Supporting information

Size-Dependent Phase Transition in Perovskite Nanocrystals

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Methods

**Nanocrystal synthesis.** The blue- and green-CH$_3$NH$_3$PbBr$_3$ NCs were synthesized by using emulsion method.\cite{1,2} To synthesize the blue-CH$_3$NH$_3$PbBr$_3$ NCs, the precursor solution formed by dissolving 0.16 mmol CH$_3$NH$_3$Br and 0.2 mmol PbBr$_2$ powder in 0.5 mL N,N-Dimethylformamide (DMF) was dropped into the solvent with mixed n-hexane (10 mL) and n-dodecylamine (40 uL). 100 uL oleic acid was added into the above mixed solution. Acetonitrile (6 mL) was used as de-emulsifier to initiate the reaction. To obtain green-CH$_3$NH$_3$PbBr$_3$ NCs, 0.16 mmol CH$_3$NH$_3$Br dissolved in 0.3 mL DMF and 0.2 mmol PbBr$_2$ dissolved in 0.5 mL DMF were dropped into a mixture of 10 mL n-hexane, 0.5 mL oleic acid and 20 uL n-octylamine. 8 mL acetone was used as de-emulsifier to initiate the reaction. The obtained solution was purified by centrifugation. After centrifuging and discarding the precipitates, the bright perovskite NCs were obtained.

**Sample fabrication.** For single-dot measurements, the NC solutions with low concentration were spin-coated on the silicon substrate with a rotation speed of 5000 rpm for 3 min. A layer of OSTE monomers were spin-coated over the NC layer with a spin speed of 5000 rpm for 2 min. Then it was exposed to the UV light to make OSTE polymerize completely, resulting in a protective film of 20-50 um thick.

**Photoluminescence measurement details.** A micro-photoluminescence system consisting of an inverted microscope (Zeiss Axio Observer Z1) equipped with a 63x (Zeiss, NA=0.75) and a 10x (Zeiss, NA=0.25) lenses, respectively, was employed for single-dot and ensemble measurement. A spectrometer (Andor SR500i) with a
thermoelectrically cooled EMCCD (Andor iXon3 at -100 °C) was used for spectra measurements. The excitation source was a 405 nm diode laser (Omicron PhoX) used in dark-field (~70° incident angle onto the sample surface). After excitation, the collected light was filtered using a 420 nm long-pass filter (Semrock). Two diffraction gratings featuring 0.9 and 0.08 nm resolution were loaded in the spectrometer. For all the PL spectra measurement, the laser wavelength was 405 nm and the excitation power was ~4 W/cm².

For time-resolved photoluminescence measurement, the filtered light was directed to an avalanche photodiode (idQuantique id100-20, ~40 ps-resolution). A pulse excitation with 50% duty cycle and a variable repetition rate ~kHz optimized for each dot was applied. The measured laser fall time was 1.3 ns. The laser pulse is generated by a pulse generator and the setting pulse width is 200 ns with a period of 50 ns. The acquisition time is 180 s for each decay trace and PL background decay traces acquired under the same conditions were subtracted from the signal curves.

For low-temperature measurements the samples were mounted on a cold copper substrate of a cryostat (Oxford instruments) under vacuum. The cooling agent was liquid nitrogen or liquid helium depending on the target temperature. The vacuum degree is about 10⁻⁶ Torr.
**Figure S1.** Size-distribution histograms of the (a) blue-CH$_3$NH$_3$PbBr$_3$ and (b) green-CH$_3$NH$_3$PbBr$_3$ NCs.

**Figure S2.** Photoluminescent spectra at various temperature of the blue-CH$_3$NH$_3$PbBr$_3$ NC ensembles.
Figure S3. Typical PL decay curves of single perovskite NCs at 295, 70 and 5 K. (a) blue-CH$_3$NH$_3$PbBr$_3$ and (b) green-CH$_3$NH$_3$PbBr$_3$ NCs.

Thermalization dynamics calculations

Rate equations for a three level system (S-T-G) with a three-fold degeneracy of the triplet state (Figure S4):

\[
\begin{align*}
\frac{d}{dt} p_S(t) &= -(\Gamma_S + 3\Gamma_{ST}) \cdot p_S(t) + \Gamma_{ST} \cdot \exp(a) \cdot p_T(t), \\
\frac{d}{dt} p_T(t) &= 3\Gamma_{ST} \cdot p_S(t) - (\Gamma_T + \Gamma_{ST} \cdot \exp(a)) \cdot p_T(t)
\end{align*}
\]

where \( a = -\Delta/kT \) is a Boltzmann thermal population factor and \( \Gamma_{TS} = \Gamma_{ST} \cdot \exp(a) \).

Figure S4. Schematics of a three level system and transition rates between them.
Solutions become:

\[ p_s(t) = \frac{\exp\left(-\frac{t}{2}(I_{ST}e^a + \Gamma_S + \Gamma_T + 3I_{ST})\right)}{2\kappa} \left[ B_1 e^{-\frac{kt}{\tau}} + B_2 e^{\frac{kt}{\tau}} \right] \]

\[ p_T(t) = -\frac{\exp\left(-\frac{t}{2}(I_{ST}e^a + \Gamma_S + \Gamma_T + 3I_{ST})\right)}{2\kappa} \left[ C_1 e^{-\frac{kt}{\tau}} + C_2 e^{\frac{kt}{\tau}} \right] \]

where

\[ \kappa = \sqrt{(I_{ST}e^a)^2 - 2I_{ST}e^a(I_S - \Gamma_T - 3I_{ST}) + (I_S - \Gamma_T + 3I_{ST})^2} \]

\[ B_{1,2} = p_S(0)(k \pm (I_S - \Gamma_T + 3I_{ST})) \pm I_{ST}(p_S(0) - 2)e^a \]

\[ C_{1,2} = (p_S(0) - 1)(k \mp (I_S - \Gamma_T - 3I_{ST})) \pm I_{ST}(p_S(0) - 1)e^a \]

Simplifying by considering \( I_{ST} \gg \Gamma_S, \Gamma_T \) the coefficient

\[ \kappa \approx I_{ST}(3 + e^a) + \frac{(I_S - \Gamma_T)(3 - e^a)}{(3 + e^a)} \]

then:

\[ p_s(t) = \frac{e^a \exp\left(-\frac{\Gamma_S e^a + 3\Gamma_T e^a}{3 + e^a} t\right)}{3 + e^a} + \exp\left(-I_{ST}e^a + 3I_{ST}t\right)\left(p_S(0) - \frac{e^a}{3 + e^a}\right) \]

\[ p_T(t) = \frac{3\exp\left(-\frac{\Gamma_S e^a + 3\Gamma_T e^a}{3 + e^a} t\right)}{3 + e^a} - \exp\left(-I_{ST}e^a + 3I_{ST}t\right)\left(p_S(0) - \frac{e^a}{3 + e^a}\right) \]

Measurable quantity (in the absence of non-radiative processes):

\[ I(t) = \Gamma_S p_S(t) + \Gamma_T p_T(t) \]

In the limit of high temperatures \((a \approx 0)\) it can be written as:

\[ I(t) = \frac{(I_S + 3\Gamma_T)}{4} \cdot \exp\left(-\frac{I_S + 3\Gamma_T}{4} t\right) + \left(p_S(0) - \frac{1}{4}\right)(I_S - \Gamma_T) \cdot \exp(-4I_{ST}t) \]

For equal probabilities of initial population in any of the excited levels \(p_s(0) = 1/4,\)
corresponding to non-resonant excitation and random thermalization to the S-T manifold the solution simplifies further:

\[ I(t) = \frac{(\Gamma_s + 3\Gamma_r)}{4} \cdot \exp\left(-\frac{\Gamma_s + 3\Gamma_r}{4} t\right) \]

So a single exponential decay is expected at high temperatures. This is not what observed experimentally, where bi-exponential decay persists over all temperatures. Therefore non-monoexponential recombination dynamics observed here does not originate from carrier thermalization process and was ascribed to the trapping/detraping and delayed luminescence.

**Phase-transition calculations**

In the calculation model, the total free energy density \( f \) of the system can be expressed as,

\[
f = a_1(p_1^2 + p_2^2 + p_3^2) + a_{11}(p_1^4 + p_2^4 + p_3^4) + a_{12}(p_1^2p_2^2 + p_1^2p_3^2 + p_2^2p_3^2) + a_{123}p_1^2p_2^2p_3^2 + a_{111}(p_1^6 + p_2^6 + p_3^6) + a_{112}[p_1^2(p_2^4 + p_3^4) + p_2^2(p_1^4 + p_3^4) + p_3^2(p_1^4 + p_2^4)]
\]

(1)

where \( P_i \) is the electrical polarization component, \( a_1, a_{11}, a_{12}, a_{111}, a_{112}, \) and \( a_{123} \) are dielectric stiffnesses, and among all the coefficients above, only \( a_1 \) is a temperature-dependent coefficient,

\[ a_1 = (T - T_c)/(2\varepsilon_0 C) \]

(2)

where \( T \) is absolute temperature, \( T_c \) is Curie temperature, \( \varepsilon_0 \) is vacuum permittivity, and \( C \) is Curie constant.
The relationship between Curie temperature and diameter of ferroelectric nanoparticles can be expressed by a theoretical formula,

\[ T_c(d) = T_c - \frac{CC}{(d - d_c)} \]  

(3)

where \( T_c(d) \) is the Curie temperature when the diameter of nanoparticles is \( d \), \( CC \) is material constant, and \( d_c \) is critical diameter. According to Eq. (3), it is obvious that diameter \( d \) has correction effect on Curie temperature, thus influences the paraelectric-ferroelectric phase transition behavior and the total free energy.

For BaTiO₃, all the Landau energy coefficients are taken from the literature, \( T_c = 388 \text{ K} \), \( CC = 700 \text{ K nm} \), and \( d_c = 110 \text{ nm} \).\(^3\)\(^4\) We take temperature at 110 K, nearing the cubic-tetragonal phase transition temperature to investigate the role of nanoparticle diameter for the paraelectric-ferroelectric phase transition temperature. As show in figure S5, the electrical polarization and Curie temperature show a sharply change around the diameter of 130 nm, which is in good agreement with the reported result,\(^4\) and the relationship between Curie temperature and diameter can be expressed by,

\[ T_c = 388 - \frac{700}{d - 110} \]  

(4)

**Figure S5.** Dependence of the (a) Curie temperature, (b) electrical polarization and Gibbs free energy on the diameter of the BaTiO₃.
For CH$_3$NH$_3$PbBr$_3$, the Landau energy coefficients are obtained by parameters fitting using experimental results and phase diagram data. Here, in order to simplify the model, we only consider one-dimensional calculation. $P_s = 0.12 \mu C/cm^2$, $T_c = 236 K$, and $C = 1.6116 \times 10^4$ are used to establish a set of Landau energy coefficients,$^5,6,7$ where

\[
\alpha_1 = 5.61 \times 10^8 \times \left(-\coth \frac{160}{T_0} + \coth \frac{160}{T}\right),
\]

$\alpha_{11} = 8.76 \times 10^9$, $\alpha_{111} = 3.75 \times 10^9$, and $T_0 = 230K$. Figure S6 show the Dependence of the electrical polarization and Gibbs free energy on the diameter of CH$_3$NH$_3$PbBr$_3$ NCs.

![Figure S6. Dependence of the electrical polarization on the diameter of CH$_3$NH$_3$PbBr$_3$ NCs.](image)

**References**


