Supporting Information File for

Broadband Multi-photon Absorption Studies of Phase Pure

Zero-dimensional Cs\(_4\)PbBr\(_6\) Perovskite Films.

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Synthesis of Cs₄PbBr₆ nanocrystals

For the synthesis of Cs₄PbBr₆ NCs, we have employed two different and popular methods i.e. for non-luminescent hot injection and for luminescent anti-solvent precipitation techniques.

Chemicals required: Cs₂CO₃ (99.9%, Aldrich), octadecene (ODE, 90%, Aldrich), oleic acid (OA, 90%, Aldrich), oleylamine (OLA, 70%, Aldrich), PbBr₂ (99.999%, Aldrich), hydrobromic acid (48% in water, 99.99%, Aldrich), dimethyl formamide (AR grade, Fisher Scientific), toluene and hexane were purchased from Finar and distilled following standard procedure.

Preparation of Cs-Oleate: 0.5625 gm Cesium carbonate and 5.4 mL oleic acid was taken in a 100 mL double necked flask and degassed for one hour at 130 °C. Temperature was raised to150 °C to prepare yellowish Cs-oleate.

Non-fluorescent Cs₄PbBr₆ NCs: 0.0367 gm PbBr₂, 5 mL octadecene, 0.2 mL oleic acid and 1.5 mL oleylamine were mixed in a 100 mL double necked flask and heated to 130 °C under vacuum until the solution becomes clear. Temperature of the solution was decreased to 80 °C and 0.36 mL of Cs-oleate solution was added quickly. After 30 seconds, the solution become turbid indicating the formation of nanocrystals. Then the solution was quickly cooled down under water stream and centrifuged. The solid was washed with toluene repeatedly and finally dissolved in toluene for measurements.

Fluorescent Cs₄PbBr₆ NCs: Firstly, 0.011 gm PbBr₂ was dissolved in 1 mL of DMF followed by addition of 20 μL of HBr, 0.1 mL of oleic acid and 0.05 mL of oleylamine. In a 50 mL of round bottom flask10 mL hexane, 5 mL oleic acid and 0.2 mL of as-prepared Cs-oleate solution were added. Previously prepared PbBr2 solution was then quickly added into the RB in vigorous stirring condition. The solution immediately turn greenish white. Then it was centrifuged and purified for further spectroscopic use.

For the Z-scan measurements thin film of the NCs were prepared by drop casting the individual NC solutions and drying under vacuum.
**Z-scan experimental details:**

We used a Ti:sapphire amplifier (Libra, M/s Coherent) delivering ~50 fs pulses at 800 nm wavelength with 1 kHz repetition rate. A broadband oscillator (~30 fs at 800 nm with a bandwidth of ~35 nm and a repetition rate of 80 MHz) was the seed for the amplifier and a nanosecond Nd:YAG laser at 532 nm was used as pump for the amplifier. The output from the laser system was ~50 fs pulses delivered with ~4 mJ energy, centered at 800 nm and a bandwidth of ~28 nm with a repetition rate of 1 kHz. In order to tune the wavelength to other parts of the EM spectrum (visible and near-IR), optical parametric amplifier (OPA) was used, delivering ~70 fs pulses. The pulses from the OPA were focused with a 15 cm plano-convex lens and the beam waists ($2\omega_o$) were estimated to be in the range of 50-140 µm (500-1500 nm). The perovskite films were placed on a linear translation stage and the transmission was collected using a photodiode, the output of which was fed to a lock-in amplifier (signal recovery 7265). All the instruments were controlled using an indigenous LabVIEW program. The Z-scan experimental schematic is provided in figure S1.

![Figure S1. Schematic of the fs Z-scan experimental setup.](image)
DFWM experimental Details:

Laser pulses at 800 nm were split into three parts with electric fields $E_1(t)$, $E_2(t-\tau)$ and $E_3(t-(\tau+T))$ [corresponding wave vectors of $\vec{k}_1$, $\vec{k}_2$, $\vec{k}_3$] using different beam splitters. We have ensured that all the three beams had equal input powers. The three beams were aligned in forward phase matching geometry (BOXCAR). A 20 cm lens is used to focus all the beams. The signal (fourth beam) in the direction $\vec{k}_4$ was collected using a photodiode which was interfaced to a lock-in amplifier. A 5-mm quartz cuvette with the sample solution was employed for the measurements. These experiments were performed in both the solution phase (dispersed in toluene) and in film phase [only for $\chi^{(3)}$ measurements]. The phase matching ($\vec{k}_4=\vec{k}_1+\vec{k}_2-\vec{k}_3$) condition was ensured by performing the DFWM measurements with (β-Barium borate) BBO crystal as shown in figure S2 (inset). The time resolved DFWM measurements were performed by delaying one of the beams and the signal was recorded at each delay. The stage, PD and the locking were interfaced to a computer and an indigenous LabVIEW program. All the measurements were performed at room temperature.

**Figure S2.** Schematic of the fs-DFWM experiment.
**Z-scan calculations**

**OA:** Z-Scan open aperture measurements where performed in the 500-1500 nm wavelength. The nonlinear absorption coefficients were measured using the following equation (1) [1].

\[ T_{OA(uPA)} = \frac{1}{\left[ 1 + (n - 1)\alpha_n L_{\text{eff}} (I_0 / (1 + (z / z_0)^2))^{n-1} \right]^{1/n-1}} \] \hspace{1cm} (1)

\[ L_{\text{eff}} = \frac{1 - e^{-\alpha_0 L}}{\alpha_0}, \quad L'_{\text{eff}} = \frac{1 - e^{-2\alpha_0 L}}{2\alpha_0}, \quad L''_{\text{eff}} = \frac{1 - e^{-3\alpha_0 L}}{3\alpha_0} \]

\[ Z_0 = \frac{\pi \omega_0^2}{\lambda} \]

Cross-sections are calculated by using \( \sigma_n = \frac{(\hbar \omega)^{n-1}}{N} \alpha_n \) where N is the concentration.

The concentration is calculated from the NCs volume for one cc.

Number of particle of Fluorescent NCs (d=40 nm) and Non-fluorscent (d=20nm) NCs.

\[ N = \frac{1}{\frac{4}{3} \times 3.14 \times (20nm)^3} \]

\[ N \text{ (fluorescent)} = 2.98 \times 10^{16} \text{ cm}^{-3} \]

\[ N = \frac{1}{\frac{4}{3} \times 3.14 \times (10nm)^3} \]

\[ N \text{ (Non-fluorescent)} = 2.39 \times 10^{17} \text{ cm}^{-3} \]

These calculations are based on the assumption that NC’s fill up the whole volume (densely packed). However, in reality the NCs will be dispersed in the film as well as in solutions. Therefore, the concentration used here is the **upper limit** and the actual concentrations will be much lower than these mentioned here. This suggests that the cross-sections mentioned in the manuscript are within the lower limit and the actual values could be much higher.
Multi-photon absorption cross-section calculations

$\sigma_{n\text{PA}}$: The cross sections are measured by using following equation (2) [1] and the calculations are shown for 500 nm ($\sigma_2$), 900 nm ($\sigma_3$) and 1400 nm ($\sigma_4$) wavelengths in the case of fluorescent Cs$_4$PbBr$_6$ NCs.

$$\sigma_n = \frac{(\hbar \omega)^{n-1}}{N} \alpha_n$$

for 2PA n=2

-------- (2)

$$\sigma_{2\text{PA}} = \frac{1.29 \times 10^{-8} \text{ cm} / \text{W} \times (3.97 \times 10^{-19} \text{ J})}{2.98 \times 10^{16} / \text{cm}^3}$$

$$\sigma_{2\text{PA}} = 1.71 \times 10^{-43} \text{ cm}^4 s$$

$$\sigma_{3\text{PA}} = \frac{6.52 \times 10^{-19} \text{ cm}^3 / \text{W}^2 \times (2.20 \times 10^{-19} \text{ J})^2}{2.98 \times 10^{16} / \text{cm}^3}$$

$$\sigma_{3\text{PA}} = 10.65 \times 10^{-73} \text{ cm}^6 s^2$$

$$\sigma_{4\text{PA}} = \frac{2.6 \times 10^{-26} \text{ cm}^5 / \text{W}^3 \times (1.418 \times 10^{-19} \text{ J})^3}{2.98 \times 10^{16} / \text{cm}^3}$$

$$\sigma_{4\text{PA}} = 24.7 \times 10^{-100} \text{ cm}^8 s^3$$

Closed Aperture Z-scan Calculations:

$$n_2 = \frac{\Delta \Phi \lambda}{2\pi I_0 L_{\text{eff}}}$$

(Fluorescent Cs$_4$PbBr$_6$ NC films)

$$\Delta \Phi = 2$$

$$\lambda = 500 \text{ nm}$$

$$L_{\text{eff}} = 4.2 \times 10^{-8} \text{ m}$$

$$I_0 = 6.1 \text{ GW/cm}^2 \quad n_2 = 0.71 \times 10^{-9} \text{ cm}^2/\text{W}$$
AFM Data: The thickness of the films was measured using an atomic force microscope.

Figure S3 AFM data of non-fluorescent (20 nm) (a) and fluorescent (40 nm) (b) thin films.
Figure S4 Intensity dependent plots of 2PA, 3PA and 4PA processes of (b,d,f) non-fluorescent and (a,c,e) fluorescent NCs of 0D-PRM measured at 600 nm, 1100 nm and 1400 nm.

References