

Supporting Information for

Anomalous emission shift of CdSe/CdS/ZnS quantum dots at cryogenic temperatures

Shaojie Liu, Yufei Shu, Meiyi Zhu, Haiyan Qin*, Xiaogang Peng

Key Laboratory of Excited-State Materials of Zhejiang Province and Department of Chemistry, Zhejiang University, Hangzhou, 310027, China

Corresponding to: hattieqin@zju.edu.cn

Section 1: Synthesis and Structural Characterizations

Chemicals and materials: Cadmium oxide (CdO, 99.99%), selenium powder (Se, 200 mesh, 99.999%), 1-octadecene (ODE, 90%), cadmium acetate dihydrate ($\text{Cd}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, >98%), oleic acid (OA, 90%), capric acid (HCA, 98%), sulfur powder (S, 200 mesh, 99.999%), zinc acetate dihydrate ($\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$, >99%) were purchased from Sigma-Aldrich. Toluene, methanol and ethanol were purchased from Sinopharm Reagents. All chemicals of analytical grade or higher were used as received without further purification.

Synthesis of CdSe core QDs: CdSe core QDs with the first exciton absorption peak at 550 nm were synthesized according to the methods in Ref. 1. Briefly, CdO (0.2 mmol) and stearic acid (0.5 mmol) mixed with 4 mL ODE were heated to 280 °C to get a colorless solution with argon protection. 0.1M of Se-suspension (Se-SUS) prepared by ultrasonic processing with Se powder and OED was injected swiftly into the solution at 250 °C. After 5-min reaction, Se-SUS was continually added into the solution at a speed of 0.2 mL/min until the first exciton absorption peak of the sample reached 550 nm. The sample purification and concentration determination can refer to Refs. 1 and 2, respectively.

Synthesis of CdSe/CdS core/shell QDs: Cd(Ac)₂·2H₂O (0.7 mmol), oleic acid (2.1 mmol), capric acid (0.7 mmol), purified CdSe core QDs (0.1 μmol) and ODE (4 mL) were added into a three-neck flask and heated to 260 °C with argon protection for 10 min. S-ODE solution (0.1 M) was added into the flask with a speed of 2 mL/h to epitaxially grow CdS shells on the CdSe cores. The reaction process was monitored by taking aliquots for UV-vis and TEM measurements.

Synthesis of CdSe/CdS/ZnS core/shell/shell QDs: Zn(Ac)₂·2H₂O (0.5mmol), oleic acid (1.2 mmol), capric acid (0.4 mmol), purified CdSe/CdS core/shell QDs (0.05 μmol) and ODE (4 mL) were added into a three-neck flask and heated to 290 °C with argon protection for 10 min. S-ODE solution (0.1 M) was added into the flask at a speed of 2 mL/h to epitaxially grow ZnS shells on the CdSe/CdS core/shell QDs. The thickness of the ZnS shells was monitored using UV-vis and TEM measurements.

Synthesis of CdSe/CdS/CdZnS/ZnS core/shell/shell/shell QDs: Zn(Ac)₂·2H₂O (0.5mmol), oleic acid (1.5 mmol), purified CdSe/CdS core/shell QDs (0.05 μmol) and ODE (4 mL) were added into a three-neck flask and heated to 290 °C with argon protection for 10 min. S-ODE solution (0.1 M) and cadmium oleate-ODE solution (Cd(OI)₂, 0.05 M) were added into the flask at a speed of 2 mL/h to epitaxially grow CdZnS shell on CdSe/CdS core/shell QDs. The thickness of the CdZnS shell was monitored by TEM. After the CdZnS shell reached the desired thickness, stop the injection of the cadmium oleate-ODE solution to epitaxially grow ZnS shell. When the QDs reached the desired size, reduce the temperature below 200 °C to stop the reaction.

Structural characterizations of QDs: The QDs were deposited on ultrathin carbon films supported by copper grids. TEM images and selected area electron diffraction (SAED) patterns were collected by a Hitachi 7700 transmission electron microscope under 100 kV.

Section 2: Optical measurements

Optical measurements of QD solution at room temperature: The samples were diluted in toluene with an absorbance below 0.2 at the first exciton absorption peak to avoid self-absorption of the sample. UV-vis absorption spectra were taken on an Agilent Technologies Cary 4000 spectrophotometer. Steady-state PL spectra were recorded using an Edinburgh Instruments FLS920 spectrometer. Time-resolved PL spectra were measured using a time-correlated single-photon counting (TCSPC) module of the same spectrometer with a 405 nm picosecond pulsed laser at a repetition frequency of 1 MHz.

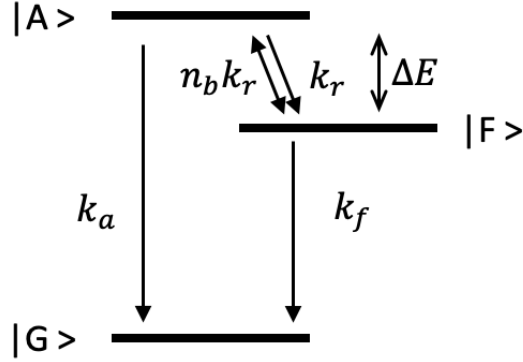
Temperature-dependent optical measurements: The QD samples diluted with PMMA (2 wt. %)/toluene solution were spin-casted onto clean quartz substrates for temperature-dependent optical measurements. The concentrations of QD solution were $\sim 1 \mu\text{M}$ and $\sim 10 \text{ pM}$ for ensemble and single-dot measurements respectively.

Optical measurements at room temperature for ensemble QD solid films and single QDs are performed using an inverted epi-fluorescence microscope system (Olympus IX83) equipped with an oil immersion objective ($\text{NA} = 1.49$) and suitable spectral filters. The PL signals are recorded by an EMCCD camera (Andor, iXon) to generate a PL intensity trace for a given QD. All PL intensity traces are subtracted by corresponding backgrounds. PL spectra are recorded by another EMCCD with a monochromator (Andor, 193i/iXon). The PL decay curves of single QDs are collected by an avalanche photodiode (PicoQuant, t-SPAD) and a TCSPC module (Becker & Hickl GmbH, DPC-230). For the measurements with different atmospheres, air and pure argon are channeled into the sample chamber respectively at a speed of $\sim 200 \text{ mL/min}$.

Optical measurements at low temperature were carried out using a closed cycle helium cryostat (Attocube Dry 2100 with attoCFM I optical head) with a far-field epifluorescence imaging microscope light-path system. The sample was mounted on the cold chamber and cooled to 1.8K. The excitation laser was reflected by a beam splitting dichroic mirror (Semrock, Di02-R561) and focused by a microscope objective ($\text{NA} = 0.82$, $\text{WD} = 0.35 \text{ mm}$) to a $\sim 1 \mu\text{m}$ sized spot on the sample. The PL signals were collected by the same objective, transmitted through the dichroic

mirror, and passed through a long-pass filter (Thorlabs, FELH0550) to remove the stray excitation light. The PL signals were focused onto the entrance slit of a spectrometer equipped with 150g/mm grating (Princeton Instrument, SP2750) and recorded with a liquid N₂ cooled CCD camera (Princeton Instrument, PyLoN-400). The PL signals can also be coupled into a fiber-based single photon avalanche photodiode (APD, Excelitas, SPCM-AQRH-16-FC) for transient PL measurements or into two APDs for second-order photon correlation measurements with a Hanbury Brown-Twiss setup. The 450 nm laser (Advanced LASER Diode Systems, PiL044X) with switchable continuous-wave mode and pulsed mode was applied as the excitation light source for the steady-state and transient PL measurements, respectively. The excitation power for all spectroscopic measurements is far below emission saturation and within the single-exciton regime. The typical excitation power density of the pulsed laser is 25 $\mu\text{J}/\text{cm}^2$ ($\langle N \rangle \sim 0.1$) in this work, unless otherwise noted.

Section 3: Dynamics of the three-level system³⁻⁵



Reproduced Figure 2b in the main text. Schematic diagram of a three-level system.

In the three-level model above, $|G\rangle$ is the ground state of exciton. $|A\rangle$ ($|F\rangle$) is the bright (dark) state, transition from which to the ground state is spin allowed (forbidden) with a radiative recombination rate of k_a (k_f). We assume the radiative yields of $|A\rangle$ and $|F\rangle$ are unity. ΔE is the energy difference between $|A\rangle$ and $|F\rangle$. k_r is the spontaneous transition rate from $|A\rangle$ to $|F\rangle$ at 0 K. $n_b k_r$ is the transition rate between $|A\rangle$ and $|F\rangle$ due to thermal mixing, where n_b is the Bose-Einstein phonon number at temperature T :

$$n_b = \frac{1}{e^{\Delta E/k_B T} - 1} \quad (S1)$$

where k_B is the Boltzmann constant.

The rate equations of populations of the three levels $A(t)$, $F(t)$ and $G(t)$ can be written as:

$$\frac{d}{dt} \begin{pmatrix} A(t) \\ F(t) \\ G(t) \end{pmatrix} = \begin{pmatrix} -(n_b + 1)k_r - k_a & n_b k_r & 0 \\ (n_b + 1)k_r & -n_b k_r - k_f & 0 \\ k_a & k_f & 0 \end{pmatrix} \begin{pmatrix} A(t) \\ F(t) \\ G(t) \end{pmatrix} \quad (S2)$$

The initial populations of $|A\rangle$, $|F\rangle$ and $|G\rangle$ can be written as:

$$\begin{pmatrix} A(0) \\ F(0) \\ G(0) \end{pmatrix} = \begin{pmatrix} p \\ 1 - p \\ 0 \end{pmatrix} \quad (S3)$$

The solution of this system of rate equations is

$$A(t) = a_1 e^{-\frac{t}{2}(\Lambda + \Delta)} + a_2 e^{-\frac{t}{2}(\Lambda - \Delta)} \quad (S4)$$

$$F(t) = f_1 e^{-\frac{t}{2}(\Lambda + \Delta)} + f_2 e^{-\frac{t}{2}(\Lambda - \Delta)} \quad (S5)$$

$$G(t) = 1 - \left[(a_1 + f_1)e^{-\frac{t}{2}(\Lambda + \Delta)} + (a_2 + f_2)e^{-\frac{t}{2}(\Lambda - \Delta)} \right] \quad (\text{S6})$$

where

$$\Lambda = k_a + k_f + k_r + 2k_r n_b \quad (\text{S7})$$

$$\Delta = \sqrt{k_a^2 - 2k_a k_f + 2k_a k_r + k_f^2 - 2k_f k_r + 4k_r^2 n_b^2 + 4k_r^2 n_b + k_r^2} \quad (\text{S8})$$

$$a_1 = \frac{1}{2\Delta} [p\Delta + p(k_a - k_f + k_r) - (1 - p)2k_r n_b] \quad (\text{S9})$$

$$a_2 = \frac{1}{2\Delta} [p\Delta - p(k_a - k_f + k_r) + (1 - p)2k_r n_b] \quad (\text{S10})$$

$$f_1 = \frac{1}{2\Delta} [(1 - p)\Delta - (1 - p)(k_a - k_f) - (1 + p)k_r - 2pk_r n_b] \quad (\text{S11})$$

$$f_2 = \frac{1}{2\Delta} [(1 - p)\Delta + (1 - p)(k_a - k_f) + (1 + p)k_r + 2pk_r n_b] \quad (\text{S12})$$

The observed emission decay $I(t)$ caused by radiative transitions from $|A\rangle$ and $|F\rangle$ to $|G\rangle$ can be written as

$$I(t) = k_a * A(t) + k_f * F(t) = C_1 e^{-k_{Fast}t} + C_2 e^{-k_{Slow}t} \quad (\text{S13})$$

where

$$C_1 = a_1 k_a + f_1 k_f \quad (\text{S14})$$

$$C_2 = a_2 k_a + f_2 k_f \quad (\text{S15})$$

and the fast and slow components are:

$$k_{Fast} = \frac{1}{2}(\Lambda + \Delta) \quad (\text{S16})$$

$$k_{Slow} = \frac{1}{2}(\Lambda - \Delta) \quad (\text{S17})$$

Substitute Equations S16 and S17 with Equations S1, S7 and S8, we have:

$$k_{Fast,Slow} = \frac{1}{2}(\Lambda \pm \Delta) = \frac{1}{2} \left[k_r \coth\left(\frac{\Delta E}{2k_B T}\right) + k_a + k_f \pm \sqrt{k_r^2 \csc^2\left(\frac{\Delta E}{2k_B T}\right) + (k_r + k_a - k_f)^2} \right] \quad (\text{S18})$$

From Equation S13, the intensity ratio of $|A\rangle$ to $|F\rangle$ can be written as

$$\frac{I_F}{I_A} = \frac{\int_0^\infty k_f * F(t) dt}{\int_0^\infty k_a * A(t) dt} = \frac{k_f}{k_a} \frac{\int_0^\infty F(t) dt}{\int_0^\infty A(t) dt} \quad (\text{S19})$$

From Equation S2, we have

$$A(\infty) - A(0) = -[(n_b + 1)k_r + k_a] \int_0^\infty A(t) dt + n_b k_r \int_0^\infty F(t) dt = -p \quad (\text{S20})$$

$$F(\infty) - F(0) = (n_b + 1)k_r \int_0^\infty A(t) dt - (n_b k_r + k_f) \int_0^\infty F(t) dt = p - 1 \quad (\text{S21})$$

Thus

$$\frac{I_F}{I_A} = \frac{k_f}{k_a} \cdot \frac{(n_b+1)k_r+(1-p)k_a}{n_bk_r+pk_f} \quad (\text{S22})$$

Assuming $p = 0.5$, that is, the initial populations of $|A\rangle$ and $|F\rangle$ are equal

$$\frac{I_F}{I_A} = \frac{k_f}{k_a} \cdot \frac{2(n_b+1)k_r+k_a}{2n_bk_r+k_f} \quad (\text{S23})$$

Plugging in the fitting results from Figure 3c ($E=2.2$ meV, $k_a=0.075$ ns⁻¹, $k_f=0.0042$ ns⁻¹ and $k_r=4.5$ ns⁻¹) gives the temperature-dependent intensity ratio of $|F\rangle$ and $|A\rangle$ (Figure S10).

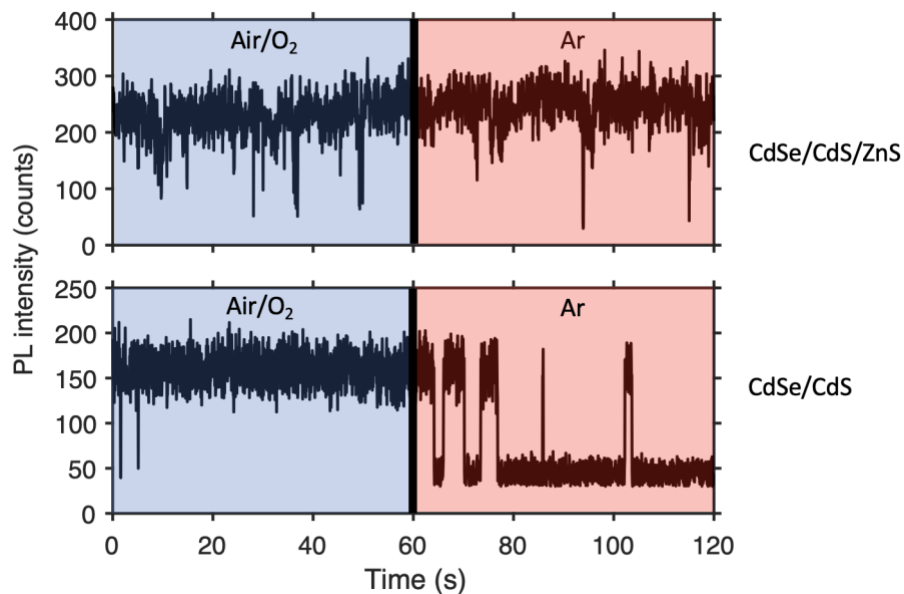


Figure S1. The PL intensity trajectories of single CdSe/CdS/ZnS (upper) and CdSe/CdS (lower) QDs in air/oxygen and Ar environment with 50 ms bin time. The experiments are performed at room temperature with an oil immersion objective of 1.49 NA and a continuous-wave laser as the excitation light.

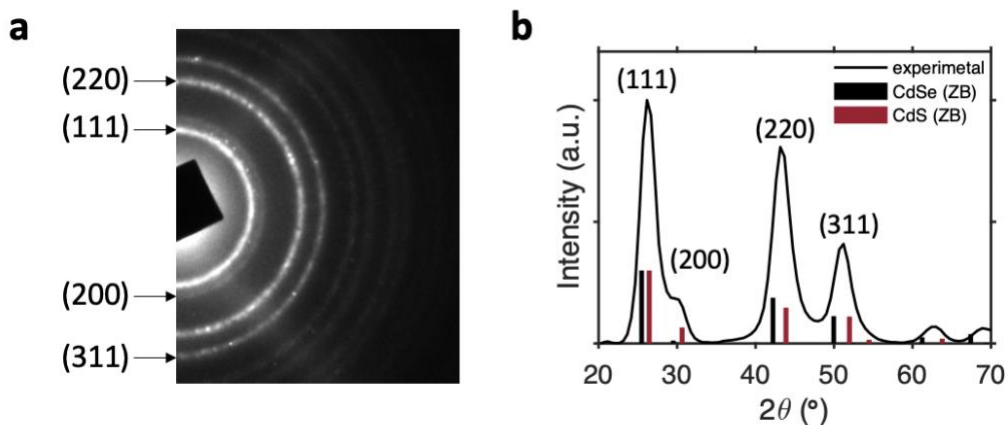


Figure S2. SAED pattern (a) and the corresponding circularly integrated intensity curve (b) of the CdSe/CdS/ZnS core/shell/shell QDs. The standard pattern for bulk zinc-blende CdSe and CdS crystals are shown as black and red bars, respectively.

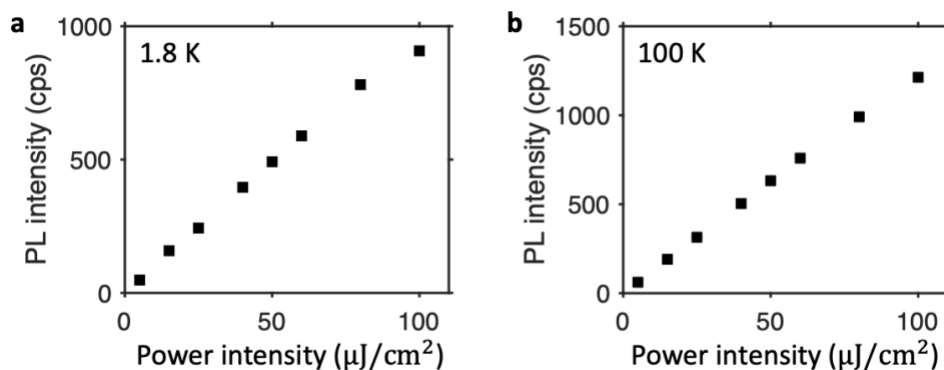


Figure S3. Excitation power-dependent PL intensity of single CdSe/CdS/ZnS QDs at (a) 1.8 K and (b) 100 K excited by a 450 nm pulsed laser with a repetition rate 2 MHz. The typical excitation power density is $25 \mu\text{J}/\text{cm}^2$ for spectroscopic measurements in this work, unless otherwise noted.

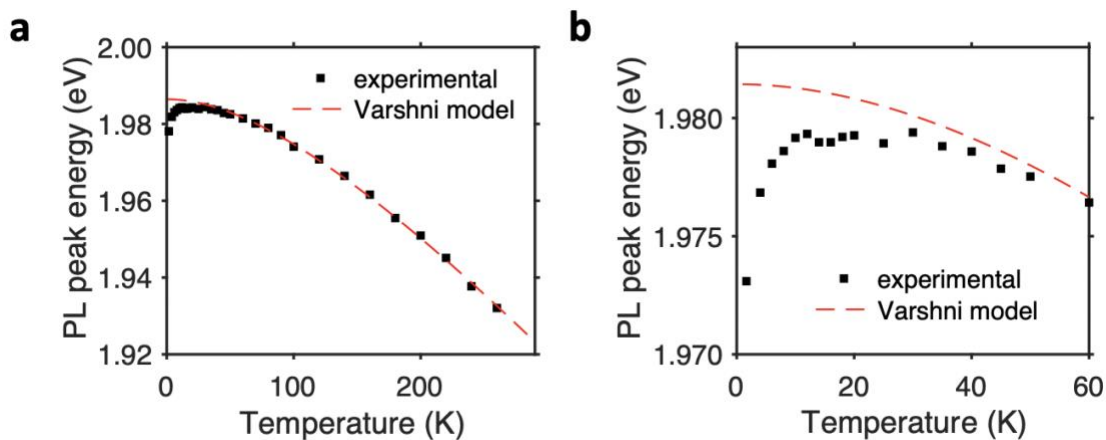


Figure S4. Temperature-dependent PL peak energy for another type of QDs (CdSe/CdS/CdZnS/ZnS) from 300 K to 1.8 K, (a) and an enlarged plot below 60 K (b). The diameter of CdSe core is 6 nm. Non-monotonic emission energy shift is also observed for this type of QDs.

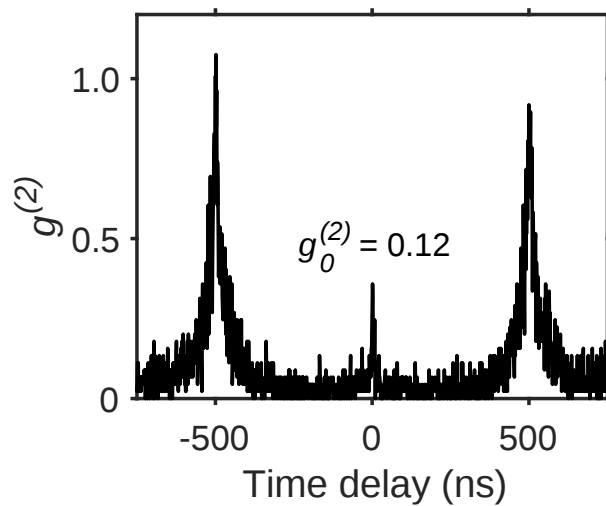


Figure S5. A typical second-order photon correlation ($g^{(2)}$) curve of a single QD under 450 nm pulsed laser excitation with power density of $10 \mu\text{J}/\text{cm}^2$ at 1.8 K.

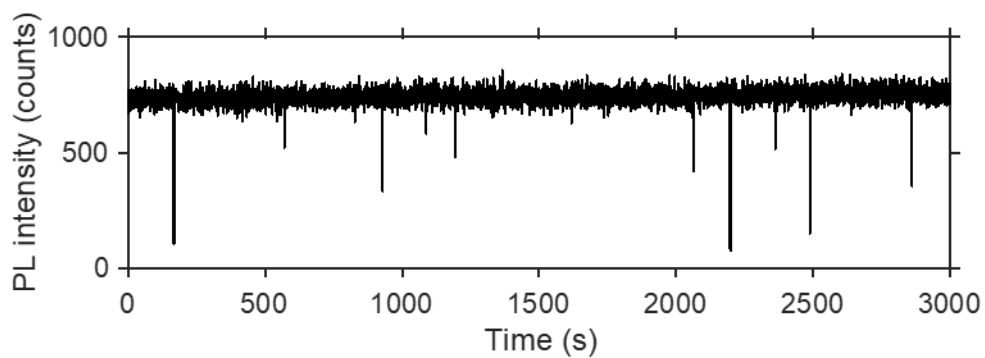


Figure S6. A representative PL intensity time trace of a single QD at 1.8 K excited by a 450 nm continuous-wave laser. Bin time is 0.5 s.

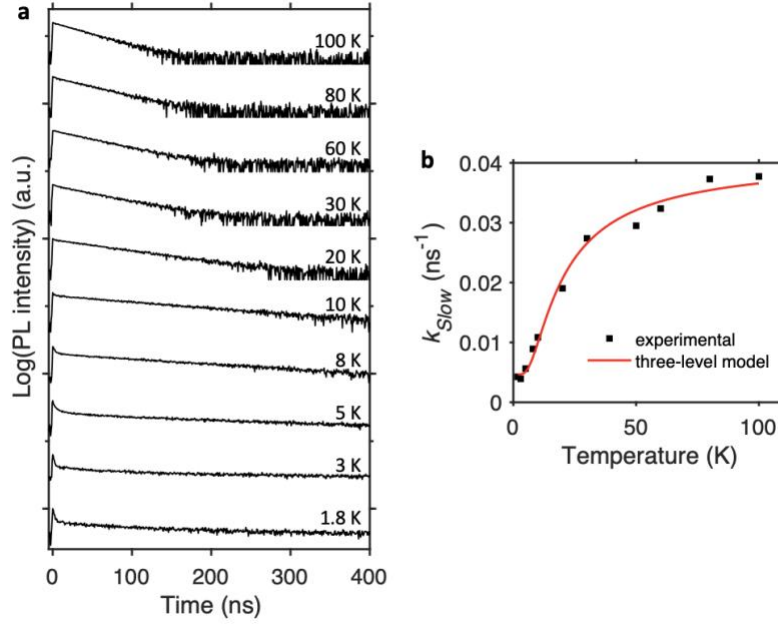


Figure S7. (a) PL decay dynamics of a typical single CdSe/CdS/ZnS QD from 1.8 to 100 K excited by a 450 nm pulsed laser with power density of $25 \mu\text{J}/\text{cm}^2$ ($\langle N \rangle \sim 0.1$) and a repetition rate of 2 MHz. (b) Temperature-dependence of the decay rate of the slow component (k_{slow} , black squares) extracted from (a). The red line is a fit to the model with $\Delta E = 2.15 \text{ meV}$, $k_a = 0.078 \text{ ns}^{-1}$ and $k_f = 0.0047 \text{ ns}^{-1}$. The energy splitting between $|A\rangle$ and $|F\rangle$ from single QD measurements agrees well with the ensemble measurements.

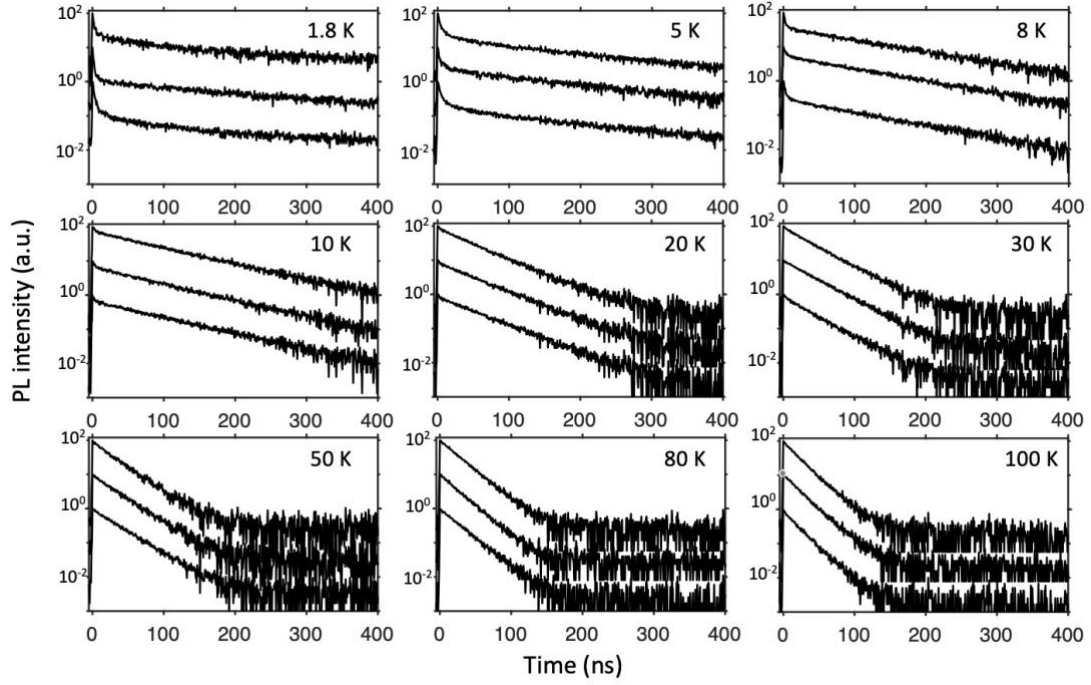


Figure S8. PL decay dynamics of randomly selected single QDs at temperatures from 1.8 to 100 K.

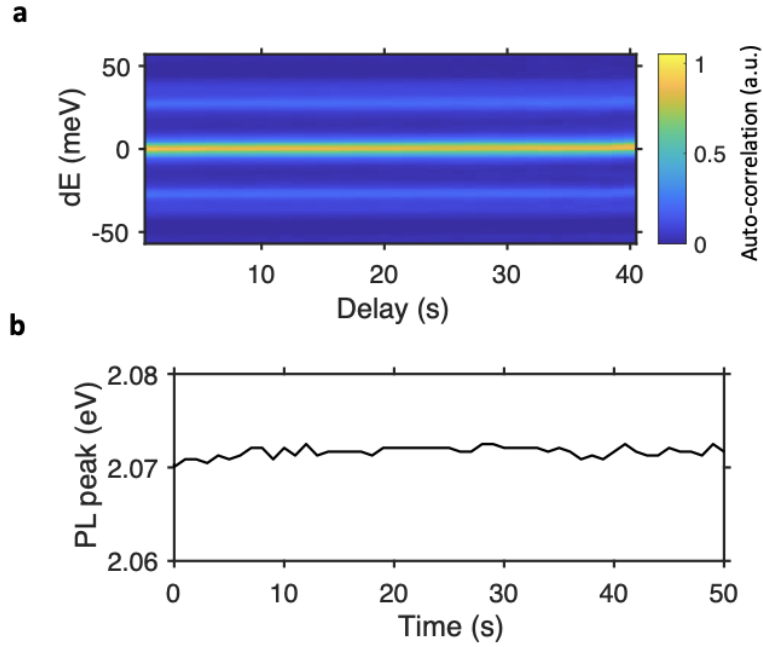


Figure S9. (a) Auto-correlation of the time-dependent single-dot emission spectrum. (b) Time-dependent emission peak energy of single dot, which corresponds to the time-dependent emission spectrum in Figure 4c in Main Text. The standard deviation of the PL peak energy over 50 s is only 0.44 meV.

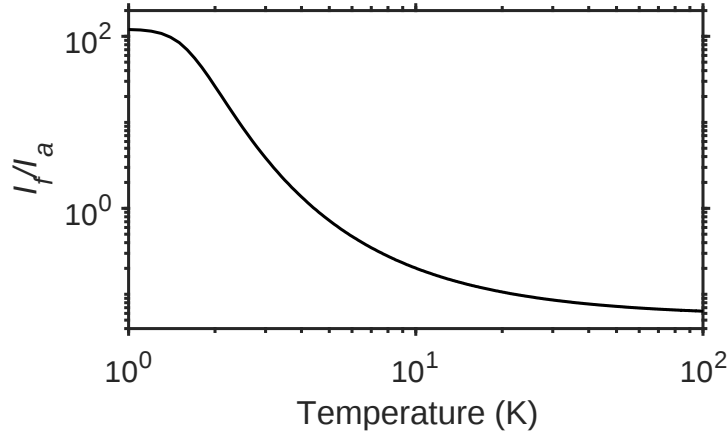


Figure S10. Temperature-dependent intensity ratio of $|F\rangle$ to $|A\rangle$ calculated by Equation S23 with parameters from the ensemble CdSe/CdS/ZnS QDs experiments.

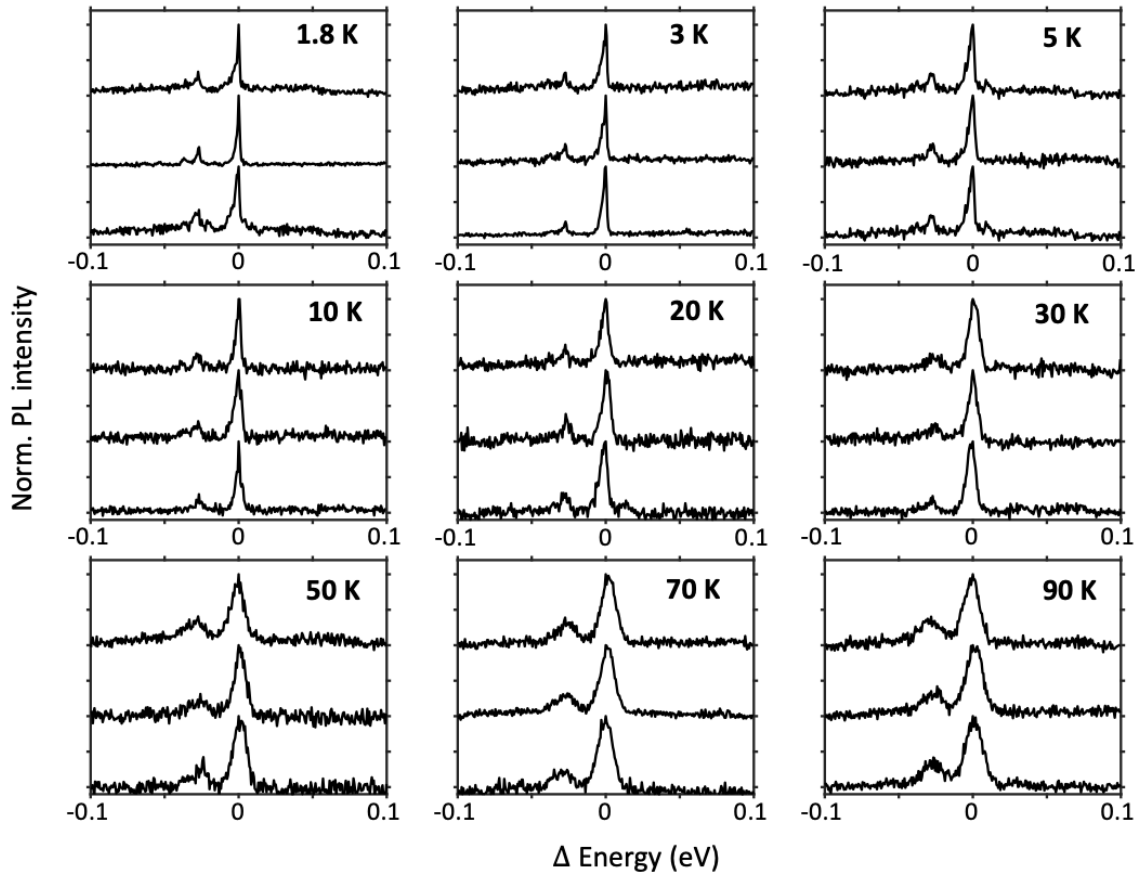


Figure S11. PL spectra of 27 randomly selected single QDs at temperature from 1.8 K to 90 K. There are 3 single-QD PL spectra at each temperature. The energy of spectra is zeroed according to the peak of the ZPL. The asymmetric profiles of the ZPLs below 5 K are obvious.

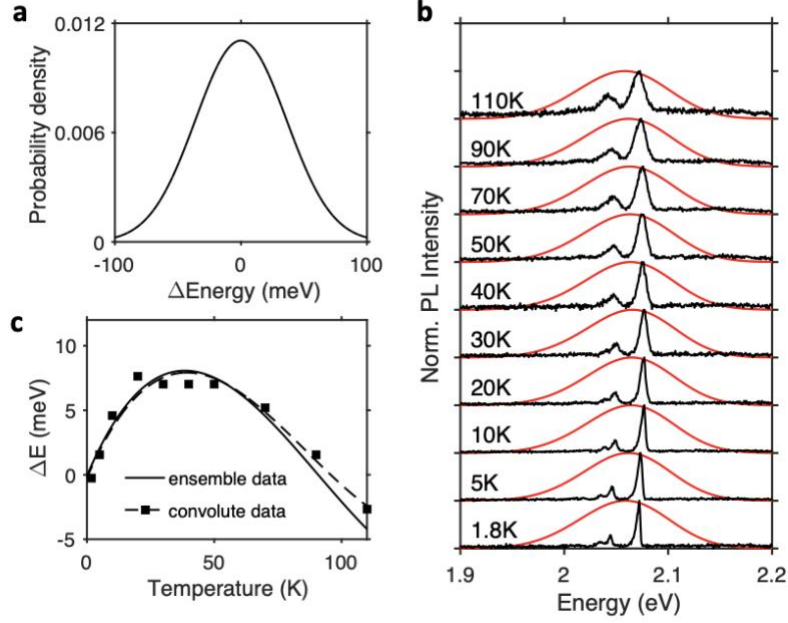


Figure S12. (a) Gaussian distribution profile with a width of 85 meV, being consistent with the ensemble PL peak width at 1.8 K. (b) Convolution (red) of the Gaussian function with the single QD PL spectra (black) at different temperatures. The resulting peak energies are plotted in (c). (c) The simulated (dash line) temperature-dependence of relative emission peak for ensemble QDs matches the measured data (solid line) in Figure 2b.

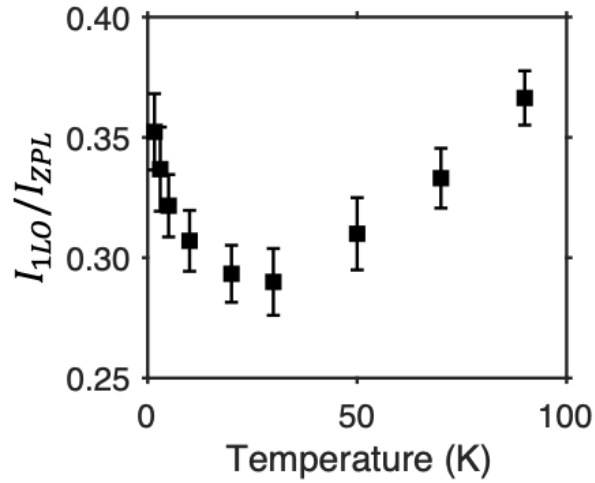


Figure S13. Statistical temperature-dependence of the intensity ratio of the 1LO to ZPL. 10 randomly selected single QDs are measured at each temperature. The average values and standard deviations are indicated by squares and error bars.

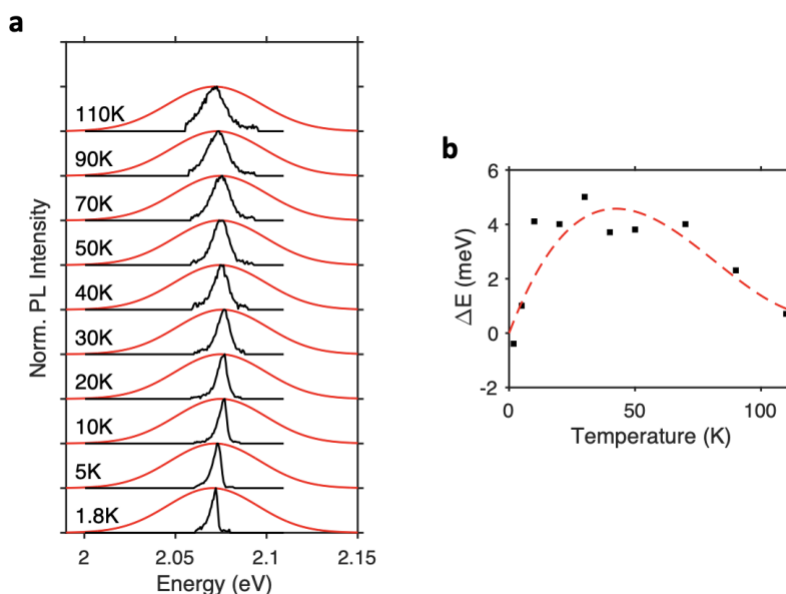


Figure S14. (a) Convolution (red) of the Gaussian function only with the ZPL spectra (black) at different temperatures. The resulting peak energies are plotted in (b). The simulated emission peak red-shift is about 4.6 meV from 40 to 1.8 K.

References

- (1) Cao, Z. Y.; Shu, Y. F.; Qin, H. Y.; Su, B.; Peng, X. G. Quantum Dots with Highly Efficient, Stable, and Multicolor Electrochemiluminescence. *Acs Central Sci.* **2020**, *6*, 1129-1137.
- (2) Li, J. Z.; Chen, J. L.; Shen, Y. M.; Peng, X. G. Extinction coefficient per CdE (E = Se or S) unit for zinc-blende CdE nanocrystals. *Nano Res.* **2018**, *11*, 3991-4004.
- (3) Labeau, O.; Tamarat, P.; Lounis, B. Temperature dependence of the luminescence lifetime of single CdSe/ZnS quantum dots. *Phys. Rev. Lett.* **2003**, *90*, 257404.
- (4) Biadala, L.; Louyer, Y.; Tamarat, P.; Lounis, B. Direct Observation of the Two Lowest Exciton Zero-Phonon Lines in Single CdSe/ZnS Nanocrystals. *Phys. Rev. Lett.* **2009**, *103*, 037404.
- (5) Shornikova, E. V.; Biadala, L.; Yakovlev, D. R.; Sapega, V. F.; Kusrayev, Y. G.; Mitioglu, A. A.; Ballottin, M. V.; Christianen, P. C. M.; Belykh, V. V.; Kochiev, M. V.; Sibeldin, N. N.; Golovatenko, A. A.; Rodina, A. V.; Gippius, N. A.; Kuntzmann, A.; Jiang, Y.; Nasilowski, M.; Dubertret, B.; Bayer, M. Addressing the exciton fine structure in colloidal nanocrystals: the case of CdSe nanoplatelets. *Nanoscale* **2018**, *10*, 646-656.