Supporting Information

Photovoltaic Performance of Precursor-Vapor-Assisted Solution-Processed Layer polymorph of $Cs_3Sb_2I_9$

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Experimental Methods

Chemicals – Cesium Iodide (CsI, 99.999 %), Antimony Iodide (SbI_3, 99.998%), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), were purchased from Alfa Aesar and used without further purification. Poly(3,4-ethylenedioxythiophene):poly(p-styrene sulfonate) (PEDOT:PSS. Clevios P) was bought from Heraeus (Germany). ITO substrates were cleaned with DI water and isopropyl alcohol and then kept in an oven overnight.

Device fabrication- UV-Ozone treatment was performed for 15 min. PEDOT:PSS (Clevios P, Heraeus Germany) was spin-coated for 60 s at 4000 rpm over the substrates and then the sample was annealed at 200 °C. A single precursor solution was prepared by mixing 0.25 M of SbI_3 (Alfa Aesar, 99.9 %)and 1 M of CsI (Alfa Aesar, 99.9 %) in DMSO:DMF (0.75:0.25) and then continuous stirring overnight at 70 °C. A drop of this solution was placed on the PEDOT:PSS-coated substrates and spin-coated for 40 s at 6000 rpm. These films (two samples at a time) were annealed at 70 °C for 15 min and then directly moved to glass bottle (diameter: 3 cm; height: 6 cm) at 250 °C. This bottle was covered with a cap after adding 30 µL (30 wt%) of SbI_3 in DMF in the corners of the bottle. The films were maintained at 250 °C for 15 min, then cooled at 200 °C for 5 min to avoid cracks (due to quenching); the temperature was decreased gradually to 150 °C before bringing the sample to room temperature to give the layered $Cs_3Sb_2I_9$. ITO substrates with PEDOT:PSS annealed at 150 °C were spin coated with the same solution and annealed at 150 °C to get dimer form. A 2% solution of $PC_{70}BM$ in chlorobenzene was spin-coated at 3000 rpm and then the sample was annealed at 100 °C for 20 min. Finally, 100 nm of Al was deposited as an electrode. The active area of each device was 10 mm^2.

Characterization- XRD patterns were recorded at room temperature using a Bruker D8 X-ray diffractometer (2□ range: 5–80°; step size: 0.008°) equipped with a diffracted beam monochromator set for Cu K□ radiation (□ = 1.54056 Å). SEM images and EDX spectra were recorded using an FEI Noval 200 scanning electron microscope (15 kV).

Glass substrates spin-coated with PEDOT:PSS were used for XRD measurements; ITO substrates spin-coated with PEDOT:PSS were used for recording SEM images. PL emission spectra of the samples were recorded using an diode laser (475 nm; pulse: 55 ps; 40 MHz; single pulse power: 160 mW; laser spot area: 5 μm) focused at a beam diameter of approximately 0.5 mm. Absorption spectra of the films were measured using a Jacobs V-670 UV–Vis spectrophotometer. UPS was performed at room temperature using a PHI 5000 Versa Probe apparatus equipped with an Al K□ X-ray source (1486.6 eV). UPS was used to measure the valance band using He I emission (21.2 eV, ca. 50 W) as the source of UV light; the take-off angle was 90°. Samples for UPS study were made on only ITO substrates with the same method as was used for active layer preparation of device. EQE spectra were recorded under short-circuit conditions. Devices were encapsulated before they were removed for EQE measurement. The light source was a 75-W Xe lamp (Enlitech, QE-R3011); the light output from the monochromator was focused on the photovoltaic cell being tested (DC mode). The devices were illuminated inside a glove box by the Xe lamp, which functioned as a solar simulator (Thermal Oriel 1000 W) providing a simulated AM 1.5 spectrum (100 mW cm–2). The light intensity was calibrated using a mono-silicon photodiode with a KG-5 color filter (Hamamatsu). For measuring stability, we stored the devices inside a glove box (O2: <20 ppm; H2O: <0.1 ppm) without encapsulation and then tested their performance.

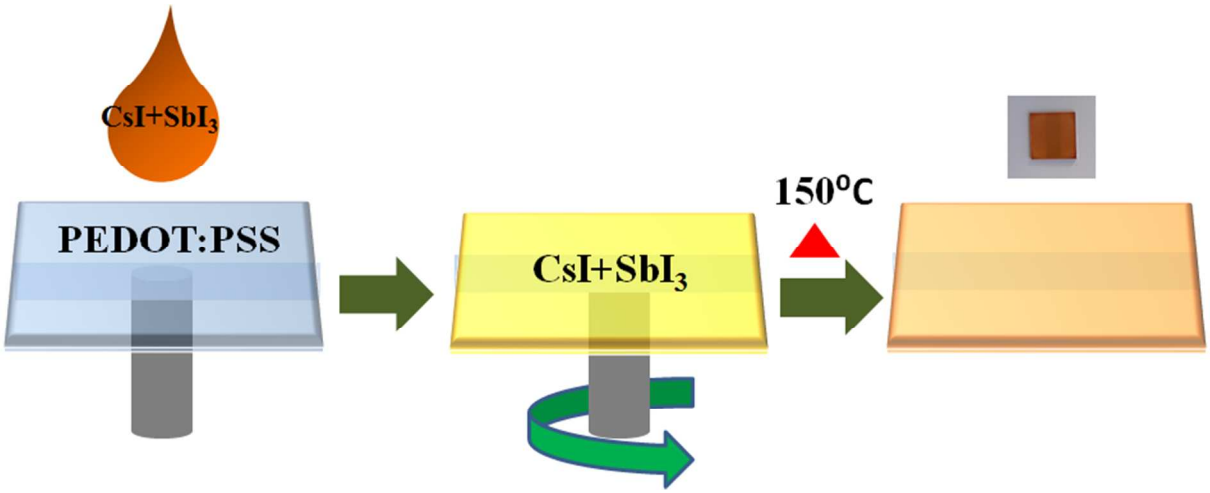

Figure S1. Schematic representation of the preparation of dimer-form $Cs_3Sb_2I_9$ with a real-time photograph of the film.

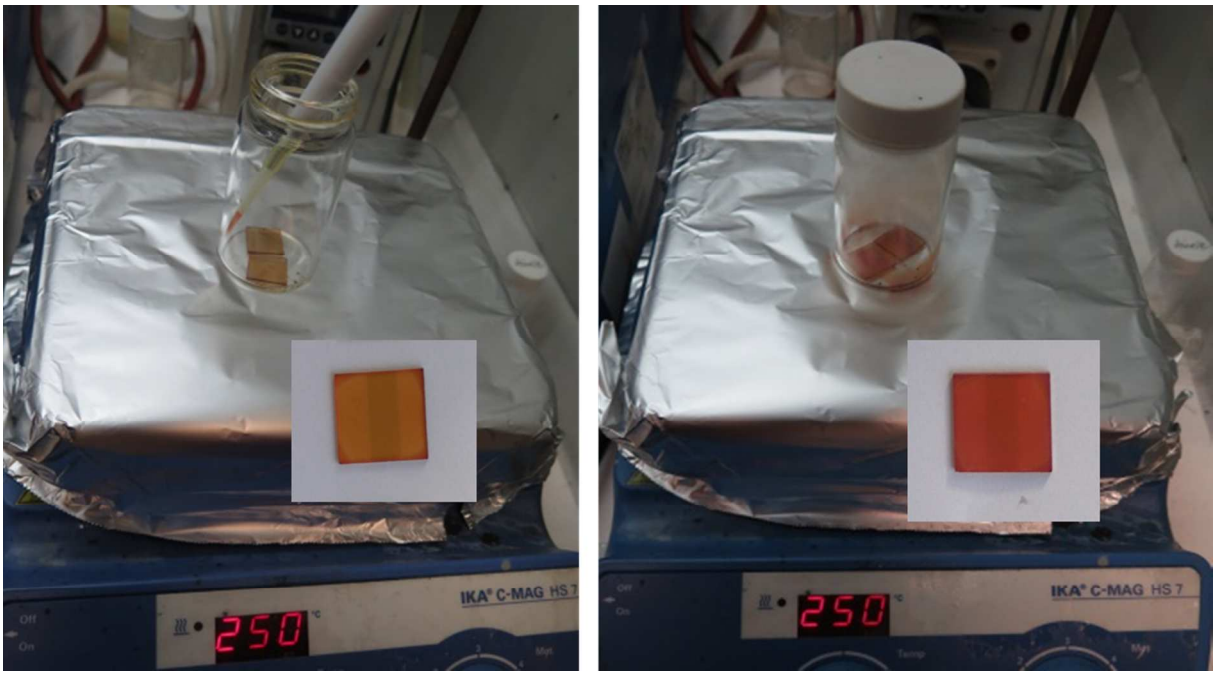

Figure S2. Real-time photographs of the dropping of a SbI_3 solution in DMF at 250 °C to provide extra SbI_3 to give a final stoichiometric layered-form $Cs_3Sb_2I_9$ at 250 °C; inset: real-time photographs of the film before and after annealing at 250 °C.

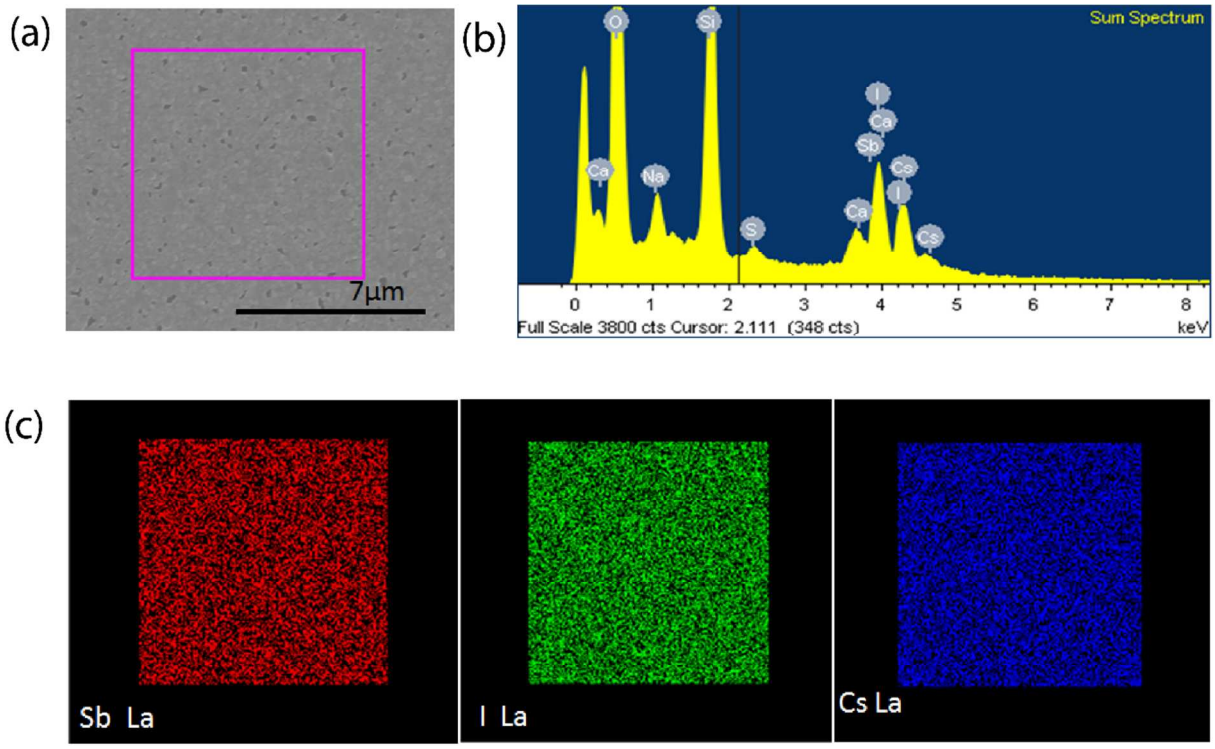

Figure S3. (a) Area scanned for EDX. (b) EDX spectra of the layer-form $Cs_3Sb_2I_9$ films with precursor composition of 0.25 M SbI_3 and 1 M CsI and annealing at 250 °C in the presence of SbI_3 and DMF vapor. (c) Pictorial visualization of the elements in the area scanned.

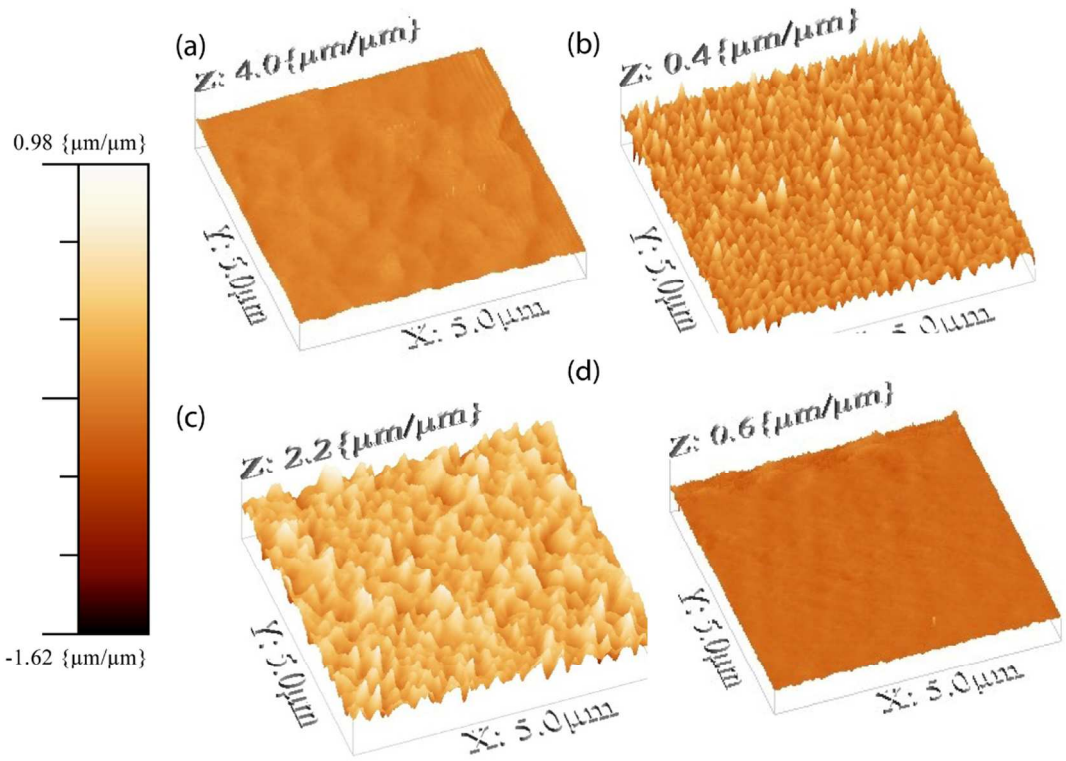

Figure S4. 3D AFM images of; (a) as spin-coated film, (b) the film pre-annealed at 70 °C, (c) the layer form, and (d) the dimer form.

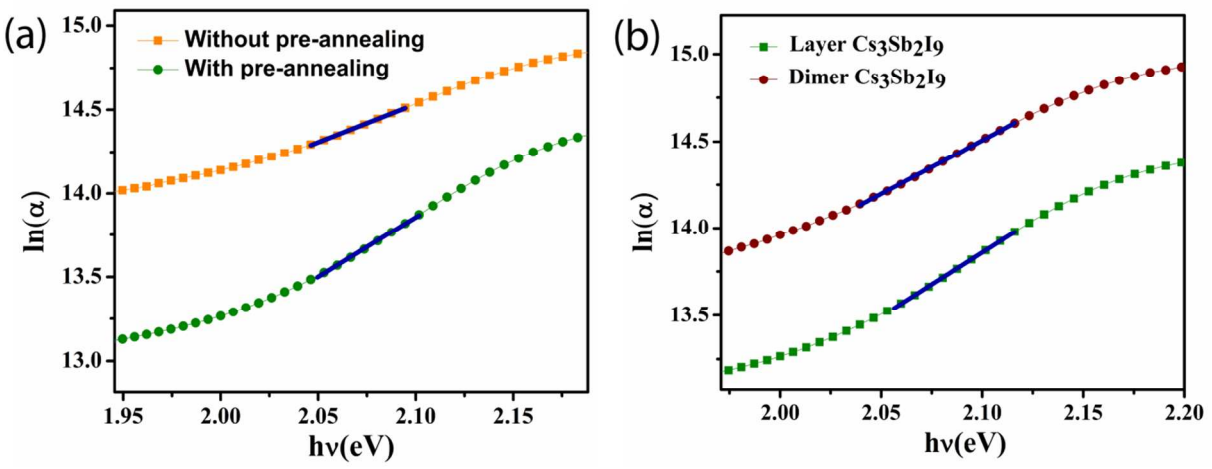

Figure S5. (a) Urbach energies for the layered form with and without pre-annealing; with pre-annealing, the Urbach energy decreased, due to the improved morphology. (b) Urbach energy for layered and dimer forms; the Urbach energy of the layered form was less than that of the dimer form.

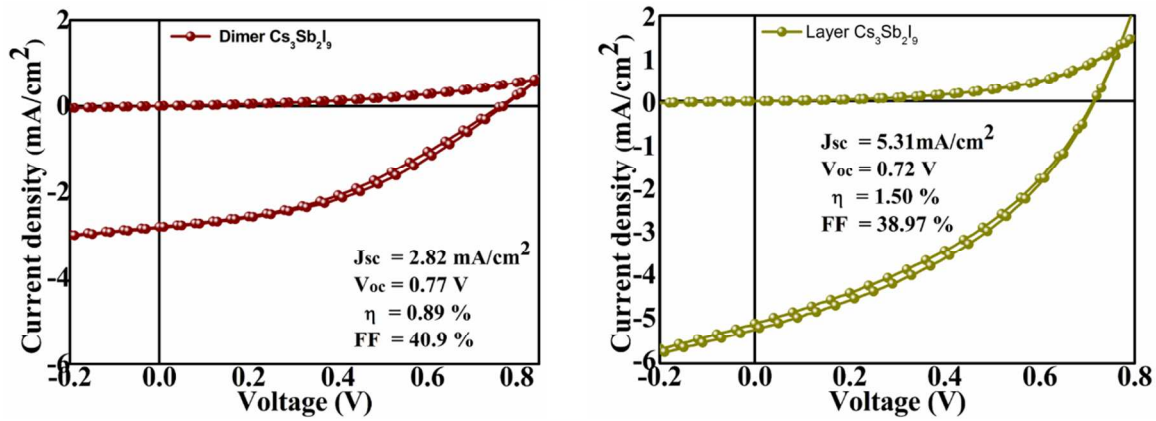

Figure S6. Forward and reverse scan for layer and dimer form

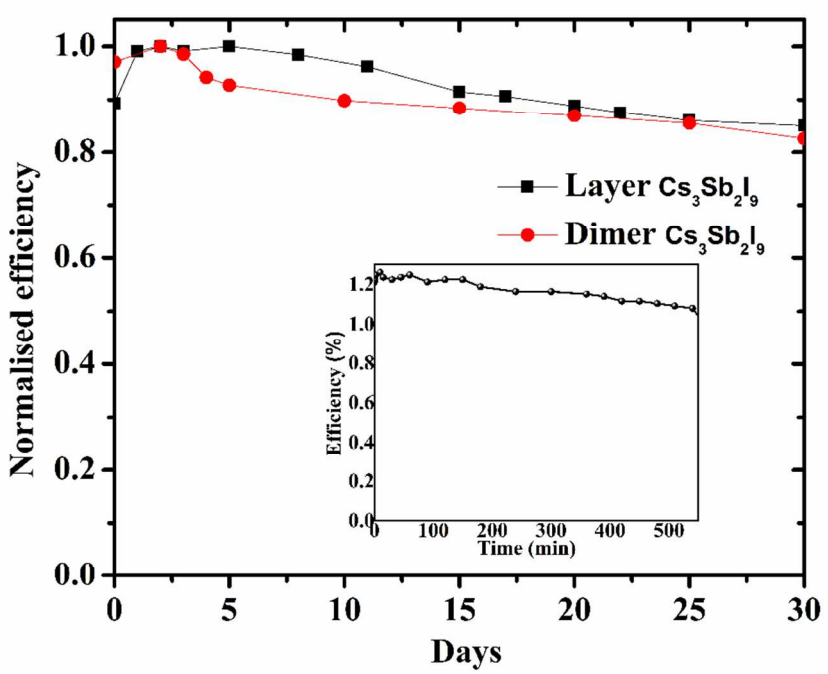

Figure S7. Stability of devices incorporating the layer (squares) and dimer (spheres) polymorphs (with only Al as the top electrode), inset showing continuous illumination for device made with layer $Cs_3Sb_2I_9$.

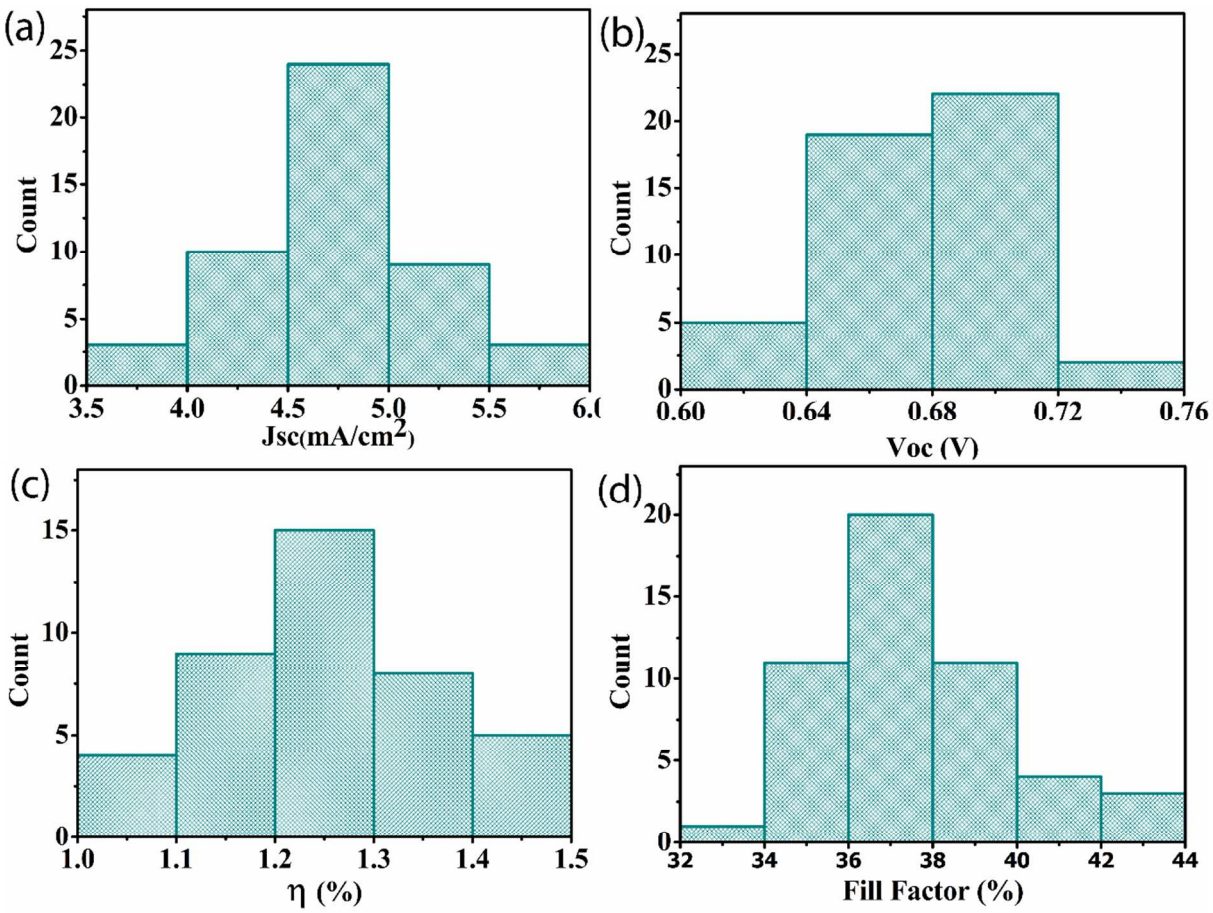

Figure S8. Statistical results for (a) Jsc, (b) Voc, (c) PCE, (d) FF for 50 devices made from the layer $Cs_3Sb_2I_9$

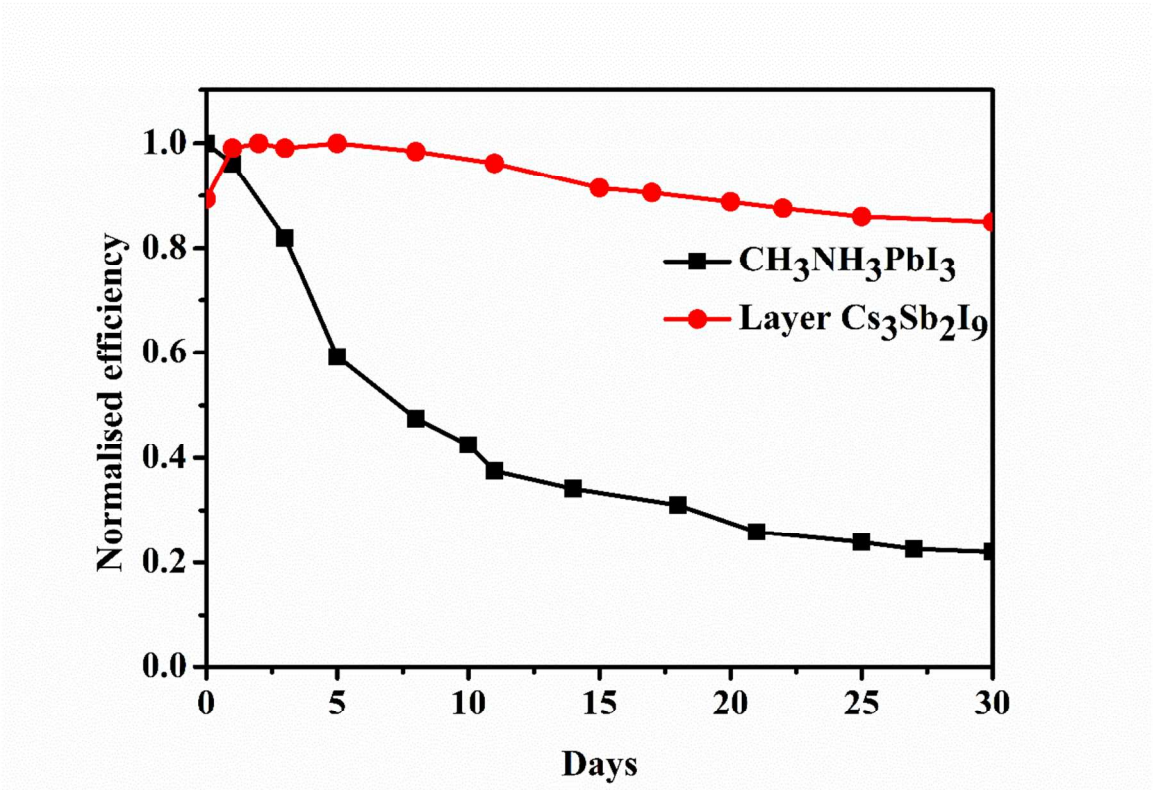

Figure S9. Stability of devices made with conventional Pb based perovskite (black squares) and layer $Cs_3Sb_2I_9$ (red spheres).

Table S1. Atomic percentages in the layer-form $Cs_3Sb_2I_9$ films prepared using various compositions of the precursor solution for spin-coating, obtained after annealing at 250 °C in the presence of SbI_3 and DMF vapor.

CsI (M):SbI_3 (M)	Cs/Sb	I/Sb	I/Cs
1:0.1	1.45	5.85	2.73
1:0.2	1.46	4.92	2.86
1:0.25	1.48	4.51	3.03
1:0.3	1.36	4.31	3.15
Expected	**1.50**	**4.50**	**3.0**

Table S2. Device performances of layer-form $Cs_3Sb_2I_9$ obtained at various compositions of the precursor solution, and at different temperatures for the best composition.

CsI (M):SbI_3 (M)	Jsc (mA cm^{-2})	V_{oc} (V)	η (%)	FF (%)
1:0.1	–	–	–	–
1:0.2	5.03	0.62	1.15	37.32
1:0.25	5.16	0.71	1.42	38.70
1:0.30	4.50	0.67	1.11	36.85
1:0.35	4.24	0.60	0.95	36.20
Temperature (1:0.25)				
250 °C	5.16	0.71	1.42	38.70
275 °C	4.00	0.65	0.96	37.10
300 °C	3.63	0.67	0.91	36.82

Table S3. Effect of film thickness on device performance.

Speed	V_{oc} (V)	J_{sc} (mA cm^{-2})	η (%)	FF (%)
4000	0.65	4.22	1.01	36.82
6000	0.69	4.32	1.11	37.41
8000	0.56	4.43	0.90	36.36

Table S4. Comparison between Pb and Sb in terms of toxicity and efficiency.

Metal	Toxicity	Efficiency
Lead (Pb)	Highly toxic (Absorbed by human body)	3.8 % (2009)[1] 22.1 % (2017)[2]
Antimony (Sb)	Moderately Toxic (Excreted through urine and faeces)	<0.1 % [3] 1.5% (Present work)

References:

(1) Kojima, A.; Teshima. K.; Shirai, Y.; Miyasaka, T. Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells. *J. Am. Chem. Soc* **2009**, *131*, 6050 6051.

(2) Yang, W.S.; Park, B.W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S.II Iodide management in formamidinium-lead-halide–based perovskite layers for efficient solar cells. *Science* **2017**, *356*, 1376-1379.

(3) Saparov, B.; Hong, F.; Sun, J.-P.; Duan, H.-S.; Meng, W; Cameron, S.; Hill, I. G.; Yan Y.; Mitzi, D. B. Thin-Film Preparation and Characterization of $Cs_3Sb_2I_9$: A Lead-Free Layered Perovskite Semiconductor. *Chem. Mater.* **2015**, *27*, 5622-5632.