Supporting Information

High External Photoluminescence Quantum Yield in Tin Halide Perovskite Thin Films

Isabella Poli¹, Guan-Woo Kim¹, E Laine Wong¹, Antonella Treglia¹,², Giulia Folpini¹ and Annamaria Petrozza¹*

¹Center for Nano Science and Technology @PoliMi, Istituto Italiano di Tecnologia, via G. Pascoli 70/3, 20133, Milan, Italy

²Dipartimento di Fisica, Politecnico di Milano, Piazza Leonardo da Vinci, 32, 20133 Milano, Italy

*Correspondence and requests for materials should be addressed to Annamaria Petrozza (annamaria.petrozza@iit.it)

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

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 FACsSnI$_3$ (red box), CsFAMASnI$_3$ (light blue box) and CsFAMAPbI$_3$ (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 $\tau=4$ ns.

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

|     | $J_{SC}$ (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  |

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 (PbI₂, 99.99%, CAS no. 10101-63-0), Lead(II) bromide (PbBr₂, ≥98%) and Tin(II) iodide (SnI₂, for Perovskite precursor) were purchased from Tokyo Chemical Industry (TCI); Tin(II) fluoride (SnF₂, 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 N₂-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 (Cs₀.₀₅(FA₀.₈₅MA₀.₁₅)₀.₉₅Pb(I₀.₈₅Br₀.₁₅)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 PbI₂/PbBr₂ 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 (FA₀.₈₅Cs₀.₁₅SnI₃) 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)/SnI₂ was 1:1. SnF₂ (10 mol% relative to SnI₂) 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:  \( PLQY = \frac{P_C - (1 - A)P_B}{L_A} \) and  \( A = 1 - \frac{L_C}{L_A} \), 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 \(\text{FACsSnI}_3\) 5 samples of \(\text{CsFAMAPbI}_3\) 1 sample of \(\text{CsFAMASnI}_3\); 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 \(\text{FACsSnI}_3\) PL spectrum. The sample was excited using a Chameleon oscillator (pulse duration 250 fs, 80 MHz 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 \(\mu\)m radius. All measurements were performed in air on an encapsulated sample.

Other characterizations. \(UV\text{-vis}\) 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 K\(\alpha_1\) (\(\lambda = 1.544060\) 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 cm². 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.