The Magic-Size Nanocluster $(CdSe)_{34}$ as a Low-Temperature Nucleant for Cadmium Selenide Nanocrystals; Room-Temperature Growth of Crystalline Quantum Platelets

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Analyses. Elemental analyses (C, H, N) were obtained from Galbraith Laboratories, Inc. (Knoxville, TN). UV-visible spectra were obtained from a Perkin Lambda 950 UV/Vis spectrometer. Photoluminescence (PL) spectra were obtained from a home-built fluorimeter. The XRD patterns were obtained from a Rigaku Dmax A vertical powder diffractometer with Cu Kα radiation (λ=1.5418 Å). Low-resolution TEM images were obtained from a JEOL 2000FX microscope operating at 200 KV. High-res TEM images were obtained from a JEOL JEM-2100F field emission (FE)- scanning transmission electron microscope. The LDI mass spectra were recorded on an ABI DE-STR MALDI TOF mass spectrometer.

The ligand-ratio study used an Agilent 7200 GC/q-TOF mass spectrometer (Agilent Technologies, Santa Clara, CA) in positive CI (chemical ionization) mode with methane as the CI reagent gas. Spectra were collected from 50-750 m/z. The samples for the calibration curve were introduced into the q-TOF MS through the GC column (Agilent HP-5MS) programmed at 80 ^{o}C for 2 min, 80-300 ^{o}C at 10 ^{o}C /min, and held at 300 ^{o}C for 6 min with 1.0 μl introduction and a split ratio of 3:1. Mass spectra of the [$(CdSe)_{34}$(*n*-octylamine)$_{16}$(di-*n*-pentylamine)$_2$] samples were obtained by introduction via a thermal-desorption probe (TDP) with a short-fused silica transfer line and no column. The thermal profile of the probe was programmed with an initial hold at 40 ^{o}C for 2 min, followed by 40-300 ^{o}C at 10 ^{o}C /min, and then a hold at 300 ^{o}C for 8 min.

Analytical-Sample Preparation. For TEM analyses of CdSe QPs, an aliquot from a reaction mixture (0.1 mL) was diluted into toluene (3-5 mL) in air. The resulting dispersion was centrifuged in a bench-top centrifuge (700 *g*) for 5 min. The colorless supernatant was discarded, and the yellowish slush was re-dispersed into 3-5 mL toluene. This process was repeated an additional 4 times to ensure complete removal of TOP and the amine cosolvents. The slushy QP precipitate was dispersed in toluene (5 mL) for subsequent TEM analysis. TEM grids were dipped into the dispersion to prepare the TEM specimen. The TEM specimens were stable in air for at least one week.

For XRD analyses of CdSe QPs, a large aliquot from a reaction mixture (5 mL) was diluted into toluene (3-5 mL) in air. The purification process was the same as above, but the cycle was conducted a total of 3 times. The resulting yellow slushy QP precipitate was dispersed in toluene (0.5 mL). This concentrated dispersion was transferred onto a glass XRD slide and dried in a fume hood (10 min). XRD patterns were recorded immediately after sample preparation.

For UV-visible spectroscopy, a small aliquot from a reaction mixture (40 μL) was diluted into toluene (12.5mL) in air. The diluted solution (2.5 mL) was used for absorption analyses. In each spectroscopic analysis, toluene was used in the reference cuvette. Absorption spectra were measured on the day of sample preparation.

For PL analyses of CdSe QPs, the reaction mixture was heated to 70 ^{o}C for 40 min prior to analysis. Toluene was purged with dry N_2 for at least 1 h, stored under N_2, and dried over molecular sieves prior to use. All sample-preparation processes were performed under N_2 at room temperature. In a typical process, a small aliquot (40μL) from an annealed reaction mixture was diluted into an oleylamine-toluene solution (12% w/w, 12.5 mL). The dilute solution (2.5 mL) was transferred into a quartz cuvette, and the cuvette was then sealed by parafilm. An absorption spectrum was obtained immediately from the freshly prepared sample, followed by the collection of a PL spectrum within 10 min after collection of the absorption spectrum. The excitation wavelength for PL spectroscopy was set at 2.95 eV (420 nm). An oleylamine-toluene solution (12% w/w) was used in the reference cuvette.

Mass-spectral Determination of the Ligand Ratio in [(CdSe)$_{34}$(*n*-octylamine)$_{16}$(di-*n*-pentylamine)$_2$]. A calibration curve for the instrument response was obtained as follows. Stock solutions (1 mM) of *n*-octylamine and di-*n*-pentylamine were prepared in acetonitrile. These stock solutions were diluted to a total concentration of 200 μM for integer ligand ratios of 1:9 to 9:1 of *n*-octylamine to di-*n*-pentylamine. Mass spectra in the CI mode (CH_5^+) were obtained in triplicate for each solution after on-line GC separation. Four ion signals were retrieved as extracted-ion chromatograms (EICs) in the range of *m*/*z* = 100-200, corresponding to *n*-octylamine, di-*n*-pentylamine, and two isomers of di-*n*-pentylamine. Signal for the ions of *m*/*z* 130.1590, 100.1121, 156.1747, and 186.2216, which were the $[M + H]^+$ of octylamine, and the $[M + H - C_4H_{10}]^+$, $[M + H - H_2]^+$ and $[M + C_2H_5]^+$ of dipentylamine, respectively, were used to quantify the four analyses. The selected ions are derived from the target amines and have little contamination (< 2%), from other sources. *n*-Octylamine:dipentylamine signal ratios were determined from the *n*-octylamine and sum of the three dipentylamine signals at each concentration. The signal ratio plotted linearly against the concentration ratio, yielding the calibration plot.

Samples of [(CdSe)$_{34}$(*n*-octylamine)$_{16}$(di-*n*-pentylamine)$_2$] were subjected to mass-spectral analysis in the CI mode (CH_5^+) by the temperature-programmed desorption described earlier in the experimental section. The integrated signal ratio was determined to be 3.7 ± 0.24, corresponding to an actual ratio of 8.1 ± 0.5. Consequently the *n*-octylamine:di-*n*-pentylamine ligand ratio of 8:1 was used to fit the elemental-analysis data (see above), yielding the molecular formula $[(\mathrm{CdSe})_{34}(n\text{-octylamine})_{16}(\text{di-}n\text{-pentylamine})_{2}]$.

Table S1. Various combinations of primary and second amines used as co-solvents

Primary Amine	**Secondary Amine**	**Temperature**	**Thickness (nm)**
Phenethyl	NA	40 ^{o}C	1.4
n-propyl *n*-pentyl *n*-octyl *n*-dodecyl	ethyl	RT	1.8
n-propyl *n*-pentyl *n*-octyl	*n*-propyl	RT	1.8
n-propyl *n*-pentyl *n*-octyl	*n*-pentyl	RT	1.8
n-propyl *n*-pentyl *n*-octyl	*n*-octyl	RT	1.8
n-octyl	*n*-octyl	70 ^{o}C	2.2

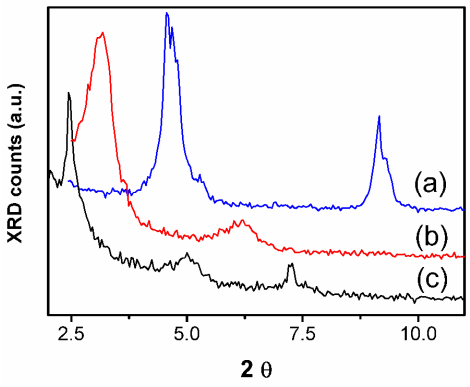

Figure S1. Low-angle XRD patterns of CdSe QPs synthesized in in diethylamine and various primary amine co-solvents. (a) *n*-pentylamine, (b) *n*-octylamine, (c) *n*-dodecylamine. These data demonstrate that the interlamellar *d* spacing within the template is determined by the primary amine, and thus that the top and bottom QP facets are passivated by the primary, rather than the secondary, amine.

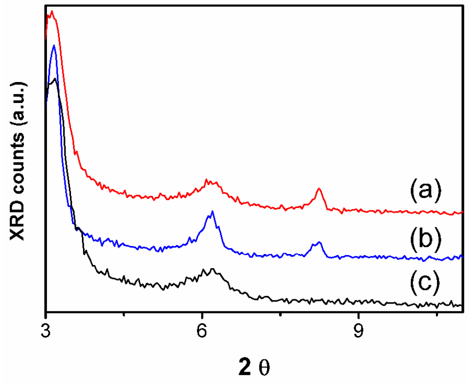

Figure S2. Low-angle XRD patterns of CdSe QPs synthesized in *n*-octylamine and various secondary amine co-solvents. (a) di-*n*-octylamine, (b) di-*n*-pentylamine, (c) diethylamine. These data demonstrate that the interlamellar *d* spacing within the template is not influenced by the secondary amine.

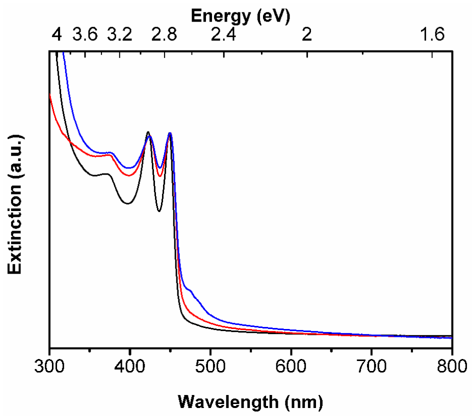

Figure S3. UV-visible extinction spectra in toluene dispersions of CdSe QPs synthesized in di-*n*-pentylamine and various primary amine co-solvents. Black curve: *n*-octylamine; blue curve: *n*-butylamine; red curve: *n*-propylamine.

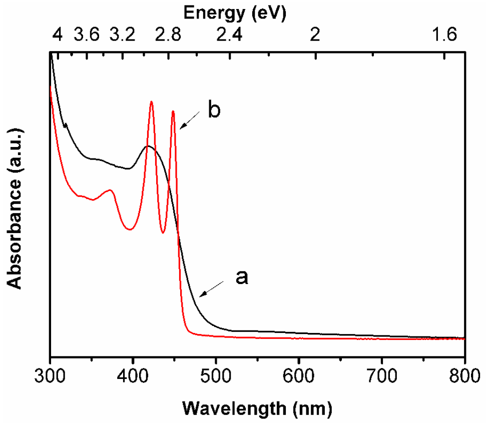

Figure S4. Spectral evolution upon transformation of $(CdSe)_{34}$ to 1.8-nm thickness CdSe QPs in an *n*-octylamine, di-*n*-octylamine co-solvent at room temperature. UV-visible extinction spectra of (a) $(CdSe)_{34}$ was observed after 1 h (black curve). (b) 1.8-nm thickness CdSe QPs (1.8-nm thickness) were observed after 2 days (red curve).

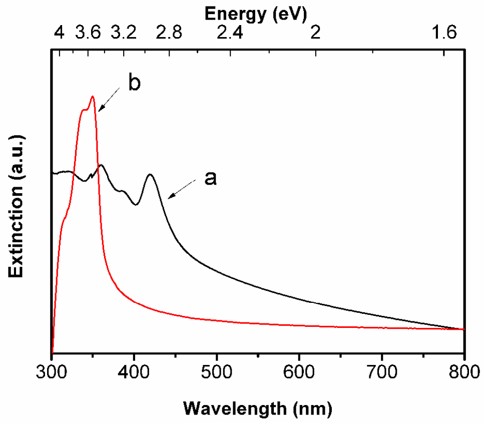

Figure S5. Spectral evolution upon transformation of $(CdSe)_{34}$ to $(CdSe)_{13}$ in *n*-propylamine and diethylamine co-solvent at 0 °C. UV-Visible extinction spectra of (a) $(CdSe)_{34}$ after 6 h (black curve). (b) Mixture of $(CdSe)_{34}$ and $(CdSe)_{13}$ after 1 week.

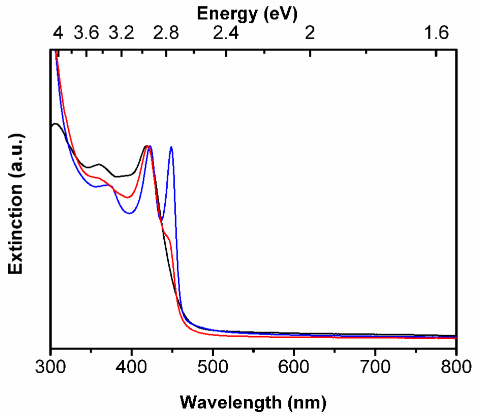

Figure S6. Spectral evolution upon transformation of $(CdSe)_{34}$ to CdSe QPs in an *n*-octylamine, di-*n*-pentylamine co-solvent. UV-visible extinction spectra of $(CdSe)_{34}$ at 0 °C (black curve) at time zero. A mixture of $(CdSe)_{34}$ and CdSe QPs was observed after 5 h (red curve). Fully transformed CdSe QPs were observed after 12 h (blue curve).

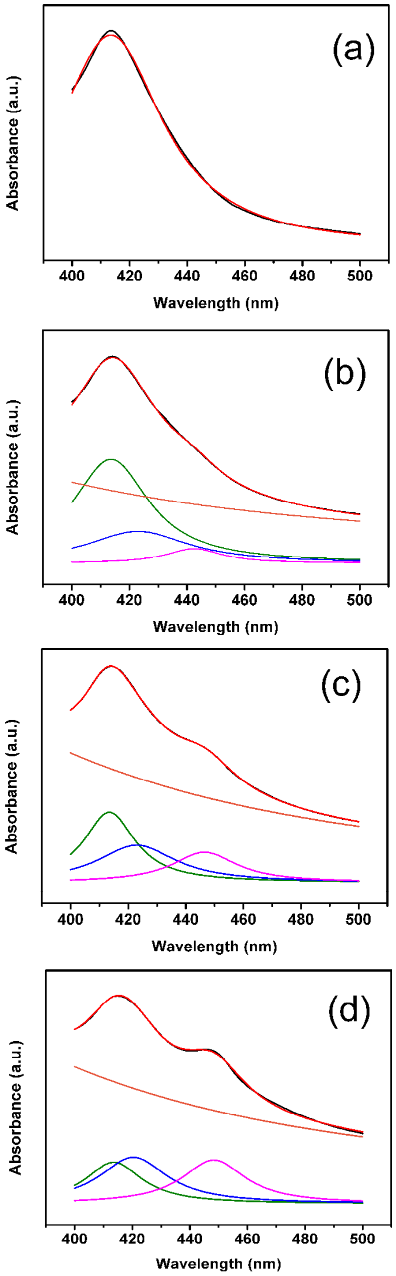

Figure S7. Curve fitting of the 418-nm absorption of $(CdSe)_{34}$, and the 423- and 448-nm absorptions of CdSe QPs observed during the conversion of $(CdSe)_{34}$ to CdSe QPs at room temperature at time (a) 0 h, (b) 5 h, (c) 10h, (d) 12h. In a-d the black curve is data, the red curve the fit, the orange curve the fitted background, and the green, blue, and magenta curves the fitted Lorentzians to the 418-, 423-, and 448-nm features, respectively. The areas of the Lorentzian fits were used in the kinetic analyses.

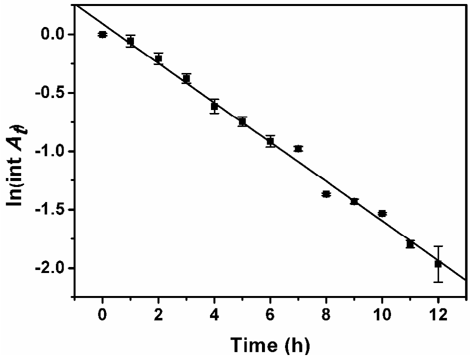

Figure S8. Kinetic data from conversion of $(CdSe)_{34}$ to CdSe QPs at room temperature. The first-order plot (black dots and curve) was constructed by monitoring decreasing of the integrated area of $(CdSe)_{34}$ absorbance at 418- nm derived from the curve fitting. A_t is the integrated area of $(CdSe)_{34}$ absorbance at 418-nm at time t.

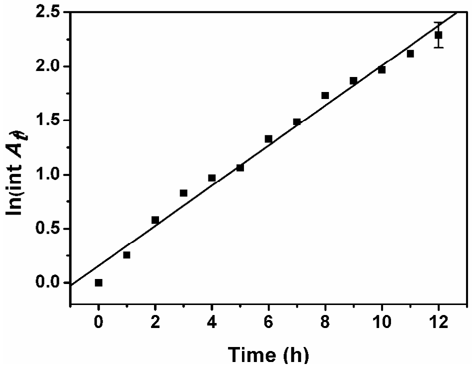

Figure S9. Kinetic data from conversion of $(CdSe)_{34}$ to CdSe QPs at room temperature. The first-order plot (black dots and curve) was constructed by monitoring increasing of the integrated area of the QP absorbance at 423- nm derived from the curve fitting. A_t is the integrated area of the QP absorbance at 423-nm at time t.

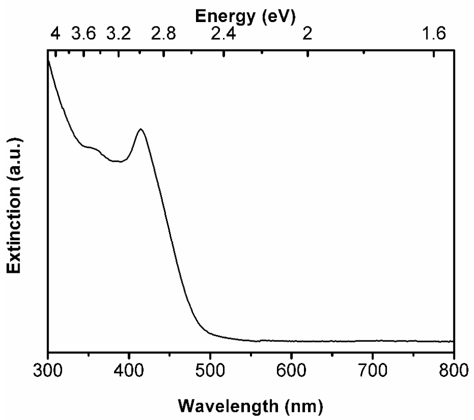

Figure S10. UV-visible extinction spectrum in toluene dispersion of isolated slushy, greenish-yellow [$(CdSe)_{34}$(*n*-octylamine)$_{16}$(di-*n*-pentylamine)$_2$] solid, prepared in *n*-octylamine and di-*n*-pentyalmine.

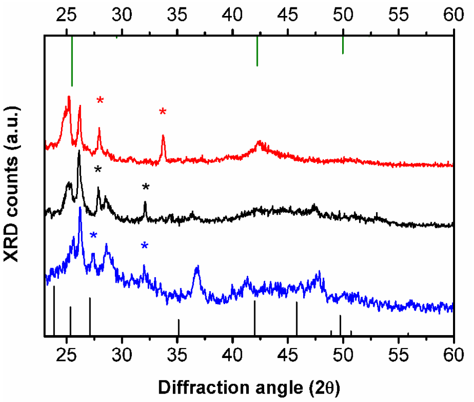

Figure S11. An XRD pattern of 1.4-nm thickness CdSe QPs (blue curve), 1.8-nm thickness CdSe QPs (black curve), and 2.2-nm thickness CdSe QPs (red curve). The black sticks are the peak positions for bulk CdSe in the wurtzite structure, and the green sticks are the peak positions for bulk CdSe in the zinc-blende structure. The indexed reflections for the wurtzite QPs are shifted to higher angle than in the bulk pattern because of the lattice contraction (see the text and ref. 22). The asterisks identify unassigned peaks.