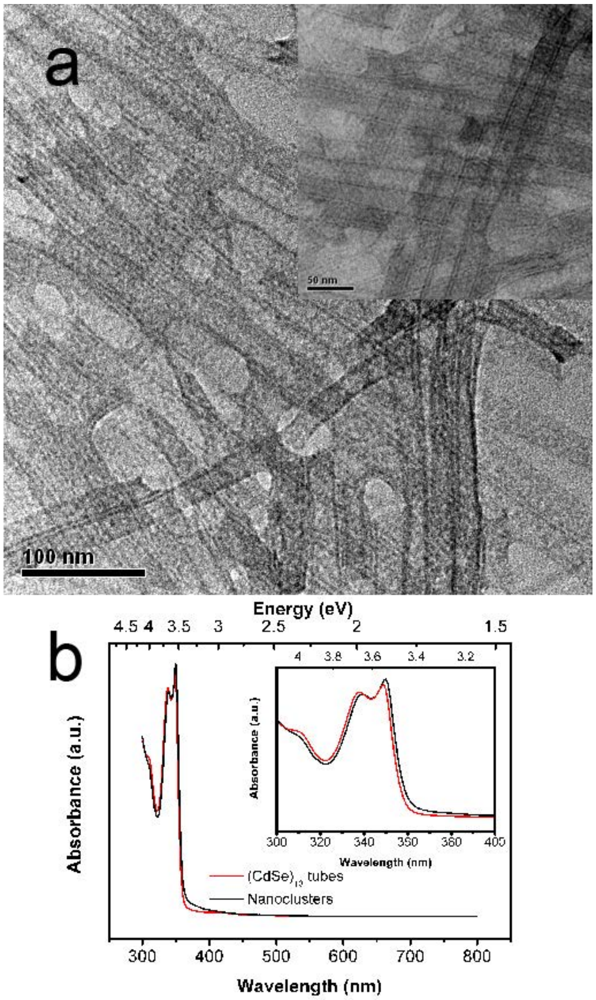

Figure S7.TEM images and UV-visible spectra of [$(CdSe)_{13}$$(oleylamine)_{13}$] nanoclusters. (a) TEM images at two magnifications of [$(CdSe)_{13}$$(oleylamine)_{13}$] obtained from the direct synthesis in oleylamine solvent. (b) Spectral comparison of [$(CdSe)_{13}$$(oleylamine)_{13}$] obtained from the direct synthesis (red curves) and by ligand exchange from [$(CdSe)_{13}$(*n*-$octylamine)_{13}$] (black curves).

Table S1. Parameters used in the LDI MS experiments.

Delay	57312 ns	Laser Attenuation	55
PIE delay	120 ns	Laser RepRate	1000 Hz
Electronic Gain	100 mV/fullscale	IS voltage 1	25 kV
SampleRate	0.25ns (4 GHz)	IS voltage 2	22.5 kV
Polarity	Positive	Lens voltage	7.75 kV
URefDet	2.367 kV	Reflector voltage 1	26.45 kV
# Shots	20000	Reflector voltage 2	13.4 kV