

Supporting Information

Piperazine Suppresses Self-doping in CsSnI₃ Perovskite Solar Cells

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Experimental Section

Materials: SnI₂ synthesis and purification was performed following our previous work.¹ Cesium iodide (CsI), piperazine, pyridine, mesoporous TiO₂ (meso-TiO₂) paste (Dyesol DSL 18NR-T), titanium isopropylate (TTIP), chlorobenzene (CB), Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), piperazine, pyridine and poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) were purchased from Sigma Aldrich. FTO-coated glass (TEC7, 2.2 mm) was purchased from Hartford Glass Co. Inc. 4-isopropyl-4'-methyldiphenyliodonium tetrakis(pentafluorophenyl)borate (TPFB) was purchased from Tokyo Chemical Industry Co, Ltd. Low temperature thermoplastic sealant (Dyesol LTD.) was purchased for encapsulation process. All these materials were used as received.

Perovskite device fabrication: TiO₂ compact layer and meso-TiO₂ layer were formed on the FTO substrate following our previous work. The thickness of meso-TiO₂ was adjusted from 700 nm to 1 μm by changing the spin speed and concentration of TiO₂ paste. CsSnI₃ solution was prepared by adding CsI and SnI₂ into a mixed solvent of DMF and DMSO (4:1 volume ratio). The ratio of CsI and SnI₂ was 0.4 with fixed amount of SnI₂ (1.0 M). 2M piperazine solution was prepared with mixed solvent of DMF and DMSO (4:1 volume ratio) and then added into CsSnI₃ solution with various molar ratios from 0-25% to SnI₂. The mixed solutions were annealed at 90 °C for 10 min. Subsequently, 45 μL of the CsSnI₃ solution was dropped onto the meso-TiO₂ substrate and the substrate was spun at 1500 rpm for 30 sec. Then, the films were annealed at 90 °C for 25 min to complete the CsSnI₃ perovskite films. The hole transport layer was prepared from 32 mg PTAA and 3.6 mg TPFB dissolved in CB. An amount of 60 μl solution was dropped onto the perovskite films, followed by spinning the substrate at 1500 rpm for 30 sec to form a hole transporting layer. Subsequently, the films were annealed at 70 °C for 5 min. Finally, 80-

nm-thick gold top electrodes were deposited in vacuum using a thermal evaporation to complete device fabrication. All devices were encapsulated using a 30- μm -thick hot-melting polymer and a microscope cover slip. These procedures were carried out in a N_2 atmosphere.

Perovskite film and device characterizations: Current density-voltage (J - V) characteristics of the devices were measured in air under 1-sun illumination (AM1.5G, 100 mW/cm^2) using a certified solar simulator (Abet Technologies) and Keithley 2400 source meter. The voltage was swept from positive bias to negative bias (namely, from V_{OC} to 0 V) unless otherwise stated. The overlapping area between the un-etched FTO glass and Au electrode was between 0.12 and 0.15 cm^2 . External quantum efficiencies (EQEs) were characterized using an Oriel model QE-PV-SI instrument equipped with a NIST-certified Si diode. Monochromatic light was generated from an Oriel 300 W lamp. Transmittance and reflectance of the perovskite films was obtained from 300 nm to 1200 nm at room temperature using a Shimadzu UV-3600 PC double-beam, double-monochromator spectrophotometer. UV-Vis absorption spectra was calculated from the transmittance by using an equation of $\alpha = -\log(1-T-R)$, where α , T and R are absorbance, transmittance and reflectance, respectively. XRD patterns were collected using a Rigaku MiniFlex600 X-ray diffractometer (Cu $K\alpha$, 1.5406 Å) operating at 40 kV and 20 mA. Either Hitachi 4800 or 8030 SEM was used for surface morphology study. Fourier-transform infrared spectroscopy (FT-IR) was performed using Nexus 870 spectrometer (Thermo Nicolet) with Attenuated total reflection (ATR) spectroscopy mode. Time-resolved photoluminescence data were collected at room temperature using a streak camera system (Hamamatsu C4334 Streakscope). 600 nm laser pulses with power of 300 μW were utilized as the excitation source, which were generated by the same high repetition rate (100 kHz) ultrafast laser system.

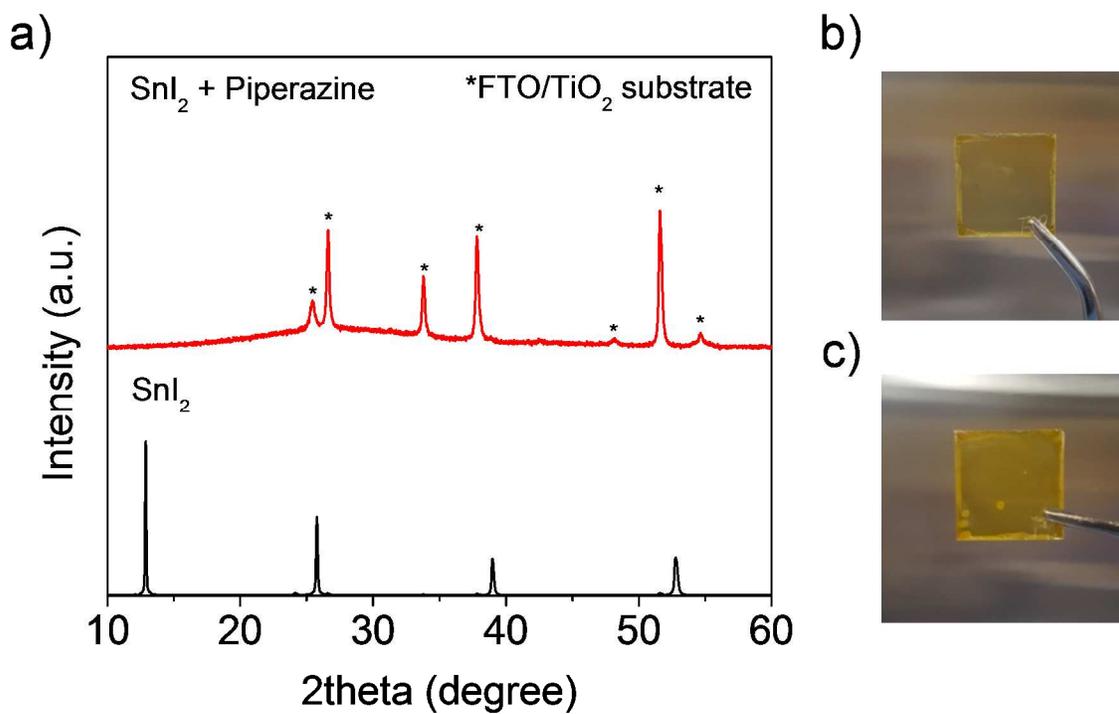


Figure S1. (a) XRD patterns of the SnI₂ films with and without 20 mol% piperazine on meso-TiO₂/c-TiO₂/FTO substrates. Pictures of SnI₂ films (b) with and (c) without 20 mol% piperazine on meso-TiO₂/c-TiO₂/FTO substrates.

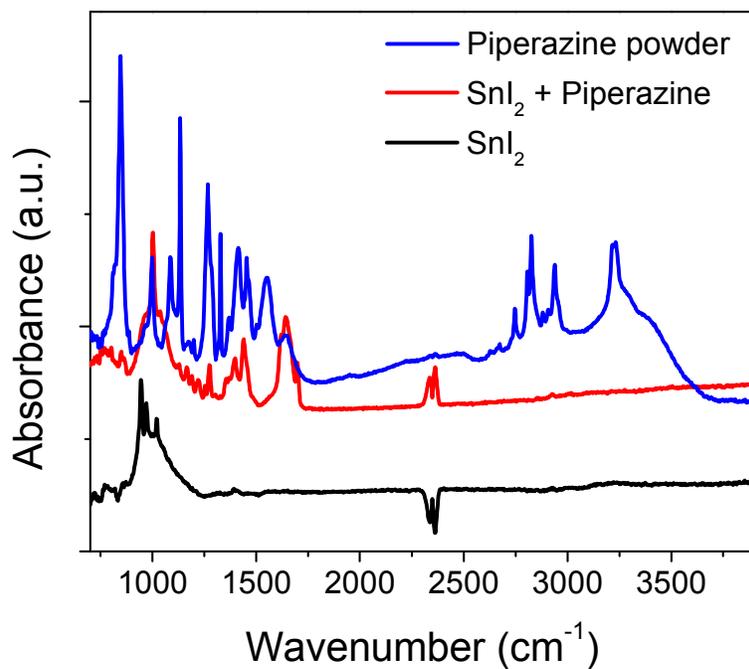


Figure S2. FTIR spectra of the SnI₂ film, piperazine powder and SnI₂-piperazine film. Piperazine still presented in the film after thermal annealing.

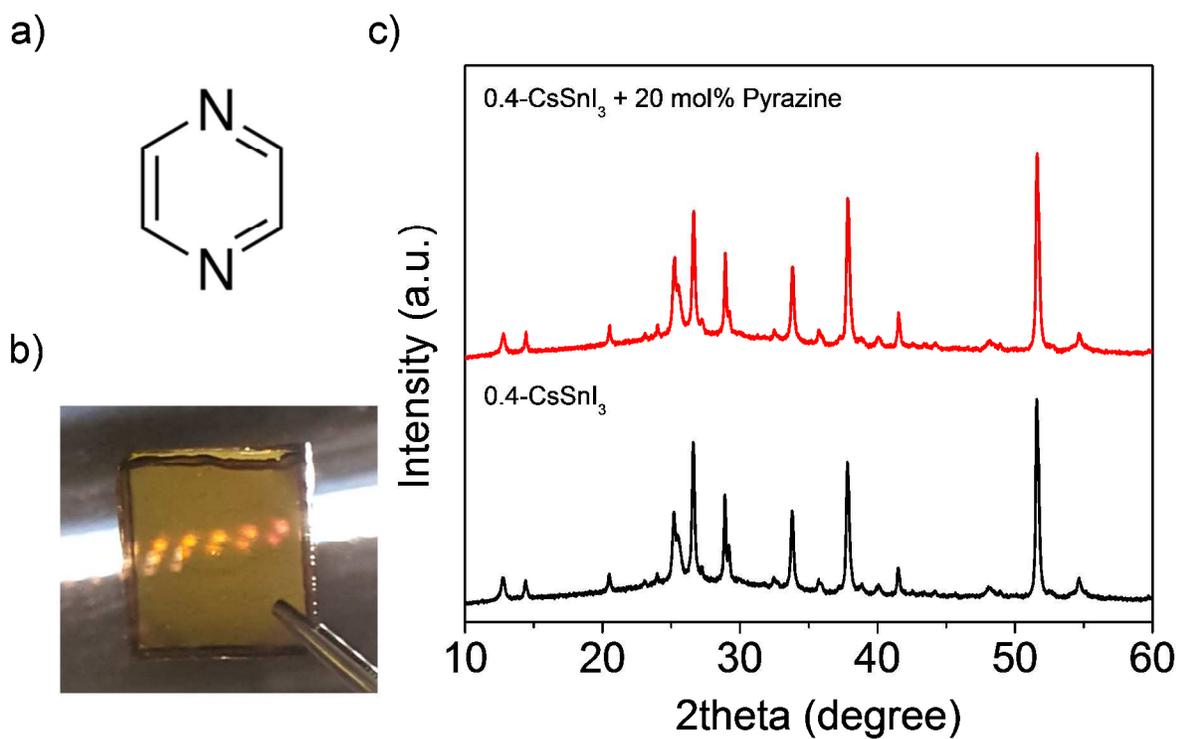


Figure S3. (a) Pyrazine molecule. (b) Picture of 0.4-CsSnI₃ film with 20 mol% of pyrazine. (c) XRD patterns of the 0.4-CsSnI₃ films with and without 20 mol% pyrazine on meso-TiO₂/c-TiO₂/FTO substrates.

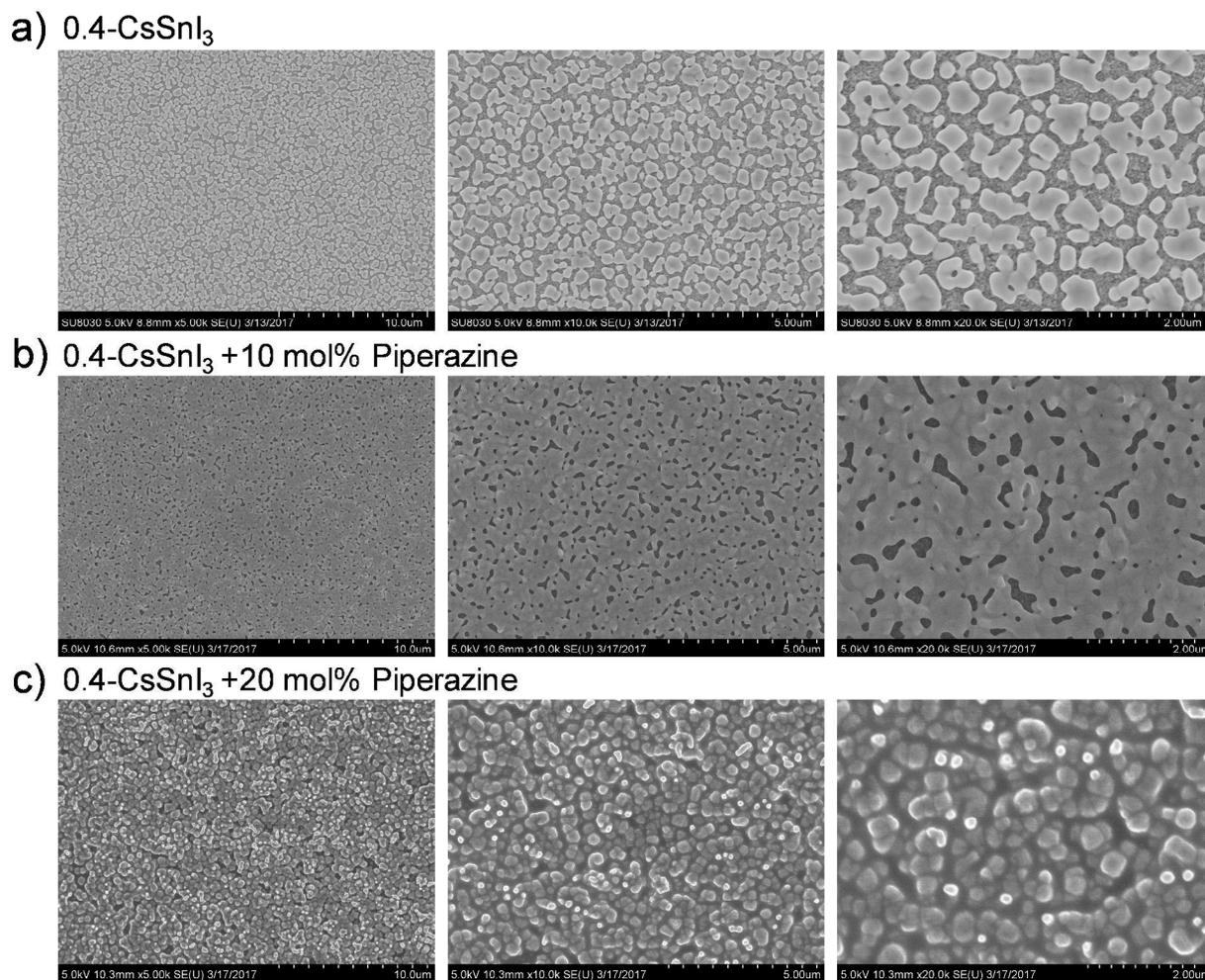


Figure S4. Various magnifications of SEM images of the 0.4-CsSnI_3 perovskite films grown with various piperazine molar ratios over meso- TiO_2 substrates: (a) 0 mol%; (b) 10 mol% and (c) 20 mol%.

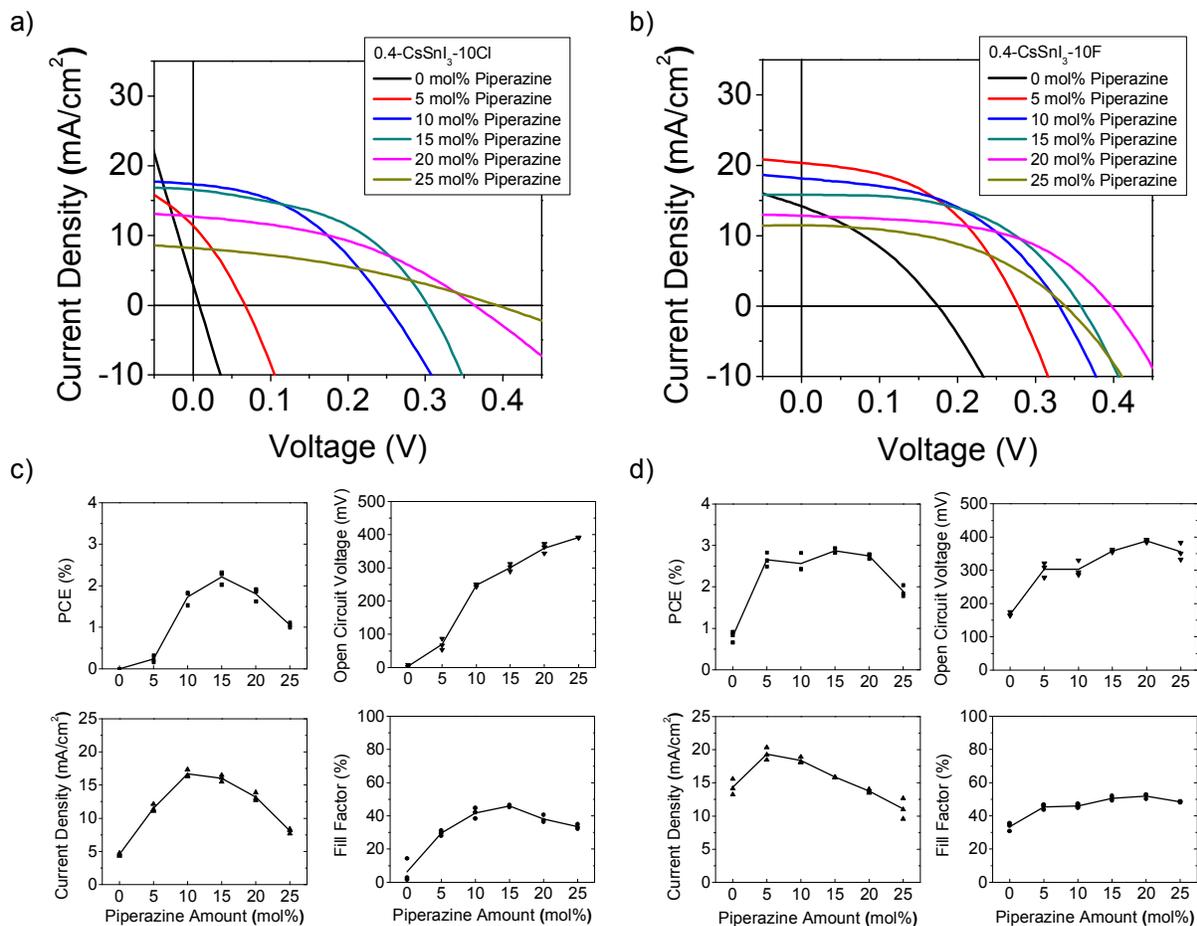
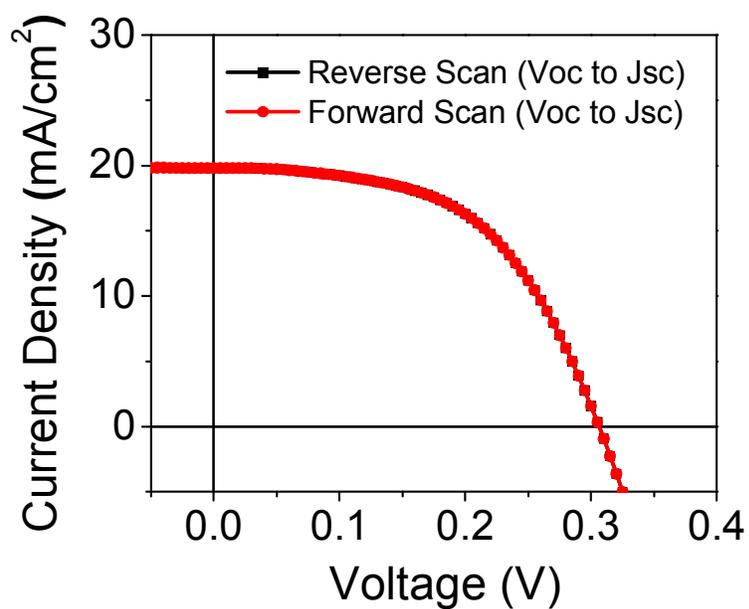


Figure S5. J-V characteristics of 0.4-CsSnI₃ devices fabricated using various molar ratio of piperazine and substituting SnI₂ with 10 mol% (a) SnCl₂ and (b) SnF₂. Each device parameter as a function of molar ratio of piperazine: substituting SnI₂ with 10 mol% (c) SnCl₂ and (d) SnF₂. Results of three devices for each system in the same batch are shown. The solid line indicates the average of the three devices.



	V_{OC} (mV)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Forward Scan ($J_{SC} \rightarrow V_{OC}$)	319.1	19.13	54.42	3.32
Reverse Scan ($V_{OC} \rightarrow J_{SC}$)	308.0	19.72	53.34	3.24

Figure S6. Hysteresis behavior of a 0.4-CsSnI₃ device fabricated using 15 mol% piperazine and substituting SnI₂ with 10 mol% SnF₂ (0.4-CsSnI₃-10F). No significant difference of the performance was observed in the forward (from J_{SC} to V_{OC}) and reverse (from V_{OC} to J_{SC}) scans.

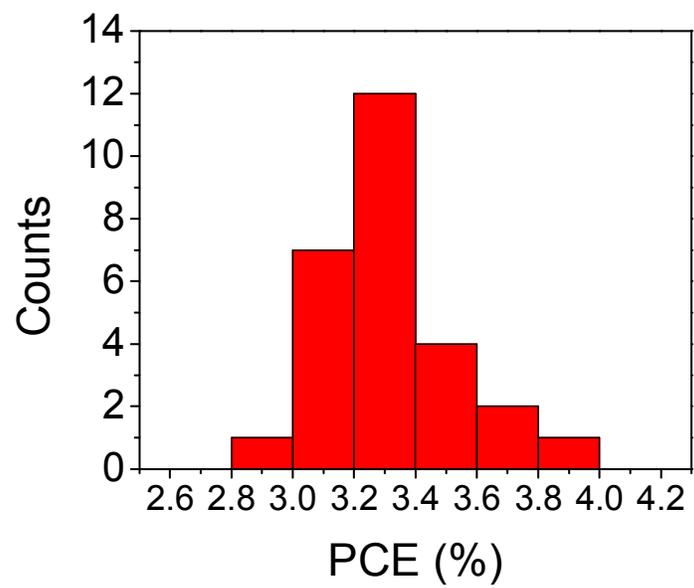


Figure S7. Histogram of PCE obtained in twenty-seven 0.4-CsSnI₃ devices fabricated using 15 mol% piperazine and substituting SnI₂ with 10 mol% SnF₂ devices (0.4-CsSnI₃-10F).

Reference

1. Yokoyama, T.; Song, T.-B.; Cao, D. H.; Stoumpos, C. C.; Aramaki, S.; Kanatzidis, M. G. The Origin of Lower Hole Carrier Concentration in Methylammonium Tin Halide Films Grown by a Vapor-Assisted Solution Process. *ACS Energy Lett.* **2016**, *2*, 22-28.