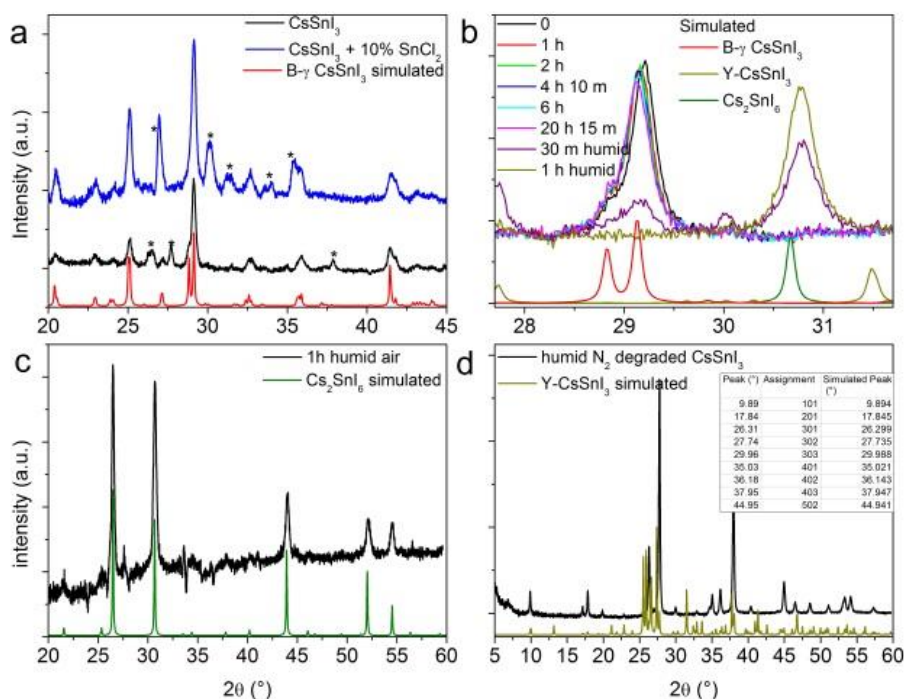


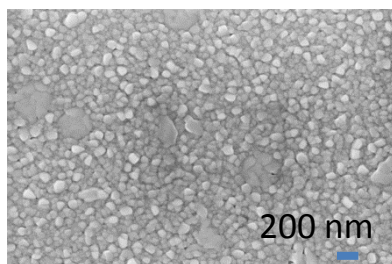
Enhanced Stability and Efficiency in Hole-Transport Layer Free CsSnI₃

Perovskite Photovoltaics

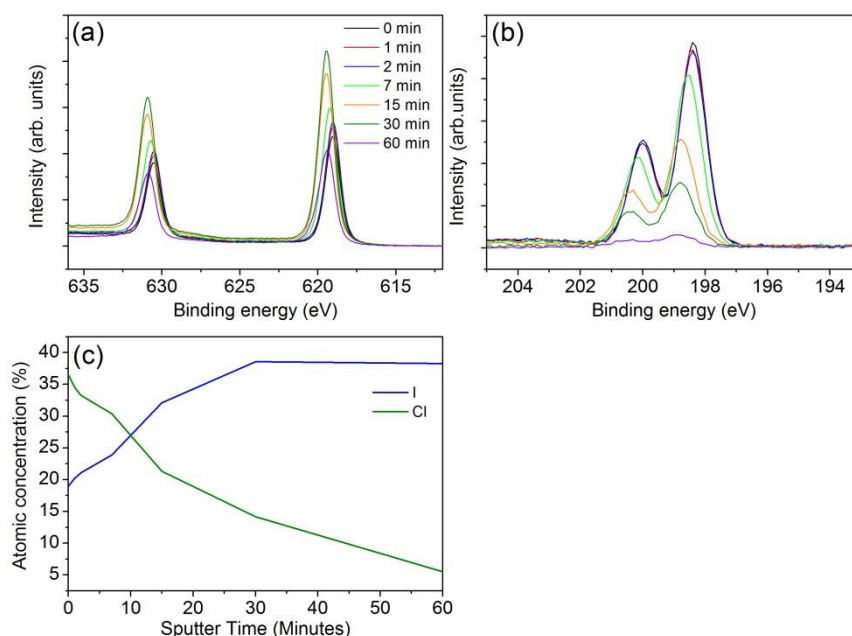
Supplementary Information



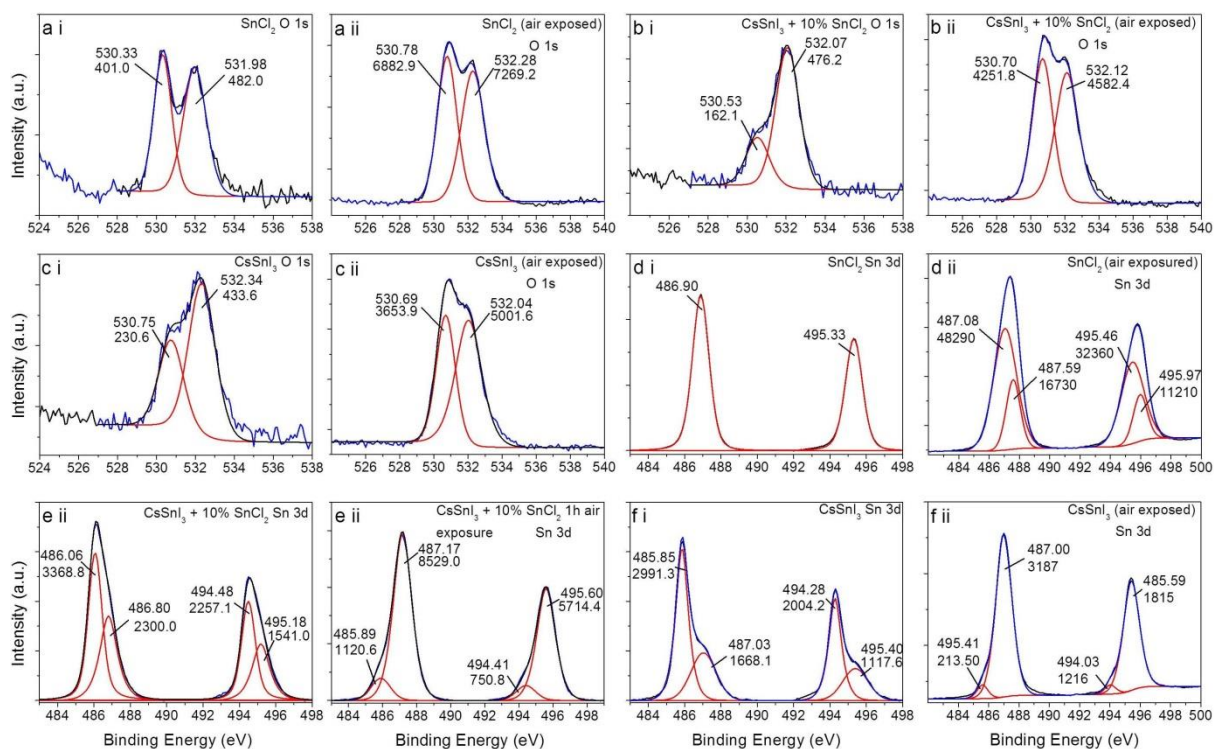
Supplementary Figure 1 | XRD patterns of thin films of CsSnI₃ with and without SnCl₂ additive stored in dry air, humid air and humid nitrogen. XRD patterns of: **a** CsSnI₃ with and without 10 mol% SnCl₂ additive.; **b** CsSnI₃ with 10 mol% SnCl₂ additive exposed to dry air for different time periods up to 19 hours, and then to humid air for 1 hour.; **c** a wider angle scan of a CsSnI₃ film exposed to humid air.; **d** a wide angle scan of CsSnI₃ with 10 mol% SnCl₂ additive exposed to humid nitrogen. * denotes sample holder peaks.



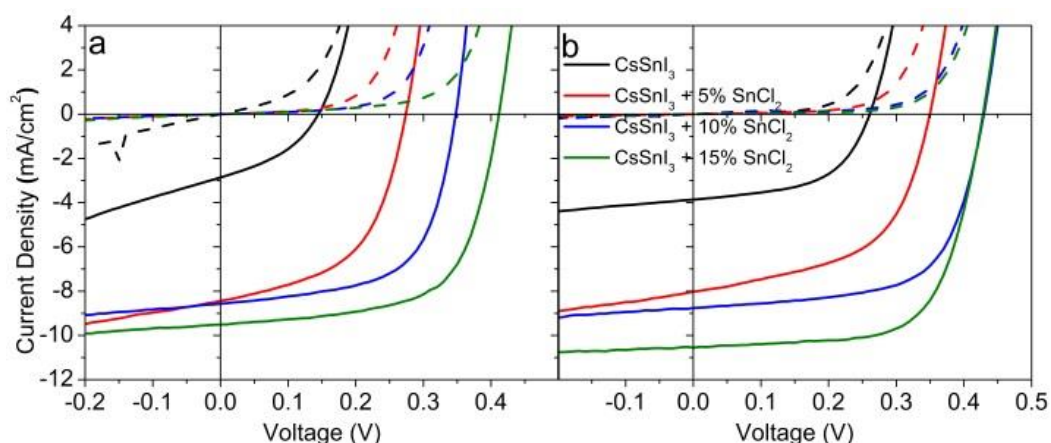
Supplementary Figure 2 | SEM image of a compact film of CsSnI_3 prepared with 10 mol% SnCl_2 additive from a 16 wt.% solution in DMF, supported on a gold substrate.



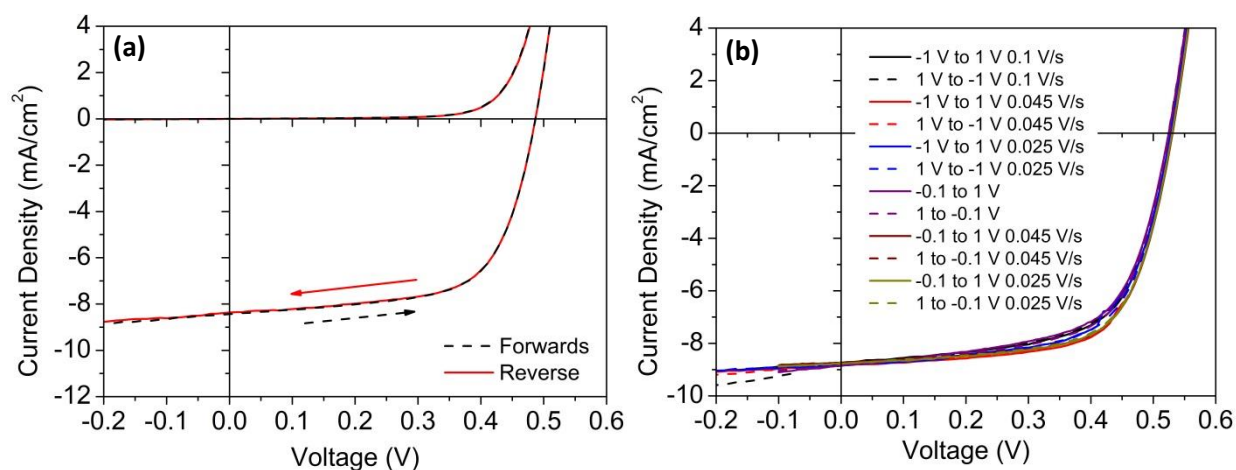
Supplementary Figure 3 | Depth profiling XPS analysis of a CsSnI_3 film with 10 mol% SnCl_2 by argon ion sputtering. High resolution (HR) XPS spectra of the surface of a ~ 80 nm thick CsSnI_3 film with 10 mol% SnCl_2 additive prepared from a 16 wt% DMF solution and supported on a gold substrate, as a function of Ar^+ sputtering time: **a** I 3d region ; **b** Cl 2p region. The evolution of the percentage composition I (blue) and Cl (green) with sputtering time is shown in **c**. Both curves in **c** are guides to the eye.



Supplementary Figure 4 | HRXPS spectra of films of SnCl_2 and CsSnI_3 with 10 mol% SnCl_2 before and after air exposure. HRXPS spectra of: **a** SnCl_2 O 1s **i** with ~1 min air exposure and **ii** after 1 hour air exposure.; **b** CsSnI_3 with 10 mol% SnCl_2 additive O 1s **i** with ~1 min air exposure and **ii** after 1 hour air exposure.; **c** CsSnI_3 O 1s **i** with ~1 min air exposure and **ii** after 1 hour air exposure.; **d** SnCl_2 Sn 3d **i** with ~1 min air exposure and **ii** after 1 hour air exposure.; **e** $\text{CsSnI}_3 + 10\% \text{SnCl}_2$ Sn 3d **i** with ~1 min air exposure and **ii** after 1 hour air exposure.; **f** CsSnI_3 Sn 3d **i** with ~1 min air exposure and **ii** after 1 hour air exposure.

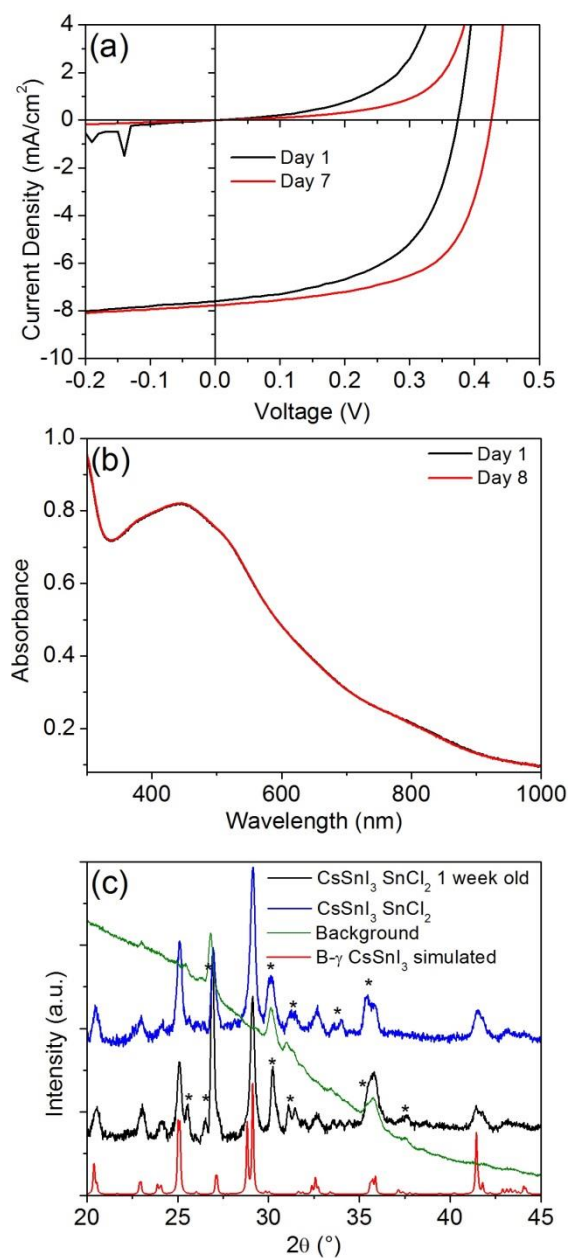


Supplementary Figure 5 | Typical current-voltage (*JV*) characteristics for CsSnI₃ based PPV devices with different loadings of SnCl₂ additive before and after an extended period of storage under nitrogen. Representative *JV* plots for devices made using CsSnI₃ with the structure: ITO glass / CsSnI₃ + X mol% SnCl₂ / PC₆₁BM / BCP / Al, with 0, 5, 10, or 15 mol% SnCl₂ additive tested **a** immediately after fabrication, and **b** after 3 weeks storage in a nitrogen glovebox. Full data set given in Supplementary Information Table S3.



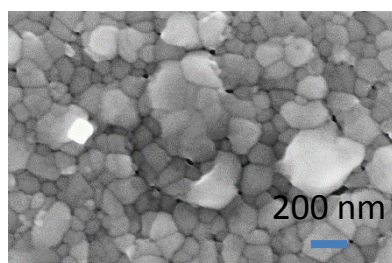
Supplementary Figure 6 | *JV* characteristics of CsSnI₃ with 10 mol% SnCl₂ showing negligible hysteresis and a very weak dependence on scan speed. **a** Representative example of *JV* characteristics for a device scanned in forward and reverse directions between -1 and + 1 V at a rate of 100 mV s⁻¹ showing no hysteresis.; **(b)** Example of *JV*

characteristics for a device scanned in forward and reverse directions for a range of starting voltages and scan rates, which shows no significant hysteresis and an optimal fill-factor for slower scan rates.

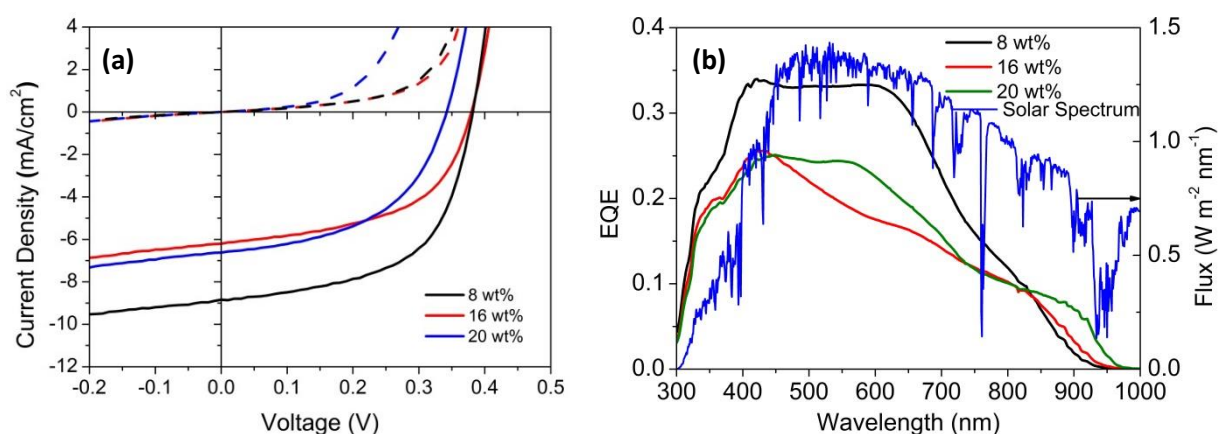


Supplementary Figure 7 | Probing the optical and structural stability of a film of $\text{CsSnI}_3 + 10 \text{ mol\% SnCl}_2$ with storage under nitrogen. **a** Representative JV plots for devices made using CsSnI_3 as the photoactive layer with the structure: ITO glass / $\text{CsSnI}_3 + 10 \text{ mol\% SnCl}_2$ (8

wt%)/ PC₆₁BM / BCP / Al, tested immediately after fabrication and after 1 week of storage in a nitrogen filled glovebox.; **b** Electronic absorption spectrum of a CsSnI₃ + 10 mol% SnCl₂ (8 wt%) immediately after deposition and after 8 days of storage in a nitrogen filled glovebox.; **c** X-ray diffraction pattern of a CsSnI₃ + 10 mol% SnCl₂ (8 wt%) film immediately after deposition (blue) and after 1 week of storage in a nitrogen filled glovebox (black). Also shown is the simulated B- γ CsSnI₃ spectrum (red) and the background spectrum (green).

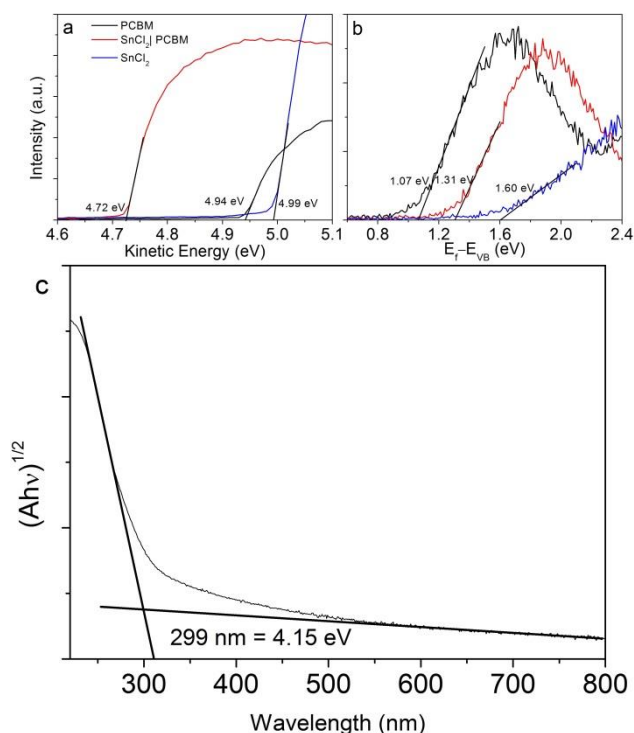


Supplementary Figure 8 | SEM image of a film of CsSnI₃ with 10 mol% SnCl₂ additive prepared using a 16 wt.% solution in DMF and supported on ITO glass.

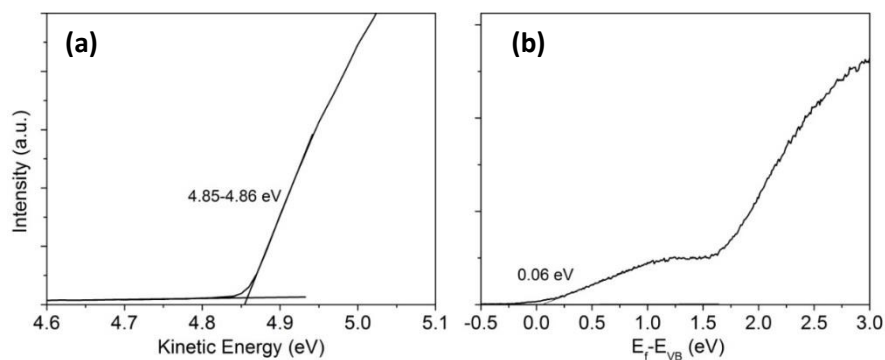


Supplementary Figure 9 | Representative current-voltage (*JV*) and external quantum efficiency (EQE) characteristics for CsSnI₃ based PPV devices with 10 mol% SnCl₂ additive

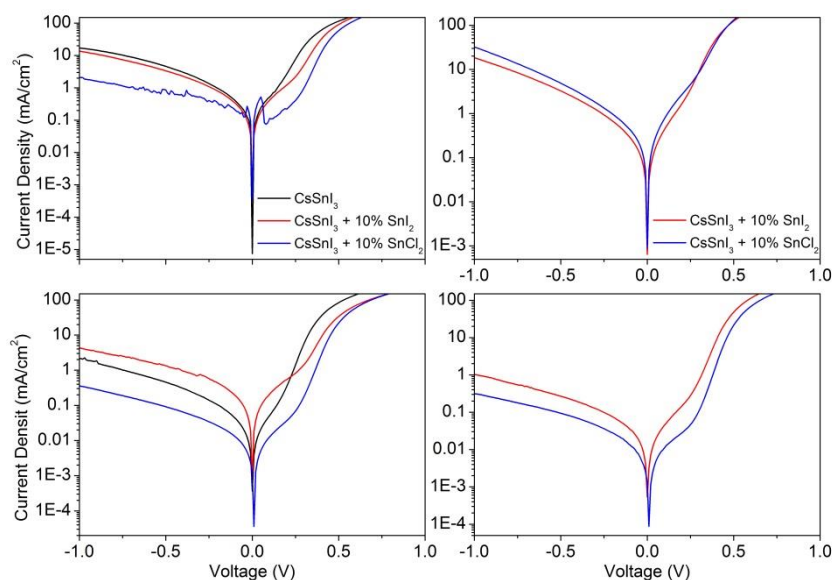
prepared from precursor solutions of different concentration. **a** Representative *JV* characteristics for devices with the structure: ITO glass / perovskite / PC₆₁BM/ BCP / Al, using CsSnI₃ with 10 mol% SnCl₂ additive. Films prepared using 8, 16, and 20 wt.% DMF solution. Full data set given in Supplementary Information Table 6. **b** Representative EQE spectra of devices made using CsSnI₃ with 10% SnCl₂ additive from 8, 16, and 20 wt% solutions in DMF immediately after fabrication. The difference between the measured J_{sc} under the solar simulator and integrated response is typically 6-7%.



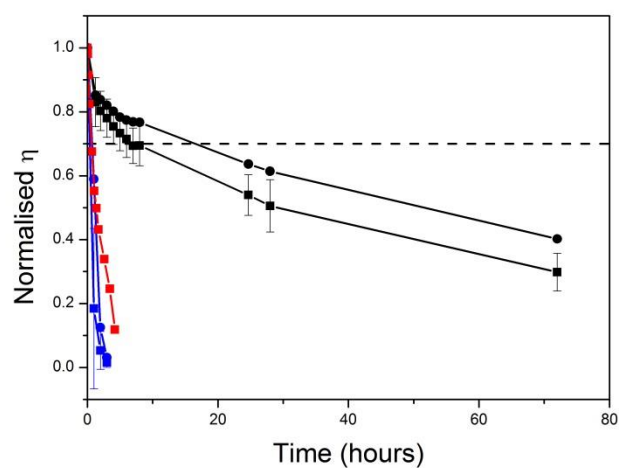
Supplementary Figure 10 | Probing the electronic structure of PC₆₁BM, SnCl₂ and SnCl₂ doped PC₆₁BM films using ultra-violet photoelectron spectroscopy and electronic absorption spectroscopy. UPS spectra of SnCl₂, PC₆₁BM (~40 nm) and bilayer SnCl₂ (<3 nm) | PCBM (~40 nm) films showing **a** the secondary electron cut-off and **b** the low binding energy edge. The electronic absorption spectrum of a SnCl₂ film on quartz is shown in **c**, and is consistent with an indirect bandgap.



Supplementary Figure 11 | Determining the ionisation potential and work function of CsSnI₃ films using valence level photoelectron spectroscopy. UPS spectra of CsSnI₃ film supported on a gold film showing: **(a)** the secondary electron cut-off; **(b)** the low binding energy edge. Importantly the samples were transferred from the glove box, in which they were fabricated, to the ultra-high vacuum system for measurement of the ionisation potential *without* exposure to air. The measured ionisation potential is in close agreement with that reported in Ref. 30 for sputtered clean CsSnI₃.

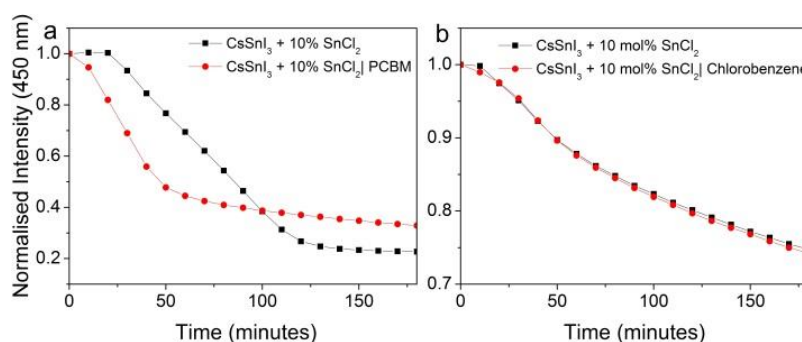


Supplementary Figure 12 | Log-linear dark current-voltage characteristics of the devices shown in Figure 5 which show that the current in reverse bias is dramatically reduced with the SnCl_2 additive; by ~ 10 times at a bias of -1 V.



Supplementary Figure 13 | PPV device stability tests under 1 sun constant illumination in ambient air for unencapsulated devices with the same architecture. Mean (squares) and champion (circles) normalised η for PPV devices *without encapsulation* tested in ambient air

under continuous 1 sun simulated solar irradiation with the structure: (black) ITO | CsSnI_3 + 10 mol% SnCl_2 | PC_{61}BM | BCP | Al at $\sim 25\%$ humidity and 50°C .; (blue) ITO | $\text{CH}_3\text{NH}_3\text{PbI}_3$ | PC_{61}BM | BCP | Al at $\sim 25\%$ humidity and 50°C .; (red) ITO | $\text{CH}_3\text{NH}_3\text{PbI}_3$ | PC_{61}BM | Bis- C_{60} | Ag reported in Ref. 29. The dotted grey line corresponds to 70% initial power conversion efficiency. All curves are guides to the eye.



Supplementary Figure 14 | Evolution of electronic absorption spectrum of CsSnI_3 films + 10 mol% SnCl_2 additive stored in ambient air, after treatment with chlorobenzene or a solution of PC_{61}BM in chlorobenzene. Normalised electronic absorbance at 450 nm for **a** CsSnI_3 + 10% SnCl_2 with and without PC_{61}BM deposited on top from a concentrated chlorobenzene solution, as used in photovoltaic device fabrication, and **b** CsSnI_3 + 10 mol% SnCl_2 either washed or not washed with chlorobenzene.

Take off angle/ $^\circ$	%Sn	%Cs	%I	%Cl
90°	23.0	21.9	18.8	36.4
30°	23.8	18.1	15.3	42.9

Supplementary Table 1 | Elemental composition analysis of the surface of a compact film of CsSnI_3 film + 10 mol% SnCl_2 , determined using XPS for two different angles of X-ray incidence. Percentage composition of the surface of an ~ 80 nm thick CsSnI_3 film with 10 mol% SnCl_2 prepared from a 16 wt% DMF solution and supported on a gold substrate.

Compositional analysis was performed for two different angles of X-ray incidence. Sampling depths for CsSnI₃ derived from NIST IMFP database calculator: Cs 3d = 6.4 nm; I 3d = 7.1 nm; Sn 3d = 7.9 nm. Sampling depths for SnCl₂: Sn 3d = 6.8 nm; Cl = 8.2 nm.

Device	Number of Pixels	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Champion η (%)
CsSnI ₃ + 10mol % SnBr ₂	12	2.32 ± 0.23	0.32 ± 0.04	0.38 ± 0.02	0.29 ± 0.05	0.35
CsSnI ₃ + 10 mol% SnF ₂	4	6.23 ± 0.58	0.14 ± 0.01	0.42 ± 0.02	0.37 ± 0.03	0.40

Supplementary Table 2 | Current-voltage (*JV*) parameters for CsSnI₃ based PPV devices with SnBr₂ and SnF₂ additives. Typical *JV* parameters (± one standard deviation) for PPV devices with the structure: ITO glass / CsSnI₃ + 10 mol% SnX₂ / PC₆₁BM / BCP / Al using CsSnI₃ with added SnBr₂ and SnF₂.

Device	number of devices	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	η (%)	Champion η (%)
CsSnI ₃	26	3.41 ± 0.63	0.15 ± 0.03	0.38 ± 0.07	0.21 ± 0.12	0.45
	28	3.06 ± 0.59	0.21 ± 0.04	0.43 ± 0.07	0.30 ± 0.15	0.58
CsSnI ₃ + 5 mol% SnCl ₂	15	8.72 ± 0.52	0.27 ± 0.01	0.50 ± 0.05	1.18 ± 0.16	1.36
	15	8.2 ± 1.0	0.33 ± 0.05	0.52 ± 0.07	1.48 ± 0.38	1.73
CsSnI ₃ + 10 mol% SnCl ₂	29	8.04 ± 0.68	0.35 ± 0.01	0.60 ± 0.06	1.71 ± 0.27	2.14
	31	8.27 ± 0.78	0.41 ± 0.06	0.60 ± 0.11	2.08 ± 0.55	2.75
CsSnI ₃ + 15 mol% SnCl ₂	17	8.9 ± 1.2	0.40 ± 0.01	0.64 ± 0.02	2.29 ± 0.34	2.71
	17	10.3 ± 1.3	0.42 ± 0.03	0.59 ± 0.07	2.55 ± 0.39	3.16

Supplementary Table 3 | Current-voltage (*JV*) characteristics for CsSnI₃ based PPV devices with different loadings of SnCl₂ additive before and after an extended period of storage under nitrogen. Typical *JV* parameters (± one standard deviation) for devices with the structure: ITO glass / CsSnI₃ + X mol% SnCl₂ / PC₆₁BM / BCP / Al with 0, 5, 10, or 15

mol% SnCl₂. Data in black - devices tested immediately after fabrication. Data in red - devices tested after storage in a nitrogen filled glove box for 3 weeks.

Device	Number of devices	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Champion η (%)
CsSnI ₃	16	3.74 ± 0.36	0.18 ± 0.06	0.43 ± 0.08	0.30 ± 0.13	0.49
	17	3.76 ± 0.34	0.20 ± 0.08	0.45 ± 0.13	0.38 ± 0.22	0.68
CsSnI ₃ + 10 mol% SnI ₂	15	7.69 ± 0.54	0.28 ± 0.03	0.40 ± 0.09	0.87 ± 0.26	1.15
	16	8.44 ± 0.61	0.35 ± 0.02	0.49 ± 0.06	1.46 ± 0.26	1.73
CsSnI ₃ + 10 mol% SnCl ₂	14	8.58 ± 0.68	0.37 ± 0.01	0.63 ± 0.03	2.00 ± 0.21	2.23
	14	8.72 ± 0.67	0.44 ± 0.01	0.66 ± 0.02	2.53 ± 0.25	2.87

Supplementary Table 4 | Current-voltage (*JV*) characteristics for CsSnI₃ based PPV devices with different tin halide additives before and after an extended period of storage under nitrogen. Typical *JV* parameters (± one standard deviation) for devices with the structure: ITO glass / perovskite / PC₆₁BM/ BCP / Al. Data in black - devices tested immediately after fabrication. Data in red - devices tested 28 days after fabrication after storage in a nitrogen filled glove box. Representative data set plotted in Figures 5a&b.

Sample	Number of devices	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Champion η (%)
CsSnI ₃ + 10% SnI ₂	15	6.80 ± 0.34	0.25 ± 0.02	0.41 ± 0.04	0.69 ± 0.12	0.88
	11	8.05 ± 0.31	0.36 ± 0.01	0.51 ± 0.02	1.50 ± 0.12	1.72
CsSnI ₃ + 10% SnCl ₂	16	9.82 ± 0.45	0.26 ± 0.05	0.42 ± 0.05	1.18 ± 0.37	1.72
	9	11.25 ± 0.83	0.40 ± 0.05	0.56 ± 0.10	2.54 ± 0.67	3.26

Supplementary Table 5 | Current-voltage (*JV*) characteristics for CsSnI₃ based PPV devices with different tin halide additives before and after an extended period of storage under nitrogen. Typical *JV* parameters (\pm one standard deviation) for devices with the structure: ITO glass / perovskite / PC₆₁BM / BCP / Al. Data in black - devices tested immediately after fabrication. Data in red - devices tested 2 months after fabrication after storage in a nitrogen filled glove box. Representative data set plotted in Figures 5c&d.

Sample	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	η (%)	Champion η (%)
8 wt%	8.89 ± 0.55	0.38 ± 0.01	0.53 ± 0.01	1.77 ± 0.20	2.06
	9.89 ± 0.55	0.50 ± 0.01	0.68 ± 0.01	3.35 ± 0.21	3.56
16 wt%	6.46 ± 0.86	0.36 ± 0.02	0.52 ± 0.07	1.21 ± 0.25	1.71
	9.1 ± 1.1	0.29 ± 0.04	0.58 ± 0.03	1.56 ± 0.45	2.52
20 wt%	6.11 ± 0.97	0.33 ± 0.02	0.49 ± 0.06	0.99 ± 0.26	1.29
	3.7 ± 1.0	0.21 ± 0.02	0.48 ± 0.03	0.38 ± 0.17	0.81

Supplementary Table 6 | Current-voltage (*JV*) characteristics for CsSnI₃ based PPV devices with 10 mol% SnCl₂ additive prepared from precursor solutions of different concentration. Typical *JV* parameters (\pm one standard deviation) for devices with the structure: ITO glass / CsSnI₃ + 10 mol% SnCl₂ / PC₆₁BM / BCP / Al. Films of CsSnI₃ + 10 mol% SnCl₂ where prepared using DMF solutions with concentrations 8, 16 and 20 wt%. Data in black - devices tested immediately after fabrication. Data in red - devices tested after 5 months storage in a nitrogen filled glove box.

Supplementary Discussion

Discussion related to Figure 1 in main text. The small difference in the absorption intensity at very short wavelengths as compared to that in reference 19 is rationalised in terms of a variability in the extent of scattering of short wavelength light, since as is evident in Figure 2 these films are polycrystalline with crystallite dimensions of 50-200 nm.