Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Materials for

High-temperature inverted annealing for efficient perovskite photovoltaics

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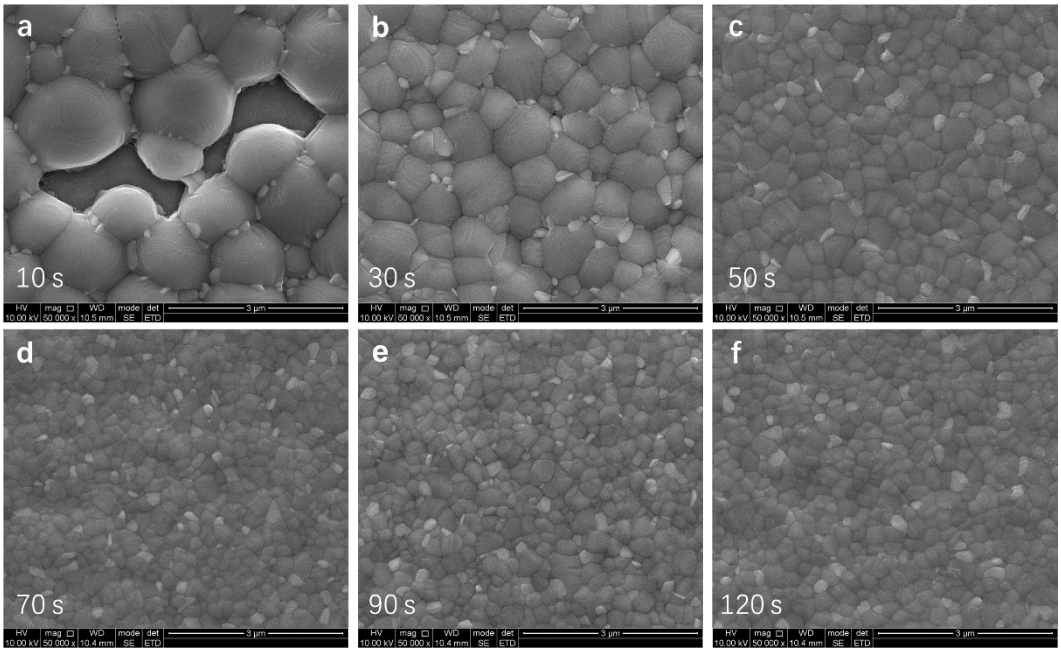

Fig. S1. Top-view SEM images of the CsFAMA hybrid perovskite films with respect to pre-annealing time at 60℃. (a) 10 s, (b) 30 s, (c) 50 s, (d) 70 s, (e) 90 s, (f) 120 s.

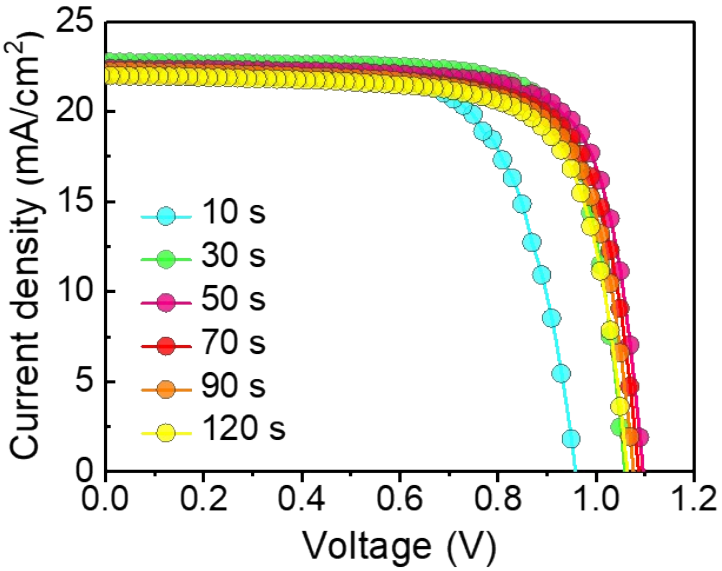

Fig. S2. Representative *J-V* curves of cells based on CsFAMA films with different pre-annealing time. Note that these *J-V* curves were recorded under reverse scan direction with a scan rate of 0.1 V/s.

Table S1. Summary of photovoltaic metrics data of each kind of cell derived from the *J-V* curves in Figure S2.

conditions	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
10 s	0.958	22.89	69.2	15.11
30 s	1.058	23.12	76.5	18.71
50 s	1.096	22.74	76.3	19.02
70 s	1.087	22.46	74.4	18.17
90 s	1.071	22.34	73.7	17.63
120 s	1.064	22.36	73.0	17.37

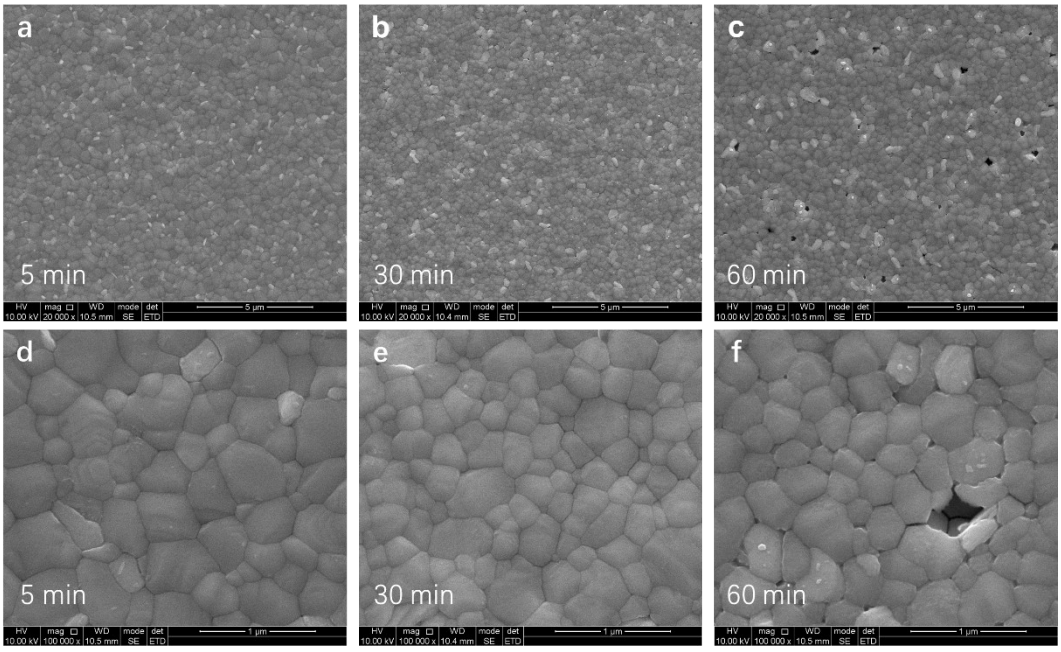

Fig. S3. Top-view SEM images of the CsFAMA triple-cation perovskite films treated by inverted annealing at 150℃ for different periods of time. (a, d) 5 min, (b, e) 30 min, (c, f) 60 min.

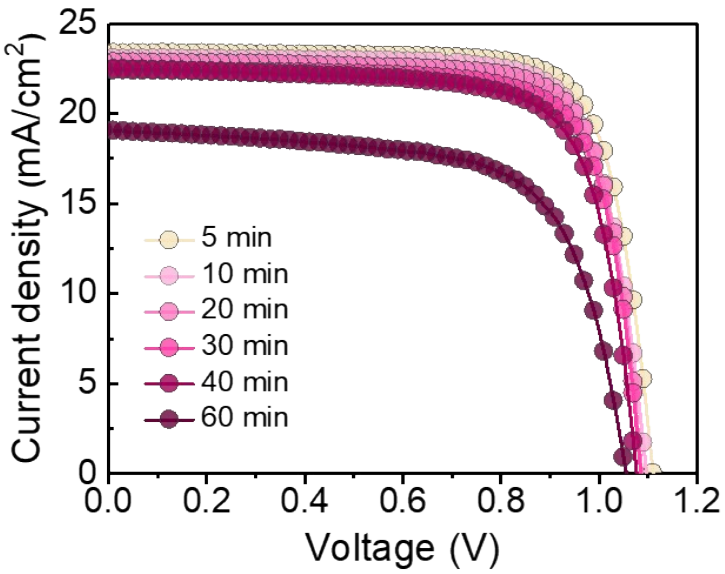

Fig. S4. Representative *J-V* curves of cells based on CsFAMA perovskite films treated by inverted annealing at 150℃ for different periods of time. Note that these *J-V* curves were measured under reverse scan direction with a sweep rate of 0.1 V/s.

Table S2. Summary of photovoltaic metrics data of each kind of device derived from the *J-V* curves in Figure S4.

conditions	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
5 min	1.110	23.37	77.7	20.16
10 min	1.097	23.06	77.0	19.48
20 min	1.087	22.85	77.4	19.22
30 min	1.085	22.40	76.3	18.55
40 min	1.076	22.06	74.1	17.59
60 min	1.063	18.69	67.7	13.45

Table S3. Summary of Full-Width-Half-Maximum (FWHM) and diffraction intensity of the main XRD

peaks for the CsFAMA perovskite films based on the XRD data shown in **Figure 3d**.

conditions	diffraction peak	FWHM (degree)	intensity (counts)
inverted	(001)	0.136	3072
	(002)	0.102	2248
	(012)	0.097	2160
	(001) of PbI_2	/	444
normal	(001)	0.130	2789
	(002)	0.106	1944
	(012)	0.097	2109
	(001) of PbI_2	/	565

Table S4. Fitting results of the TRPL decay curves for CsFAMA perovskite films prepared on glass substrates.

conditions for CsFAMA films	τ_1 (ns)	Fraction 1	τ_2 (ns)	Fraction 2	τ_{ave} (ns)
Normal annealing	4.9	4.1%	173.1	95.9%	172.9
Inverted annealing	4.2	2.6%	235.1	97.4%	235.0

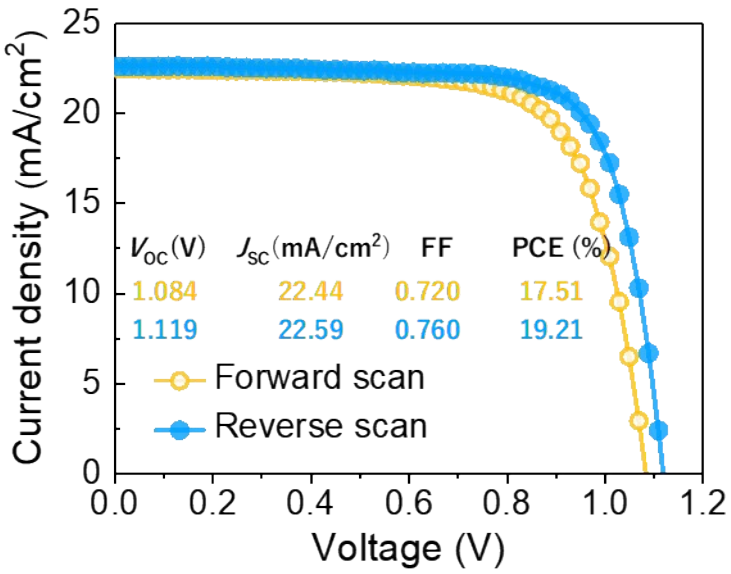

Fig. S5. J-V curves of the best-performing cell based on a normal annealed CsFAMA perovskite film measured from reverse and forward scan with a sweep rate of 0.1 V/s.

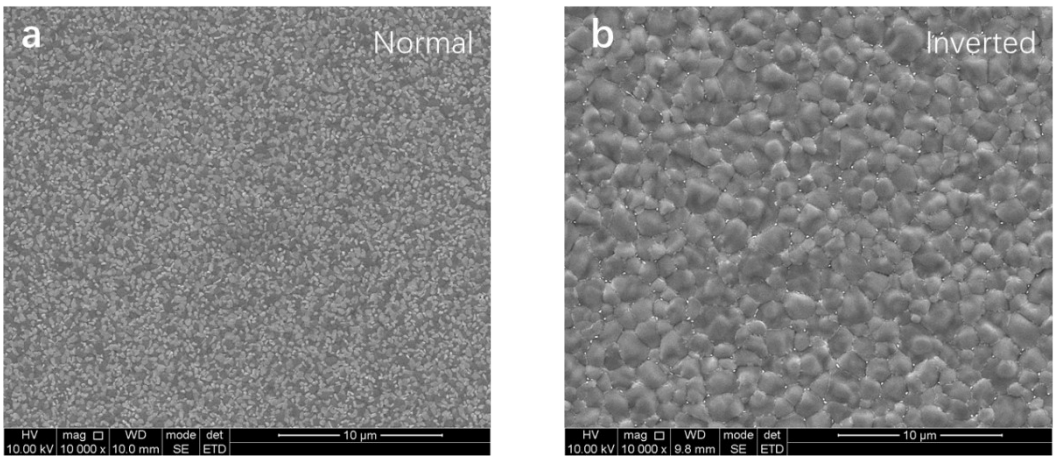

Fig. S6. Surface-view SEM images of $MAPbI_3$ perovskite films treated by normal annealing (a) or inverted annealing (b) at 150℃ for 5 min.

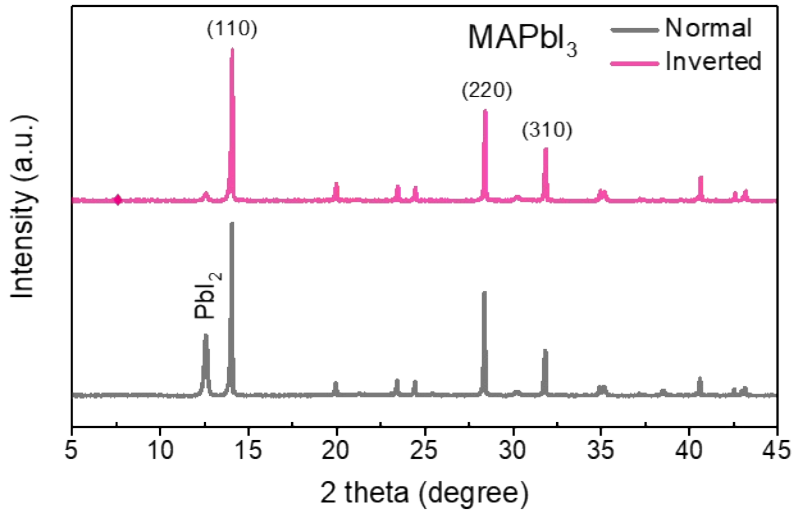

Fig. S7. XRD patterns of normal annealed and inverted annealed $MAPbI_3$ perovskite films.

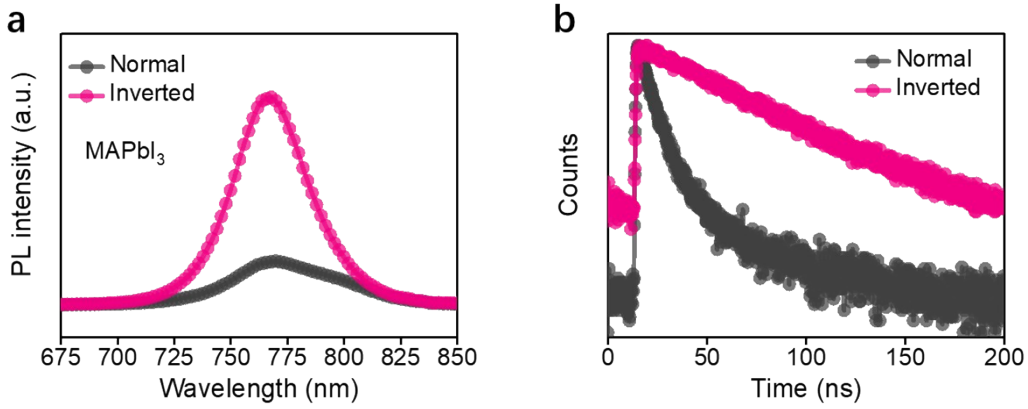

Fig. S8. Steady-state PL spectra (a) and TRPL decay curves (b) of the two types of $MAPbI_3$ perovskite films deposited on glass substrates.

Table S5. Fitting results of the TRPL decay curves for $MAPbI_3$ films prepared on glass substrates.

conditions for $MAPbI_3$ films	τ_1 (ns)	Fraction 1	τ_2 (ns)	Fraction 2	τ_{ave} (ns)
Normal annealing	8.3	59.0%	46.9	41.0%	39.1
Inverted annealing	14.0	9.6%	70.6	90.4%	69.4

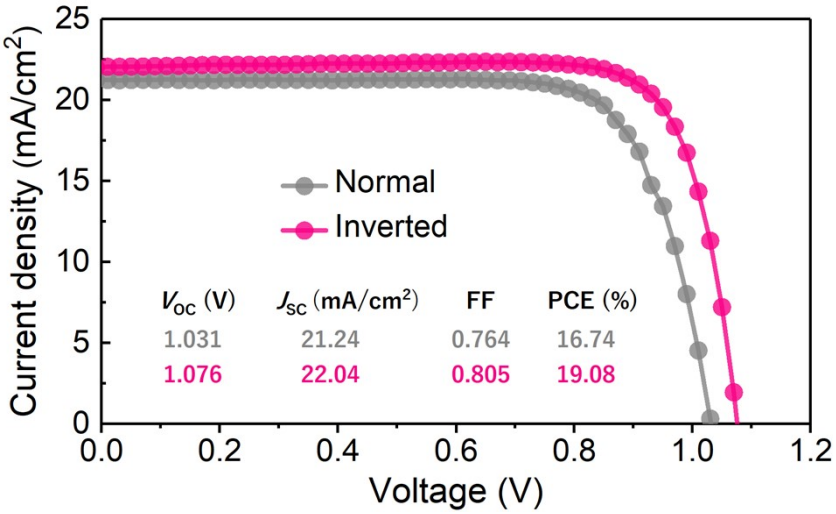

Fig. S9. *J-V* curves of the best-performing photovoltaic device based on the normal annealed or inverted annealed $MAPbI_3$ perovskite films. Note that the *J-V* curves were recorded under reverse scan with a scan rate of 0.1 V/s.

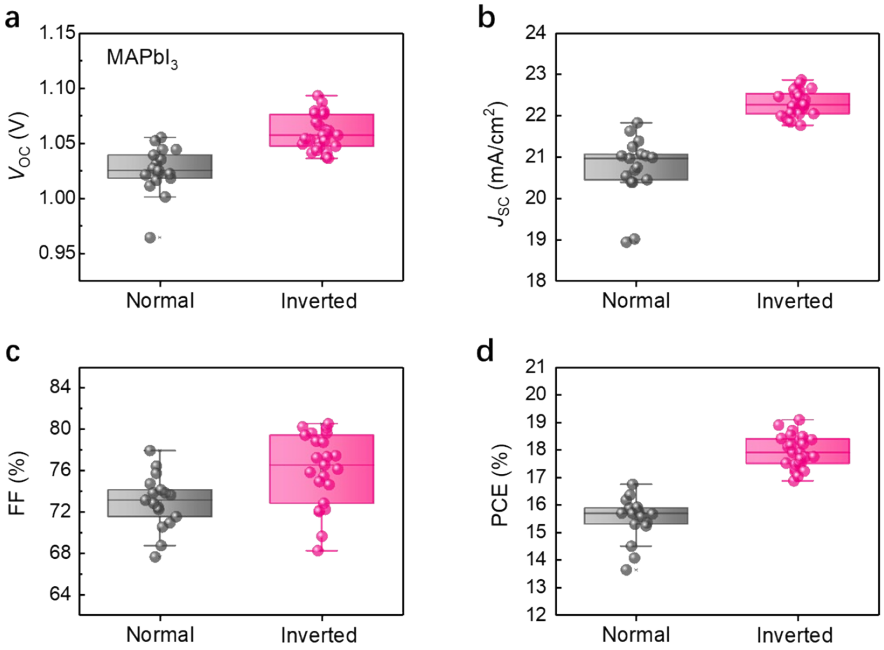

Fig. S10. Statistical distributions of photovoltaic metrics collected from around 20 independent cells of the two types of $MAPbI_3$ photovoltaic devices. (a) V_{OC}, (b) J_{SC}, (c) FF, (d) PCE.

Table S6. Summary of the photovoltaic metrics collected from around 20 independent cells of the two types of $MAPbI_3$ perovskite photovoltaic devices.

devices	V_{OC} (V)	J_{SC} (mA/cm^2)	FF (%)	PCE (%)
Normal	1.025±0.021	20.72±0.75	72.9±2.5	15.48±0.77
Inverted	1.060±0.016	22.30±0.30	76.0±3.4	17.93±0.58