

Supporting Information

The role of mid-gap states in all-inorganic CsPbBr₃ nanoparticle one photon up-conversion

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Experimental Methods

Materials and chemicals. Cesium carbonate (Cs₂CO₃, Alfa Aesar, 99.995% trace metals basis), lead (II) bromide (PbBr₂, Alfa Aesar, 98+%), oleylamine (OAm, Sigma Aldrich, technical grade 70%), oleic acid (OA, Sigma Aldrich, technical grade 90%), 1-octadecene (ODE, Sigma Aldrich, technical grade 90%), hexanes (Sigma Aldrich, anhydrous mixture of isomers, 99%), Rhodamine 6g (Acros Organics, 99% pure), toluene (Sigma Aldrich, anhydrous, 99.8%), fluorescein (Sigma Aldrich, for fluorescence, free acid), Ammonium thiocyanate (Sigma Aldrich, 99.99% trace metals basis).

Preparation of Cs-oleate: Cs₂CO₃ (0.200 g), OA (0.624 mL), and ODE (10 mL) were added to a 25-mL 3-neck round bottomed flask and heated for 1 hour at 120°C under vacuum to dry. After 1 hour, the flask was put under argon and heated to 150°C until all the Cs₂CO₃ had reacted.

Synthesis of CsPbBr₃ NCs: PbBr₂ (0.069 g) and ODE (5 mL) were added to a 25-mL 3-neck round bottomed flask and heated under vacuum to 120 °C for 1 hour. The solution was then placed under argon, and dried OAm (0.5 mL) and dried OA (0.5 mL) were injected to solubilize the PbBr₂. The temperature increased to 180°C, and the Cs-oleate (0.4 mL) was swiftly injected. After 1 minute, the solution was cooled with an ice bath. The final solution was centrifuged at 3000 g-forces for 5 minutes and the supernatant was discarded. The precipitate was dispersed in hexane.

NH₄SCN Treatment of CsPbBr₃ NCs: NH₄SCN was added to a vial of CsPbBr₃ suspended in hexane and vigorously stirred for between 20 and 30 minutes. The resulting cloudy solution was centrifuged at 3000 g-forces for 5 minutes, and the supernatant was decanted and analyzed.

Absorbance: UV-VIS spectra from 300 to 800 nm were collected on an Ocean Optics Flame-S-UV-Vis spectrometer with an Ocean Optics DH-200-Bal deuterium and halogen lamp light source.

Above-gap Excitation Photoluminescence (SSPL): SSPL was measured on a PTI QuantaMaster spectrofluorometer with a xenon arc lamp for steady state excitation, using a holographic grating to select for 462 nm excitation. The emission was detected using A PMT (Hamamatsu R928). The

photoluminescence quantum yield (PLQY) was calculated relative to a fluorescein standard with a PLQY of 95%. The excitation wavelength for PLQY measurements was 460 nm.

Below-gap Excitation Photoluminescence (ASPL): ASPL was measured using a 532 nm Nd:YAG CW laser ported through a WITec alpha 300 RA confocal microscope, focused on the sample using a long working distance 0.55 numerical aperture objective. The solutions were analyzed in capped quartz cuvettes placed under the objective. The PLQY was calculated relative to a Rhodamine 6g standard with a QY of 95%. The absorbance of the samples at 532 nm was determined by measuring their transmission and using the relationship $A = \log_{10}(T)$.

Temperature Dependence of ASPL: Samples were sandwiched between two quartz slides and heated using a Linkam Instruments TS1500 thermal stage attached to the WITec alpha 300 RA confocal microscope.

Powder X-ray Diffraction (XRD): XRD measurements were taken with a Bruker-AXS D8 Advanced Bragg-Brentano diffractometer equipped with Cu K- α x-ray radiation and a Lynxeye position sensitive detector.

Energy Dispersive X-Ray Spectroscopy (EDS): EDS spectra were collected on a FEI Tecnai G2 F20 ST FE-TEM microscope using a Fischione ultra-high resolution STEM HAADF detector coupled with an EDAX instruments EDS detector.

Transmission Electron Microscopy (TEM): TEM images were collected on a FEI Tecnai G2 F20 ST FETEM microscope operated at 200 kV.

Characterization of CsPbBr₃ Nanocrystals:

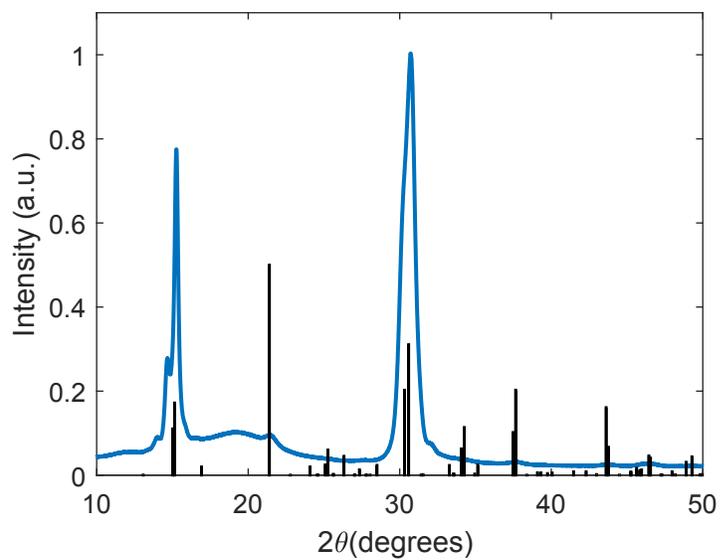


Figure S1. X-Ray diffractogram of CsPbBr₃ nanocrystals (blue) plotted against the crystal structure determined by Cottingham et al.¹

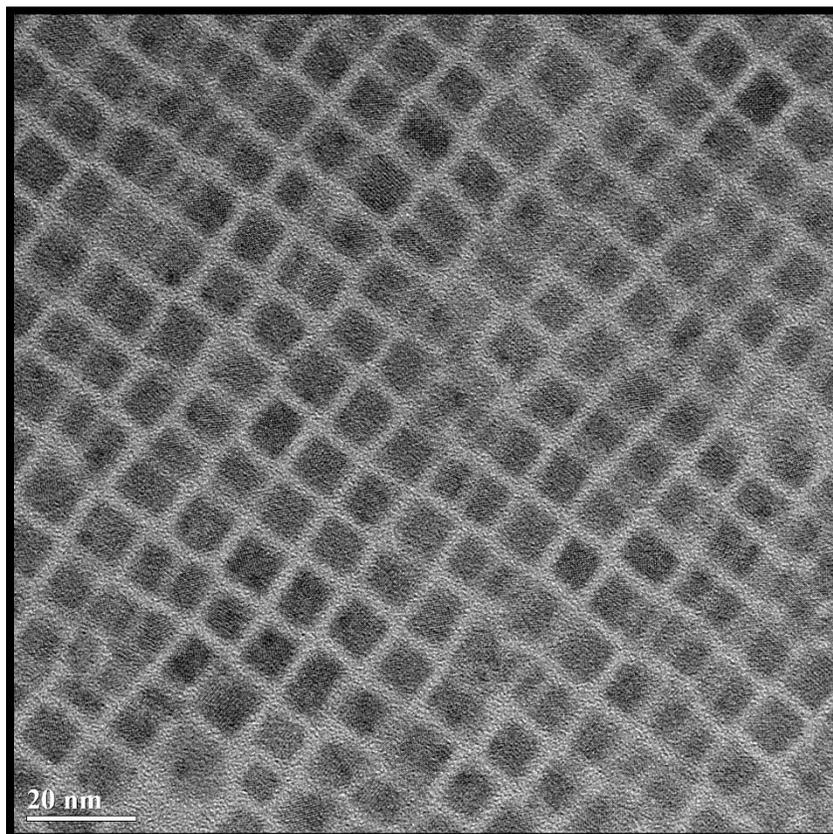


Figure S2. Transmission electron micrograph of CsPbBr₃ nanocrystals.

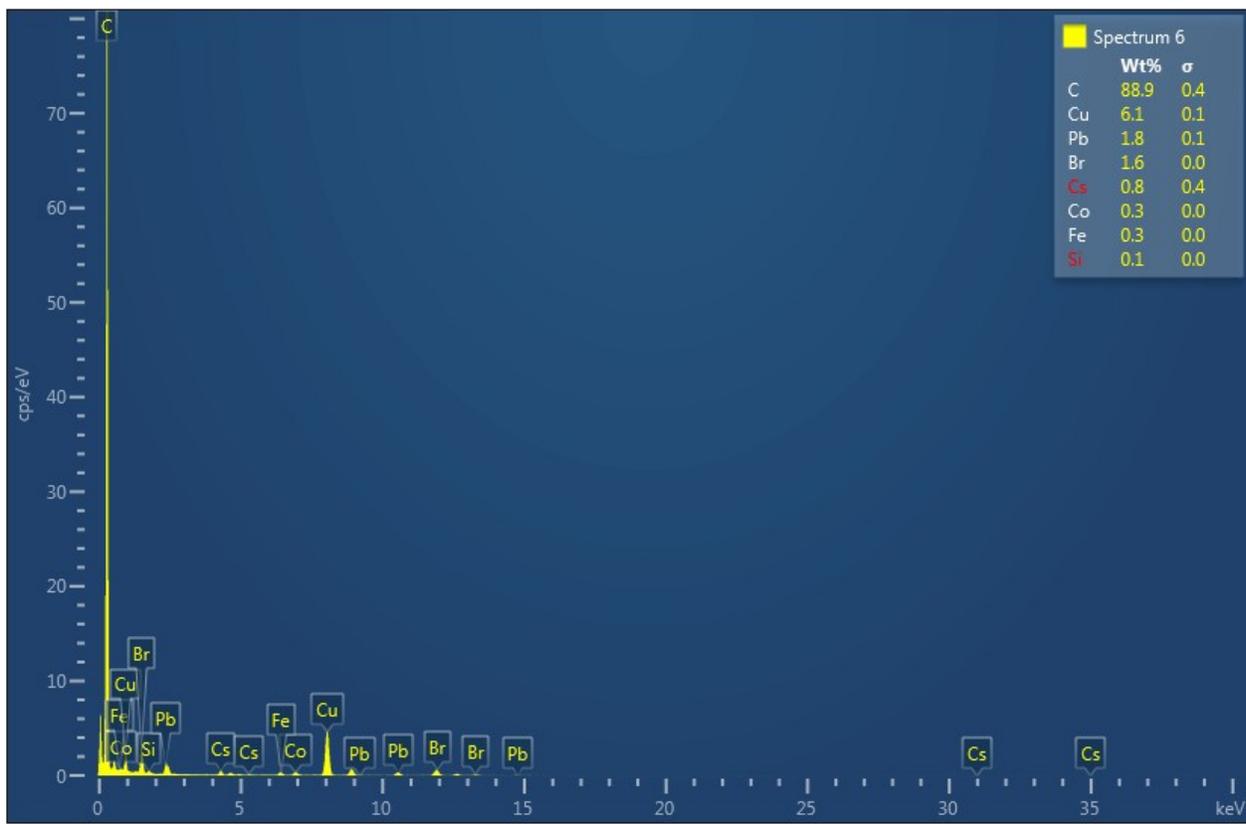


Figure S3. Energy dispersive x-ray spectrum of CsPbBr₃ nanocrystals. Molar ratios are calculated to be Cs₁Pb_{1.44}Br_{3.33}. Excess Pb and Br is likely due to excess PbBr₂ salt.

References:

1. P. Cottingham and R. Brutchey, *Chem Commun*, 2016, **52**, 5246.