

# Supporting information: Printing of Tin Perovskite Solar Cells via Controlled Crystallization

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Table S 1: Parameters of each film during the gas pulse trigger and after annealing estimated from PL.

Additives Used for FASnI <sub>3</sub> Films	Band gap (eV) Gas Pulse Trigger	Band gap (eV) Prior annealing	Band gap (eV) Annealed	$\Delta E$ (eV) Gas Pulse Trigger to before annealing	$\Delta E$ (eV) Gas Pulse Trigger to Annealed	$\Delta E$ (eV) Gas Pulse Trigger to Annealed	Intensity Annealed	FWHM (eV)
SnCl <sub>2</sub>	1.82	1.57	1.41	-0.25	-0.16	-0.41	7259	0.087
MACl	-	-	1.52	-	-	-	3434	0.105
MASnCl <sub>3</sub>	1.73	1.51	1.42	-0.22	-0.09	-0.31	17205	0.095
SnF <sub>2</sub>	1.81	1.51	1.42	-0.30	-0.09	-0.39	9003	0.090

Table S 2: XRD peaks and corresponding species.

Additive/Species	NA	SnI <sub>4</sub>	FASnI <sub>3</sub> (100)	SnI <sub>4</sub>	NA	FASnI <sub>3</sub> (200)	FASnI <sub>3</sub> (122)
SnCl <sub>2</sub>		12.75 12.94	14.30	25.73	26.24	29.18	
MAI		12.87	14.04	25.53	26.13	28.71	31.55
MASnCl <sub>3</sub>			14.31			29.08	
SnF <sub>2</sub>	12.24		14.17			28.91	

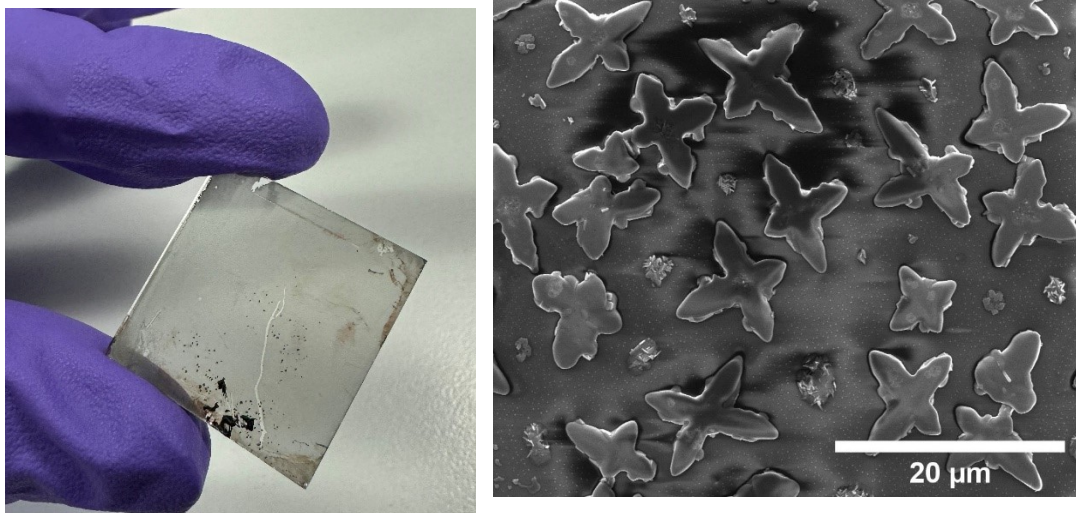


Figure S 1: Photo and SEM image of FASnI<sub>3</sub> films produced without the gas pulse step.

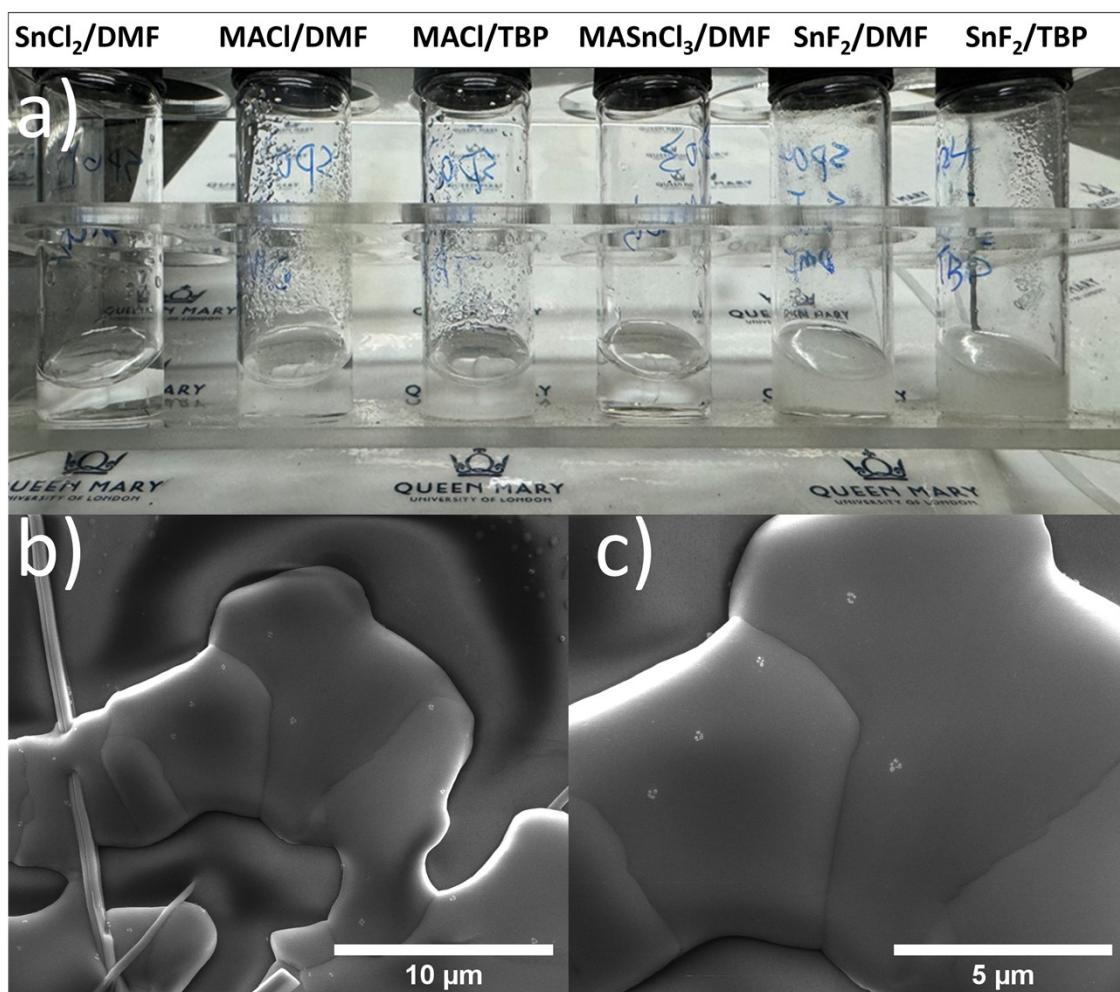


Figure S2: a): Solubility test of additives in DMF (1 M concentration tested); b) and c): SEM images of spin coated 1 M  $\text{MASnCl}_3$  in DMF from gas pulse quenching similar to the spin coating process for the  $\text{FASnI}_3$  film. Massive grains were observed under SEM. This indicates the possibility to prepare pure  $\text{MASnCl}_3$  films.

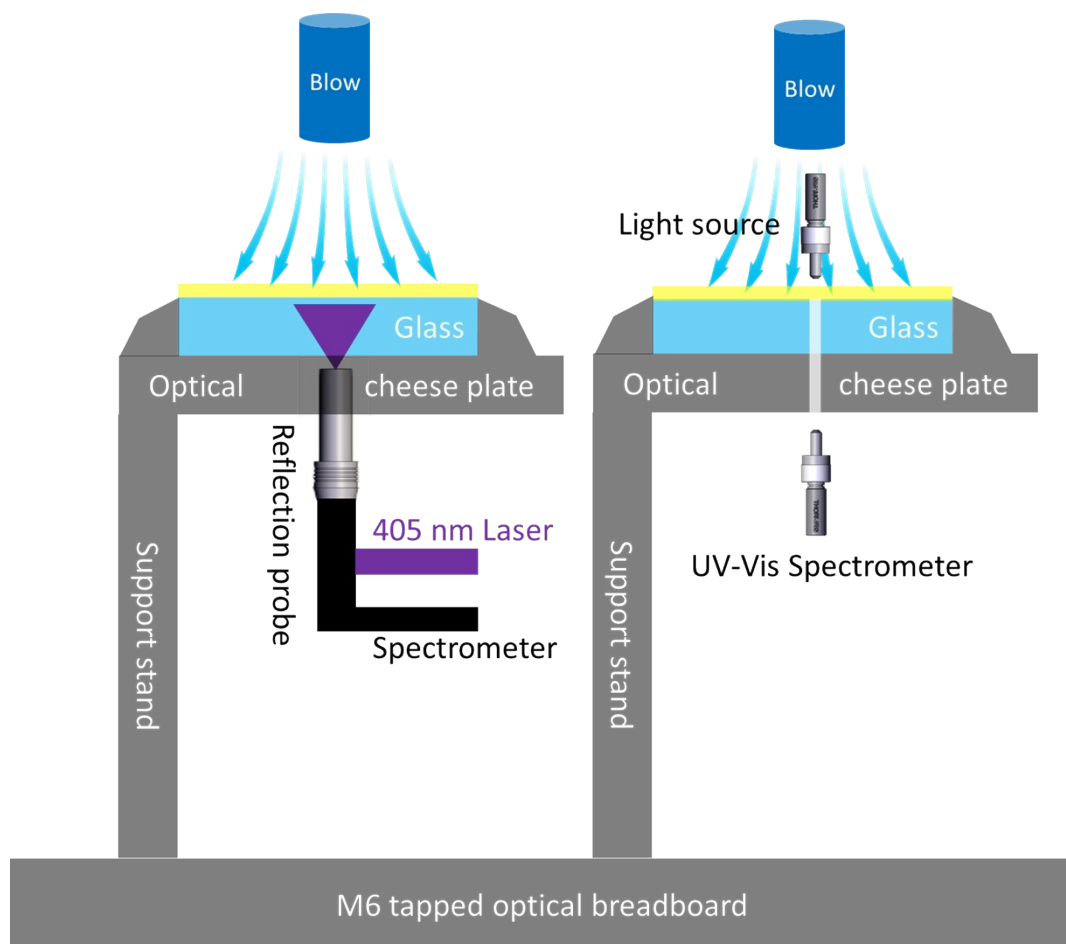


Figure S 3: Set-up of the in-situ measurement. Wet film was placed immediately on to the cheese plate after printing and in-situ monitoring started right before gas pulse applied.

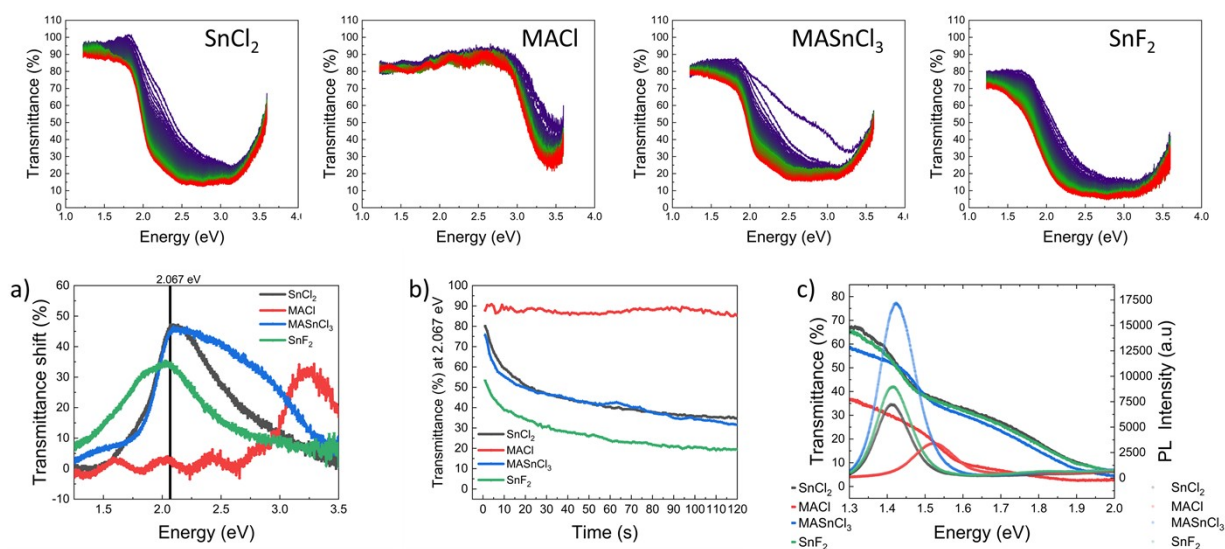


Figure S 4: Top row: In-situ transmittance data during 120 s after gas pulsing (blue being the 1<sup>st</sup> measurement and red being the final 120<sup>th</sup> measurement). a): Transmittance shift (the mathematical difference between the 1<sup>st</sup> transmittance data after the gas pulse and the 120<sup>th</sup> final transmittance data after gas pulse), indicating the energy location where the biggest change happened. b): Transmittance shift tracking at 2.067 eV. c): Steady-state final PL and final transmittance after thermal annealing.

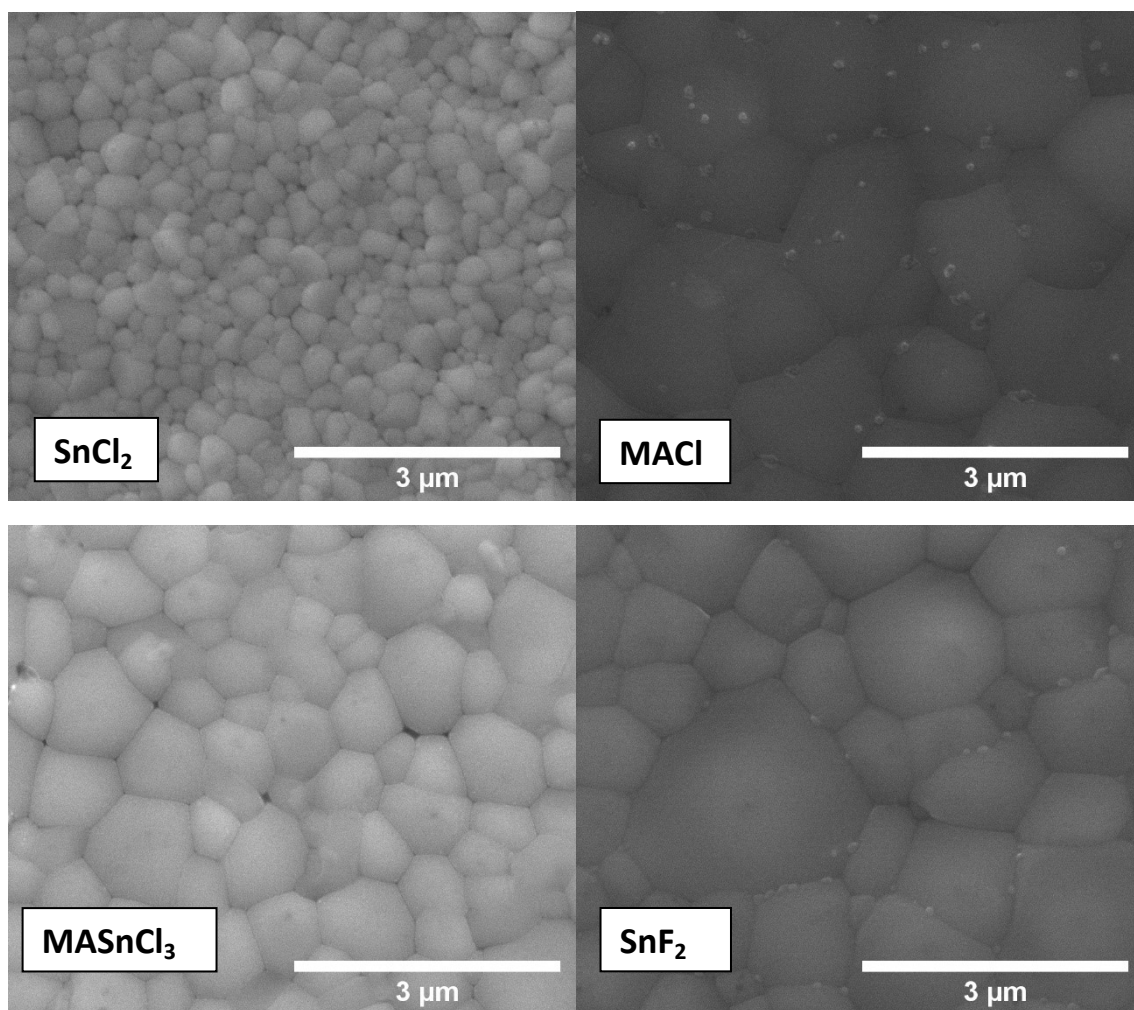


Figure S 5: SEM images of slod die coated FASI- $\text{SnCl}_2$ , FASI- $\text{MACl}$ , FASI- $\text{MASnCl}_3$  and FASI- $\text{SnF}_2$  films on glass substrates produced using gas pulse trigger and heating.



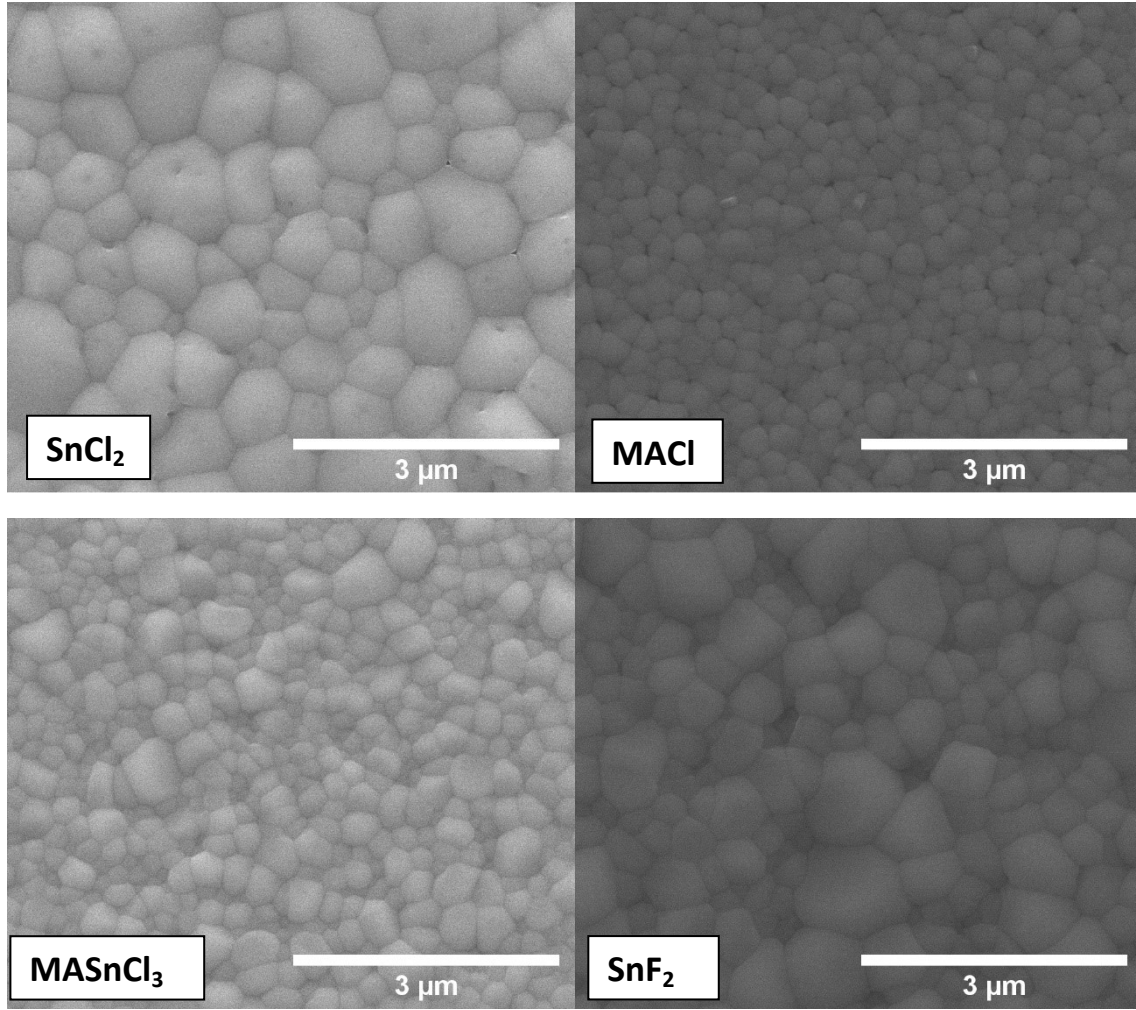


Figure S 6: SEM images of slod die coated FASI-SnCl<sub>2</sub>, FASI-MACl, FASI-MASnCl<sub>3</sub> and FASI-SnF<sub>2</sub> films on PEDOT:PSS/ITO glass substrates produced using a gas pulse trigger and heating.

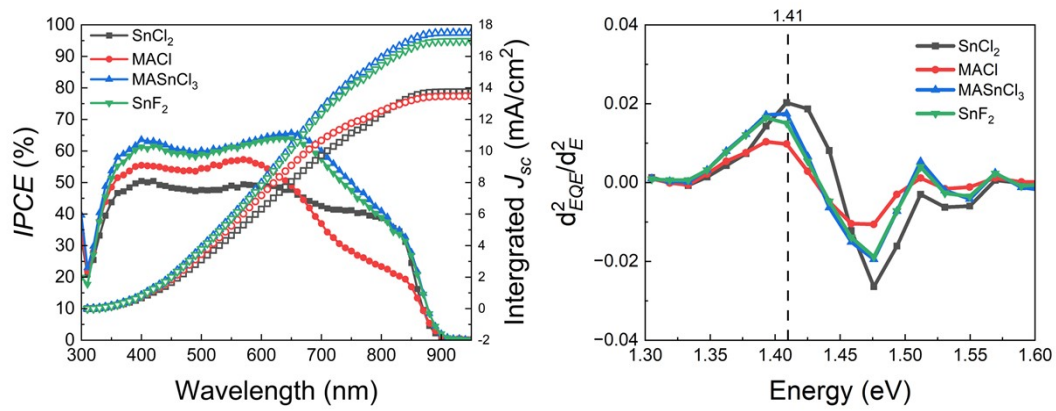


Figure S 7: IPCE measurement of the champion pixels of each FASI-Additive device, and the corresponding  $(d_{EQE})^2/(dE)^2$  plot identifying the band gap value. The IPCE values integrate to a higher JSC than the estimates from our JV measurements.

Figure S7: The IPCE values integrate to a higher JSC than the estimates from our JV measurements. The results from the JV

scans of the record pixels are reported as they were recorded right after fabrication. The IPCE and JV measurements show the same trend in photocurrent changes with additive.

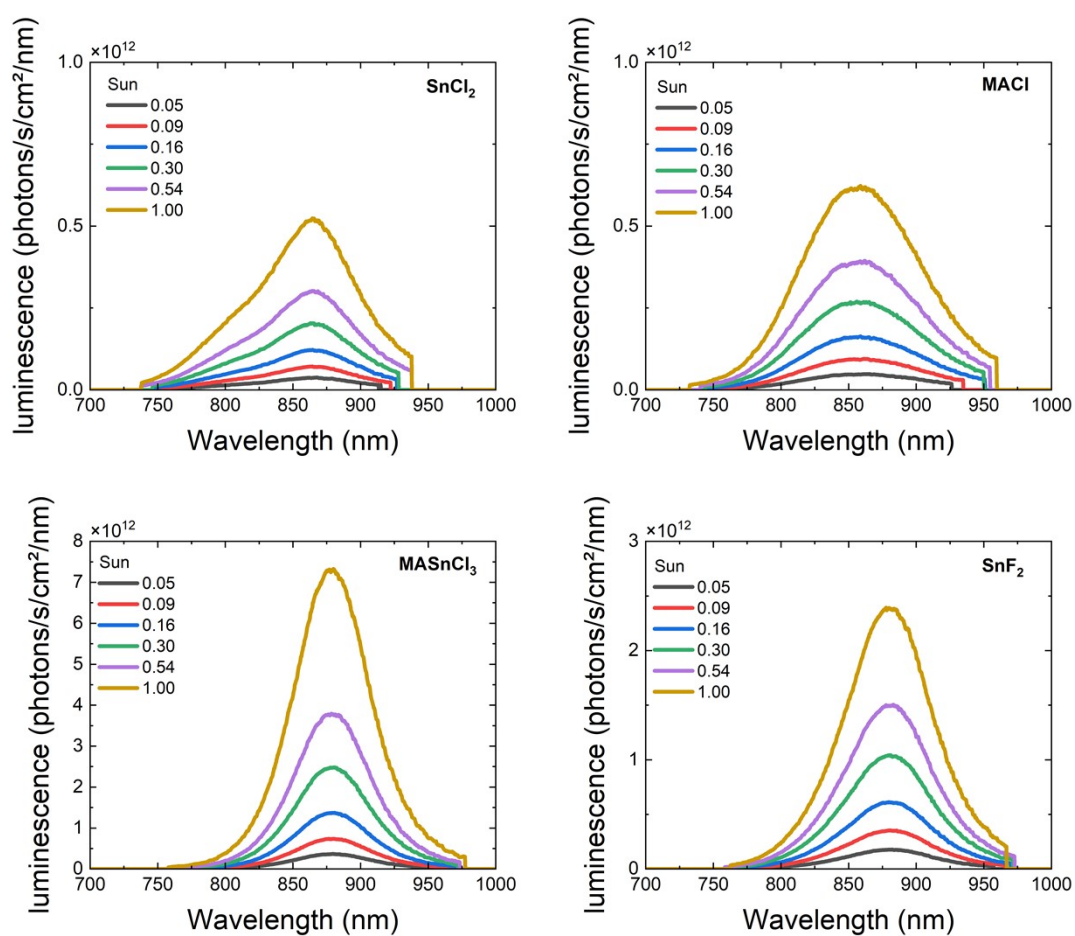


Figure S 8: Light-dependent photoluminescence spectra of each device with different additives. Note the scale bar differences that FASI-MASnCl<sub>3</sub> device has the highest PL intensity.

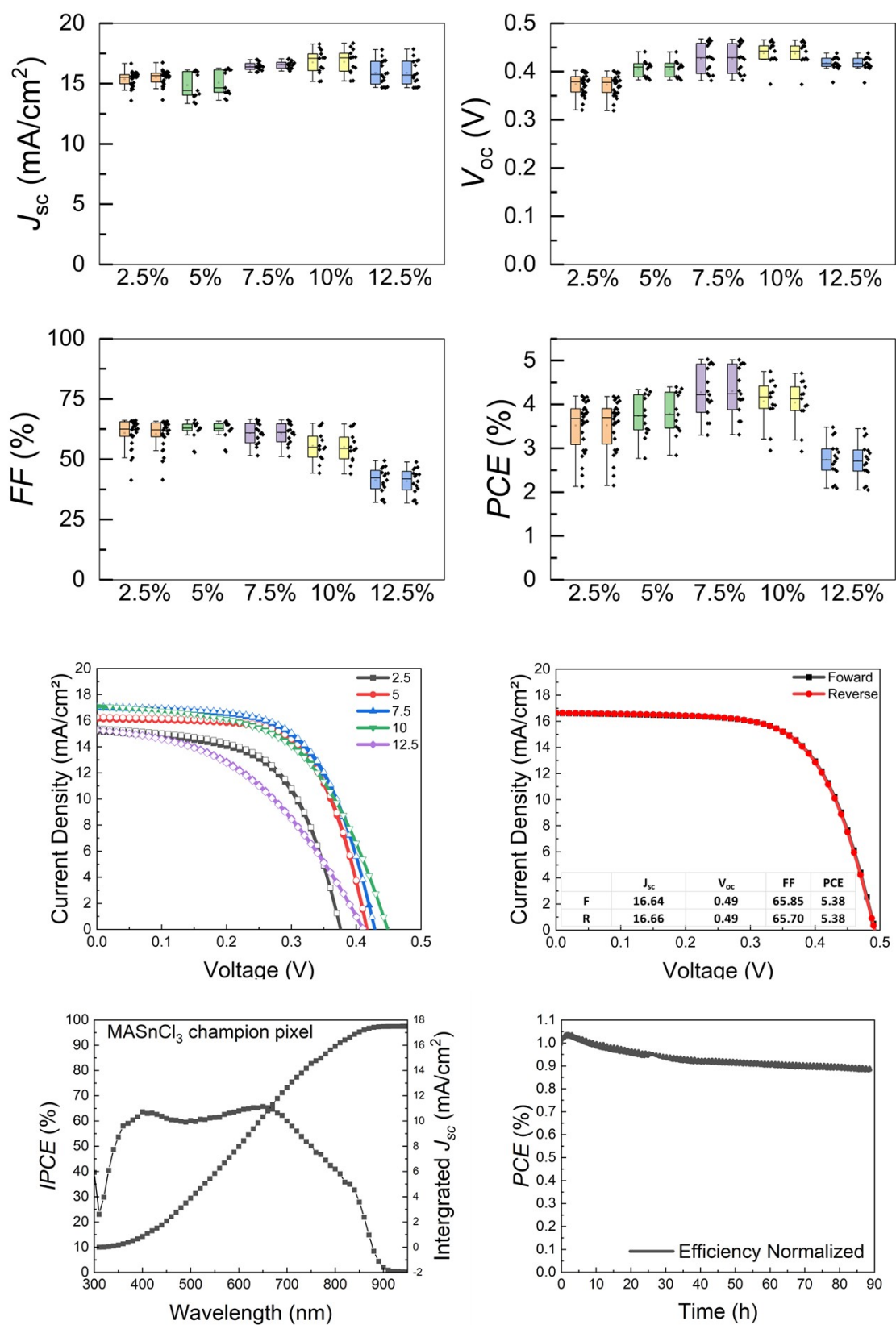
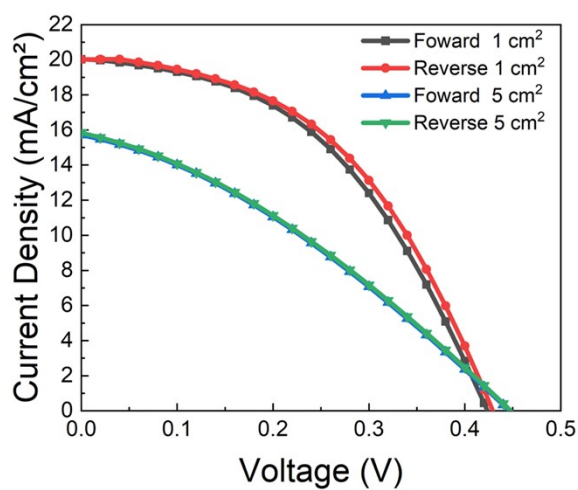
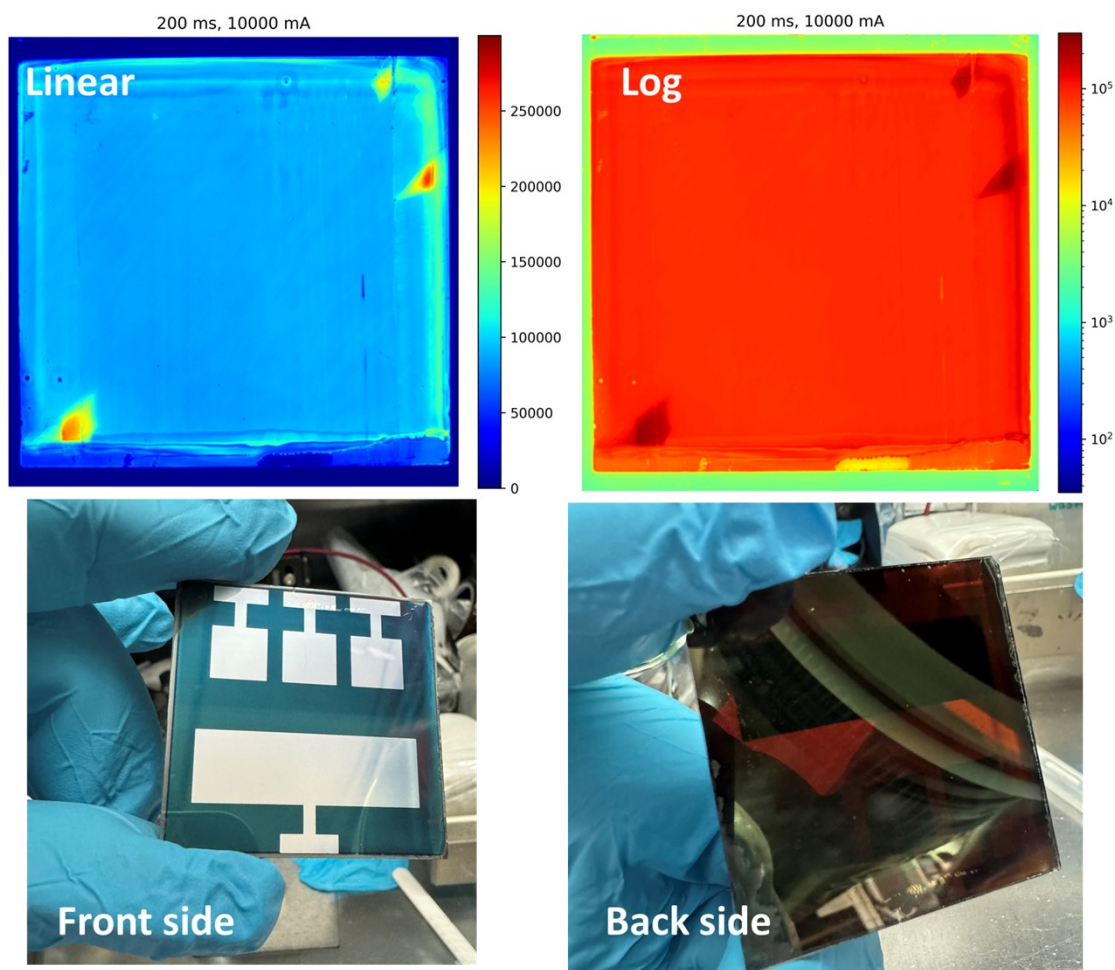


Figure S 9: Performance (forward and reverse scans) distribution of MASnCl<sub>3</sub> molar concentration. The champion pixel is from 7.5 M.

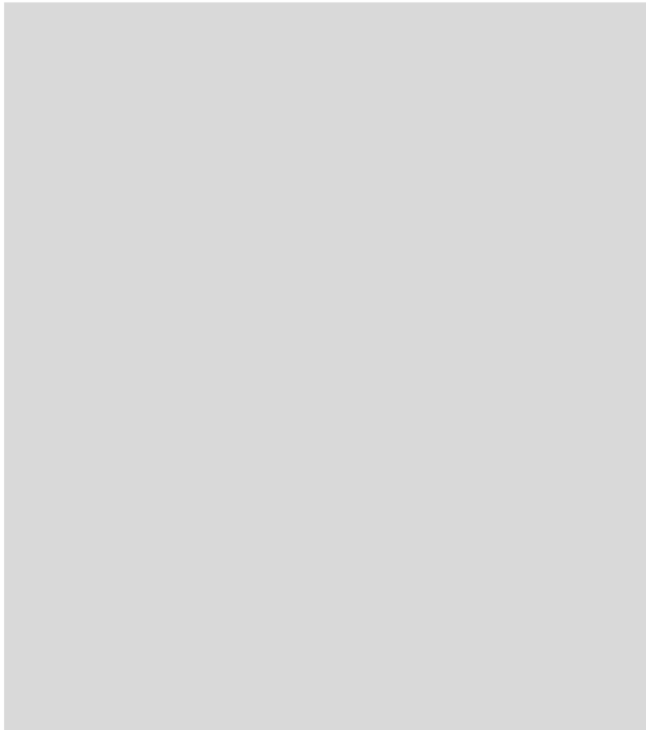
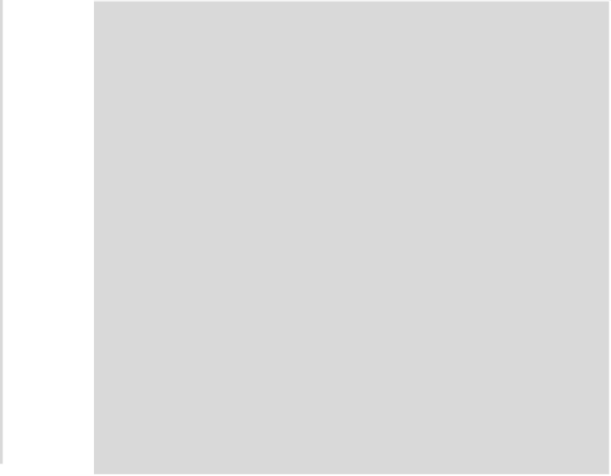
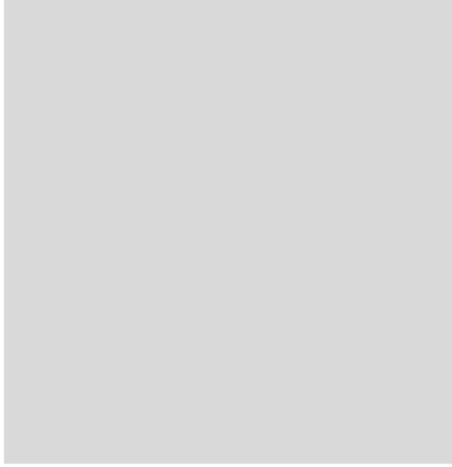
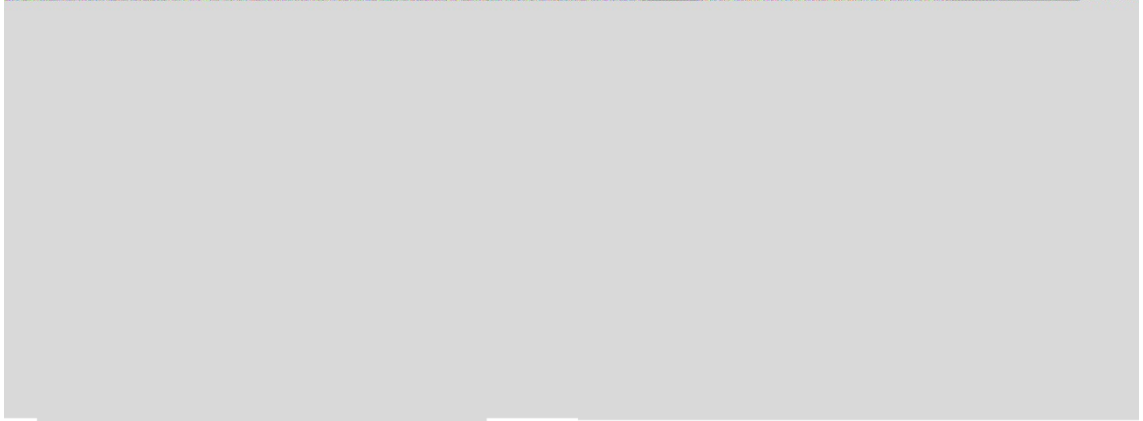




Area	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE (%)
1 cm <sup>2</sup> F	20.02	0.42	45.7	3.88
1 cm <sup>2</sup> R	20.01	0.43	46.9	4.02
5 cm <sup>2</sup> F	15.71	0.45	32.7	2.29
5 cm <sup>2</sup> R	15.83	0.44	32.68	2.31

Figure S 10: Photoluminescence Imaging of the deposited  $FASnI_3$  films on ITO/PEDOT:PSS, the bright spots in the absolute plot corresponds to uncovered PEDOT layer from spin coating process. The photos of the front and back side of the 50x50mm device. The JV scan results of the champion performances of the 1 cm<sup>2</sup> and 5 cm<sup>2</sup> pixels.





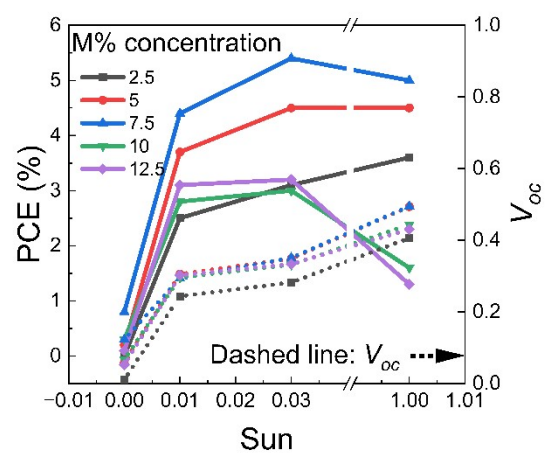


Figure S 11: Device response to low light level LED illumination, including  $V_{oc}$  changes (broken lines connect  $V_{oc}$  data points) as a function of light intensity. PCE data corresponds to data in Figure 4 in the main text.