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Supplementary Information

Vertically-aligned quasi-2D cesium lead halide perovskite solar cells

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Perovskite films were prepared on the substrate without preheating and then annealed at 210 °C, and images of these perovskite films are shown in Fig. S1. The perovskite film with DMF/DMSO = 1:1 started transforming to the black phase after being annealed for 4 seconds, while it started after 6 seconds for the perovskite film with DMSO only, suggesting a slower crystallization rate when the DMSO proportion increased. And the spin-coating processes of perovskite films prepared by hot-casting with DMSO only and DMF/DMSO of 4:1 are shown in Video S1 and Video S2, respectively, which also suggests a slower rate for higher DMSO proportion.

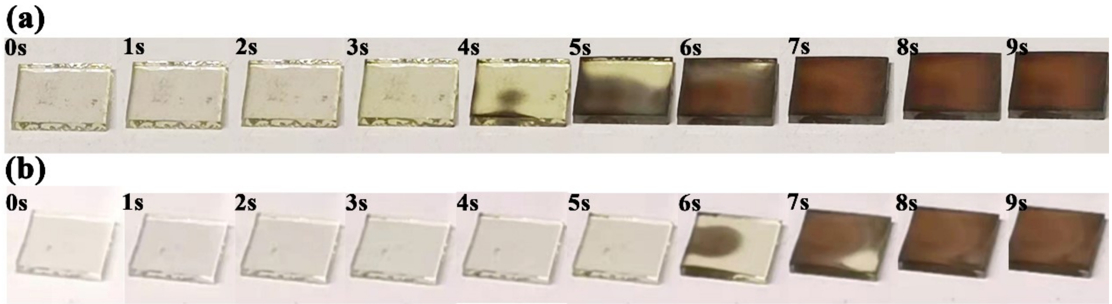

Fig. S1 Images of perovskite films with (a) DMF/DMSO = 1:1, and (b) DMSO only during the crystallization process

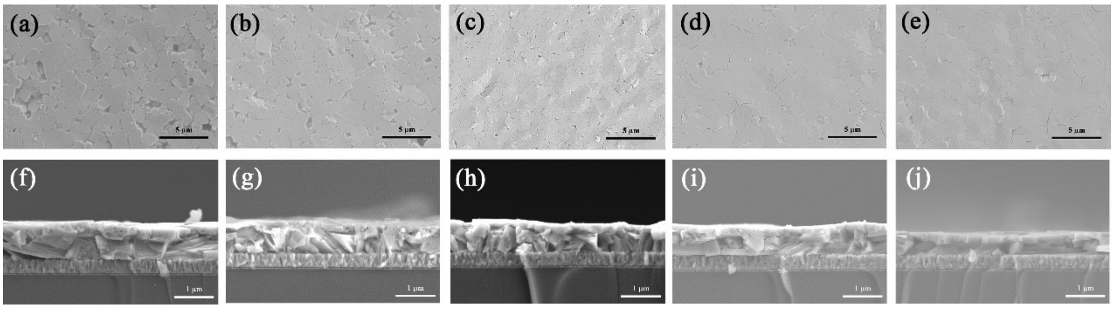

Fig. S2 Top-view SEM images of perovskite films without MACl and with DMF/DMSO ratio of (a) 4:1; (b) 7:3; (c) 1:1; (d) 3:7 and (e) DMSO only; cross-sectional SEM images of perovskite films without MACl and with DMF/DMSO ratio of (f) 4:1; (g) 7:3; (h) 1:1; (i) 3:7 and (j) DMSO only.

The average perovskite film thicknesses of different DMF/DMSO ratios are shown in Table S1. The average film thickness was obtained by calculating a simple arithmetic mean of thicknesses measured from three different parts of the cross-sectional SEM image.

Table S1 Average thicknesses of perovskite films

DMF/DMSO / Additives	4:1	7:3	1:1	3:7	DMSO only
w/ MACl	1106.4 nm	1031.9 nm	975.2 nm	726.3 nm	517.8 nm
w/o MACl	886.0 nm	793.0 nm	745.6 nm	724.6 nm	480.7 nm

The average crystal sizes D of perovskite films were calculated with the Scherrer equation:

$$D=0.89\lambda/(\beta\cos\theta) \quad (1)$$

The λ represents the wavelength of the X-ray, β represents the FWHW of diffraction peaks and the θ is the corresponding diffraction peak position[1]. The average crystal sizes of perovskite films with different solvents were calculated with the FWHW of the (202) diffraction peak at 28.9°, and the results are shown in Table S2.

Table S2 The intensity, FWHW, and calculated average crystal sizes of $(PEA)_2Cs_3Pb_4I_{13}$ perovskite films prepared with different solvents (DMF/DMSO = 4:1, 7:3, 1:1, 3:7, and DMSO only) at (111) and (202) diffraction peaks (Extracted from Fig. 2(a))

DMF/DMSO	Intensity of (111) (a.u.)	Intensity of (202) (a.u.)	FWHW of (111) (°)	FWHW of (202) (°)	Crystal size (nm)
4:1	26574	37084	0.1347	0.2129	40.39
7:3	34135	44161	0.1306	0.2002	42.95
1:1	43615	65908	0.0936	0.1478	58.18
3:7	24811	40865	0.1492	0.1776	48.42
DMSO only	16590	21099	0.1416	0.2161	39.79

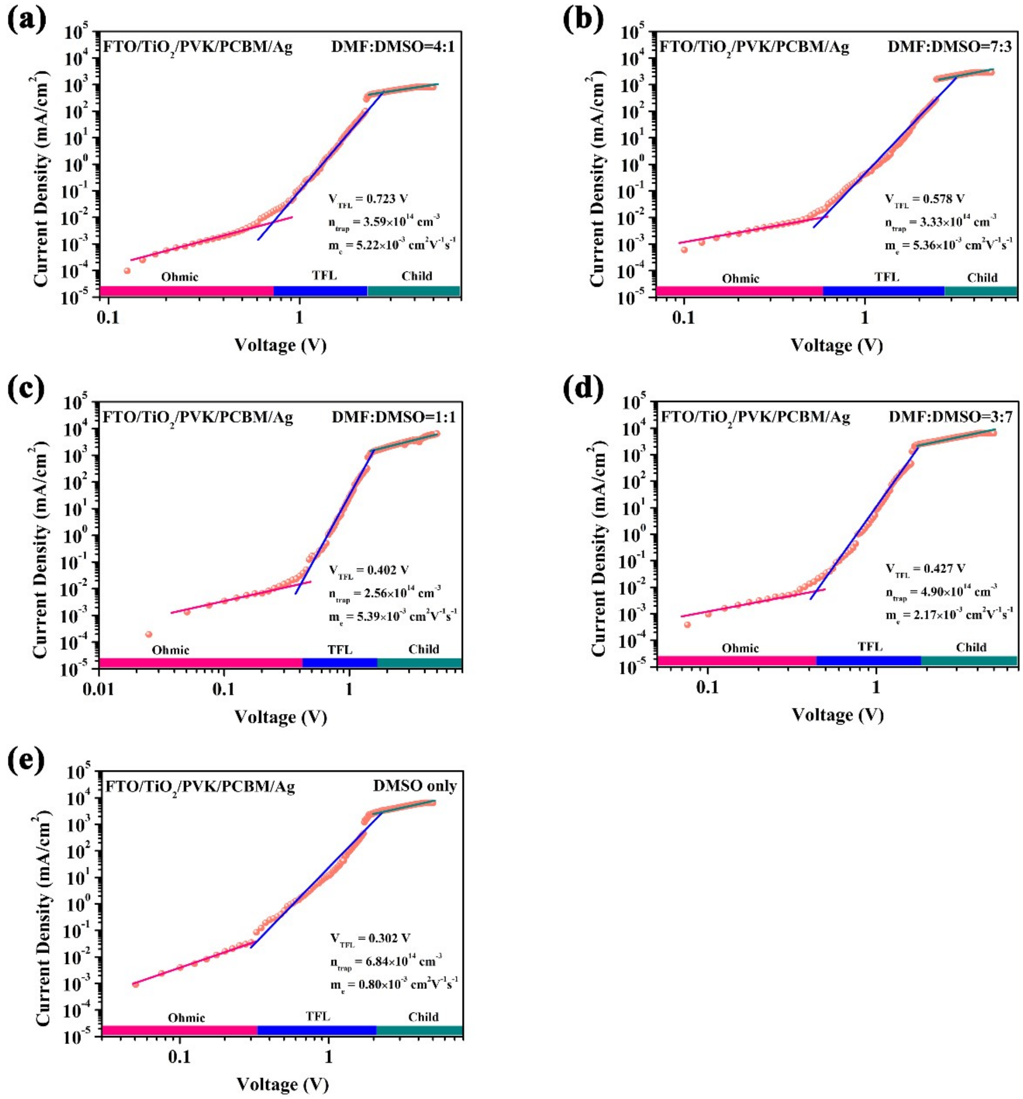

Fig. S3 Dark current–voltage curves of electron-only devices with different DMF/DMSO ratios

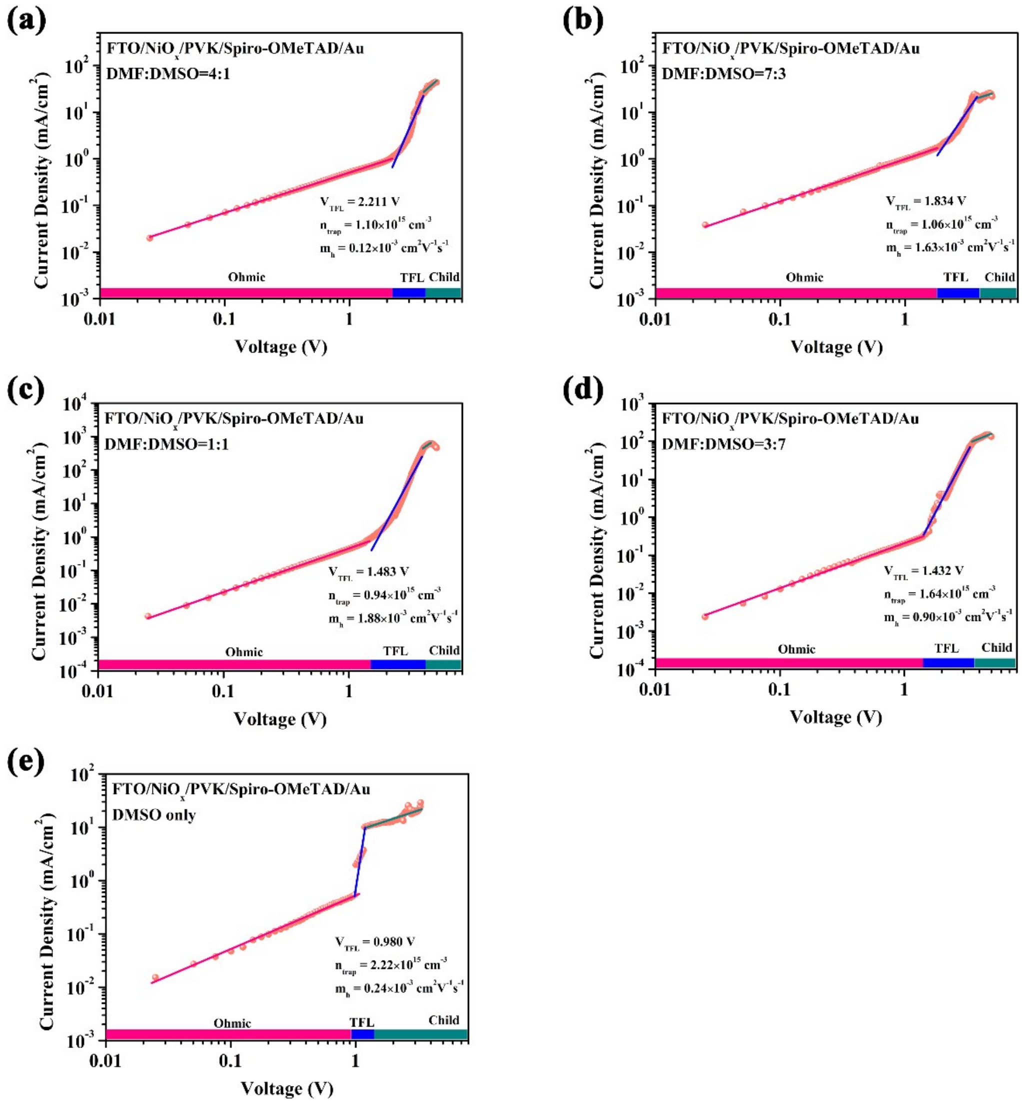

Fig. S4 Dark current–voltage curves of hole-only devices with different DMF/DMSO ratios

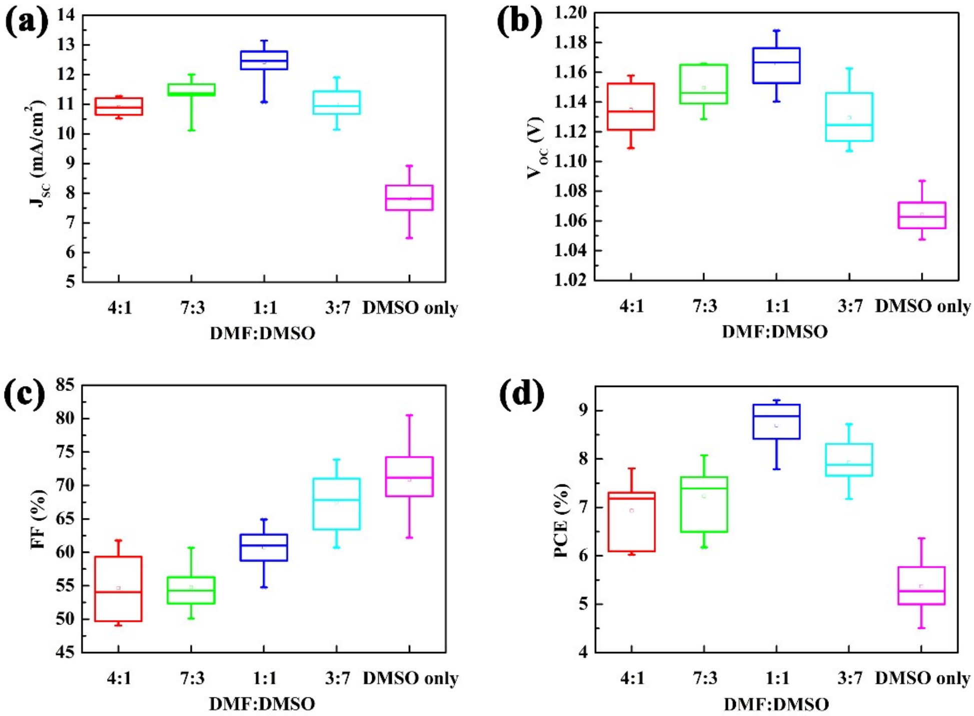

Fig. S5 (a) short current density (J_{SC}), (b) open-circuit voltage (V_{OC}), (c) fill factor (FF), and (d) photovoltaic conversion efficiency (PCE) distributions of devices with different DMF/DMSO ratios

Table S3 Photovoltaic parameters of the best devices with different DMF/DMSO ratios

	4:1	7:3	1:1	3:7	DMSO only
V_{oc}(V)	1.12	1.13	1.18	1.11	1.07
J_{sc} (mA/cm^2)	11.27	12.00	12.31	11.06	8.26
FF (%)	61.76	59.62	63.43	71.17	71.42
PCE (%)	7.80	8.08	9.21	8.72	6.30

The average crystal sizes of perovskites with and without MACl were also calculated by using the Scherrer equation with the FWHW of the diffraction peak at 28.9°, and the results are presented in Table S4.

Table S4 The intensity, FWHW, and the average crystal sizes of $(PEA)_2Cs_3Pb_4I_{13}$ perovskite films prepared with and without MACl (Extracted from Fig. 4(a))

	Intensity of (111) (a.u.)	Intensity of (202) (a.u.)	FWHW of (111) (°)	FWHW of (202) (°)	Crystal size (nm)
w/o MACl	9200	14322	0.1247	0.1957	43.94
w/ MACl	43615	65908	0.0936	0.1478	58.18

Table S5 Fitting results for time-resolved PL spectra of perovskite films with and without MACl prepared on the glass substrate

	A_1	τ_1 (ns)	A_1	τ_2 (ns)	τ_{avg} (ns)
Perovskite films without MACl	0.03	11.65	0.97	382.24	381.89
Perovskite films with MACl	0.01	15.01	0.99	1206.53	1206.38

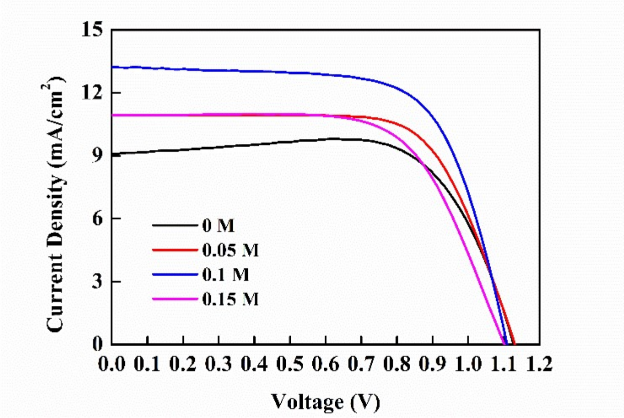

Fig. S6 J-V curves of devices with MACl of different molar concentrations (0 M, 0.05 M, 1 M, 1.5 M)

Table S6 Photovoltaic parameters of the best devices with MACl of different molar concentrations (0 M, 0.05 M, 1 M, 1.5 M)

	0 M (without)	0.05 M	0.1 M	0.15 M
V_{oc}(V)	1.13	1.13	1.10	1.10
J_{sc} (mA/cm^2)	9.10	10.93	12.97	10.93
FF (%)	0.74	0.69	0.69	0.66
PCE (%)	7.57	8.56	9.84	7.91

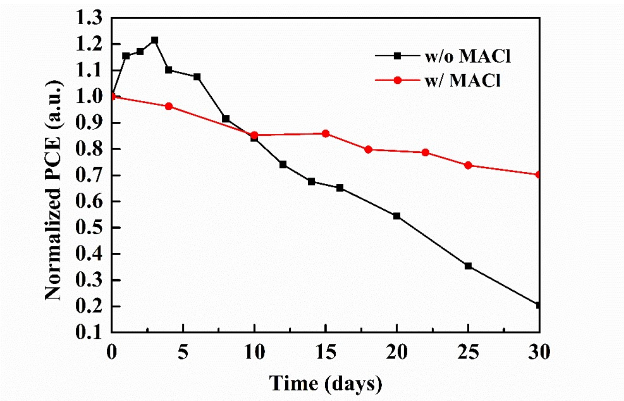

Fig. S7 Long-time stability of unencapsulated quasi-2D $PEA_2Cs_3Pb_4I_{13}$ solar cells without and with MACl stored in air under 10%-20% relative humidity

1. F. Zheng, C. Zuo, M. Niu, C. Zhou, S. J. Bradley, C. R. Hall, W. Xu, X. Wen, X. Hao, M. Gao, T. A. Smith and K. P. Ghiggino, *ACS Applied Materials & Interfaces*, 2020, **12**, 25980-25990.