Supporting information

Title: The Scaling of Ligand Concentration and Soret Effect Induced Phase Transition in CsPbBr$_3$ Perovskite Quantum Dots

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S1. Experimental section

Materials and chemicals

Lead bromide (PbBr2, Aladdin, 99%), cesium bromide (CsBr, Aladdin, 99%), oleic acid (OA, Aladdin, AR), oleylamine (OAm, Aladdin, 90%), dimethylformamide (DMF, Aladdin, ≥99.9%), P-xylene (C8H10, Aladdin, 98%) and ethyl acetate (C2H3O2, Aladdin, 99%) were used as received without further purification.

Synthesis of CsPbBr3 Nanocrystals

The synthesis process was carried out at room temperature. 0.4 mmol of PbBr2 and 0.4 mmol CsBr were dissolved in 10 ml of DMF. Various amount of OA and OLA were added to achieve different ligand/Pb molar ratio (Clig). After completely stirring, 0.2 ml of precursor was rapidly rejected in to 2 ml of P-xylene solution with continuing stirring. Green emission can be observed under ultraviolet light which indicated that CsPbBr3 had been successfully formatted.

Temperature gradient generation

The temperature gradient with length in solution was generated by a refrigeration module integrated under the reaction container. The refrigeration system was made up with a high power (100W) semiconductor cooling chip and two cooling fans. With continues refrigerating, the temperature at bottom of reaction container kept at 255K. Around 25K temperature difference from room temperature (280K) was generated in 1mm thick solution.
S2. Characterization of CsPbBr$_3$ and Cs$_4$PbBr$_6$ nanocrystal

Table S1. Transition temperature, phase system, space group of CsPbBr$_3$ and Cs$_4$PbBr$_6$ nanocrystal.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Phase system</th>
<th>T (K)</th>
<th>Space Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>CsPbBr$_3$</td>
<td>Cubic</td>
<td>404</td>
<td>PM3M</td>
</tr>
<tr>
<td></td>
<td>Tetragonal</td>
<td>363</td>
<td>P4/MBM</td>
</tr>
<tr>
<td></td>
<td>Orthorhombic</td>
<td></td>
<td>PMBN</td>
</tr>
<tr>
<td>Cs$_4$PbBr$_6$</td>
<td>Hexagonal</td>
<td></td>
<td>R-3C</td>
</tr>
</tbody>
</table>

**XRD:** X-ray diffraction (XRD) patterns were recorded with film diffractometer (Rigaku SmartLab SE Multipurpose X-ray diffraction system) with Cu r K-α wavelength pf 1.54 Å.

**TEM:** High-resolution TEM (HR-TEM) was performed by TECNAI F30.

**In-situ PL characterization and analysis:** PL signal was collected through optical fiber to spectrometer (Ocean Optics USB 2000+) under 365nm UV LED excitation. A 400nm long-pass filter was applied to prevent high power excitation light. A customized high-throughput spectrum analyzer is used to extract the demand optical information from spectrum files generated by spectrometer software, shown in Figure S2(a). Center wavelength and intensity of peaks was firstly identification. Then multi-peak Lorentz fitting is applied based on SciPy $^1$. The emission wavelength and FWHM (Full width at half maximum) of the product are calculated from a Lorentz curve with maximum peak value. Additionally, bandgap of CsPbBr$_3$ QDs mapping from PL information was correlated by considering the size-dependent Stokes-shift, data from Kuno et al.$^2$. 

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$^1$ SciPy: Scientific Python library for scientific computing

$^2$ Kuno et al.: Reference for bandgap correlation
Time-resolved PL characterization:

**Table S2.** Parameters of fitted Time-resolved PL of middle state and CsPbBr$_3$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_1$ (Counts)</th>
<th>$A_2$ Counts</th>
<th>$A_3$ (Counts)</th>
<th>$\tau_1$ (ns)</th>
<th>$\tau_2$ (ns)</th>
<th>$\tau_3$ (ns)</th>
<th>$\tau_a$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Middle state</td>
<td>2.69(0%)</td>
<td>1111.2(0.23%)</td>
<td>478950(99.77%)</td>
<td>5.85</td>
<td>0.84</td>
<td>0.28</td>
<td>0.28</td>
</tr>
<tr>
<td>CsPbBr$_3$</td>
<td>244.06(1.48%)</td>
<td>4334.10(26.42%)</td>
<td>11825(72.08%)</td>
<td>69.07</td>
<td>9.0</td>
<td>2.69</td>
<td>18.24</td>
</tr>
</tbody>
</table>

Time-resolved PL for our two samples is performed to discuss the lifetime of excitons. As Figure S6 showed, it is easy to distinguish that the instrument response function (IRF) has much larger dynamics than the decays of two samples. The decay curves show totally different trends that intensity decreasing speed of CsPbBr$_3$ is much slower than the middle state sample, which indicated they have different optical properties. To analyze the numerical details, PL decay curves were convoluted using multiple
exponential functions. After comparing the chi-square with 1, we find that curves were best fitted by tri-
exponential function and their parameters were listed in Table 3, where

\[ I(t) = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) + A_3 \exp \left( -\frac{t}{\tau_3} \right) \]

Eq S1

After estimate the PL decay for CsPbBr\textsubscript{3} we get three components of 69.07 ns (1.48%), 9.0 ns (26.42%) and 2.69 ns (72.08%), also presented in Table S3; the former originates from the power dependent process in the perovskite active layer and the latter is from free carrier recombination in the radiative channel and the last one is from auger effect.\textsuperscript{3,4} While the PL decay for CsPbBr\textsubscript{3}/Cs\textsubscript{4}PbBr\textsubscript{6} hybrid structure have three components 5.85 ns (0%), 0.8384 ns (0.23%) and 0.27901 ns (99.77%). The average lifetime was calculated, the weight mean of each sample were taken as following equation

\[ \tau_{avg} = \frac{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3}{A_1 + A_2 + A_3} \]

Eq S2

So, the average lifetime of CsPbBr\textsubscript{3} (18.24 ns) is much larger than the middle state (0.28 ns), which indicate the emission ability of Cs\textsubscript{4}PbBr\textsubscript{6} is more possible to be by induced by the hybrid structure induced defects, which agree with recent report.\textsuperscript{5}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure_s2.png}
\caption{The XRD pattern of Cs\textsubscript{4}Pb(Br\textsubscript{2}I\textsubscript{4}) hybrid with CsPb(Br\textsubscript{1}I\textsubscript{2}) nanocrystals. (110), (200) crystal plane (marked in red) of CsPb(Br\textsubscript{1}I\textsubscript{2}) and (120), (024), (006) plane (marked in black) which belong to Cs\textsubscript{4}Pb(Br\textsubscript{2}I\textsubscript{4}) nanocrystals were observed to prove the hybrid of two phases.}
\end{figure}
Supporting References


