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# Electronic Supplementary Information (ESI)

## Efficient and reproducible $CH_3NH_3PbI_{3-x}(SCN)_x$ perovskite based planar solar cells†

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## Experimental Sections

**Materials.** All chemicals were purchased from J&K Scientific, Ltd (China) unless indicated, and used as received. The phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) was purchased from Nano-C, Inc.

**Sample preparation.** 462 mg/mL $PbI_2$ in the presence / absence of $Pb(SCN)_2$ (wt % = 1, 5, 10) and 40 mg/mL $CH_3NH_3I$ were first dissolved in dimethylformamide (DMF) and 2-propanol, respectively. A hot solution of $PbI_2$ or $PbI_2$:$Pb(SCN)_2$ mixture at 80 ºC was spin-coated onto the substrate at 3000 rpm for 40 s and $CH_3NH_3I$ solution was spin-coated onto the as-prepared $PbI_2$ layer at 3000 rpm for 40 s immediately. Subsequently, the film was annealed at 100 ºC for 5 min to obtain the perovskite films.

**Characterization**. Optical absorption and photoluminescence (PL) spectra of samples were acquired on Agilent 8453 UV-Visible spectrophotometer and a Horiba FluoroMax®-4 spectrofluorometer, respectively. X-ray diffraction (XRD) pattern data for 2θ values were collected with a Bruker AX D8 Advance diffractometer with nickel filtered Cu Kα radiation (λ = 1.5406 Å). Scanning Electron Microscopy (SEM) images were acquired on a JEOL JSM-6701F field-emission SEM at an accelerating voltage of up to 30 kV and coupled with energy-dispersive X-ray (EDX, 20 kV) elemental analysis abilities. Raman spectra were obtained on an XploRA laser Raman spectrometer (HORIBA JOBIN YVON, Inc.) using a He-Cd laser (532 nm).

**Device Fabrication and Measurements.** Patterned indium tin oxide (ITO) substrates (12 Ω/□, Thin Film Devices, Inc.) were cleaned sequentially in an ultrasonic solvent bath of deionized water, acetone, and isopropyl alcohol. After blow-drying with nitrogen, the substrates were treated in UV-ozone for 20 min. A thin layer (~30 nm) of PEDOT:PSS (Clevios™ P VP AI 4083, Heraeus) was spin-coated onto the ITO at 3000 rpm for 60 s and then baked in air at 120 ºC for 30 min. The PEDOT-coated substrates were immediately transferred to a $N_2$-filled glovebox for making the active layer. For preparing the perovskite layer, a hot solution of $PbI_2$ with or without the presence of $Pb(SCN)_2$ was firstly spun onto the PEDOT:PSS-coated ITO substrate at 3000 rpm for 40s. Then a fresh $CH_3NH_3I$ solution of 40 mg/mL in anhydrous isopropanol was spin-coated onto the as-prepared $PbI_2$ or $PbI_2$/ $Pb(SCN)_2$ layer at 3000 rpm for 40s immediately, followed by thermal annealing at 100 ºC for 5 min. After the perovskite film was formed, 2 wt% $PC_{61}BM$ in 1,2-dichlorobenzene was spin-coated onto the perovskite layer at 1000 rpm for 60 s. The samples were then loaded into a glovebox-

integrated deposition chamber and pumped down to a pressure of $<10^{-4}$ Pa. A sequence of Ca (20 nm) and Al (100 nm) layers were sequentially deposited by thermal evaporation through a shadow mask at a rate of 0.1 Å/s and 2 Å/s, respectively. The active area as defined shadow mask is ~0.11 $cm^2$. The *J*–*V* data were acquired with a Keithley 2400 source–meter unit. The light *J*–*V* curves were measured under illumination with a Newport-Oriel (Sol3A Class AAA Solar Simulator, 94043A) AM 1.5G light source operating at an intensity of 100 mW $cm^{-2}$. The light intensity was calibrated by a certified Oriel reference cell (91150V) and verified with a NREL calibrated, filtered silicon diode (Hamamatsu, S1787-04). For the measurement of hysteresis, the J-V curves were obtained in the air through reverse (1.2 V → −1.2 V) or forward scan (−1.2 V → 1.2 V) with a scan rate of 10 mV/s or 50 mV/s. External quantum efficiency (EQE) spectra were measured on a commercial EQE set-up (QE-R, Enli Technology Co., Ltd). A calibrated silicon diode with a known spectral response was used as a reference.

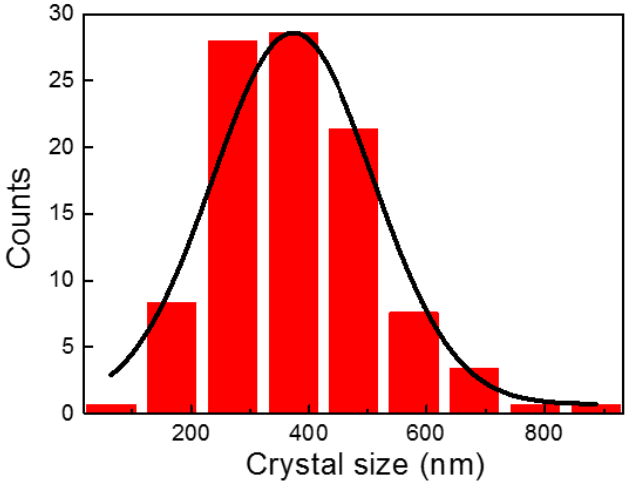
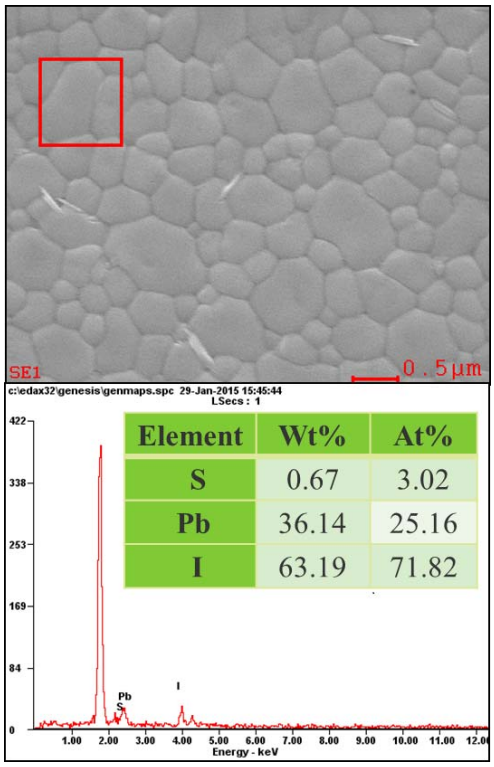



**Fig. S1** Crystal size distribution within $CH_3NH_3PbI_{3-x}(SCN)_x$ perovskite film on Si substrate.




| Element | Wt% | At% |
|---|---|---|
| S | 0.67 | 3.02 |
| Pb | 36.14 | 25.16 |
| I | 63.19 | 71.82 |

**Fig. S2** Energy dispersive X-ray (EDX) analysis of $CH_3NH_3PbI_{3-x}(SCN)_x$ perovskite film on Si substrate.

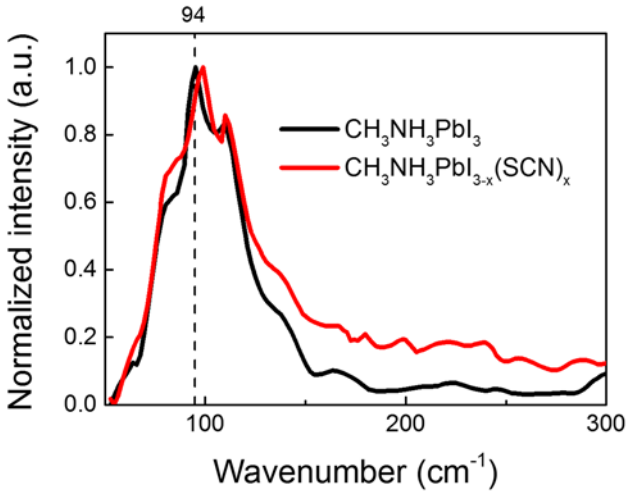



**Fig. S3** Comparison of Raman spectra of $CH_3NH_3PbI_3$ and $CH_3NH_3PbI_{3-x}(SCN)_x$ films.

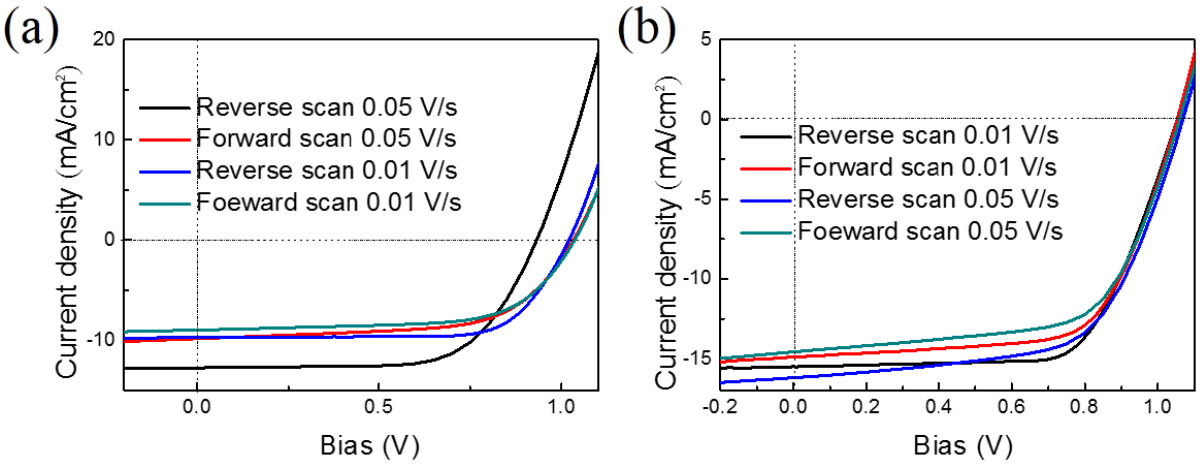



**Fig. S4** Photocurrent density−voltage characteristics with forward and reverse scan directions and at a scan rate of 50 mV/s for fast scan and 10 mV/s for slow scan, respectively. (a) $CH_3NH_3PbI_3$ and (b) $CH_3NH_3PbI_{3-x}(SCN)_x$ based perovskite solar cells.

**Table S1** Summary of photovoltaic performance of $CH_3NH_3PbI_{3-x}(SCN)_x$ based devices (at least 12 individual cells) with various amounts of $Pb(SCN)_2$

| $Pb(SCN)_2$ (wt %) | Sweep Direction | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| 0% | Forward | 7.79 ± 1.18 | 1.00 ± 0.05 | 65 ± 1 | 5.03 ± 1.01 |
| | Reverse | 8.95 ± 0.78 | 0.99 ± 0.04 | 70 ± 4 | 6.18 ± 1.06 |
| 1% | Forward | 9.24 ± 0.80 | 0.93 ±0.08 | 60 ± 1 | 5.18 ± 0.95 |
| | Reverse | 10.22 ± 0.91 | 0.95 ± 0.05 | 64 ±1 | 6.29 ± 0.99 |
| 5% | Forward | 15.48 ± 0.04 | 1.03 ± 0.03 | 64 ± 2 | 9.64 ± 0.69 |
| | Reverse | 15.48 ± 0.05 | 1.03 ± 0.03 | 65 ± 3 | 10.32 ± 0.75 |
| 10% | Forward | 11.59 ± 1.09 | 0.85 ± 0.01 | 65 ± 5 | 6.39 ± 1.04 |
| | Reverse | 11.80 ± 1.39 | 0.88 ± 0.03 | 69 ± 3 | 7.10 ± 0.93 |

**Table S2** Summary of photovoltaic performance of $CH_3NH_3PbI_{3-x}(SCN)_x$ and $CH_3NH_3PbI_3$ based devices within one-hour sunlight irradiation time

| Device | Time (h) | $J_{sc}$ (mA/cm$^2$) | $V_{oc}$ (V) | FF (%) | PCE (%) |
|---|---|---|---|---|---|
| $CH_3NH_3PbI_{3-x}(SCN)_x$ | 0 | 16.19 | 1.03 | 65 | 10.88 |
| | 0.5 | 15.51 | 1.05 | 68 | 11.07 |
| | 1 | 14.59 | 1.05 | 66 | 10.1 |
| $CH_3NH_3PbI_3$ | 0 | 9.72 | 1.02 | 73 | 7.24 |
| | 0.5 | 8.25 | 1.04 | 65 | 5.55 |
| | 1 | 6.53 | 1.05 | 61 | 4.17 |