

Supporting Information

CH₃NH₃PbI₃ from non-iodide lead salts for perovskite solar cells *via* formation of PbI₂

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Experimental

Chemicals: PbI₂ was purchased from Alfa Aesar, Pb(SCN)₂, Pb(NO₃)₂ and HI (57 % in water) were purchased from Sigma-Aldrich. Methylamine (40 % in methanol) was purchased from TCI America chemicals. P3HT (molecular weight of 55,000) was purchased from One Material. Methylammonium lead iodide was synthesized by following the literature procedure.¹

Thin film and perovskite solar cell fabrication: Over the clean FTO coated glass slides (13 Ω/sq, Aldrich) compact TiO₂ layer was spin coated and sintered at 550 °C in air. The substrate was subsequently immersed in 50 mM aqueous TiCl₄ solution for 30 minutes at 70° C and finally sintered to 550 °C for 30 minutes in air.²

Formation of Perovskite Films: Complete vapor grown perovskite film with PbCl₂

Compact TiO₂ coated FTO films were placed in an evaporating chamber under the base pressure of 2×10^{-7} . PbCl₂ was evaporated at the rate of 1Å/s to get a film with thickness of around 200 nm. The lead chloride deposited substrate was moved into the glove box where the methylammonium iodide (MAI) was spread out around the vapor deposited PbI₂ film in a petri dish with cover. The graphite vessel / petri-dish containing MAI and substrate was heated to 180° C for 3 hours to form the desired perovskite

thin film with thickness of around 440 nm. The thin film formed was kept in vacuum (7×10^{-7} torr) overnight at room temperature to remove excess MAI deposited on the top of perovskite.

Partially vapor grown perovskite film with $\text{Pb}(\text{SCN})_2$ and $\text{Pb}(\text{NO}_3)_2$

Lead thiocyanate or lead nitrate solution (1M in DMF) was stirred at 70° C for 30 minutes. The solution was filtered and spin coated over TiO_2 coated FTO films at the spin rate of 4000 rpm for 30 s. The films were then annealed at 110° C for 20 minutes. The MAI was evaporated over the spin coated lead salt in the glove box by the same process as discussed above.

Over the perovskite film, the hole transporting layer containing P3HT was spin coated from 12 mg/mL solution of chlorobenzene at 4000 rpm for 30s. The P3HT coated perovskite thin films were annealed at 110° C for 15 minutes before depositing 90 nm of gold by thermal evaporation at 8×10^{-7} Torr.

Film Characterization: XRD was done on Siemens D500 X-ray diffractometer with a copper target X-ray tube set to 45 KV and 30 mA. SEM-EDS was done on FEI Quanta 250 FE SEM setup equipped with Oxford Aztec energy-dispersive X-ray analysis system using an 80mm² silicon drift detector.

Device Characterization: For IV: Keithly SMU model 236 was used to measure current and source voltage. For light source a GE ELH bulb operating at 110V was used and intensity adjusted to 1 sun using a calibrated silicon photodiode of 5 mm sq. area. For QE: This is a system built in house using a chopped light source from Horiba monochromator model H2O. The intensity of the beam is measured with a calibrated silicon photodiode. The signal of the sample is measured with Stanford Research System lock-in amplifier model SR830 using Ithaco current preamplifier model 1211.

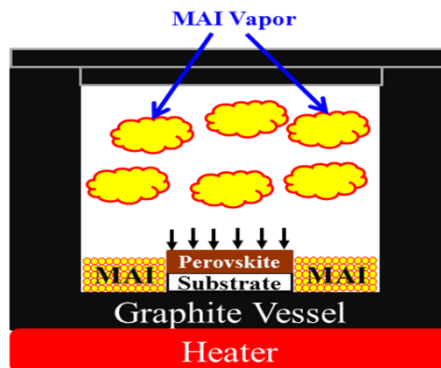


Figure S1: Schematic representation of vapor assist growth of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite formed by the exposure of methylammonium iodide vapors to substrate containing lead salts

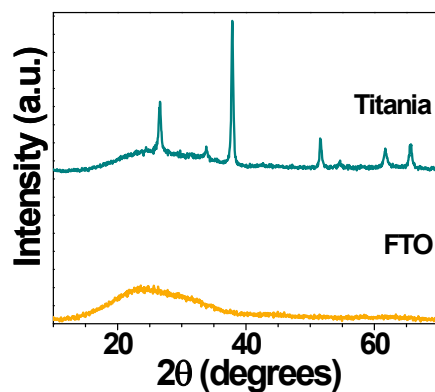


Figure S2: XRD of FTO and TiO_2 coated FTO substrate

Table S1: Relative atomic ratios of carbon, nitrogen, oxygen, sulfur, chlorine, iodine and lead in perovskites formed from different lead precursors

Precursor	C	N	O	S	Cl	I	Pb	Pb : I ratio
Thiocyanate	23.71	6.08	5.86	0.00	0.24	47.99	16.13	1 : 2.98
Nitrate	25.54	4.57	3.58	0.11	0.26	49.08	16.87	1 : 2.91
Chloride	26.54	3.19	3.54	0.00	0.00	48.11	18.62	1 : 2.58

Table S2: Relative atomic ratios of carbon, nitrogen, oxygen, sulfur, chlorine, iodine and lead at different stages of perovskite formation

Precursor	C	N	O	S	Cl	I	Pb	Pb : Cl : I ratio
Precursor	13.15	0.31	0.15	0.00	54.94	0.00	31.46	1 : 1.8 : 0
Intermediate	21.52	0.00	3.91	0.31	5.30	44.16	24.80	1 : 0.2 : 1.8
Perovskite	26.54	3.19	3.54	0.00	0.00	48.11	18.62	1 : 0 : 2.6

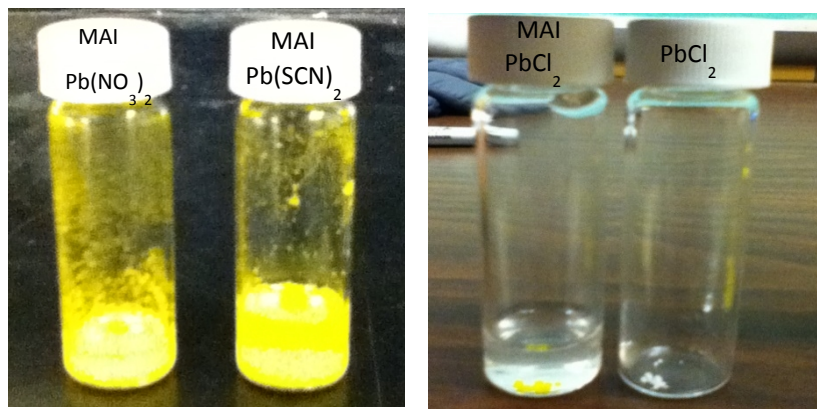


Figure S3: Formation of golden yellow spangles (lead iodide) upon addition of colorless lead nitrate and lead thiocyanate to aqueous MAI (left) and lead chloride beads before and after the addition of aqueous of methylammonium iodide (right).

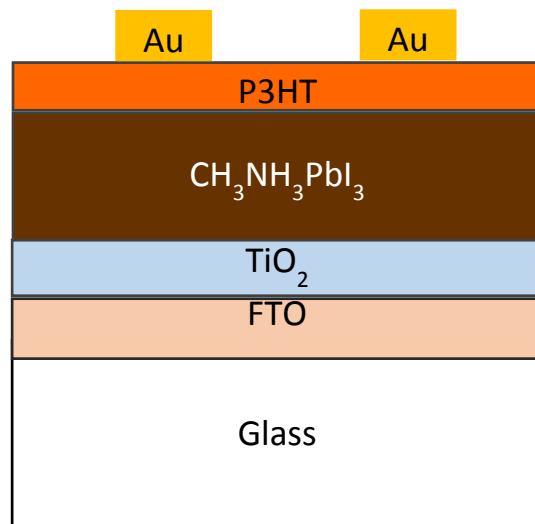


Figure S4: Device architecture for perovskite solar cells made from different lead precursors

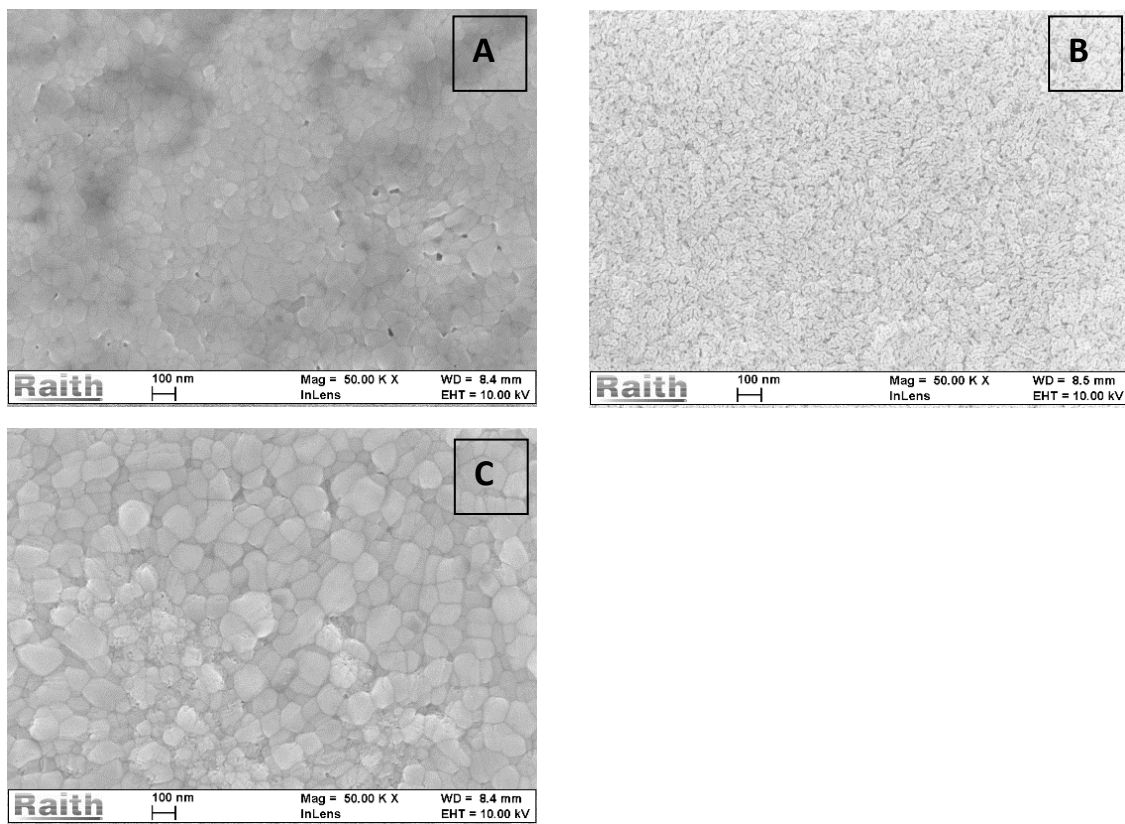


Figure S5. SEM images of lead precursors (A) $\text{Pb}(\text{NO}_3)_2$ (B) $\text{Pb}(\text{SCN})_2$ (C) PbCl_2

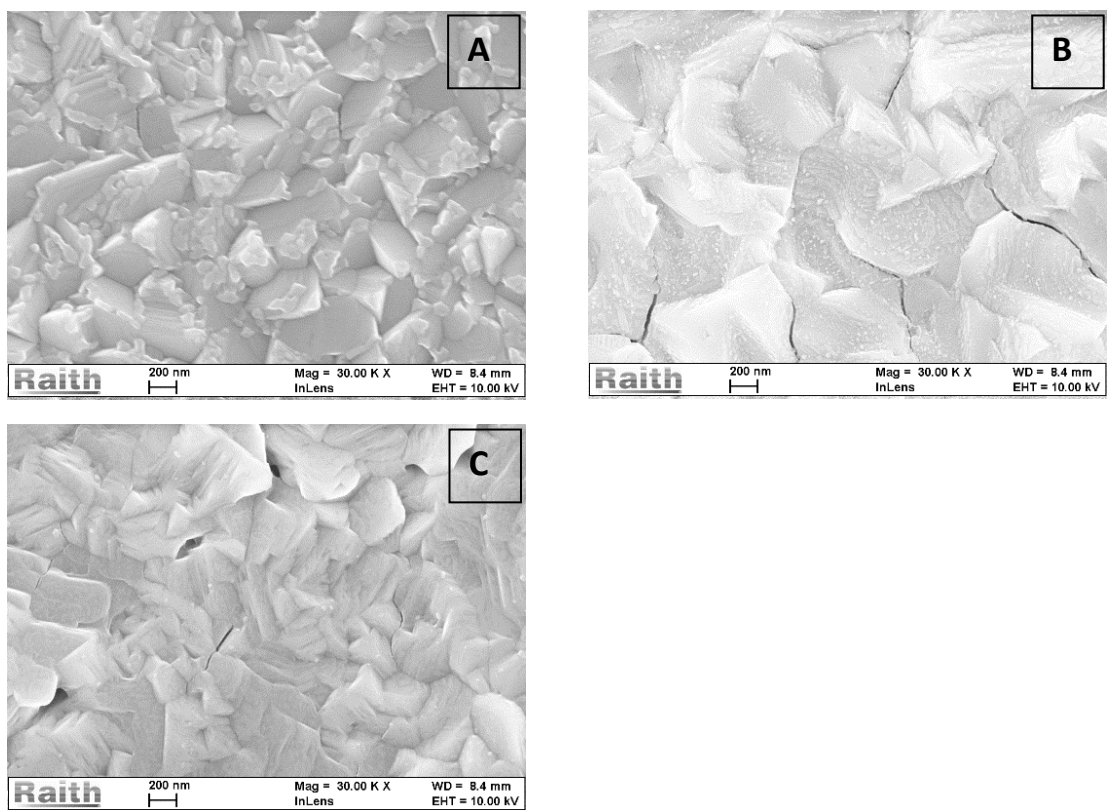


Figure S6. SEM images of $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskites formed from (A) $\text{Pb}(\text{NO}_3)_2$ (B) $\text{Pb}(\text{SCN})_2$ (C) PbCl_2

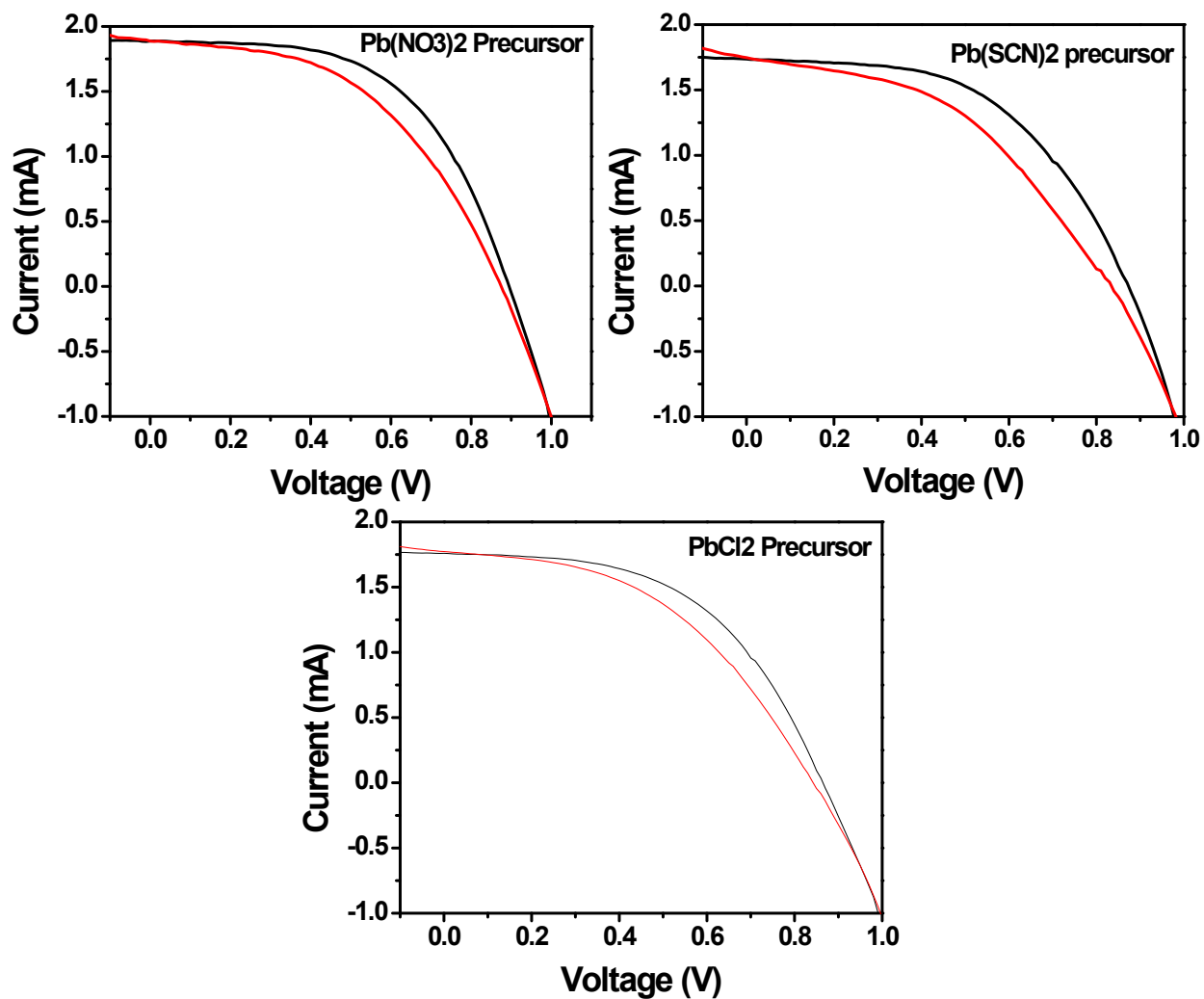


Figure S7. Hysteresis curve for $\text{CH}_3\text{NH}_3\text{PbI}_3$ cells formed from different lead precursors. The black curve going from V_{oc} to J_{sc} and the red curve going from J_{sc} to V_{oc} .

References

1. Burschka, J.; Pellet, N.; Moon, S. -J.; Humphry – Baker, R.; Gao, P.; Nazeeruddin, M. K.; Grätzel, M. *Nature*, **2013**, *499*, 316.
2. Chen, Q.; Zhou, H.; Hong, Z.; Luo, S.; Duan, H, -S.; Wang, H. -H.; Liu, Y.; Li, G.; Yang, Y. *J. Am. Chem. Soc.* **2014**, *136*, 622.