Highly efficient radiative recombination in intrinsically zero-dimensional perovskite micro-crystals prepared by thermally-assisted solution-phase synthesis

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Experimental section

CsBr (1.6g) and $PbBr_2$ (0.69g) were dissolved in 5 mL of H_2O and N,N-dimethylformamide (DMF) respectively. The CsBr solution was drop-cast on glass substrates that were cleaned by ultrasonication followed by washing for 10 minutes sequentially in each solvent; acetone, ethanol and deionized water. The substrates were kept at 110℃ until formation of the solid CsBr became evident at the edge of the droplet. $PbBr_2$ solution was added into the CsBr droplet gradually. This reaction was kept at 110℃. Finally, the perovskite micro-crystals were formed after solvent evaporation. Residual impurities were removed by washing in DMF several times.

X-ray diffractometry was performed using a Rigaku Ultima IV instrument. A field emission scanning electron microscope equipped with an energy dispersive X-ray spectrometer was used to observe the structure and chemical element distribution of the micro-crystals. Selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) were performed using a FEI Tecnai F20 instrument. Photoluminescence quantum yield (PLQY) measurements were performed using an integrating sphere accessory (F3018, Horiba Jobin Yvon) on a Fluorolog®-3 fluorimeter. All spectra for the absolute quantum yield measurements were corrected for the light source noise, wavelength sensitivity and the transmittance of the filters. The emission from the sample was collected using an integrating sphere. Fluorescence spectra were collected with a Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) equipped with a liquid N_2 cooled cryostat (OptiStatDN, Oxford Instruments). Power-dependent PL spectra were measured by exciting with 405 nm continuous-wave (CW) laser and collecting the emission using an Ocean Optics (HR2000) optical fiber-based spectrometer.

For time-resolved PL measurements, the excitation light was the frequency doubled output (450 nm) of a cavity-dumped, mode-locked Titanium: sapphire laser (Coherent Mira 900f/APE PulseSwitch) operating at 67 kHz. The excitation energy density ranged

from 0.1 nJ/cm^2 to 10 nJ/cm^2. The emission was collected through a thin film polarizer set at the magic angle, f#1 lens and monochromator (Jobin Yvon, H20), detected by a microchannel plate photomultiplier (Eldy, EM100) and acquired with a time-correlated single photon counting-based system based on NIM bin electronics comprising a constant fraction discriminator (Ortec 9307 Picotiming CFD), time-to-amplitude converter (EG&G Ortec 457) and multichannel analyzer (FAST Commtec, GmbH, MCA-3). The fluorescence wavelength was set at 520 nm. Time-resolved emission microscopy (TREM) images were acquired using an inverted microscope (Olympus IX71) with confocal scanning unit (FV300), which was coupled with a TCSPC imaging system comprising a PMT (Becker & Hickl, DCC-100) and SPC-150 card (B&H), with a highpass optical filter. FLIM images were analyzed using the associated software package (Becker & Hickl, SPCImage 5.5).

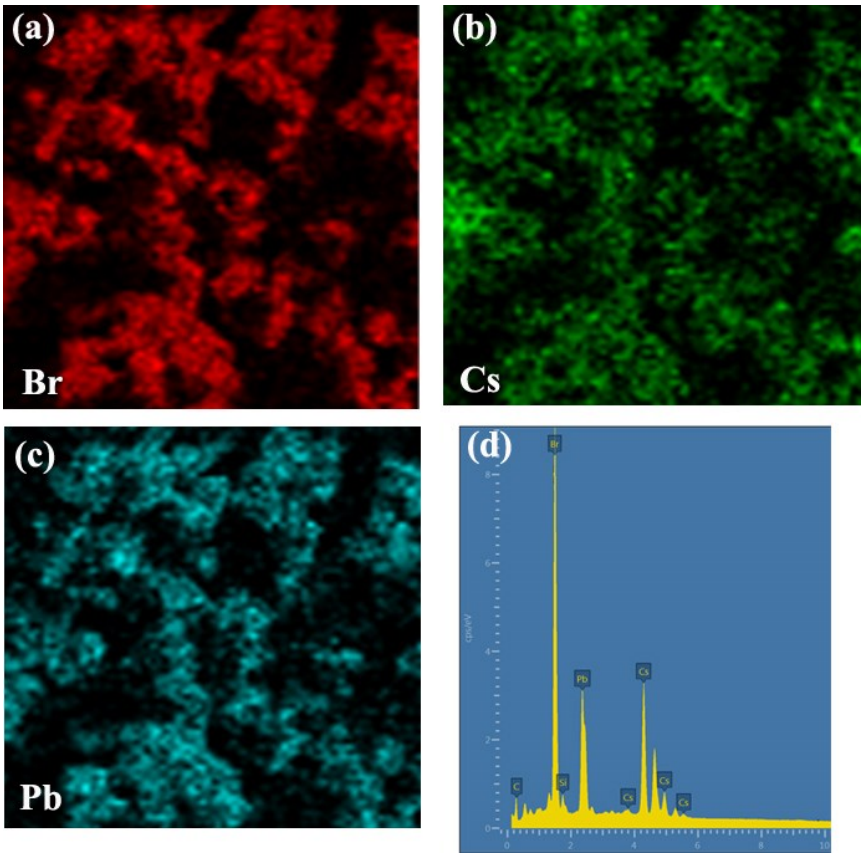

Figure S1. (a-c) Br, Cs and Pb elemental distribution images of zero-dimensional perovskite micro-crystals; (d) Energy dispersive spectrometer analysis of zero-dimensional perovskite micro-crystals.

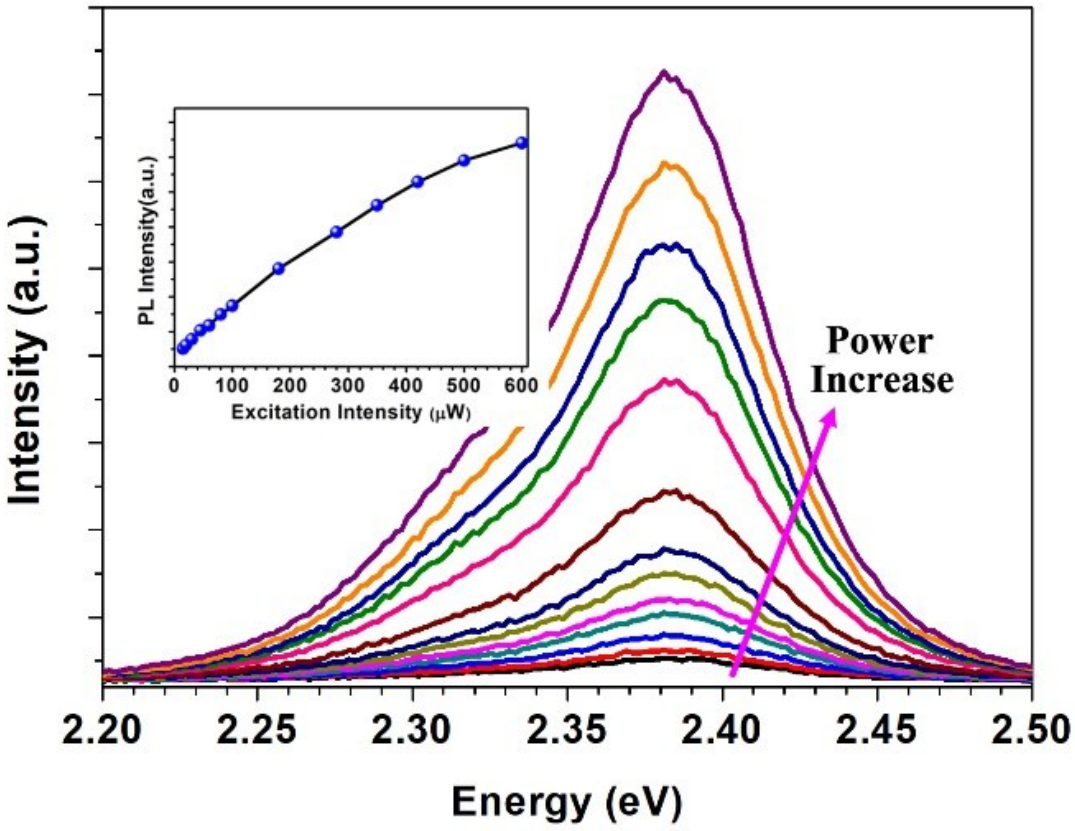

Figure S2. PL spectra of zero-dimensional perovskite micro-crystals under different excitation power. The inset is the fluorescence intensity vs the excitation intensity.

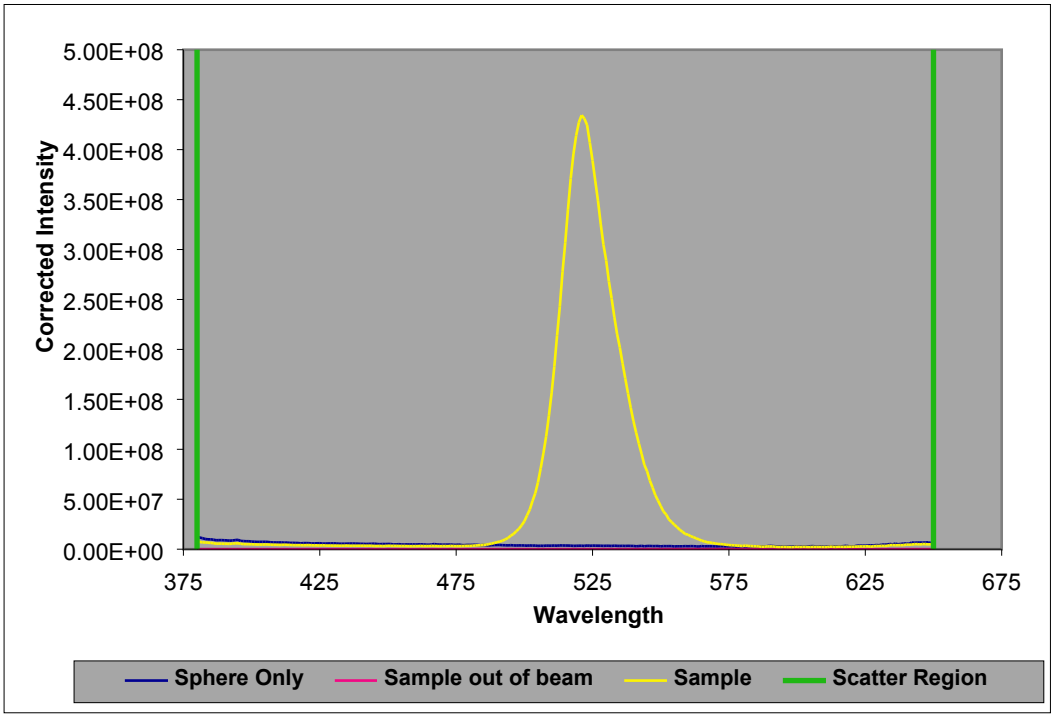

Figure S3. Fluorescence quantum yield measurement of zero-dimensional perovskite micro-crystals in an integrating sphere. Blue line stands for the measurement without excitation; pink line stands for that the excitation light is not focused on the sample; yellow line the emission from the sample; green line is the scattering region.

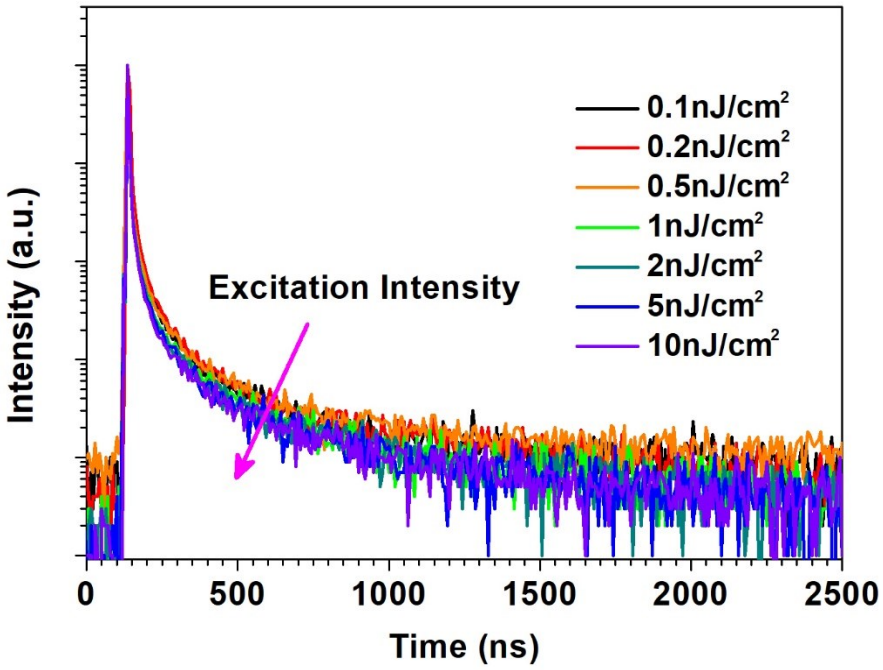

Figure S4. Excitation intensity dependent time-resolved PL spectra at 77K.

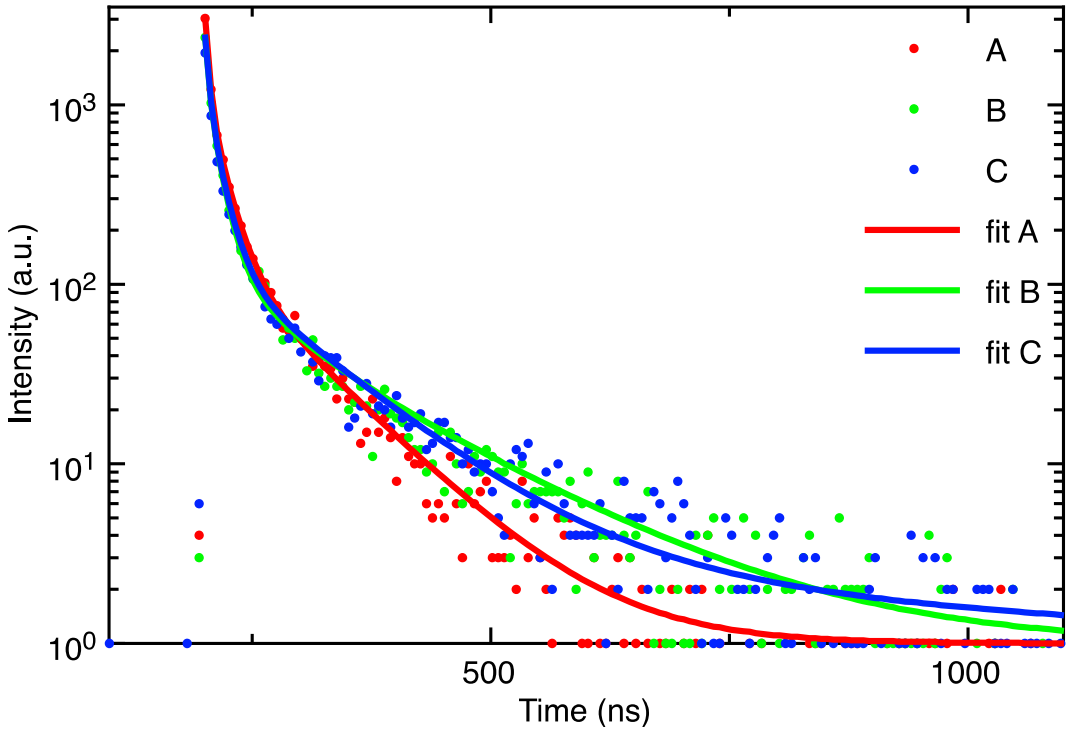

Figure S5. PL decay profiles of a single perovskite micro-crystal recovered from the TREM image shown in Figure 4 (b), but fit using four exponential parameterization functions, where decay times and pre-exponential factors were varied to obtain the best fit.