

Supporting Information

Unexpected Red Emission From Cs₄PbI₆ Nanocrystals

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Experimental Methods

Chemicals:

Lead (II) iodide (PbI_2 , 99.99%), Cesium carbonate (Cs_2CO_3 , 99.99%) and oleic acid (OA, 85%) were purchased from Aladdin. Cesium iodide (CsI, 99.9%), tetra-n-octylammonium bromide (TOAB, 98%), octadecene (ODE, 90%), ethyl acetate (EtAc, 99%) and oleylamine (OLA, 80-90%) were purchased from Macklin. N,N-dimethylformamide (DMF, 99.5%) and n-hexane (Hex, 98%) were purchased from Tianjin Fuyu Fine Chemical Co., Ltd., and toluene (TOL, 99.5%) was purchased from Yantai Far East Fine Chemical Co., Ltd., China. All chemicals were used as received without further purification.

Preparation and Purification of Cs_4PbI_6 Nanocrystals (NCs):

The luminescent Cs_4PbI_6 nanoparticles were synthesized by a reprecipitation method.¹ Typically, 36.88-mg of PbI_2 and 20.78-mg of CsI were loaded in a vial containing 2-ml DMF at room temperature under vigorous stirring to form a CsPbI_3 precursor (0.04 M). 200 μl of the precursor solution was mixed with ligands of OA and OLA (5 μl for each) under a vortex mixer before injecting into 2-ml toluene. Note that the dose of ligands is vital to form the emissive Cs_4PbI_6 nanoparticles (See Figure S1). The reaction was allowed to proceed for 10 minutes at room temperature before centrifugation. The purified particles at bottom pellet were dispersed in 2-ml toluene for further characterization.

Preparation and Purification of CsPbI_3 Nanocrystals (NCs):

CsPbI_3 nanocrystals were synthesized by a hot-injection method.² Typically, 2.25-g of Cs_2CO_3 was mixed with 21.5-ml of OA in a three-neck flask and heated at 120 °C for 1 hour under a N_2 atmosphere, generating a Cs-oleate precursor. Thereafter, 10-mL ODE and 0.17-g PbI_2 were loaded into a 50-mL three-neck flask and dried under vacuum for 1 h at 120 °C. OA and OLA (1 mL each) were injected at 120 °C under N_2 . After a complete dissolution of PbI_2 , the temperature was elevated to 130 °C before a rapid injection of 156- μL Cs-oleate precursor. 5 s later, the reaction mixture was cooled by

an ice-water bath. The reaction mixture was loaded into a centrifuge tube, followed by addition of an equivalent volume of ethyl acetate. The mixture was then centrifuged at 4000 rpm for 3 min. The supernatant was discarded and the pellet was dispersed with 5-mL toluene, followed by centrifugation at 4000 rpm for 3 min. Thereafter, the supernatant was kept as the target product.

Photoluminescence and Absorption.

The nanocrystals dispersed in toluene were cast on a glass slide for steady-state spectral measurement of photoluminescence, excitation, and absorption, respectively. Absorption measurements in the range of 300 nm to 800 nm were performed using a Cary-5000 UV-vis spectrometer (Agilent Technologies). Photoluminescence, PL QY and excitation spectra were recorded using a FS5 spectrofluorometer (Edinburgh Instruments). The emission slit was set to 0.2 nm in PL QY measurement.

X-ray Diffraction Measurements.

Powder X-ray diffraction was carried out using a Bruker AXS D8 diffractometer with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) at a scanning speed of 10°/min in steps of 0.02°.

Time-Resolved Photoluminescence (TRPL) Measurement.

The TRPL measurement was conducted on a home-made device with a single-photon detector (DU420A-OE). A 408-nm nanosecond diode laser was used as the excitation source with a pulse frequency of 1 MHz.

Raman Spectral Measurement.

The nanocrystals were drop cast on a glass slide, followed by fixing on the sample stage after drying. The Raman spectra were collected by 532-nm laser irradiation (Horiba Labram HR800 Raman spectrometer), while the PL spectra were collected by irradiating the sample with a 325-nm laser. The low-temperature measurement was performed in a microscope-coupled stage with a temperature-controlling module (HCS421VXY, Instec Inc).

Scanning Electron Microscope Measurement.

Scanning electron microscope images were collected using a Regulus-8100 FESEM from HITACHI.

Transmission Electron Microscopic Measurement.

HR-TEM images were obtained using a JEOL 2100F transmission electron microscope. Cs₄PbI₆ nanocrystal samples were unstable under electron beam irradiation and tend to decompose in a short time (< 5 s).

Confocal Microscope Measurement.

The sample was excited with a 647-nm laser using a confocal microscope (Nikon, A1R), and the light signal between 663-738 nm was collected for image acquisition through a 60× objective lens (NA=1.27, oil immersion).

Details of PL stability experiments.

Both anion exchange experiment and photobleaching experiment were conducted under ambient condition (25 °C and 30% of humidity). Typically, the toluene solutions of tetra-n-octylammonium bromide were injected into the toluene dispersions of CsPbI₃ and Cs₄PbI₆, respectively, and kept stirring. PL spectra were recorded under 450-nm laser (~ 7 mW/cm²) excitation to track the anion exchange process. As to photobleaching experiment, a 450-nm laser of a higher power density (~74.9 mW/cm²) was used to irradiate the toluene solutions of CsPbI₃ and Cs₄PbI₆, respectively, and the PL was recorded with the aid of ND filter (OD=2).

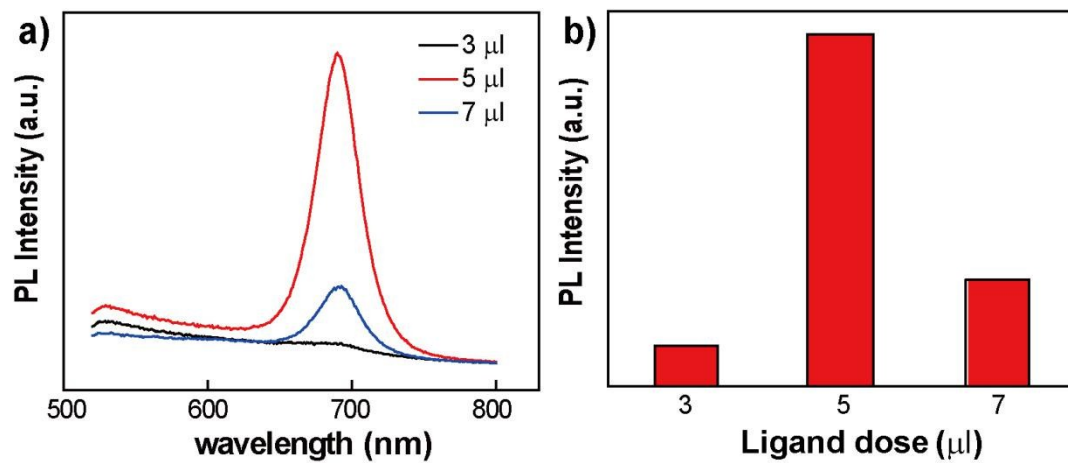


Figure S1. (a) PL spectra of Cs_4PbI_6 samples synthesized with different dose of ligands (OA or OLA). (b) Integrated PL intensity of Cs_4PbI_6 was plotted against ligand doses.

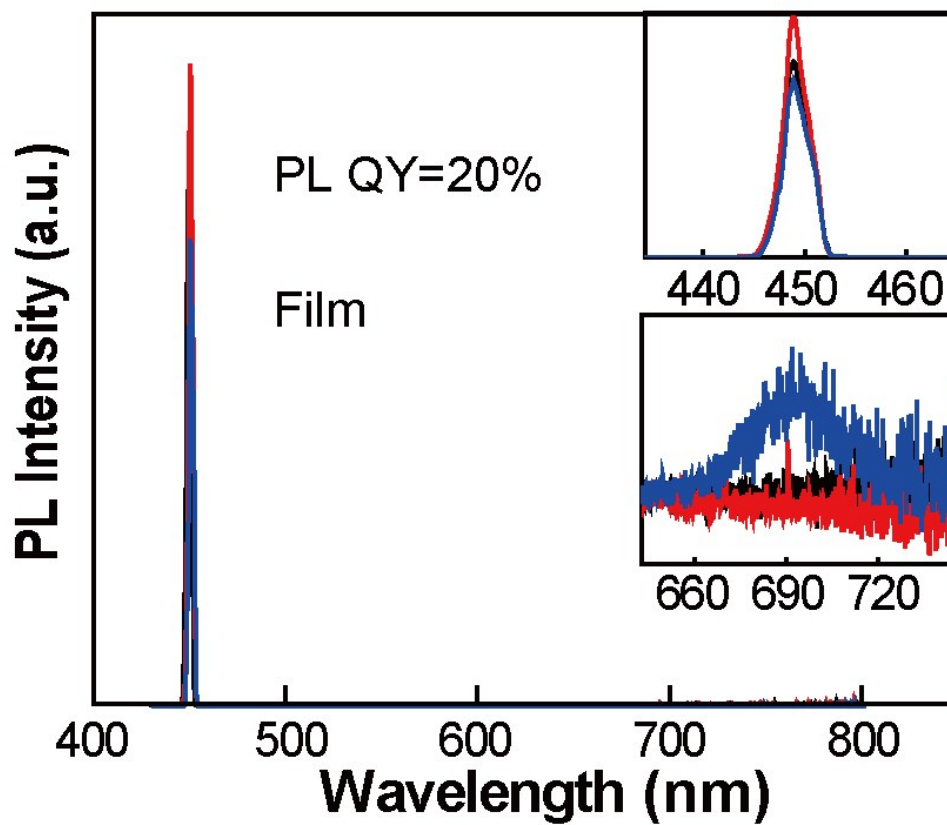


Figure S2. The PL QY measurement of the solid Cs₄PbI₆ sample. Note that an indirect configuration was used to minimize the scattering effect.

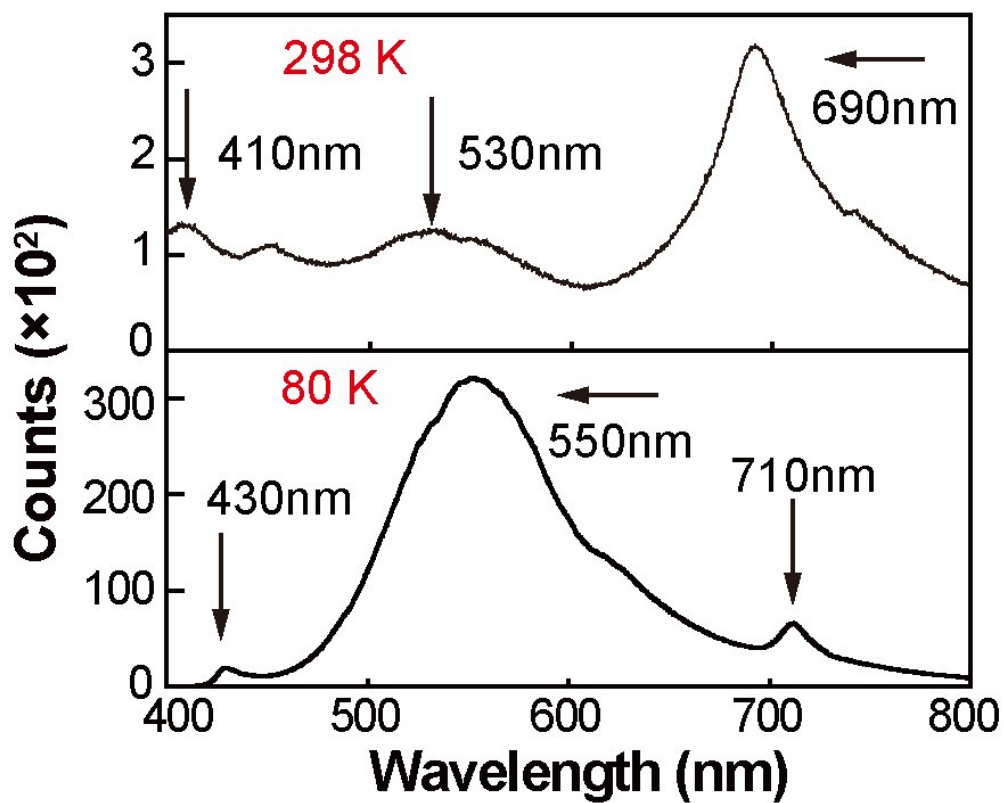


Figure S3. PL spectra of Cs₄PbI₆ crystal at temperature of 80 K and 298 K excited by 325-nm laser.

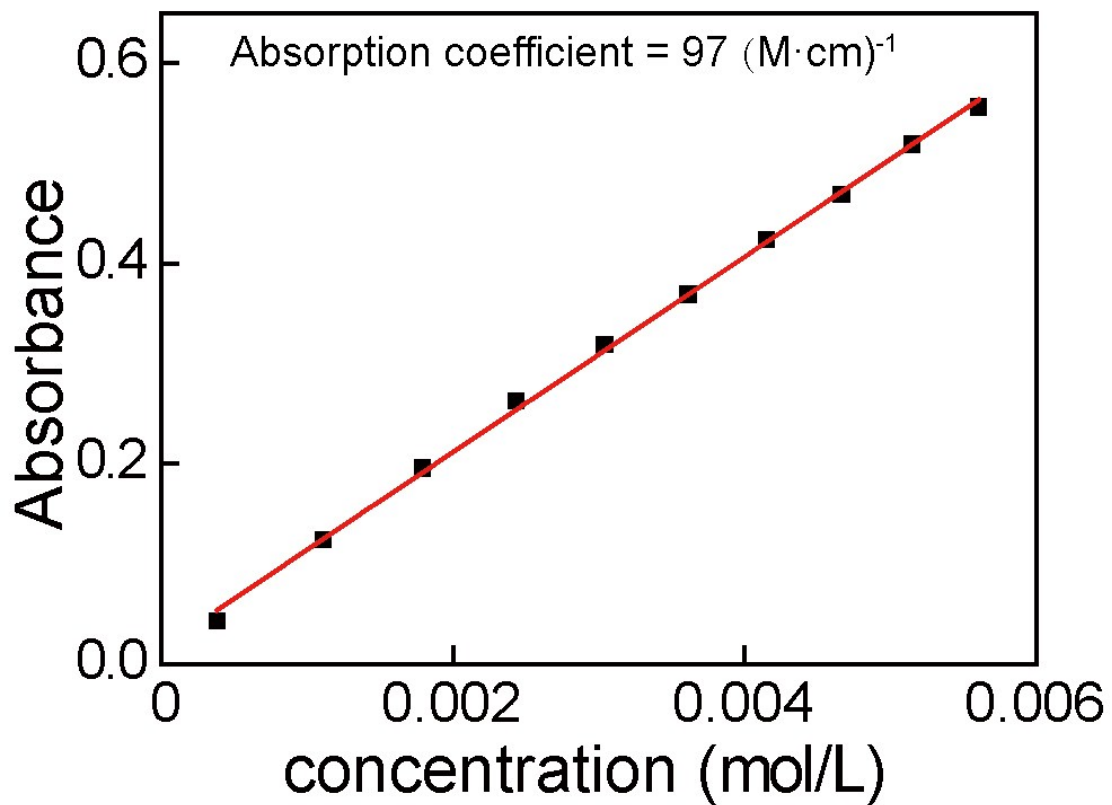


Figure S4. The absorbance is proportional to the concentration and the slope is the absorption coefficient according to Beer-Lambert law (the red line is the fitted curve).

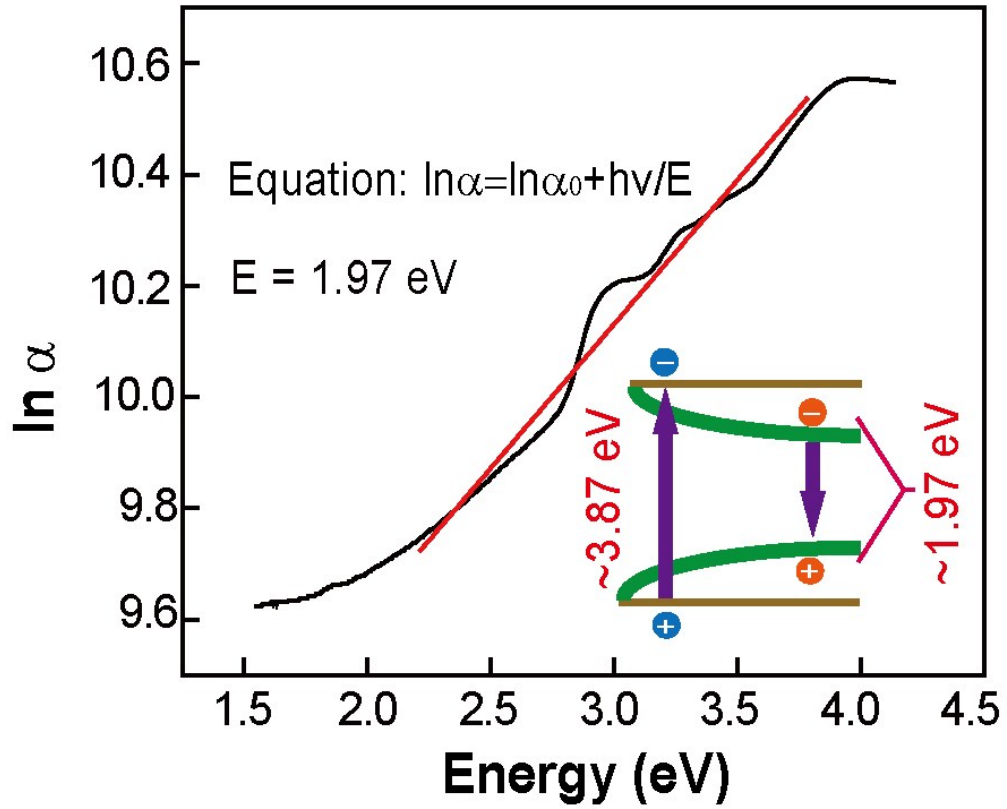


Figure S5. Urbach energy value obtained by fitting Urbach equation shown above, and the inset is schematic diagram of the Urbach energy, whereby localized states shrink the bandgap.

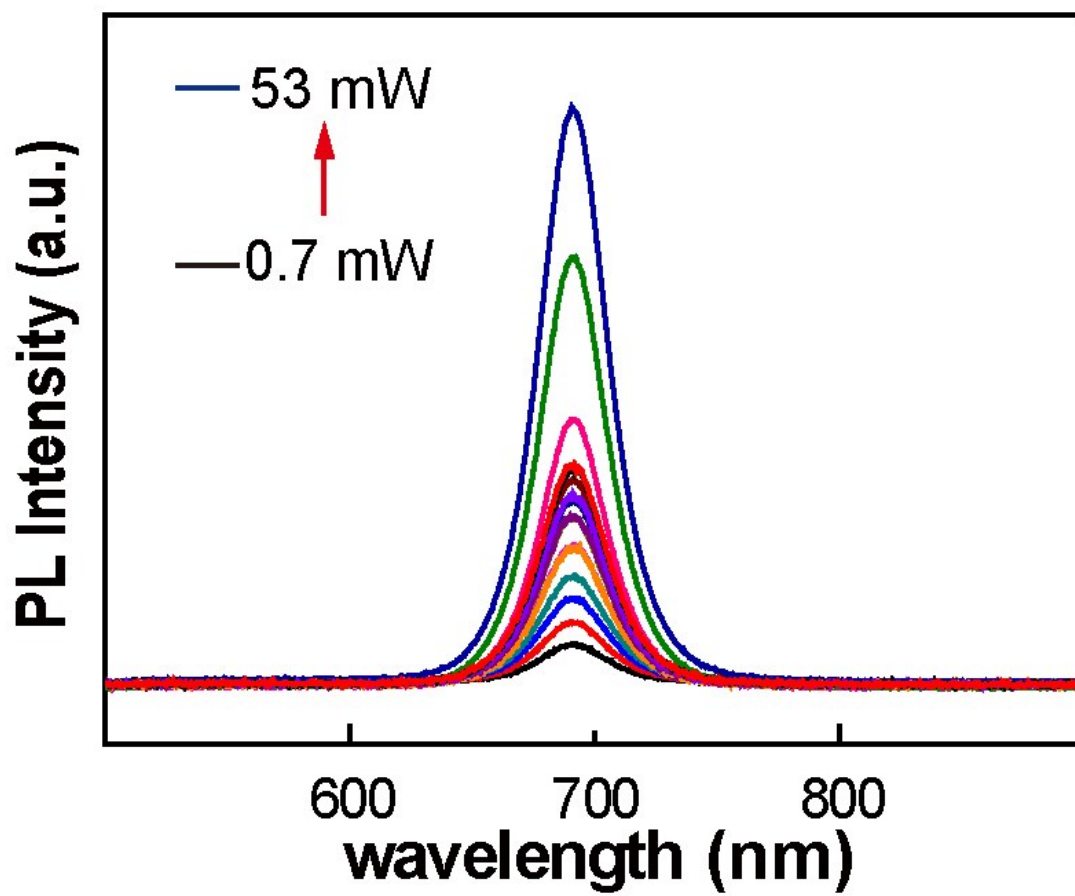


Figure S6. PL spectra obtained by 450-nm excitation with different output powers.

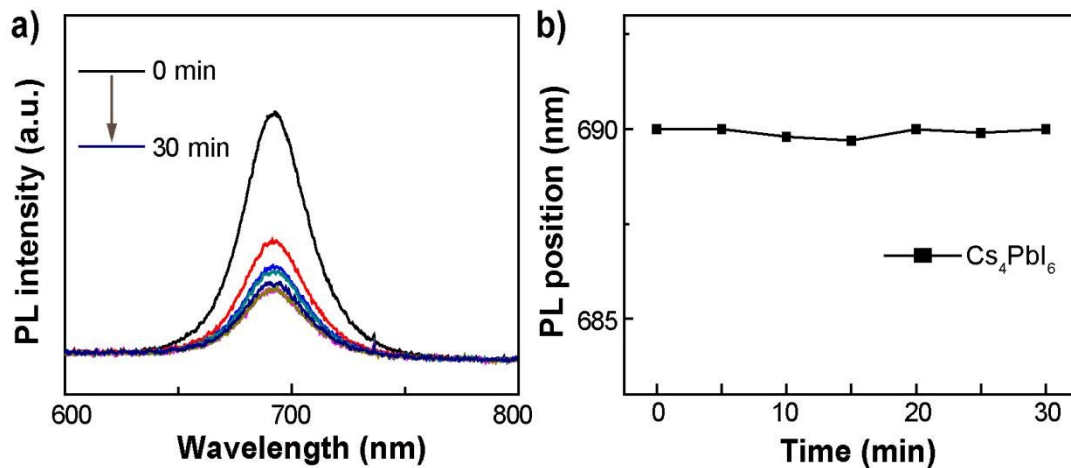


Figure S7. Long-run evolution for 30 min of (a) PL spectrum and (b) peak position after adding a toluene solution of TOAB to Cs_4PbI_6 sample, suggesting a robust resistance to anion exchange in Cs_4PbI_6 system.

Table S1: Fitting parameters of PL lifetime at 680 nm.

Sample	I ₀	A	τ _c (ns)	β
Cs ₄ PbI ₆	5361	21.5	24.1	0.56

The effective PL lifetime (τ_{PL}) is composed of the radiation life (τ_r) and the non-radiation lifetime (τ_{nr}) by the equation:³

$$\tau_{PL}^{-1} = \tau_r^{-1} + \tau_{nr}^{-1} \quad (1)$$

Radiation lifetime and non-radiation lifetime are related to PL internal quantum efficiency (η_{int}) by the equation:³

$$\eta = \tau_{nr} / (\tau_r + \tau_{nr}) \quad (2)$$

Through equations (6) and (7), the radiation lifetime can be expressed as:³

$$\tau_r = \tau_{PL} / \eta_{int} \quad (3)$$

In order to obtain an effective PL lifetime, the parameters obtained by fitting Figure 2d are brought into the following equation:³

$$\tau_{PL} = \frac{\tau_c}{\beta} \Gamma\left(\frac{1}{\beta}\right) \quad (4)$$

$$\Gamma\left(\frac{1}{\beta}\right) = \int_0^{\infty} x^{(1-\beta)/\beta} e^{-x} dx \quad (5)$$

It is worth noting that the PLQY of the Cs₄PbI₆ film was 20% measured by

integrating sphere at room temperature. We take the measured PLQY as a reasonable approximation of the internal quantum efficiency (η_{int}).

The effective PL lifetime and internal quantum efficiency were brought into equation (3) to obtain a radiation lifetime of 199 ns, and the non-radiation lifetime obtained by equation (1) was 50 ns.

Table S2: Basic parameters of Cs₄PbI₆, Cs₄PbBr₆ and (CH₃ (CH₂)₃NH₃)₂PbI₄.

	(CH ₃ (CH ₂) ₃ NH ₃) ₂ PbI ₄	Cs ₄ PbBr ₆	Cs ₄ PbI ₆
PL position	550 nm	515 nm	680 nm
FWHM	37 nm	22 nm	33 nm
binding energy	4.42 meV	353 meV	172 meV
lifetime	1.52 ns	3.35 ns	24 ns
quantum yield	88%	83%	20%
$\hbar\omega$	29 meV	42 meV	80 meV

In order to further clarify the characteristics of Cs₄PbI₆, we compared the parameters of Cs₄PbI₆, Cs₄PbBr₆ and (CH₃ (CH₂)₃NH₃)₂PbI₄.⁴⁻⁶ It can be seen that the FWHM of Cs₄PbI₆ is smaller than that of (CH₃ (CH₂)₃NH₃)₂PbI₄, indicating a better monochromaticity. Cs₄PbI₆ has larger optical phonon energy than the other two, indicating a stronger interaction between phonon and exciton.

Reference

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