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$CsPbBr_3$ and Cs_4PbBr_6 perovskite nanoparticles: hidden potential of Cs_4PbBr_6 or ineffective fluorescence?

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Experimental section

Materials: *Cs_2CO_3* (99.9%, SigmaAldrich), *$PbBr_2$* (99.999%, SigmaAldrich), *oleic acid* (97.4%, Ruskhim), *oleylamine* (98%, SigmaAldrich), *pentadecylamine* (98%, Sigma-Aldrich), *octadecene* (90%, Alfa Aesar), *mineral oil* (VM-5c, FOXY), *dimethylformamide* (99%, Aldrich) and *n-hexane* (chemically pure, Himmed) were used without additional purification. All actions were carried out according to the modified procedures described in studies[S1,S2] at different temperatures in an argon atmosphere and in air using absolute solvents.

Dispersion was carried out with an ultrasonic homogenizer (USH) SONOPULS HD 3100, BANDELIN, using a power of 10–30, 60 W and two probes with diameters of 13 and 3 mm. Suspensions were purified using a Sigma 3–30 KS centrifuge at 2000 and 9000 rpm.

Synthesis of $CsPbBr_3$ NPs (113):[S1] *The synthesis of cesium oleate.* 0.814 g (2.5 mmol) of Cs_2CO_3, 40 ml of ODEmineral oil and 2.5 ml of oleic acid were mixed in a 100 ml three-necked flask. The resulting mixture was heated (T = 150 °C) in an argon atmosphere until the reaction of cesium carbonate with oleic acid was complete with the formation of a yellow-brown transparent solution. *The synthesis of $CsPbBr_3$ NPs.* $PbBr_2$ weighing 0.069 g (0.188 mmol) and pentadecylamine weighing 0.318 g (0.0014 mol), 10 ml octadecene or mineral oil, 0.5 ml oleylamine and 1 ml oleic acid were mixed in a three-necked flask. The resulting mixture was heated (T=180 °C) in an argon atmosphere until the salt was completely dissolved. After complete solubilization of the lead bromide, 0.4 ml of cesium oleate (0.125 M in octadecene or mineral oil) was rapidly added. Because cesium oleate precipitates at room temperature, the solution must be heated to 150 ºC before injection. Within 5 seconds after injection, the reaction mixture was rapidly cooled in an ice bath.

Synthesis of $CsPbBr_3$ NPs (113 UT):[S2] A mixture of 0.1289 g (0.4 mmol) Cs_2CO_3, $PbBr_2$ weighing 0.4404 g (1.2 mmol), pentadecylamine weighing 0.6216 g (0.0027 mol), 1 ml oleylamine and 2 ml oleic acid were placed in a beaker with a volume of 50 ml, dispersed in 40 ml of octadecene using an ultrasonic homogenizer with a power of 20 W and a probe diameter of 13 mm for 30 min in an ice bath. The resulting solution was centrifuged at 9000 rpm for 10 min. The precipitate was dispersed in 20 ml of n-hexane using a 10 W ultrasonic generator with a probe diameter of 3 mm for 10 min. The solution was additionally centrifuged at 2000 rpm for 10 min. A yellow colloidal solution with green luminescence was obtained.

Synthesis of Cs_4PbBr_6 (416): A mixture of 0.39 g (1.2 mmol) Cs_2CO_3, 0.2202 g (0.6 mmol) $PbBr_2$, 1 ml oleic acid, 0.5 ml oleylamine and 0.6212 g pentadecylamine were placed in a 50 ml beaker and dispersed in 30 ml of octadecene using an ultrasonic homogenizer with a power of 20 W and a probe diameter of 13 mm for 10 min in an ice bath, as a result a white dispersion was obtained. The resulting solution was centrifuged at 9000 rpm for 10 min. The precipitate was dispersed in 20 ml of n-hexane using a 10 W ultrasonic generator with a probe diameter of 3 mm. To obtain a dispersion with a particle size of about 50 nm, the solution was additionally centrifuged at 2000 rpm for 10 min.

Sample preparation for XRD analysis: Silicon (Si) was chosen as the substrate. The substrates were preliminarily cleaned in several stages with various solvents: placed in DMF for 10 min, then treated with distilled water, acetone and again with water. Preparation of films by drop deposition. 50 μl of a suspension of NPs dispersed in n-hexane was applied by drop method onto a prepared substrate, covered with dark glass to prevent sunlight, until the solvent completely evaporated.

Characterization

The phase analysis of the samples was determined by X-ray phase analysis using D8 Advance powder X-ray diffractometer (CuKα radiation) in the angle range of 10°–50° with a step of 0.02° 2θ and an exposure of at least 0.4 s per step. X-ray diffraction patterns were indexed using the ICDD PDF2 database (2012).

Scanning electron microscopy (SEM) images were obtained using a Tescan Amber GMH microscope. Images were taken at an accelerating voltage of 30 kV, using a secondary electron detector (Everhart-Thornley) at working distance of 5 mm and × 500000 magnifications. Images in scanning transmission microscopy (STEM) mode were carried out at an accelerating voltage of 30 kV; STEM images were obtained in bright field mode at 30 kV.

TEM characterization of NPs was performed using a JEM-2010F transmission electron microscope (JEOL, Japan), operating at an accelerating voltage of 200 kV. Samples for TEM were prepared by dissolving a sol of perovskite NPs in ethanol in a volume ratio of 1 : 10, applying a drop of it to a carbon coated TEM-grid followed by drying. with a Lacey-type carbon film after which it was deposited on a copper grid with a Lacey-type carbon film.

The electron absorption spectra of colloidal solutions were recorded on a two-beam Cary-5000 UV-VIS-NIR spectrometer (resolution 0.05 nm). Photoluminescence spectra were recorded at room temperature on a Perkin Elmer LS-55 single-beam luminescence spectrometer (resolution 0.5 nm) in the wavelength range from 500 nm to 750 nm at an exciting light wavelength of 365 nm, the slit sizes were 10 nm.

Table S1 Lattice parameters for rhombohedral and cubic phases/Full profile analysis of diffraction patterns.

Sample	Space Group	a/Å	Angle β/ deg
$CsPbBr_3$	*Pm-3m*	5.8013	90
Cs_4PbBr_6	*R-3c*	13.3683	89.282

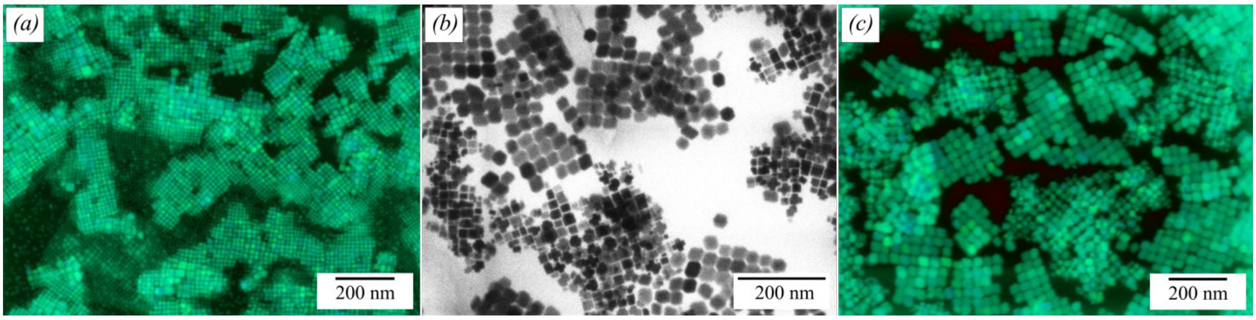

Figure S2 STEM-images of perovskite (*a*) $CsPbBr_3$ NPs (113 HI); (*b*) $CsPbBr_3$ (113 UT); (*c*) Cs_4PbBr_6 (416).

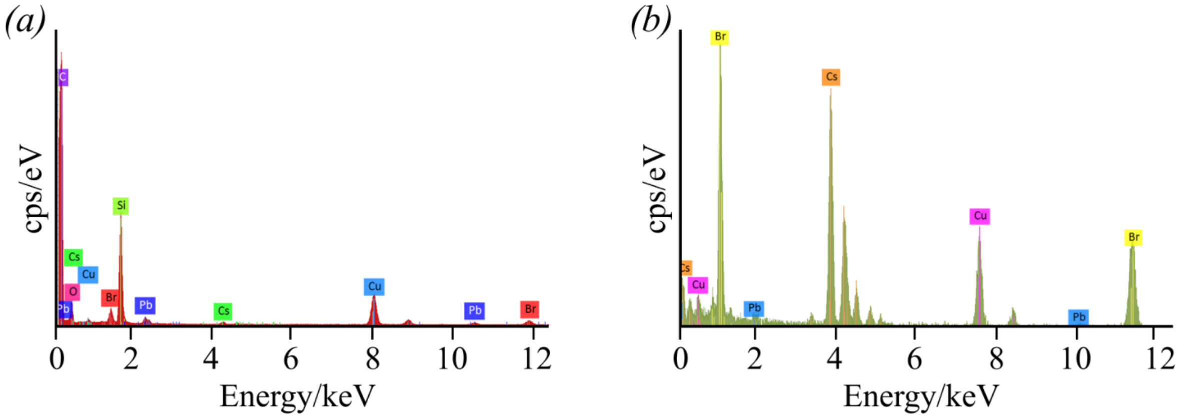

Figure S3 EDX spectra of (*a*) $CsPbBr_3$ NPs (113 HI) and (*b*) Cs_4PbBr_6 (416).

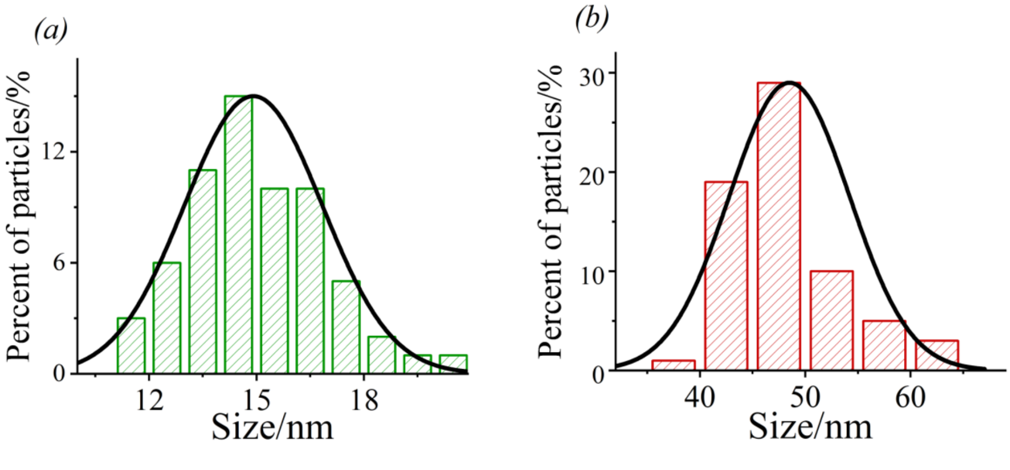

Figure S4 Particle size distribution according to TEM-images: (*a*) $CsPbBr_3$ NPs (113 HI) and (*b*) Cs_4PbBr_6 (416).

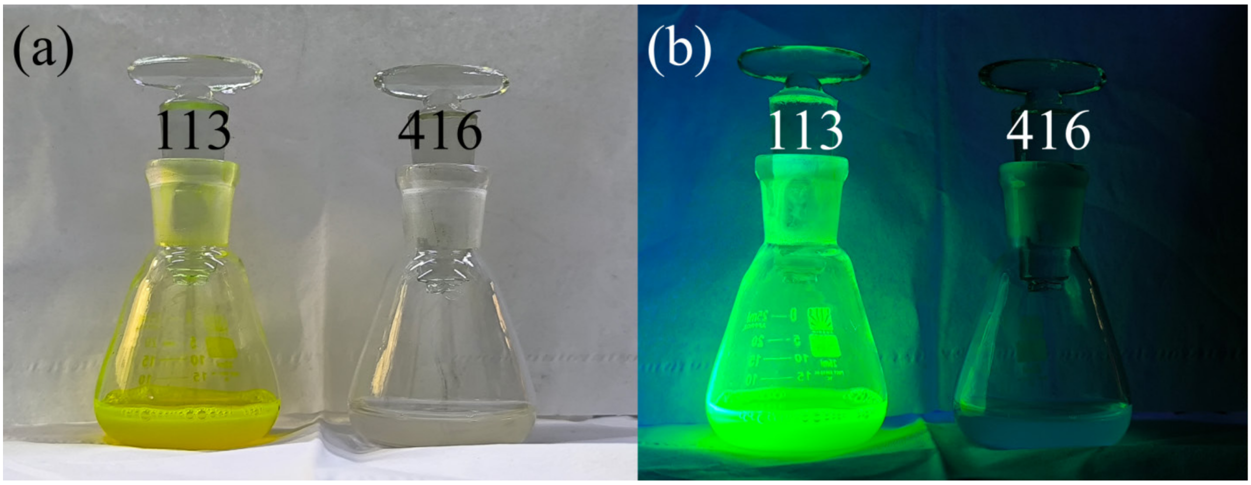

Figure S5 Colloidal solutions of $CsPbBr_3$ (113 HI) and Cs_4PbBr_6 (416) perovskite NPs: (*a*) general view; (*b*) under UV exposure (λ_{exc} = 290 nm).

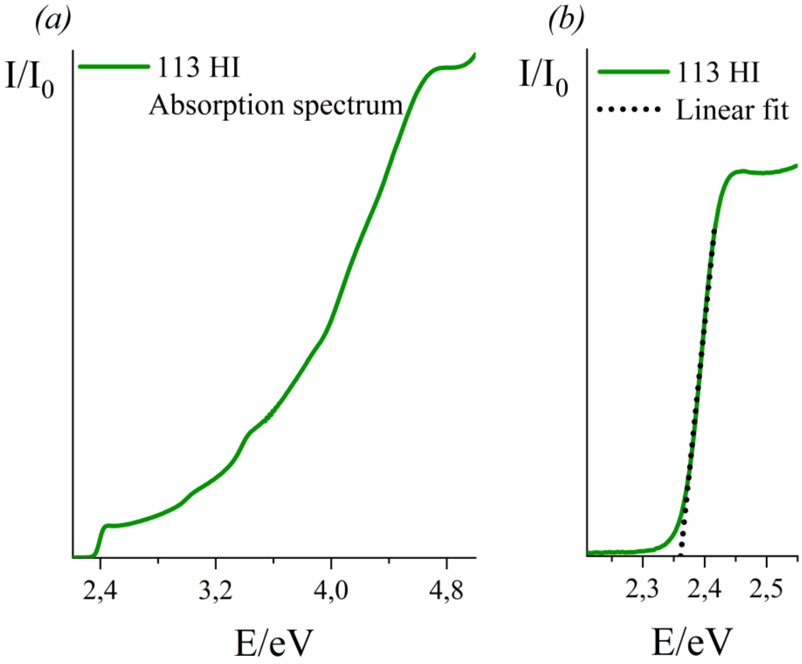

Figure S6 The optical band gap estimation of nanoparticles by Tauc method:[S3] (*a*) absorption spectrum of NPs $CsPbBr_3$ (113 HI) in the energy range from 2.4 eV to 4.8 eV; (*b*) enlarged view of the absorption edge in the narrow energy range from 2.3 eV to 2.5 eV with linear fitting to determine the energy of the band gap (2.34 eV).

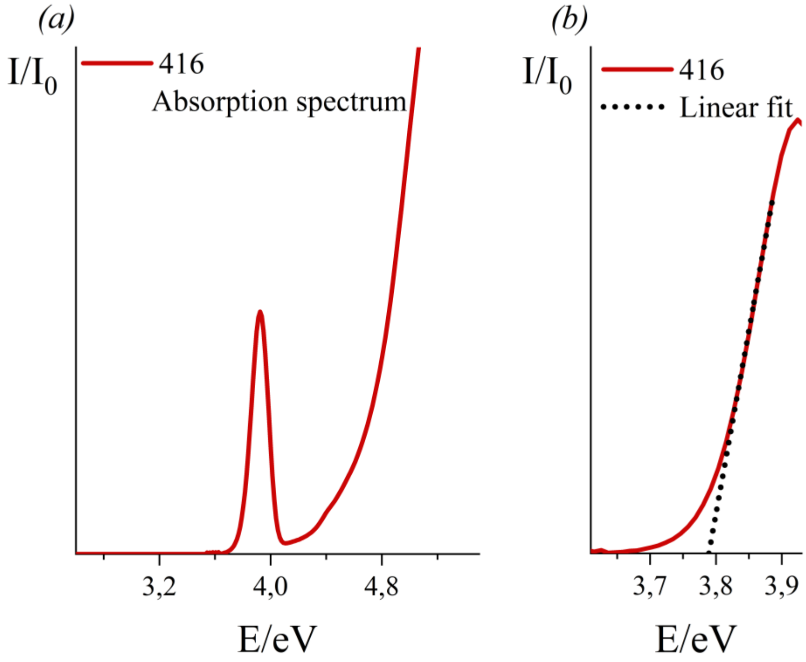

Figure S7 The optical band gap estimation of nanoparticles by Tauc method:[S3] (*a*) absorption spectrum of Cs_4PbBr_6 (416) in the energy range from 3.2 eV to 5.0 eV; (*b*) enlarged view of the absorption edge in the narrow energy range from 3.7 eV to 3.9 eV with linear fitting for band gap determination (3.73 eV).

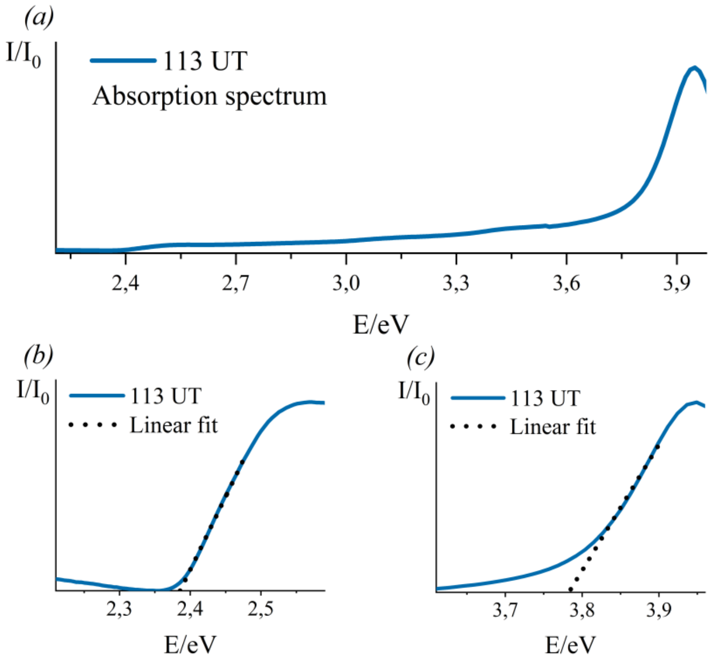

Figure S8 The optical band gap estimation of nanoparticles by Tauc method:[S3] (*a*) absorption spectrum of $CsPbBr_3$ (113 UT) in the energy range from 2.4 eV to 4.0 eV; (*b*) enlarged view of the absorption edge in the narrow energy range from 2.3 eV to 2.5 eV with linear fitting for band gap determination (2.38 eV) and (*c*) Enlarged view of the second absorption edge in the narrow energy range from 3.7 eV to 3.9 eV with linear fitting for band gap determination (3.77 eV).

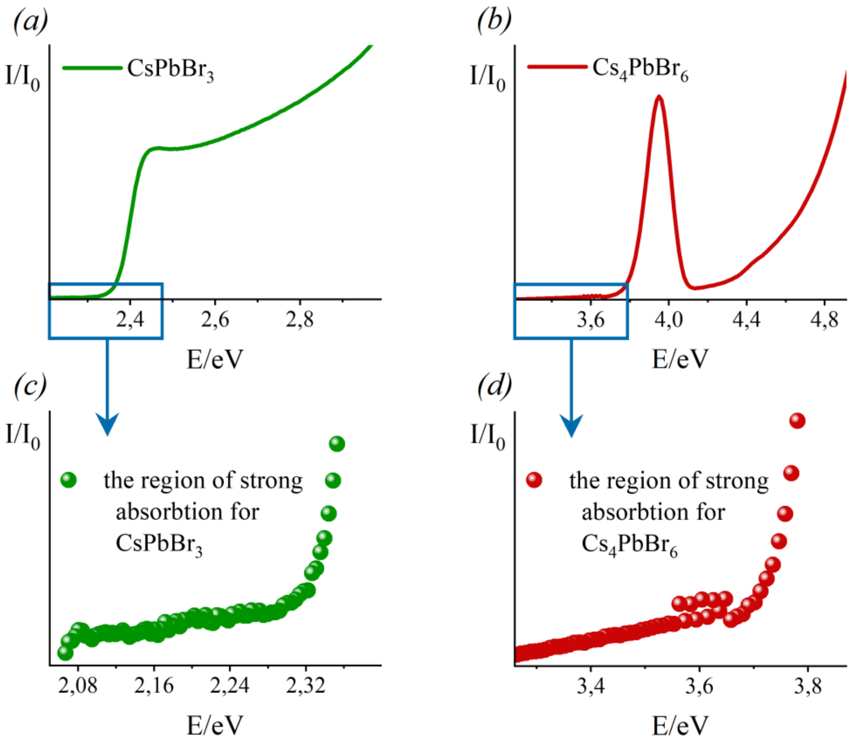

Figure S9 Absorption spectra: (*a*) The absorbance dependence of energy for $CsPbBr_3$ (113 HI); (*b*) the absorbance dependence of energy for Cs_4PbBr_6 (416); (*c*) region of strong absorbance for $CsPbBr_3$ (113 HI); (*d*) region of strong absorbance for Cs_4PbBr_6 (416).

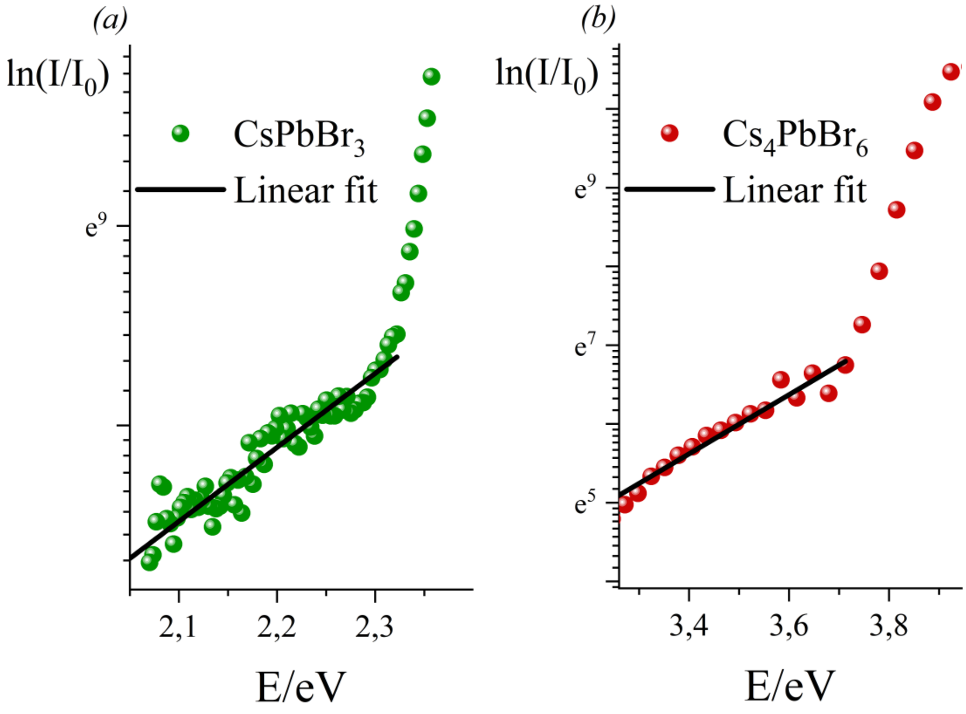

Figure S10 The Urbach energy estimation of nanoparticles[S4] by the dependence of ln(I/I$_0$) on energy for (*a*) $CsPbBr_3$ (113 HI) and (*b*) Cs_4PbBr_6 (416).

References

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