

Supporting Information

Photoinduced Transformation of $\text{Cs}_2\text{Au}_2\text{Br}_6$ into CsPbBr_3 Nanocrystals

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Experimental section

Chemicals. Cesium carbonate (Cs_2CO_3 , 99.9%, Sigma Aldrich), Lead (II) bromide (PbBr_2 , 99.99%, Sigma Aldrich), Oleic acid (OLA, 90%, Sigma Aldrich), Oleylamine (OLAm, technical grade 70%, Sigma Aldrich), 1-Octadecene (ODE, technical grade 90%, Sigma Aldrich), Methyl acetate (MeOAc, 99.98%, Gold(III) bromide (AuBr_3 , 99.99%, Sigma Aldrich), Toluene (Anhydrous, 99.99%, Sigma Aldrich), Ethanol (200 proof, Koptec).

Synthesis of CsPbBr_3 nanocrystals (NCs). CsPbBr_3 NCs were synthesized following a modified procedure adapted from Protesescu et al.¹ Cs-oleate was prepared by mixing 0.153 g of Cs_2CO_3 , 1.4 mL of OLA, and 3 mL of ODE in a 25 mL round bottom flask. The mixture was degassed at 80 °C for 1 hour. The lead bromide precursor was prepared by adding 3 mL of OLA, 3 mL of ODE, and 0.414 g of PbBr_2 to a 25 mL round bottom flask and degassing for 1 hour at 80 °C. After one hour, the temperature was raised to 170 °C, and 1.5 mL of OLAm was added to the mixture. The solution was degassed for one more minute. The vacuum was then turned off, and the flask was put into a nitrogen environment. Simultaneously, the Cs-oleate precursor was brought up to 120 °C and put under a nitrogen atmosphere. Once both solutions have reached the target temperatures, 2 mL of the Cs-oleate solution was injected into the lead-bromide precursor with a heated syringe (from the oven). The mixture was then immediately put in an ice bath until it reached a temperature of 65 °C.

The nanocrystals were washed with approximately 20 mL of 1-Octadecene and transferred to a 50 mL centrifuge tube. This was then spun down for 10 minutes at 7800 rpm. The supernatant was discarded, and the pellet was washed with 5 mL of ODE. The nanocrystals were again centrifuged for 10 minutes at 7800 rpm. The pellet was dispersed in 5 mL toluene and washed with 5 mL of methyl acetate. The nanocrystals were spun down again for 10 minutes at 7800 rpm. The supernatant was discarded, and the pellet was dispersed in 3 mL toluene and again centrifuged for 10 minutes at 7800 rpm. The supernatant was collected and preserved for further experiments.

Synthesis of $\text{Cs}_2\text{Au}_2\text{Br}_6$ nanocrystals. AuBr_3 was dissolved in 1:10 v/v ethanol/toluene mixture to get 10 mM solution. 19 μL OLA was added to 1 mL of 10 mM AuBr_3 solution and the solution was used within an hour of preparation. The prepared AuBr_3 solution was added to CsPbBr_3 nanocrystals in toluene to obtain 1 mM AuBr_3 in 100 nM $\text{Cs}_2\text{Au}_2\text{Br}_6$ nanocrystal suspension. The ssuspension was stirred for 10 minutes.² The molar ratio of precursors, $[\text{AuBr}_3]:[\text{CsPbBr}_3]$ was 10,000 - CsPbBr_3 concentration being expressed in terms of nanocrystal concentrations. The stability of CsPbBr_3 in 0.5% ethanol containing toluene was checked by monitoring absorption and emission spectra (Figure S1). It was found to be stable.

Preparation of PbBr_2 stock solution. PbBr_2 (0.828 g) was placed in a three-necked round bottom flask with 3 mL ODE, 3 mL OLA and 1.5 mL OLAm under nitrogen atmosphere. This solution was heated to 150 °C until it turned clear. The final solution (0.30 M) was cooled and stored for later use.

Characterization Methods. UV-visible absorption spectra were recorded using a Cary 50 Bio spectrophotometer (Varian). Emission spectra were collected using a Horiba Jobin Yvon Fluorolog-3 spectrophotometer. The photoluminescence decay of the samples was monitored and recorded by time-correlated single-photon counting (TCSPC) using a Horiba Jobin Yvon system with a IBH Data Station Hub

for timing with a 371nm nano LED light source. Transmission electron microscopy (TEM) and Scanning Transmission Electron Microscopy (STEM) imaging were carried out using FEI Titan 80-300 (300 kV) high-resolution transmission electron microscope. X-ray diffraction (XRD) analysis was performed by using D8 Advance Davinci, Bruker X-ray diffractometer with Cu K α X-ray ($\lambda = 1.5406 \text{ \AA}$) and for all the samples, the value of 2θ was varied from 10° to 70° with a scan rate of $0.3^\circ \text{ min}^{-1}$.

The colloidal suspension of nanocrystals in a quartz cuvette was subjected to 1Sun ($\lambda > 400 \text{ nm}$, 100 mW/cm^2) visible light excitation. The absorbance and emission spectra and other spectral characterization were made on samples irradiated at different irradiation times.

Transient Absorption Experiments. Femtosecond transient absorption measurements were carried out using a Spectra-Physics Solstice Ace laser system (800 nm fundamental, $\sim 5 \text{ mJ/pulse}$, $\text{fwhm} = \sim 30 \text{ fs}$, repetition rate of 1 kHz) with detection software from Ultrafast Systems (Helios). A small portion of the fundamental beam was frequency-doubled to 400 nm (using a 1 mm thick BBO crystal) to generate the pump beam, and another part of the fundamental beam was passed through an optical delay stage and focused onto a sapphire crystal to generate a white-light continuum probe pulse. The pump and probe beams are spatially overlapped onto the sample such that the probe is within the area of pump irradiation. The pump beam was sent through an iris of known diameter and the power was adjusted via a neutral density filter wheel to keep the power density at $\sim 15 \text{ } \mu\text{J/cm}^2$ for these experiments. Under these conditions the transient absorption experiments do not show any evidence of multiple exciton/Auger recombination effects. The measurements were done using 2 mm cuvette under argon atmosphere to eliminate any potential interactions with oxygen.

Determination of concentration of CsPbBr₃ nanocrystals

The intrinsic absorption cross section of the nanocrystals depends on their size and shape. The intrinsic absorption coefficient (μ_i) can be used to calculate the molar extinction coefficient (ϵ), of CsPbBr₃ NCs.³ We have taken the molar extinction coefficient (ϵ) and absorbance at 335 nm to determine the concentration of our samples.

$$\epsilon_{335} = \frac{N_A V_{NC}}{\ln 10} \mu_i$$

Here, N_A is the Avogadro constant, V_{NC} is the volume of nanocrystal and μ_i at 335 nm = $1.98 \times 10^5 \text{ cm}^{-1}$

$$\epsilon_{335} = 0.0518 \times d^3 \text{ cm}^{-1} \mu\text{M}^{-1}$$

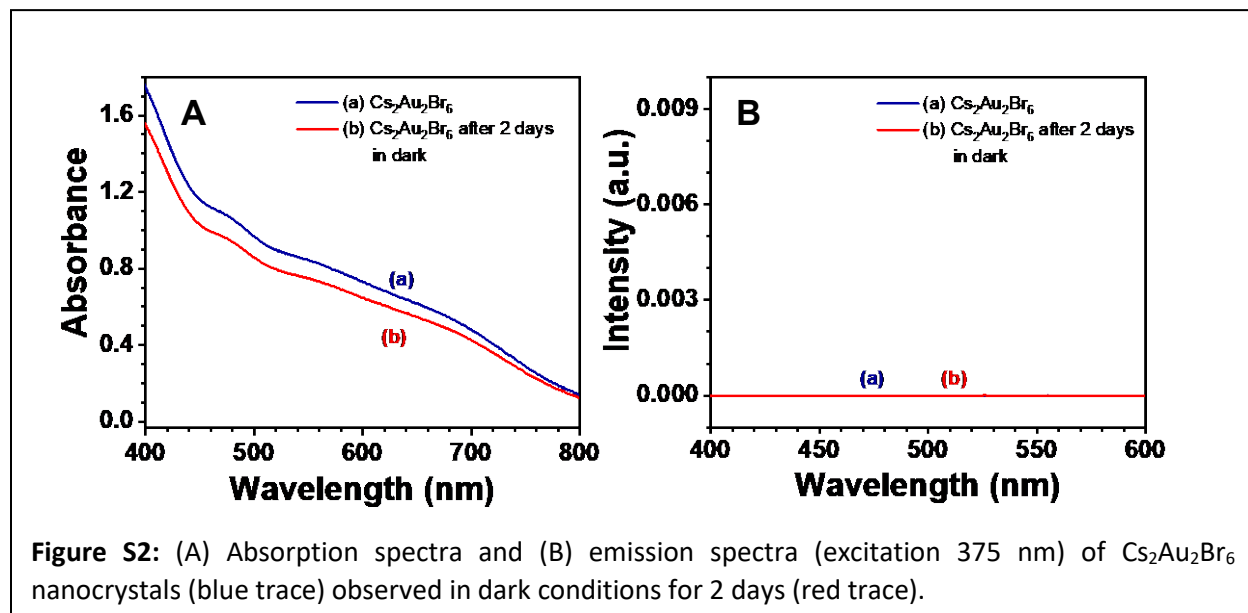
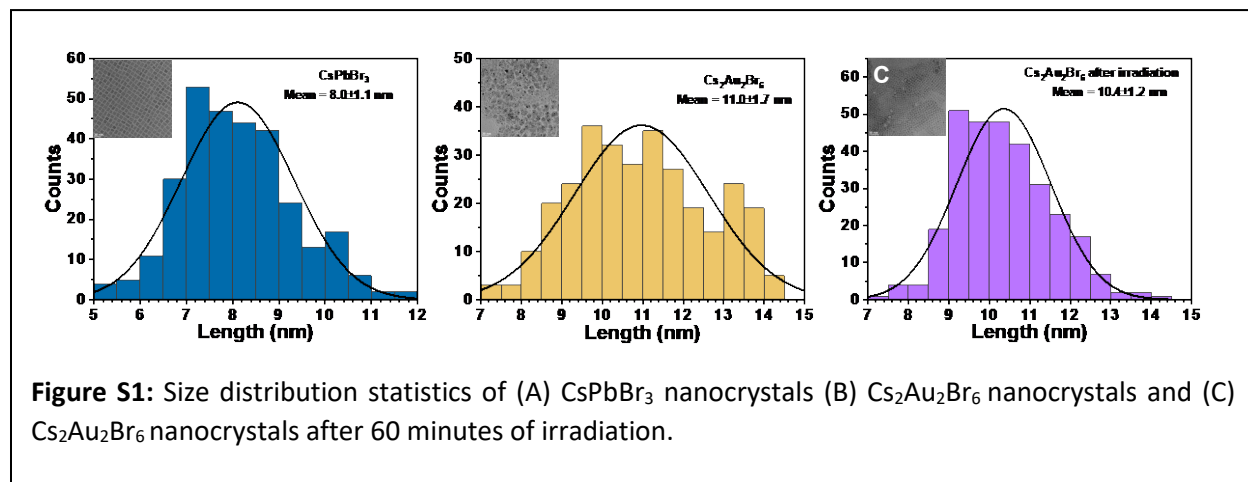
where, d is the cube edge in nanometer and found to be 8.1 nm.

$$\epsilon_{335} = 27.12 \text{ cm}^{-1} \mu\text{M}^{-1}$$

Absorbance, $A = \epsilon Cl$

$C = A/\epsilon l$

The path length, $l = 1\text{cm}$ and the corresponding absorbance value at 335 nm is used to calculate the concentration, C .



	A ₁ (%)	τ ₁ (ps)	A ₂ (%)	τ ₂ (ps)	<τ> (ps)
CsPbBr ₃ (510 nm)	68.3	36.3	31.7	259.6	107.1
Cs ₂ Au ₂ Br ₆ (520 nm)	60.6	5.3	39.4	207.9	85.2
Cs ₂ Au ₂ Br ₆ (750 nm)	-	12.3	-	-	12.3

Table S1: Kinetic analysis of the TA data for CsPbBr₃ (510 nm) and Cs₂Au₂Br₆ (520 nm and 750 nm) calculated from the ultrafast transient absorption/bleach recovery measurements. The induced absorption of Cs₂Au₂Br₆ (750 nm) was fit to a monoexponential function $y = A_1 e^{-t/\tau_1}$. The bleach kinetics were fit to a biexponential function $y = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2}$ and the average lifetime was found using the following equation:

$$\tau_{avg} = \frac{\sum_{n=1}^i (A_i \tau_i)}{\sum_{n=1}^i (A_i)}$$

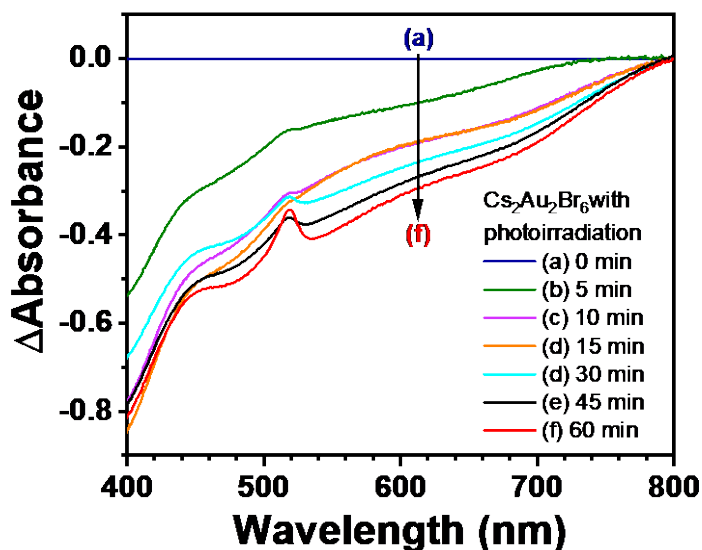
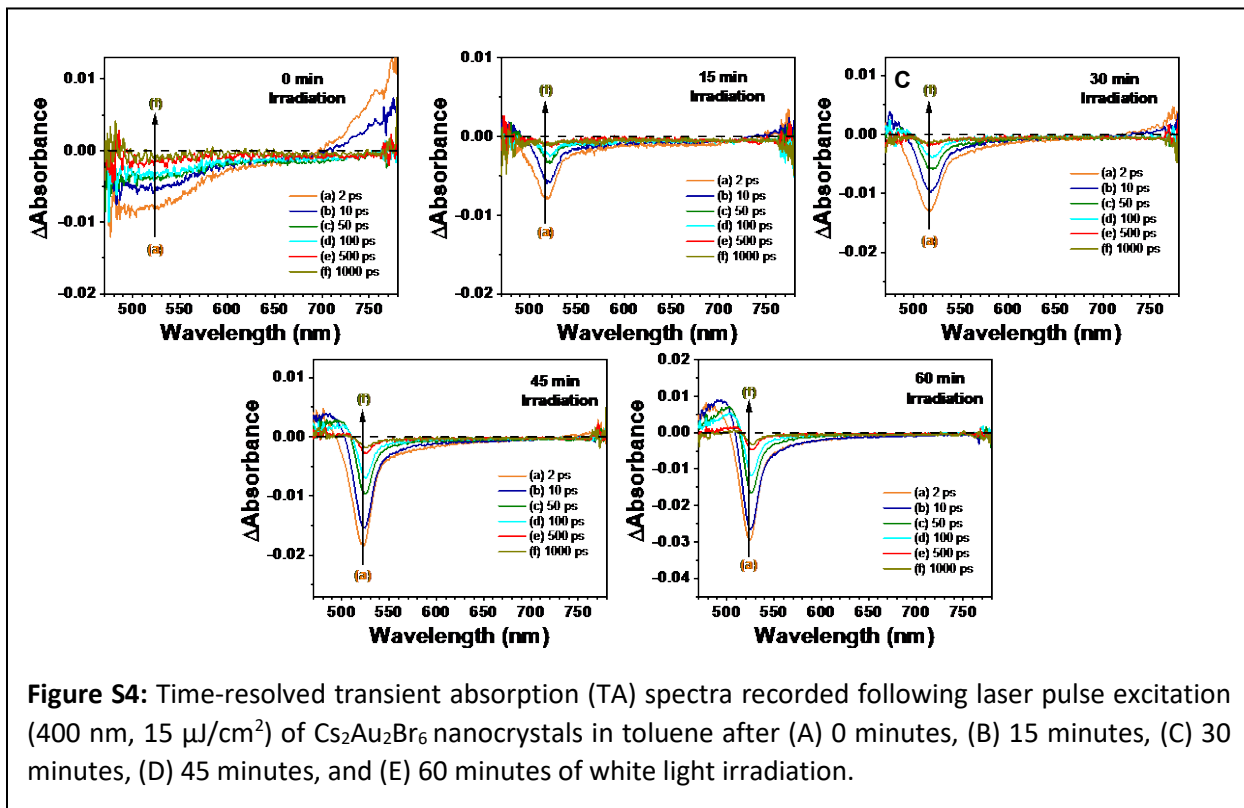


Figure S3: Difference absorption spectra recorded for the Cs₂Au₂Br₆ nanocrystals at different irradiation times in toluene.



$\text{Cs}_2\text{Au}_2\text{Br}_6$ (irradiation)	$A_1(\%)$	τ_1 (ps)	$A_2(\%)$	τ_2 (ps)	$\langle\tau\rangle$ (ps)
0 min	60.6	5.3	39.4	207.9	85.2
15 min	62.6	4.8	37.4	157.7	62.0
30 min	58.9	14.1	41.1	148.6	69.4
45 min	43.1	11.2	56.9	119.4	72.8
60 min	58.3	23.1	41.7	149.2	75.7

Table S2: Kinetic analysis of the TA data for $\text{Cs}_2\text{Au}_2\text{Br}_6$ (520 nm) at different irradiation times calculated from the ultrafast transient absorption/bleach recovery measurements. The bleach kinetics were fit to a biexponential function $y = A_1e^{-(t/\tau_1)} + A_2e^{-(t/\tau_2)}$ and the average lifetime was found using the following equation:

$$\tau_{avg} = \frac{\sum_{n=1}^i (A_i \tau_i)}{\sum_{n=1}^i (A_i)}$$

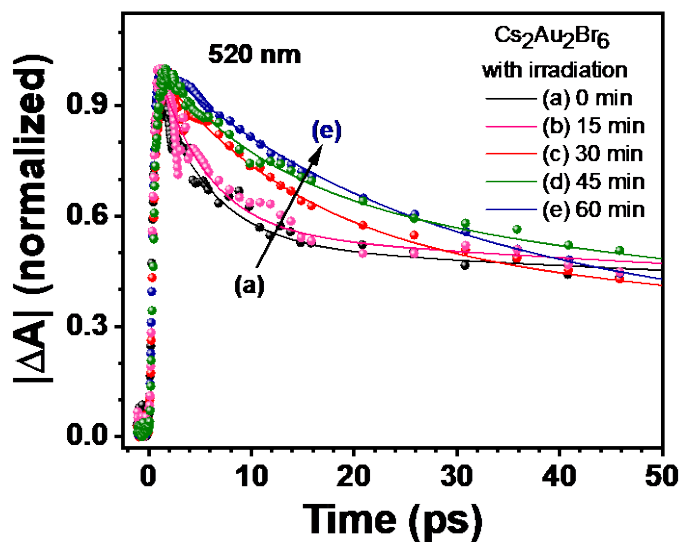


Figure S5: Bleach growth and recovery recorded at 520 nm for $\text{Cs}_2\text{Au}_2\text{Br}_6$ nanocrystals at different irradiation times in toluene over 50 ps timescale.

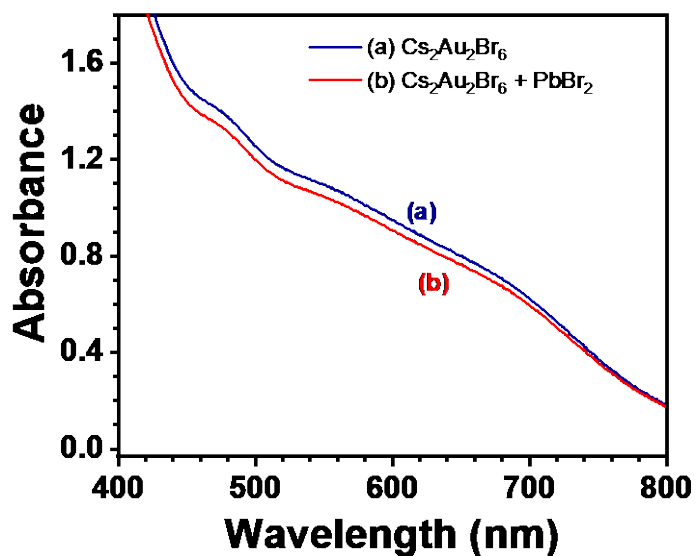


Figure S6: Absorption spectra of $\text{Cs}_2\text{Au}_2\text{Br}_6$ nanocrystal (100 nm) suspension in toluene before and after the addition of 30 μM PbBr_2 .

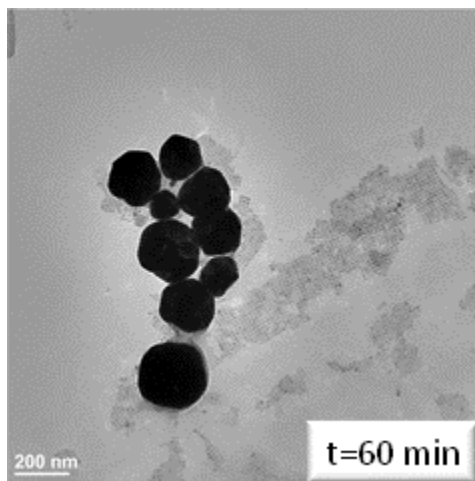


Figure S7: TEM images of $\text{Cs}_2\text{Au}_2\text{Br}_6$ nanocrystal samples following photoirradiation (white light, 100 mW/cm^2) at 60 minutes.

References

1. Protesescu, L.; Yakunin, S.; Bodnarchuk, M. I.; Krieg, F.; Caputo, R.; Hendon, C. H.; Yang, R. X.; Walsh, A.; Kovalenko, M. V., Nanocrystals of Cesium Lead Halide Perovskites (CsPbX_3 , X= Cl, Br, and I): Novel Optoelectronic Materials Showing Bright Emission with Wide Color Gamut. *Nano Lett.* **2015**, *15*, 3692-3696.
2. Roman, B. J.; Otto, J.; Galik, C.; Downing, R.; Sheldon, M., Au Exchange or Au Deposition: Dual Reaction Pathways in Au– CsPbBr_3 Heterostructure Nanoparticles. *Nano Lett.* **2017**, *17*, 5561-5566.
3. De Roo, J., et al., Highly Dynamic Ligand Binding and Light Absorption Coefficient of Cesium Lead Bromide Perovskite Nanocrystals. *ACS Nano* **2016**, *10*, 2071-2081.