Supporting Information

High External Photoluminescence Quantum Yield in Tin Halide Perovskite Thin Films

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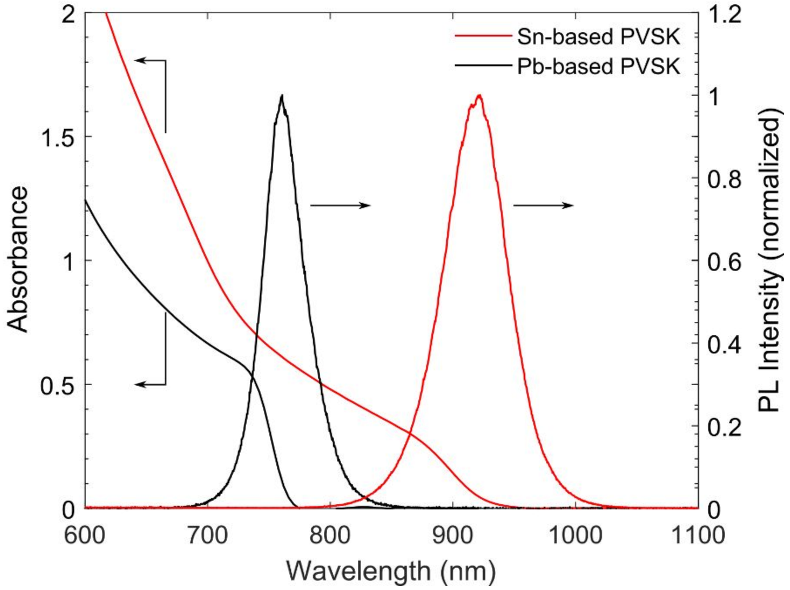


Figure S1: UV-Vis absorption spectra and PL peaks of Sn-based (red curves) and Pb-based (black curves) thin film perovskites (PVSK).

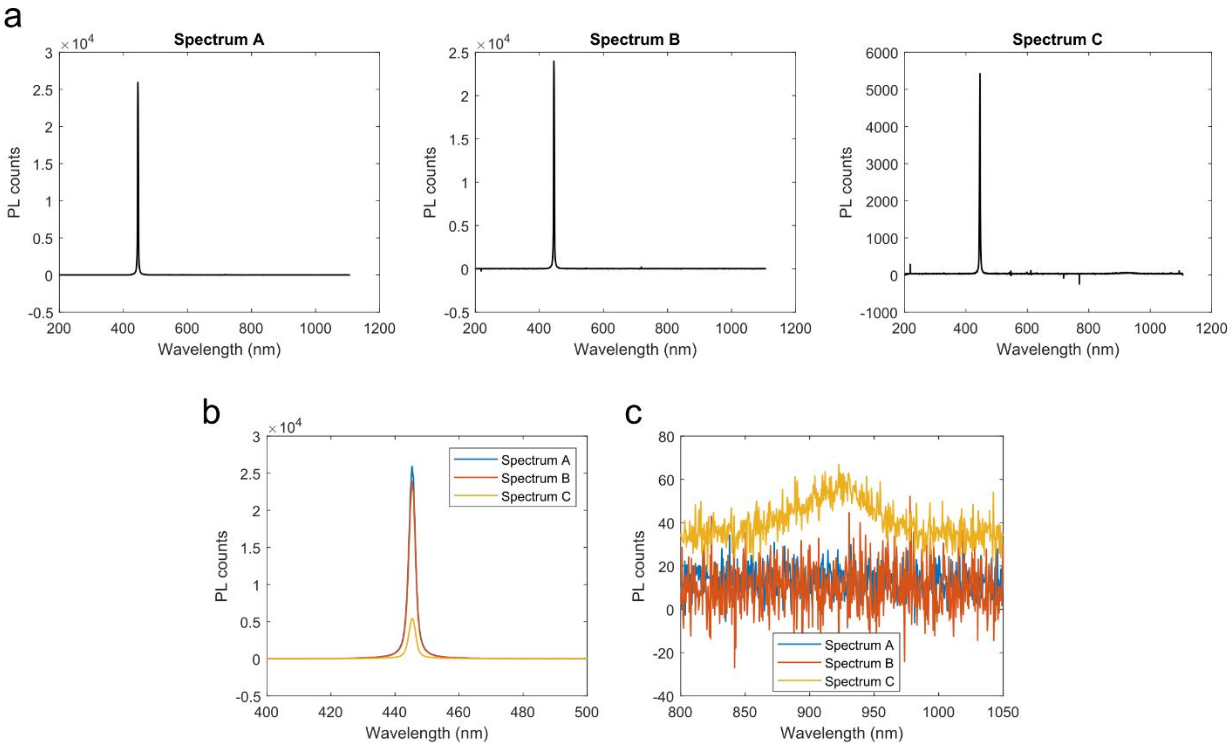


Figure S2: Raw data of FACsSnI$_3$ thin film measured in an integrating sphere system for the calculation of the absolute PLQY. (a-c) PL spectra of FACsSnI$_3$ acquired for the empty sphere, for the film placed in the sphere out of the laser beam path and for the film placed in the sphere and directly hit by the laser. (b) Magnification of the spectra between 400-500 nm to highlight the excitation light. (c) Magnification of the spectra between 800-1050 nm highlighting the emitted PL.

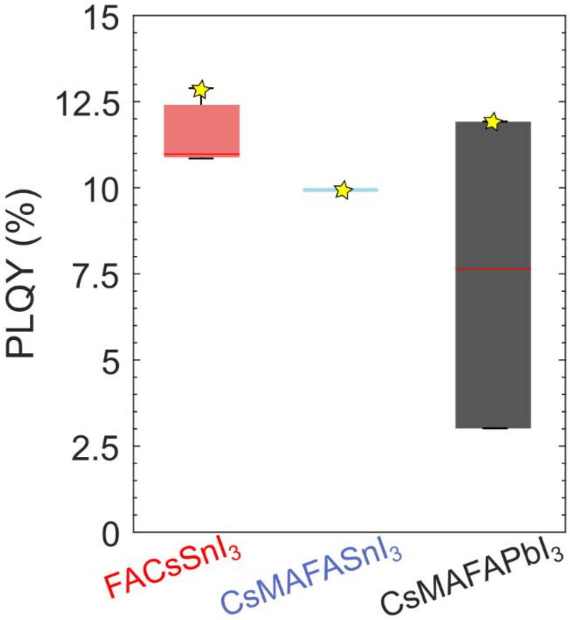


Figure S3: External PLQY of FACsSnI3 (red box), CsFAMASnI$_3$ (light blue box) and CsFAMAPbI3 (black box) thin films measured using an integrating sphere system at ~10 Wcm^{-2}. The red lines and stars indicate the average and champion values, respectively. The number of samples tested are: 3 samples of $FACsSnI_3$, 1 sample of $CsFAMASnI_3$ and 3 samples of $CsFAMAPbI_3$.

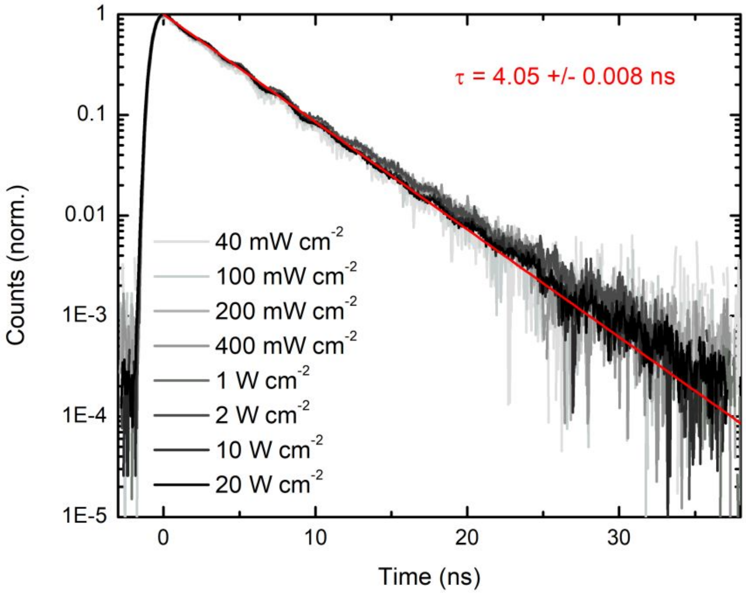
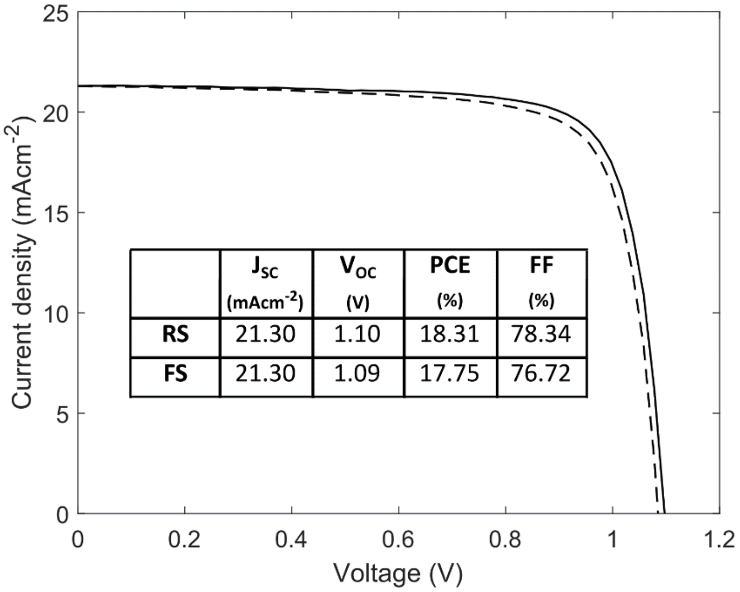


Figure S4: Time resolved PL (TRPL) of a $FACsSnI_3$ thin film measured at different excitation densities. TRPL decays can be fitted with a single exponential (red line) to give a lifetime τ=4 ns.



	J_{SC} (mAcm^{-2})	V_{OC} (V)	PCE (%)	FF (%)
RS	21.30	1.10	18.31	78.34
FS	21.30	1.09	17.75	76.72

Figure S5: Current density-voltage (JV) curve of an average performing neat Pb-based PSC under reverse (solid line) and forward (dashed line) scan.

EXPERIMENTAL METHODS

Sample preparation. N,N-dimethylformamide (DMF, anhydrous, 99.8%), chlorobenzene (anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, ≥99.9%) Anisole (anhydrous, 99.7%) and tin powder (<150 μm, 99.5%) were purchased from Sigma-Aldrich; methylammonium bromide (MABr) and methylammonium iodide (MAI) were purchased from Dyesol; Lead(II) iodide (PbI_2, 99.99%, CAS no. 10101-63-0), Lead(II) bromide ($PbBr_2$, ≥98%) and Tin(II) iodide (SnI_2, for Perovskite precursor) were purchased from Tokyo Chemical Industry (TCI); Tin(II) fluoride (SnF_2, 97.5%) was purchased by Alfa Aesar. All chemicals were used without any further purification. Glass substrates were cleaned in acetone and isopropyl alcohol (IPA) for 10 min by sonication. The cleaned glass substrates were treated with oxygen plasma for 10 min before any further deposition. Thin-film perovskite deposition was done in a N_2-filled glovebox and thin-films were glass encapsulated immediately after thermal annealing (in the glovebox to avoid oxygen).

Pb-based thin films: to make Pb-based ($Cs_{0.05}(FA_{0.85}MA_{0.15})_{0.95}Pb(I_{0.85}Br_{0.15})_3$) thin-film perovskite, the precursor solution (concentration of 1.2 M) was prepared in mixed solvents of DMF and DMSO with a volume ratio of 4:1. The molar ratio for FAI/MABr and $PbI_2/PbBr_2$ were 0.85/0.15, respectively. The precursor solution was stirred at 60°C until solved clearly and then, a small volume (5 %) of CsI precursor (1.5 M in DMSO) was added. The perovskite films were prepared in 2 step (1000 r.p.m for 10 s, 6000 r.p.m for 20 s), and 300 μL of chlorobenzene was dropped 5 s before the end of 2nd step. Resulting films were annealed at 100 °C for 45 min.

Sn-based thin films: to make Sn-based ($FA_{0.85}Cs_{0.15}SnI_3$) thin-film perovskite the precursor solution (concentration of 1.2 M) was prepared in mixed solvents of DMF and DMSO with a volume ratio of 4:1. The molar ratios for FAI/CsI was 0.85:0.15 and the molar ratio of (FAI+CsI)/ SnI_2 was 1:1. SnF_2 (10 mol% relative to SnI_2) and tin powders (5 mg ml^{-1}) were added in the precursor solution. The precursor solution was stirred at 60°C for 30 min and then filtered through 0.20-μm PTFE membrane before use. The perovskite films were deposited with one-step spin-coating procedures at 5000 r.p.m. for 50 s. Anisole (200 μl) was dropped on the spinning substrate at 25 s before the end of the procedure. The substrates were annealed at 120°C for 20 min.

Photoluminescence. The excitation source was an unfocused beam of a 450 nm c.w. diode laser (Oxxius). Photoluminescence was collected in reflection mode at a right angle from the excitation line and focused into a fiber coupled to a spectrometer (Ocean Optics Maya Pro 2000) with an intensity of ~100 mW cm^{-2}. PL was measured in air on glass encapsulated samples. For relative PLQY measurements, the integrated photoluminescence was measured at varying excitation intensities and plotted as: Relative PLQY $= \frac{I_{PL}}{I_{pump}}$.

Absolute values of PLQY were obtained from measurements performed in an integrating sphere (Labsphere) on encapsulated thin films deposited on non-conductive glass. Excitation was provided by a c.w. diode laser (450 and 405 nm, beam diameter ~370 nm) and spectra acquired through an optical fiber coupled from the sphere to a spectrometer (Ocean Optics Maya Pro 2000) with an excitation power of 0.1 mW and 10 mW. PLQY values were calculated employing the method proposed by de Mello et al [1] using the equations: $PLQY = \frac{P_C - (1-A)P_B}{L_A A}$ and $A = 1 - \frac{L_C}{L_B}$, where P_B and P_C are the integrated intensity of the diffused PL when the sample is placed inside the sphere out of the laser beam path and directly hit by the laser, respectively. L_A, L_B and L_C are the integrated intensity of the excitation light when the sample is out of the sphere, inside the sphere and out of the laser beam path and in the sphere and directly hit by the laser, respectively. The total samples tested in this work are 13: 8 samples of $FACsSnI_3$ 5 samples of $CsFAMAPbI_3$ 1 sample of $CsFAMASnI_3$; each sample was measured only at 1 excitation density and measurements were taken on set of samples measured on different days with films fabricated in different batches.

TRPL measurements were performed using a nitrogen cooled Hamamatsu Time Correlated Single Photon Counting (TCSPC) detector in a 50 ns measurement window, corresponding to a temporal resolution of 1 ns (FHM of the instrument response function). The decays were collected at 1.33 eV (930 nm), corresponding to the maximum of $FACsSnI_3$ PL spectrum. The sample was excited using a Chameleon oscillator (pulse duration 250 fs, 80 MH repetition rate) with central wavelength 750 nm; the repetition rate was reduced to 2 MHz through a pulse picker. The beam was focused on the sample with a 100 mm focal lens to a spot size of 40 μm radius. All measurements were performed in air on an encapsulated sample.

Other characterizations. *UV-vis* steady state absorption spectra were measured on perovskite thin films deposited on bare glass using a UV/VIS/NIR spectrophotometer Lambda 1050, PerkinElmer, in the wavelength range 400–1100 nm, a step size of 2 nm. *XRD* patterns were recorded with a Bruker D8 Advance diffractometer with Bragg–Brentano geometry equipped with a Cu Kα1 ($\lambda = 1.544060$ Å) anode, operating at 40 kV and 40 mA. All the diffraction patterns were collected at room temperature, with a step size of 0.03 in symmetric scan reflection mode and an acquisition time of 1 s. Perovskite films were prepared on bare glass substrates. *SEM* images were obtained using a MIRA3 TESCAN microscope with an accelerating voltage of 4 kV. Perovskite films were prepared on ITO/PEDOT:PSS/PTAA substrates. *Solar cell devices* were measured under simulated AM1.5 solar illumination using a class AAA solar simulator (Oriel Sol3A, Newport). The illumination intensity was calibrated using an unfiltered certified Si reference diode (area = 4 cm2, Newport) to be 100 mW cm^{-2}. The *current density–voltage (J–V)* characteristics were recorded with a Keithley 2440. The illuminated electrode area, defined with a holed black anodized aluminium mask, was 0.0935 cm^2. Devices were measured in an ambient atmosphere at 23 ± 2 °C and 40–60% relative humidity. The scan rates of the J–V sweep were 0.2 V s^{-1}. The forward scan was from -0.1 V to 1.2 V, and the backward scan was from 1.2 V to -0.1 V.

References

(1) de Mello, J.C., Wittmann, H.F. and Friend, RH (1997), An improved experimental determination of external photoluminescence quantum efficiency. Adv. Mater., 9: 230-232.