Electronic Supplementary Information

A Relationship Between Crystal Structures and Spectroscopic Properties in Cesium Lead Bromide (CsPbBr$_3$) Perovskite Nanocrystals: Focusing on the Photoluminescence Efficiency

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Experimental Section

1. Synthesis of CsPbBr$_3$ nanocrystals (CPB)

CsPbBr$_3$ nanocrystals were prepared following previously reported procedures with modifications$^{1,2}$

1) Preparation of cesium oleate solution: Cs$_2$CO$_3$ (0.163 g, Aldrich, 99.9%), 1-octadecene (8 mL, Uniam, 99%) and oleic acid (0.5 mL, Uniam, 99%) were loaded into 100 mL of 3-neck flask. And then the solution was dried under vacuum at 110 °C for 2 h. After drying, the temperature of the solution was further raised to 150 °C under N$_2$ and kept until the injection.

2) Synthesis of pristine-CPB and ZnBr$_2$-CPB: We note that the samples are denoted as “pristine-CPB” or “ZnBr$_2$-CPB” depending on the presence of ZnBr$_2$ in the synthesis. 0.138 g of PbBr$_2$ (Aldrich, ≥98%), 1 mL of oleic acid (degassed, Uniam, 99%), and 1 mL of oleylamine (degassed, Aldrich, 70%) were placed into 100 mL 3-neck flask (0.095 g of ZnBr$_2$ (Aldrich, 99.999%) was added for the synthesis of ZnBr$_2$-CPB). The flask containing precursor solution is dried under vacuum at 110 °C for 2 h. And then, the solution was further heated to 170 °C under N$_2$, and 0.8 mL of prepared Cs-oleate solution (150 °C) was swiftly injected. Approximately 10 s from the injection, the flask was rapidly cooled down in an ice bath.

3) Isolation of CsPbBr$_3$ nanocrystals: Reaction crude solution was centrifuged for 12 min at 10000 rpm. And then the precipitates were redispersed in 3 mL of anhydrous toluene with strong vortexing. When the NCs were completely redispersed, the NC solution was centrifuged for 32 min at 13000 rpm (temperature was set to 18 °C during centrifugation). After the centrifugation, the precipitates were redispersed in 4 mL of anhydrous hexane, and again centrifuged for 10 min at 6000 rpm. Finally, supernatant was collected and filtered with syringe filter (pore size 0.45 µm) while the precipitates were discarded. We note that all isolation procedures were performed under inert condition.

2. UV-Visible & Photoluminescence spectroscopy

Steady-state absorption spectra were measured on a UV/Vis spectrometer (Cary5000, Varian) and photoluminescence spectra were recorded by using a fluorescence spectrophotometer (F-
Photoluminescence spectra are spectrally corrected by using correction factor of the fluorescence spectrophotometer. All steady-state measurements carried out by using a quartz cuvette with a pathlength of 1 cm at ambient temperatures.

3. Femtosecond transient absorption spectroscopy

The femtosecond time-resolved transient absorption (fs-TA) spectrometer consists of an optical parametric amplifier (OPA; Palitra, Quantronix) pumped by a Ti:sapphire regenerative amplifier system (Integra-C, Quantronix) operating at 1 kHz repetition rate and an optical detection system. The generated OPA pulses have a pulse width of ~ 100 fs in the range of 280-2700 nm, which are used as pump pulses. White light continuum (WLC) probe pulses were generated using a sapphire window (4 mm thick) by focusing a small portion of the fundamental 800 nm pulses which was picked off by a quartz plate before entering the OPA. The time delay between pump and probe beams was carefully controlled by making the pump beam travel along a variable optical delay (ILS250, Newport). Intensities of the spectrally dispersed WLC probe pulses are monitored by a High Speed Spectrometer (Ultrafast Systems) for both visible and near-infrared measurements. To obtain the time-resolved transient absorption difference signal (ΔA) at a specific time, the pump pulses were chopped at 500 Hz and absorption spectra intensities were saved alternately with or without pump pulse. Typically, 4000 pulses excite the samples to obtain the fs-TA spectra at each delay time. The polarization angle between pump and probe beam was set at the magic angle (54.7°) using a Glan-laser polarizer with a half-wave retarder in order to prevent polarization-dependent signals. Cross-correlation fwhm in pump-probe experiments was around 200 fs and chirp of WLC probe pulses was measured to be 1.2 ps in the 450-800 nm region. To minimize chirp, all reflection optics were used in the probe beam path. A quartz cell of 2 mm path length was employed. After completing each set of TA experiments, the absorption spectra of all samples were carefully checked to rule out the presence of artifacts or spurious signals arising from, for example, degradation or photo-oxidation of the samples in question.

4. Single molecule confocal microscopy

Samples for single molecule confocal measurements were prepared by spin-coating NC solutions on rigorously cleaned quartz coverslips at 3000 rpm for 30s. The NC solutions were composed of NCs in hexane containing 20 mg·mL⁻¹ polystyrene (M.W. = 40000, Aldrich). The confocal microscope (TE2000-U, Nikon) was equipped with a sample scanning stage at RT. Circular polarized light from a picosecond pulsed diode laser (LDH-D-C-450, Picoquant, 1 MHz repetition rate, prepared using a Berek compensator (5540, New Focus)) excited the samples. It was passed through a laser line filter (FF01-420/10-25, Semrock) and collimating lens. Then, it subsequently focused on the sample via an oil immersion objective (Plan Fluor, 1.3 NA, 100×, Nikon) with a power density corresponding to an average number of excitons per pulse, \( \langle N_x \rangle = 0.1 \). Fluorescent signals were passed through a dichroic mirror (T425lpxr, Chroma Technology), spectrally filtered using a notch filter (HNPF-420.0AR-1.0, Kaiser optical systems) and a band pass filter (FF-01-430/LP-25, Semrock), and then split by using a non-polarizing 50:50 beam splitter. Half of the fluorescence was dispersed via a spectrograph.
(SpectraPro 2150i, Princeton Instruments) and projected onto an EMCCD camera (PL PROEM:512B EMCCD, Princeton Instruments). The other half was detected by an avalanche photodiode (APD) module (SPCM-AQR-16-FC, EG&G). The fluorescent signal detected by the APD was registered by a time-correlated single photon counting (TCSPC) PC (SPC 830, Becker & Hickl). The TCSPC was operated in first-in-first-out regime in which the arrival time after the beginning of acquisition and the time lag with respect to the excitation pulse were stored for each detected photon. The full-width half maximum (FWHM) of the overall instrumental response function approximately corresponded to 500–600 ps. The data were processed by using a BIFL data analyzer software (Scientific Software Technologies Center) to obtain fluorescence intensity trajectories and the time-resolved fluorescence decays.

5. Auger ionization efficiency

The probability (P) of creating multiple excitons within a given bin time should be considered to understand the on-time kinetics using Auger ionization processes. The probabilities of creating n excitons in a single pulse and multiexciton (MX, n ≥ 2) were calculated by Equation 1 and 2.

$$P_{\langle N_x \rangle}(n) = e^{-\langle N_x \rangle} \cdot \langle N_x \rangle^n / n! \quad (1)$$

$$P_{MX} = 1 - e^{-\langle N_x \rangle} - \langle N_x \rangle \cdot e^{-\langle N_x \rangle} \quad (2)$$

Here, the average number of generated excitons $\langle N_x \rangle$ can calculated by multiplying the absorption cross section ($\sigma$, cm$^{-2}$) at the excitation wavelength and the intensity of laser ($i$, photons/cm$^2$·pulse) ($\langle N_x \rangle = i \cdot \sigma$).

The Auger ionization efficiency influences the fall-off time of on-time distribution since $P_{\text{fall-off}}$ is the probability of forming the multiexciton state ($P_{MX}$) and the ionization probability ($P_{\text{ionize}}$).

$$P_{\text{fall-off}} = \Delta T_{\text{rep}} / \tau_{\text{fall-off}} = P_{MX} \times P_{\text{ionize}} \quad (3)$$

$$P_{\text{ionize}} = P_{\text{fall-off}} / P_{MX}$$

where $\Delta T_{\text{rep}}$ is a repetition rate of the pulsed laser.

6. PL intensity-lifetime scaling

Intensity-lifetime scaling or the ratio of radiative rates between two distinct intensity levels ($\beta$)

$$\beta = \frac{\tau_{on}}{\tau_{off}} \times \frac{l_{off}}{l_{on}}$$

where $\tau$ and I are the PL lifetime and intensity of the corresponding “on” and “off” states.

In Figure 4(a), the radiative lifetime ratio of the the brightest state and dark state is calculated
Thus, the dark state emission arises from trion.

In Figure 4(d), the radiative lifetime ratio of the brightest state and dark state is calculated as

$$\frac{\tau_{\text{on}}}{\tau_{\text{off}}} \times \frac{l_{\text{on}}}{l_{\text{off}}} = \frac{4.24}{95.2 - 2(\text{background})} \times \frac{15.6 - 2(\text{background})}{0.49} \approx 1.3$$

Thus, the dark state emission results from the trapping of band-edge electrons and holes.
Supporting Figures

Table S1 Basic optical parameters of CsPbBr₃ NCs.

<table>
<thead>
<tr>
<th></th>
<th>E₉ [eV]</th>
<th>Δₓ [meV]</th>
<th>δᵦ [meV]</th>
<th>σ₁₅ [10⁻¹⁵ cm²]</th>
<th>Δₓₓ [meV]</th>
<th>QY [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>2.46</td>
<td>45</td>
<td>14</td>
<td>9.27</td>
<td>77</td>
<td>72</td>
</tr>
<tr>
<td>ZnBr₂</td>
<td>2.47</td>
<td>56</td>
<td>67</td>
<td>8.50</td>
<td>81</td>
<td>38</td>
</tr>
</tbody>
</table>

ₐ The band gap energy yielded from first excitonic absorption peak λₐₚₑ. ₐ The Stokes shift is defined as the energy difference between the first minimum in the δ²/δλ² spectrum and the emission peak. ₐ The transition line width. ₖ Absorption cross section at 3.1 eV. ₖ Biexciton binding energy.

![Fig. S1 PL spectra and PL quantum yield of fresh Pristine- and ZnBr₂-CPB.](image-url)
Fig. S2 Representative blinking dynamics for individual NCs: (a) fresh Pristine-, (b) 7-days Pristine-, (c) fresh ZnBr$_2$- and (d) 7-days ZnBr$_2$-CPB.

Fig. S3 Femtosecond transient absorption (fs-TA) spectra of (a) Pristine-CPB and (b) ZnBr$_2$-CPB at early time before aging.
**Fig. S4** Histograms of the net spectral shifts of a single CsPbBr$_3$ NCs for (a) fresh Pristine-CPB (b) Pristine-CPB after aging (c) fresh ZnBr$_2$-CPB and (d) ZnBr$_2$-CPB after aging.

**Fig. S5** The Auger lifetime obtained from fitting the multiexciton dynamics by mono-exponential decay for (a) fresh Pristine-CPB (b) fresh ZnBr$_2$-CPB (c) Pristine-CPB after aging and (d) ZnBr$_2$-CPB after aging.
Fig. S6 (a) Pb/Cs and (b) Br/(Cs+Pb) atomic ratios of Pristine- and ZnBr$_2$-CPB from XPS data.

Fig. S7 Energy diagrams of Pristine-CPB (left) and ZnBr$_2$-CPB (right). The bandgap energy is obtained from first excitonic absorption peak (Table S1). The subband gap energy is measured as the difference between the first transition energy and the second transition energy. The intraband gap energy changes depending on the type of ligands adsorbed on the substrate surface.
**Fig. S8** Typical PL scan images of CsPbBr$_3$ NCs in single crystal measurements.
Reference


