

Supplementary Information

Stepwise Polymerization Enables Tailored Perovskite Ink for Scalable Flexible Perovskite Solar Cells

Weifu Zhang^{1,2,3†}, Zhaojin Wang^{4†}, Hengyu Zhou^{1†}, Wei Song^{1*}, Chenfan Xing¹, Jiahan Xie¹, Jintao Zhu⁵, Jiaming Huang^{6*}, Xiaowei Xu^{1*}, Mengjin Yang^{1*}, Yang Bai⁴, Ziyi Ge^{1,3*}

¹ Zhejiang Provincial Engineering Research Center of Energy Optoelectronic Materials and Devices, Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, Ningbo 315201, China.

² CAS Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences Beijing 100190, China.

³ Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing 100049, China.

⁴ Faculty of Materials Science and Energy Engineering, Shenzhen University of Advanced Technology, Shenzhen, China

⁵ Department of Chemical and Environment Engineering, University of Nottingham Ningbo China, Ningbo 315100, China.

⁶ Department of Electrical and Electronic Engineering, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China.

* Corresponding authors.

E-mail: songwei@nimte.ac.cn; jiaming1993.huang@polyu.edu.hk; xuxiaowei@nimte.ac.cn; yangmengjin@nimte.ac.cn; geziyi@nimte.ac.cn

† These authors contributed equally to this work.

Calculation Methods

Note S1: Residual stress calculation based on GIXRD results

According to Bragg's Equation and generalized Hooke's Law, the residual stress (σ) can be determined by 2θ - $\sin^2\varphi$ method:

$$\sigma = -\frac{E}{2(1+\nu)} \frac{\pi}{180^\circ} \cot \theta_0 \frac{\partial(2\theta)}{\partial(\sin^2\varphi)}$$

Where φ and E are the diffraction vector angle respective to the sample surface normal and the perovskite modulus, respectively. ν is the Poisson's ratio of the perovskite, θ_0 is half of the scattering angle $2\theta_0$ (the (012) crystallographic plane oriented at near 31.6°). By linear fitting 2θ as a function of $\sin^2\varphi$, the σ could be obtained. Positive slope indicates compressive stress, and negative slope indicates tensile stress.

Note S2: Carrier recombination lifetime and exciton lifetime calculation

The carrier recombination lifetimes can be derived from time-resolved photoluminescence (TRPL), the TRPL decay curves were fitted by the bi-exponential function:

$$y(t) = A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) + y_0$$
$$\tau_{ave} = \frac{\sum A_i \tau_i^2}{\sum A_i \tau_i}$$

where, A_1 and A_2 are the relative amplitudes, τ_1 and τ_2 represent time constants for fast and slow decay lifetimes in relation to nonradiative recombination of surface traps near the GBs and radiative recombination from the bulk perovskite film, respectively.

Note S3: Analyzation of space-charge-limited current (SCLC) model

The dark J - V curves display three typical regions: (I) the Ohmic region at low bias region, (II) the trap-filled limited region at intermediate bias region, and (III) a trap-free SCLC region at high bias region. In the trap-filled limited region, the trap density levels are continuously filled as bias increases, and all of traps are filled until the trap-filled limit voltage (V_{TFL}). The trap density is estimated according to the equation:

$$N_t = \frac{2\varepsilon\varepsilon_0 V_{TFL}}{qL^2}$$

Where N_t is the trap density, ε is the dielectric constants of perovskite, ε_0 is the vacuum permittivity, L is the thickness of the perovskite film, and q the elementary charge. V_{TFL} is obtained by fitting the dark I - V data with the equation.

Note S4: The dependence of J_{sc} and V_{oc} of the PSCs on light intensity

The ideality factor nKT/q can be calculated by equation:

$$V_{oc} = \frac{nKT}{q} \ln(P_{light})$$

The exponential factor α can be calculated by equation:

$$\alpha = \frac{\ln(J_{sc})}{\ln(P_{light})}$$

Note S5: Hysteresis index (HI)

The J - V hysteresis index (HI) is defined by the following equation:

$$HI = \frac{PCE_{Reverse} - PCE_{Forward}}{PCE_{Reverse}}$$



Figure S1. Crosslinking of BFDGE molecules occurred via ring opening polymerization of epoxide following a thermal treatment with IPDA as crosslinking initiator.

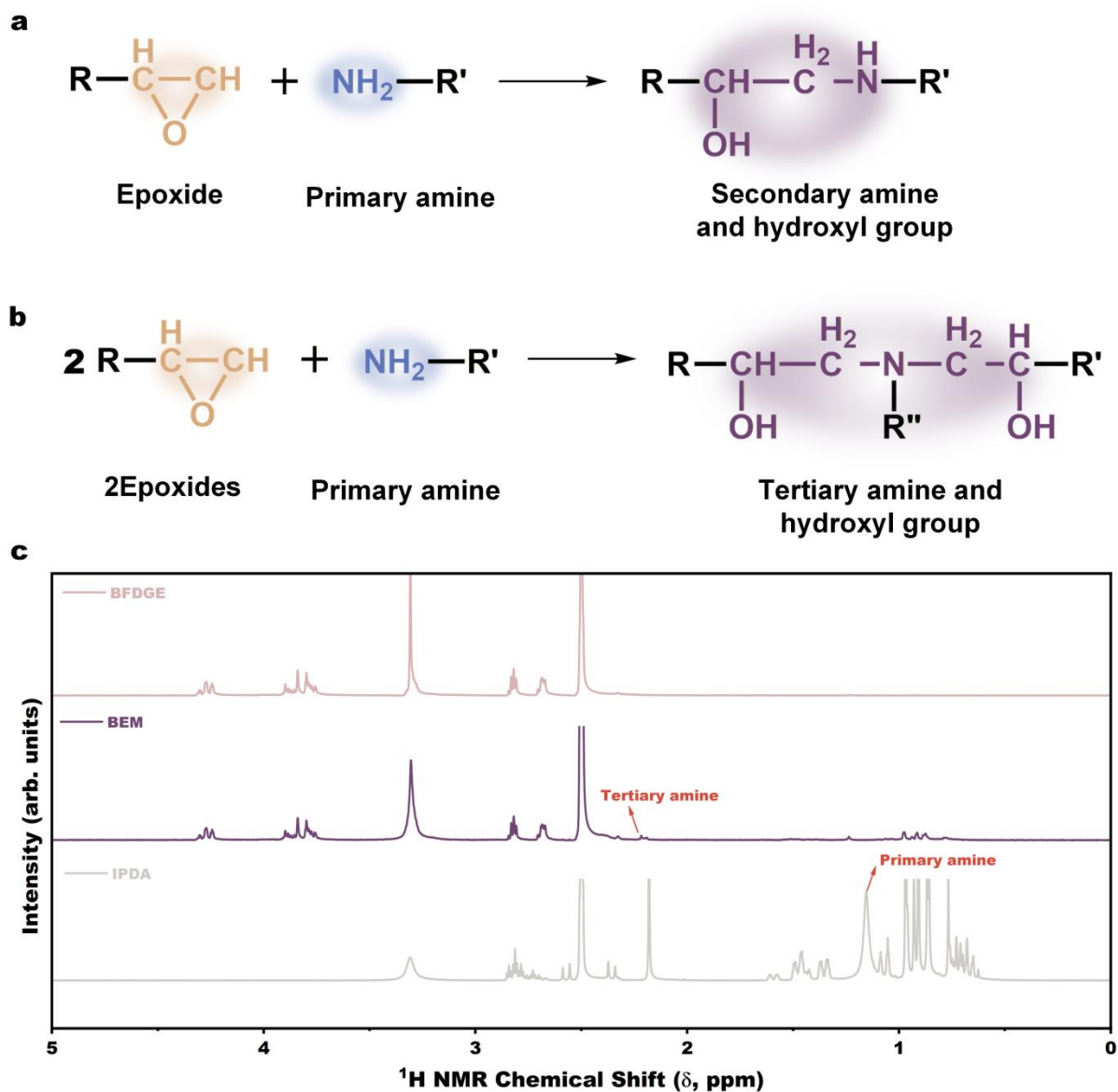


Figure S2. Ring-opening reactions of epoxide within amine and hydroxyl groups forming. (a) Secondary amine, (b) Tertiary amine and (c) ¹H NMR spectra for BFDGE, IPDA and BEM dissolved in DMSO-*d*₆.

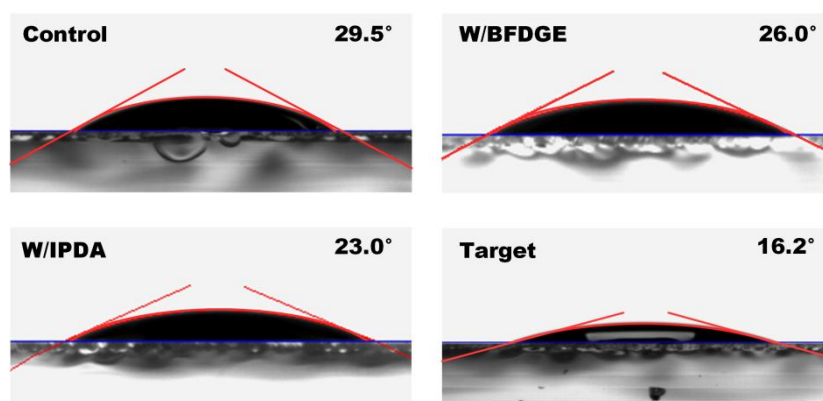


Figure S3. Contact angles of the perovskite precursor on the glass/ITO/SAM substrates.

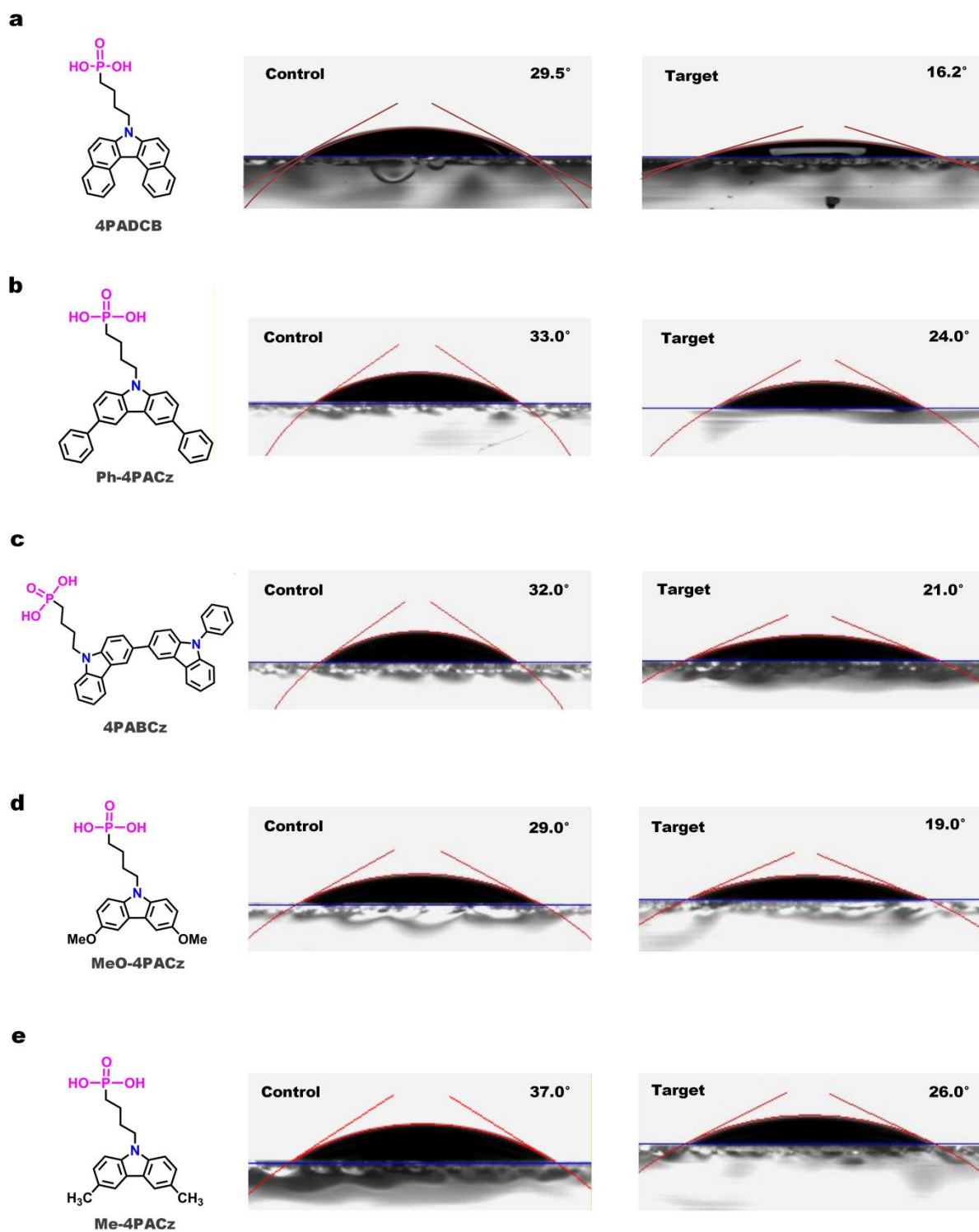


Figure S4. Comparison of contact angles for control and target perovskite inks on diverse SAM-based hole transport layers.

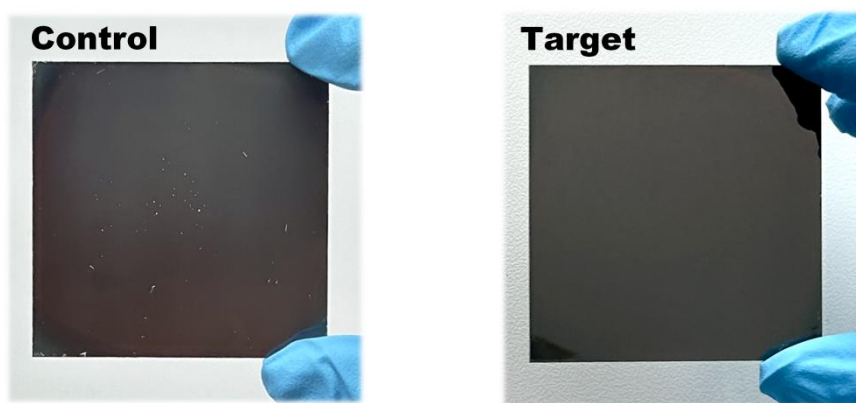


Figure S5. Photographic images of large-area perovskite films deposited on $5 \times 5 \text{ cm}^2$ glass/ITO/SAM substrates.

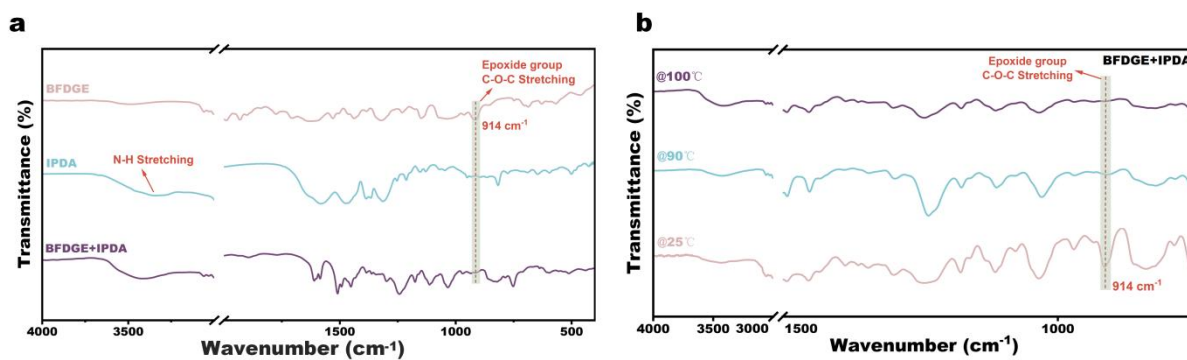


Figure S6. Confirmation of polymerization process. (a) Fourier-transform infrared spectra (FTIR) of the BFDGE monomers, pure IPDA, and BFDGE + IPDA mixture after heating at $100\text{ }^{\circ}\text{C}$ for 5 min. (b) varied-temperature FTIR spectra of BFDGE + IPDA mixture.

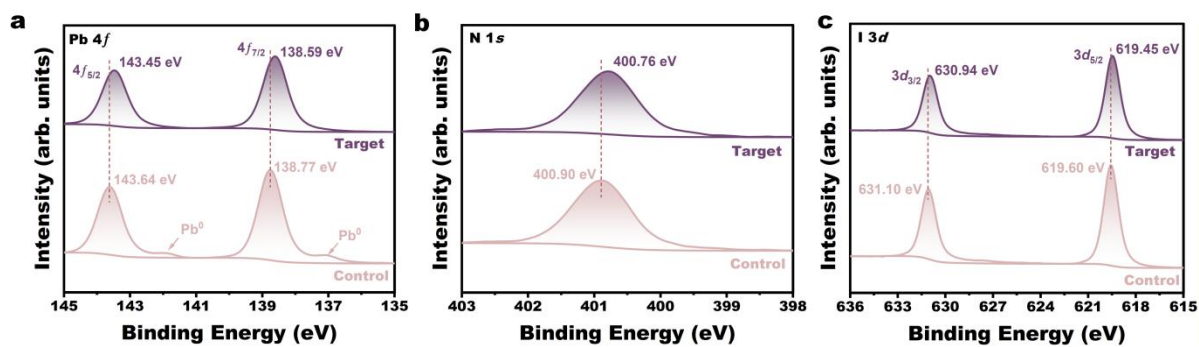


Figure S7. High-resolution XPS spectra of Pb 4f (a), N 1s (b), I 3d (c) core levels for control and target perovskite films.

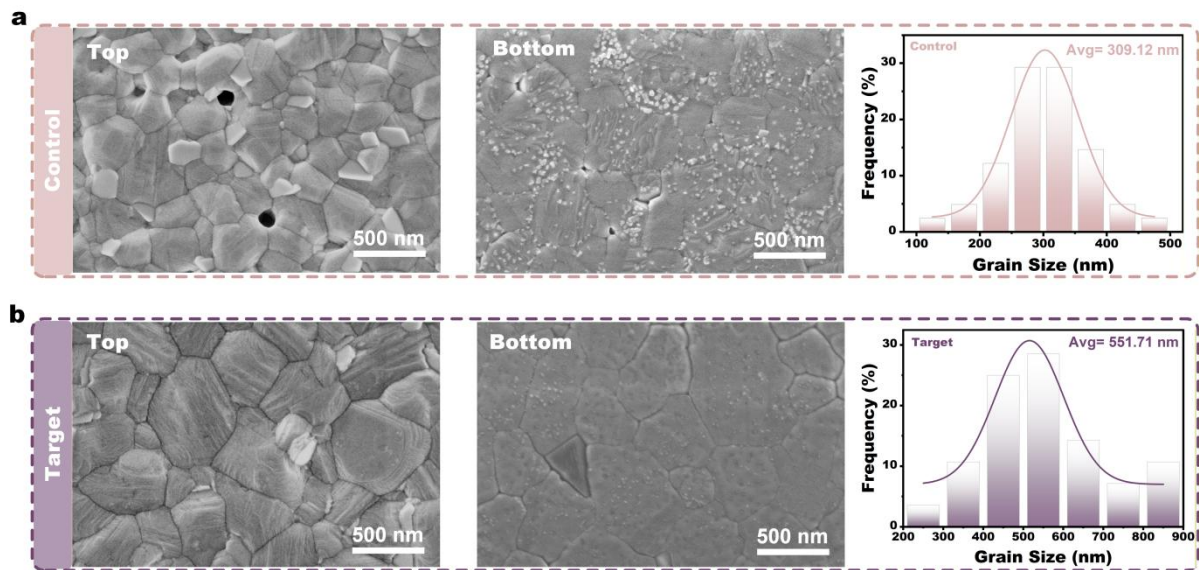


Figure S8. SEM images and the corresponding grain size distribution of the control (a), target (b) perovskite films.

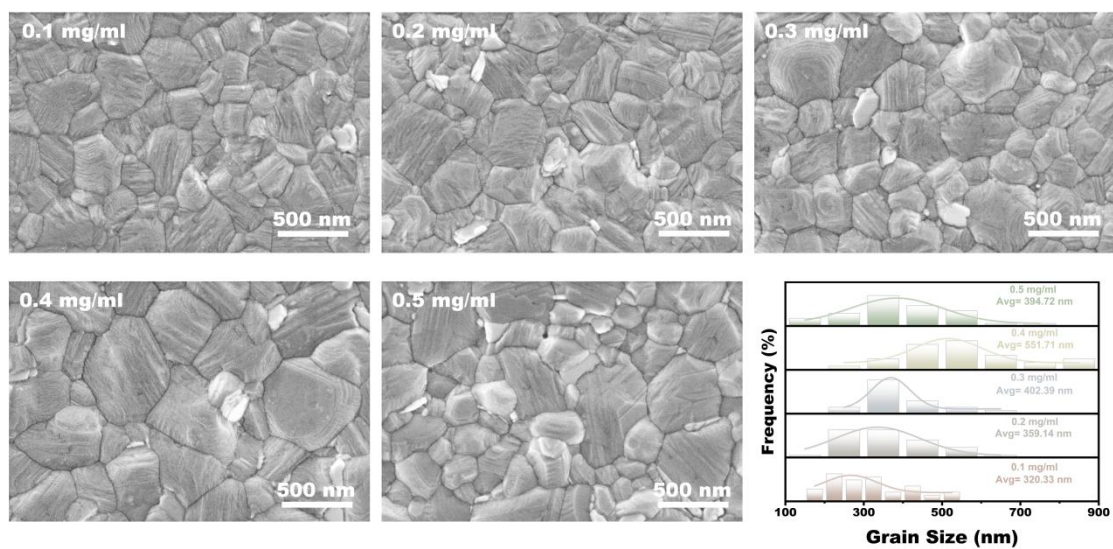


Figure S9. SEM images of perovskite films with different concentrations of BFDGE.

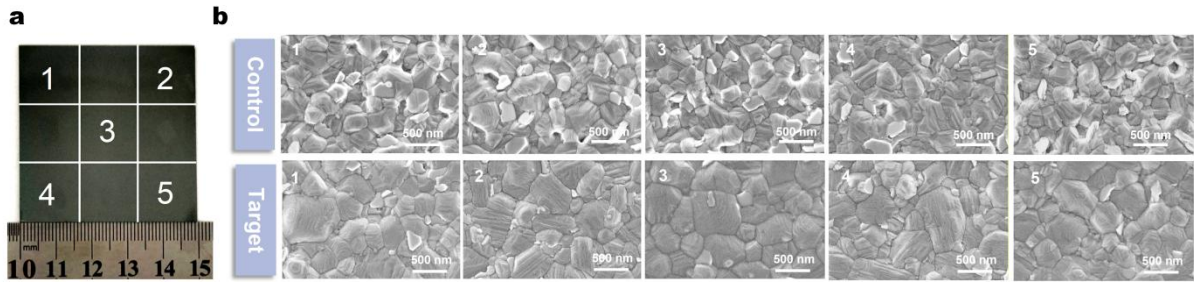


Figure S10. (a) Photograph of perovskite film deposited on 5×5 cm² substrate. (b) SEM images of five regions in the large-area perovskite films.

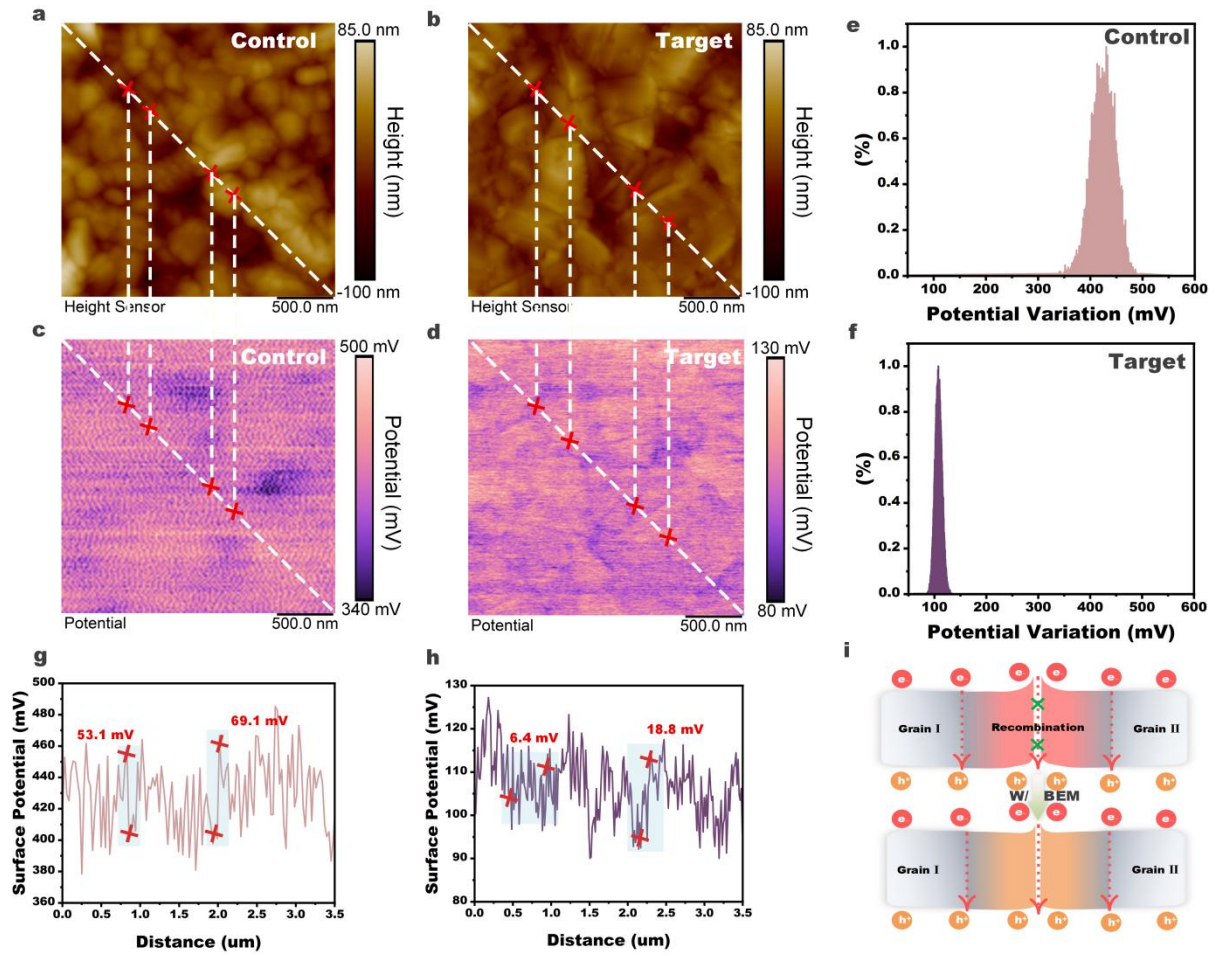


Figure S11. Surface morphology and potential distribution of perovskite films. (a, b) AFM images of control (RMS= 23.6 nm) and target (RMS= 14.3 nm) perovskite films. (c-f) KPFM images and the surface potential variation of perovskite films (g, h) The corresponding surface potential variation between grains and grain boundaries along the diagonal line for control and BEM-modified perovskite films. (i) Schematic diagram of the intergranular carrier transfer process.

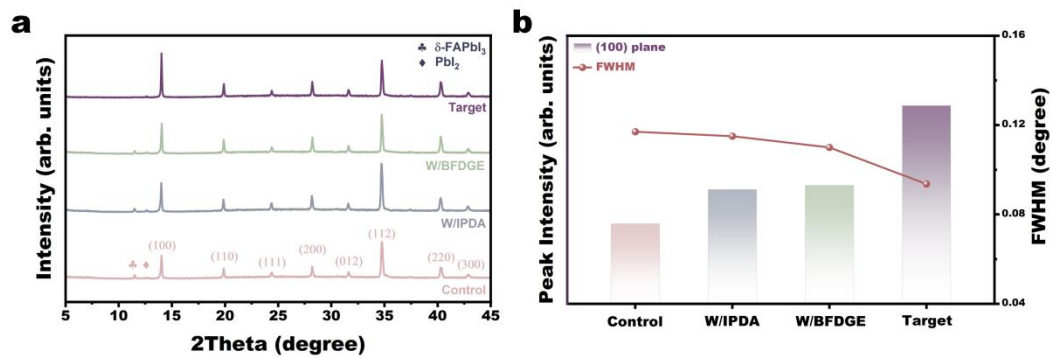


Figure S12. XRD patterns of control, target perovskite films and the corresponding FWHM of (100) facet.

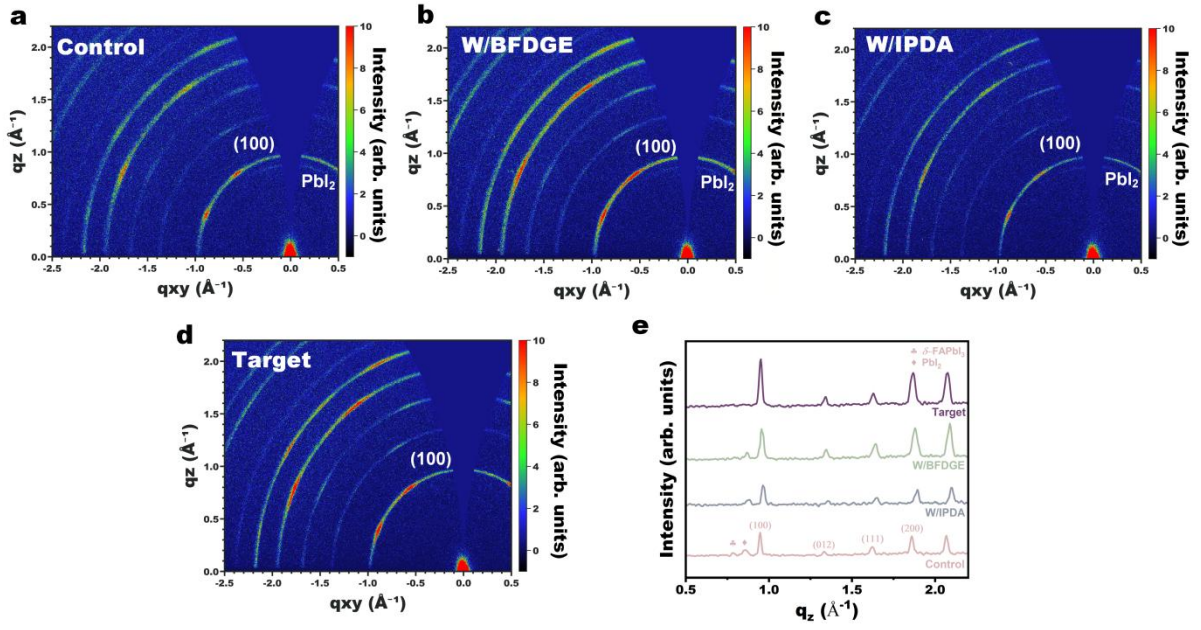


Figure S13. 2D-GIWAXS patterns of (a) Control, (b) pure BFDGE treated-, (c) pure IPDA treated-, and (d) Target perovskite films. (e) The corresponding line cuts of GIWAXS patterns.

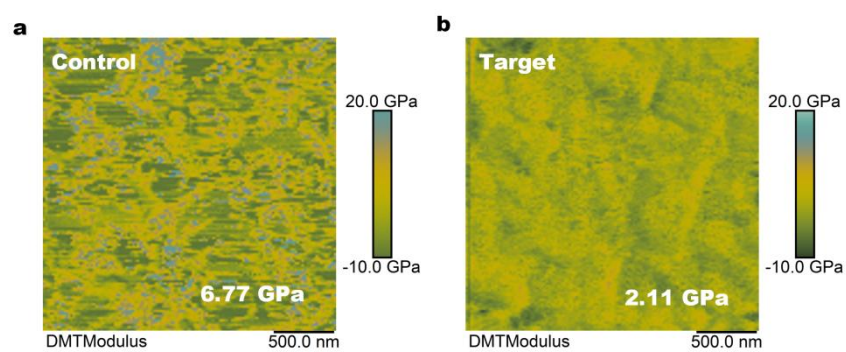


Figure S14. Young's modules of perovskite films.

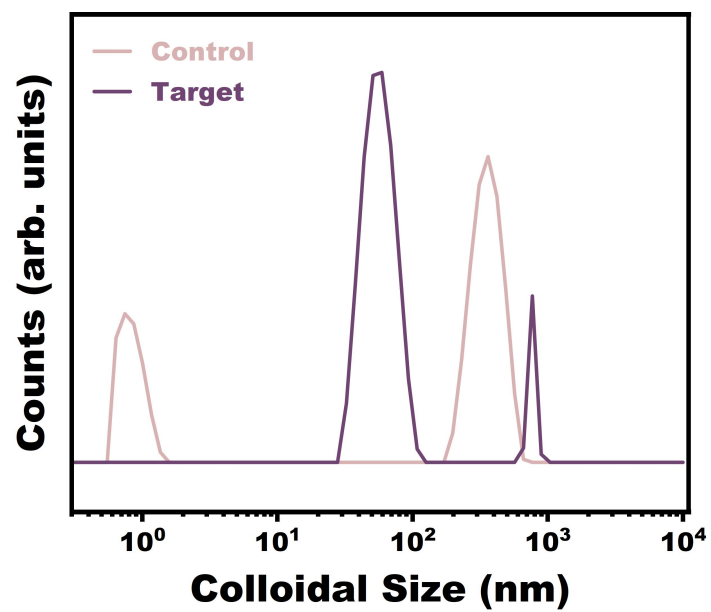


Figure S15. Dynamic Light Scattering (DLS) spectra of the control and target perovskite precursor.

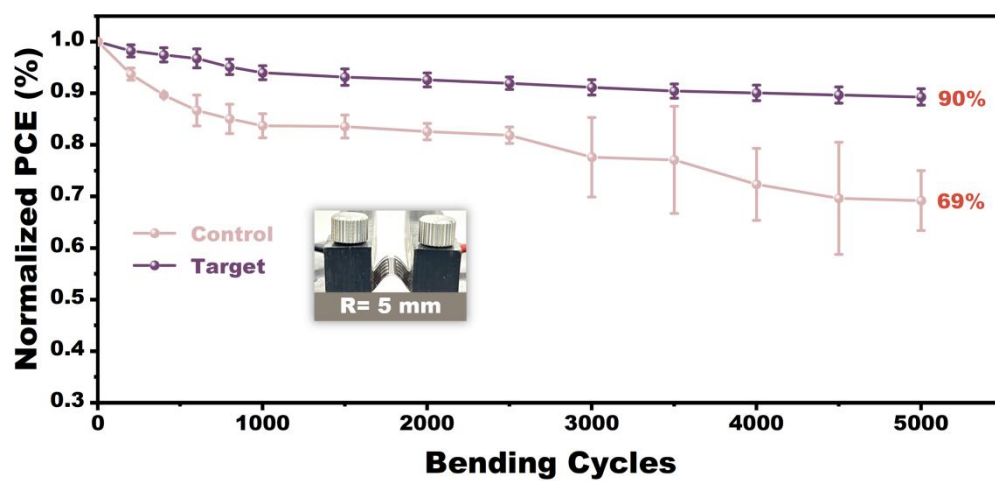


Figure S16. Mechanical stability of the f-PSCs versus bending cycles at a radius of 5 mm.

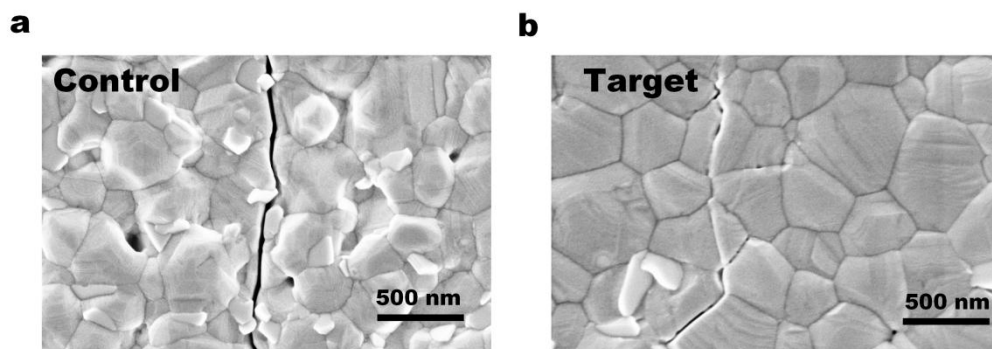


Figure S17. Top-view SEM images of the control and target perovskite films after 5000 bending cycles.

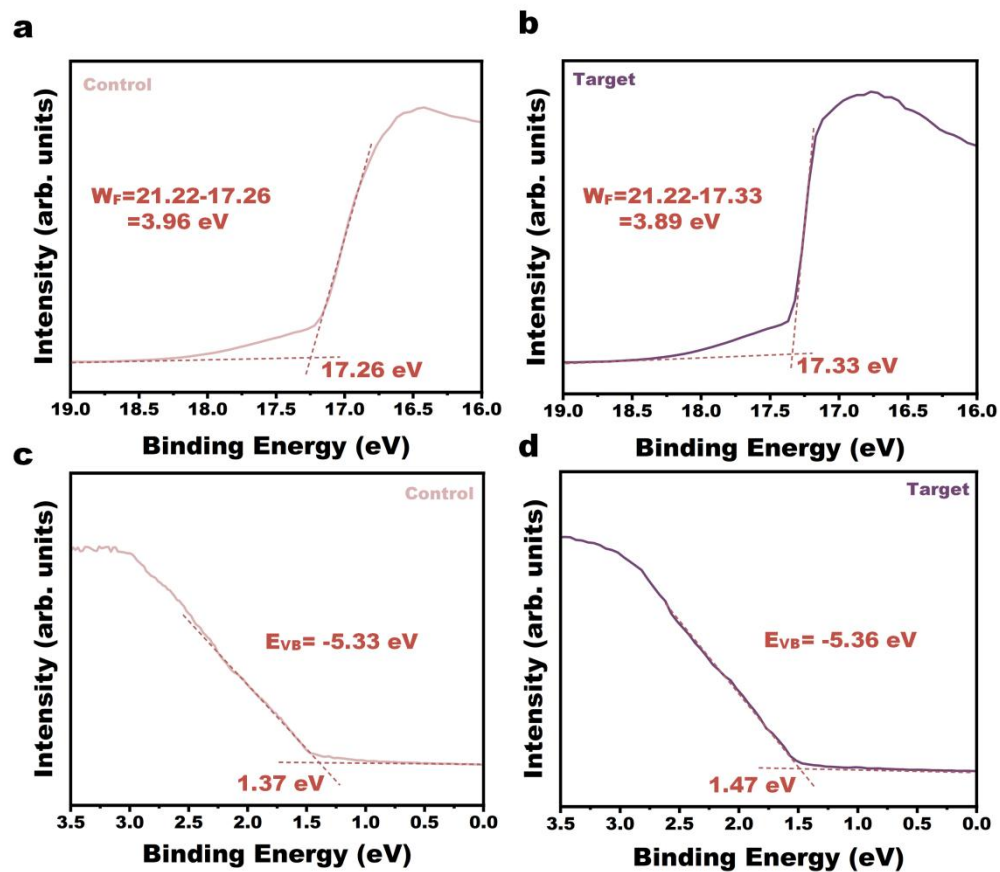


Figure S18. UPS spectra of perovskite films. (a, b) in the secondary-cutoff region. (c, d) in the valence band region.

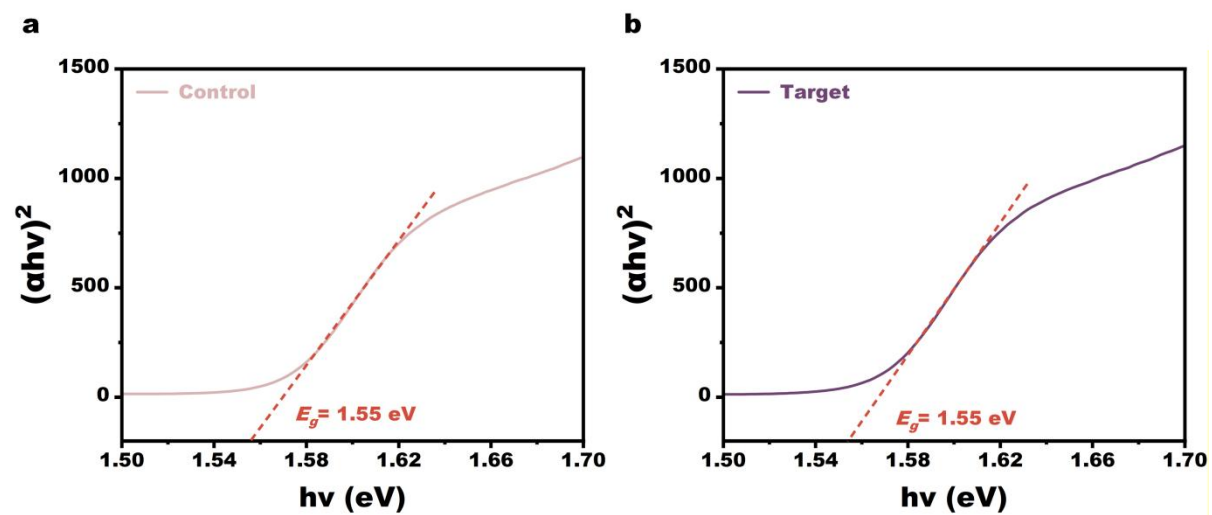


Figure S19. The UV-vis absorbance spectrum of the perovskite films.

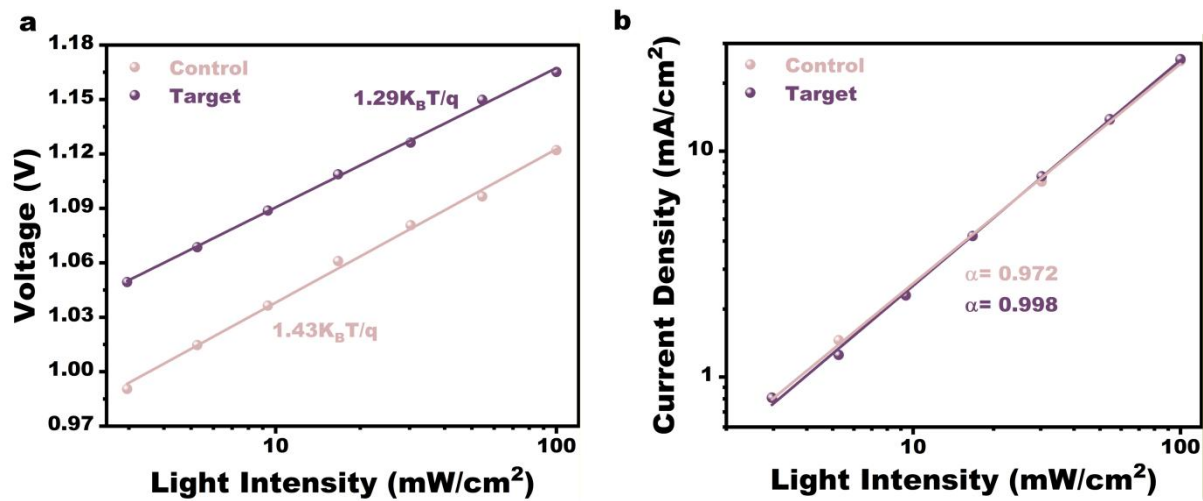


Figure S20. The light intensity dependence of the devices. (a) V_{oc} versus light intensity of the devices. (b) J_{sc} versus light intensity of the devices.

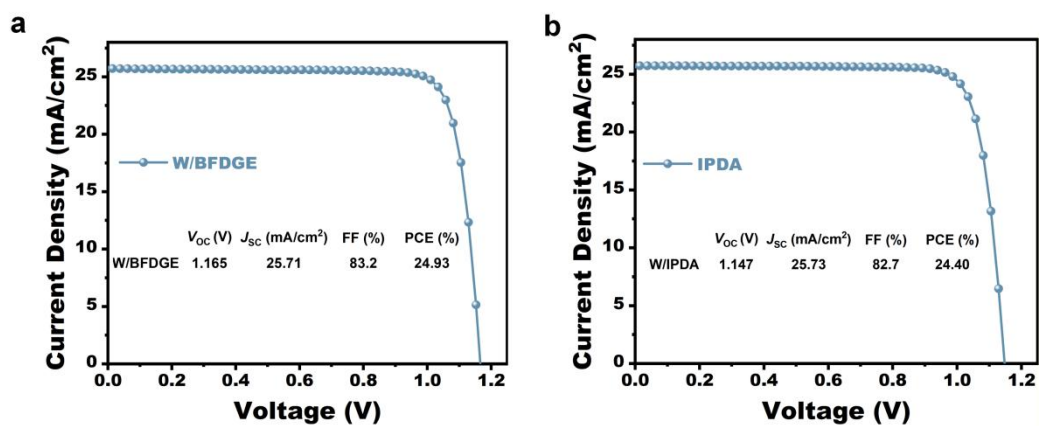


Figure S21. J - V curves of devices modified solely with BFDGE and solely with IPDA.



Report No. 25TR112502

Sample Information	
Sample Type	p-i-n perovskite solar cell
Serial No.	6-8
Lab Internal No.	25112501-2#
Measurement Item	I-V characteristic
Measurement Environment	(23.5±2.0) °C, (35.5±5.0) %RH

Measurement of I-V characteristic

Reference cell	PVM1121, mono-Si, WPVS, calibrated by NIM (Certificate No. GXG2025-01762)
Calibration Value/Date of Calibration for Reference cell	143.3 mA/ May, 2025
Measurement Conditions	Standard Test Condition (STC): AM1.5, 1000W/m ² , 25°C
Measurement Equipment/ Date of Calibration	AAA Steady State Solar Simulator (YSS-T155-2M) / Oct.2025 IV test system (ADCMT 6246) / June, 2025 Measuring Microscope (MF-82017C) / July.2025 SR Measurement System (CEP-25ML-CAS) / May.2025
Measurement Method	A bidirectional logarithmic voltage sweep, from open circuit voltage (Voc) to short circuit current (Isc) and back, was performed within a single flash in accordance with IEC 60904-1:2020. Spectral Mismatch factor was calculated and the I-V correction was performed according to IEC 60891:2021.
Measurement Uncertainty	Area: 1.0%(k=2); Isc: 2.0%(k=2); Voc: 1.0%(k=2); Pmax: 2.4%(k=2); FF: 2.5%(k=2)

2 / 4



Report No. 25TR112502

===Measurement Results ===

	Forward Scan (Isc to Voc)	Reverse Scan (Voc to Isc)
Area	5.43 mm ²	
Isc	1.439 mA	1.439 mA
Voc	1.177 V	1.175 V
Pmax	1.423 mW	1.459 mW
Ipm	1.375 mA	1.388 mA
Vpm	1.035 V	1.051 V
FF	84.00 %	86.28 %
EFF	26.21 %	26.87 %

- Spectral Mismatch Factor SMM=1.0040.
- Designated illumination area defined by a thin mask was measured by measuring microscope.
- Test results listed in this measurement report refer exclusively to the mentioned measured sample.
- The results apply only at the time of the test, and do not imply future performance.

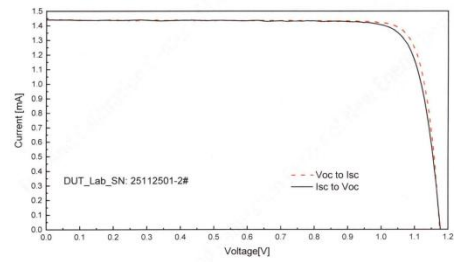


Fig.1 I-V curves of the measured sample

3 / 4

Figure S22. Certification report of the small-area target device.

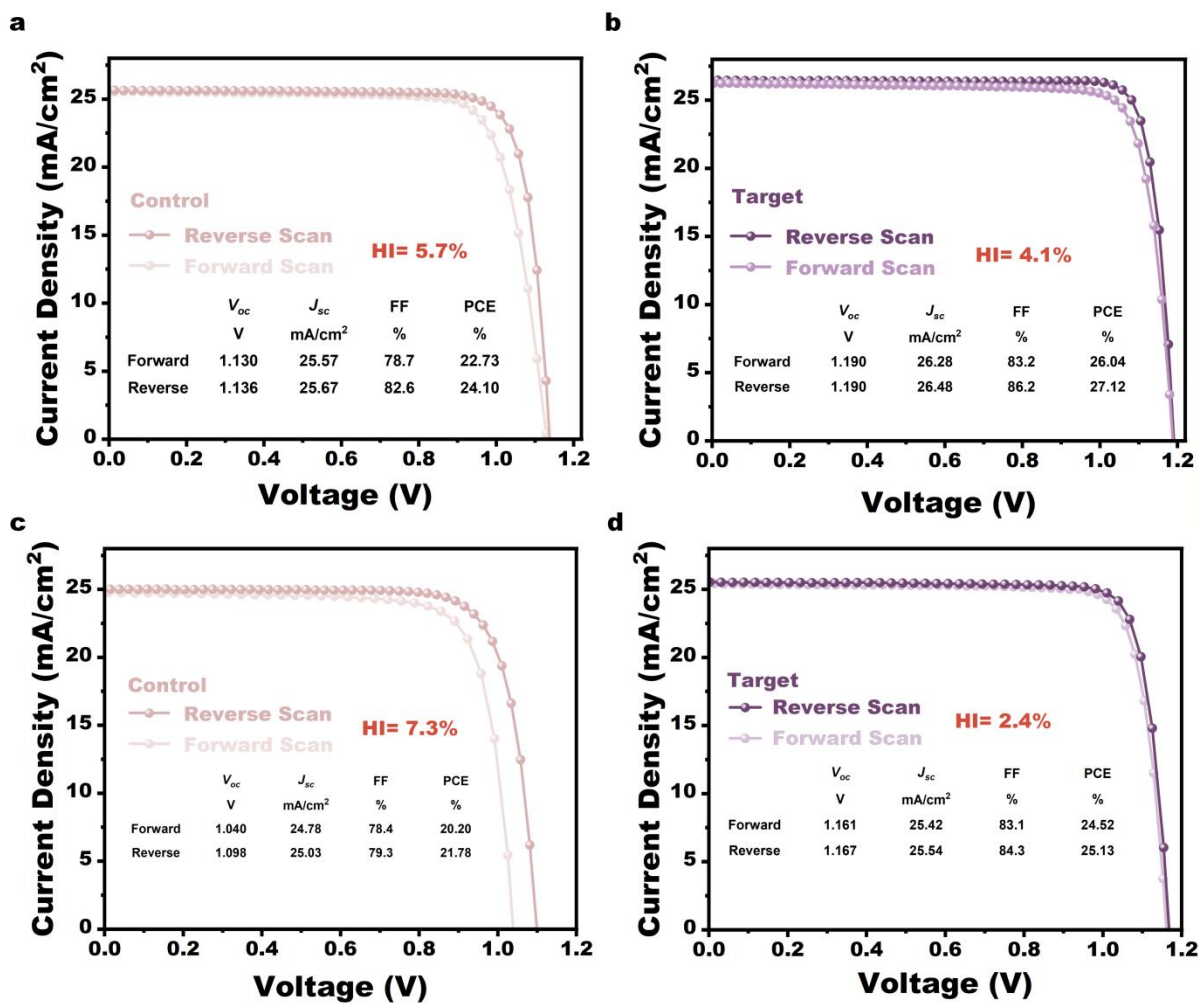


Figure S23. J - V curves with forward and reverse scan for devices. (a, b) Rigid PSCs. (c, d) Flexible PSCs.

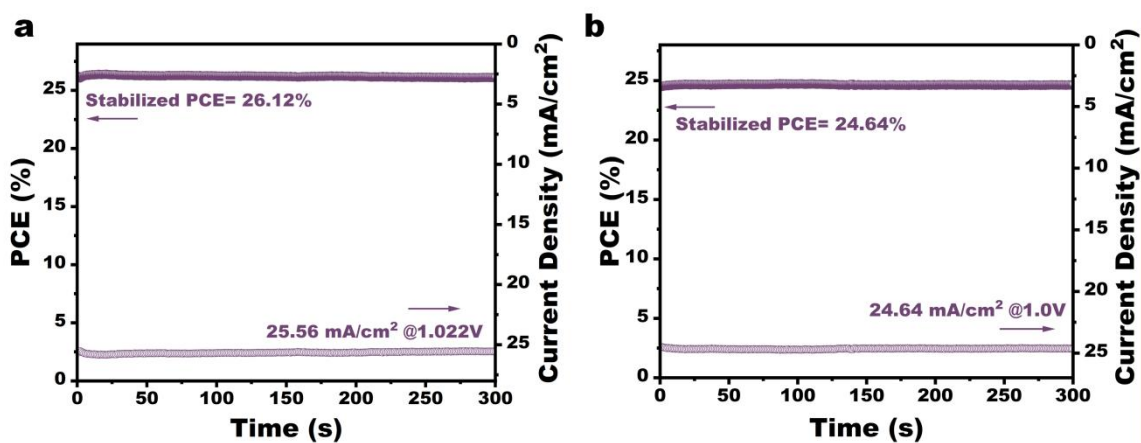


Figure S24. The stable power output and steady-state current density of the best-performance target devices, (a) rigid device, (b) flexible device.

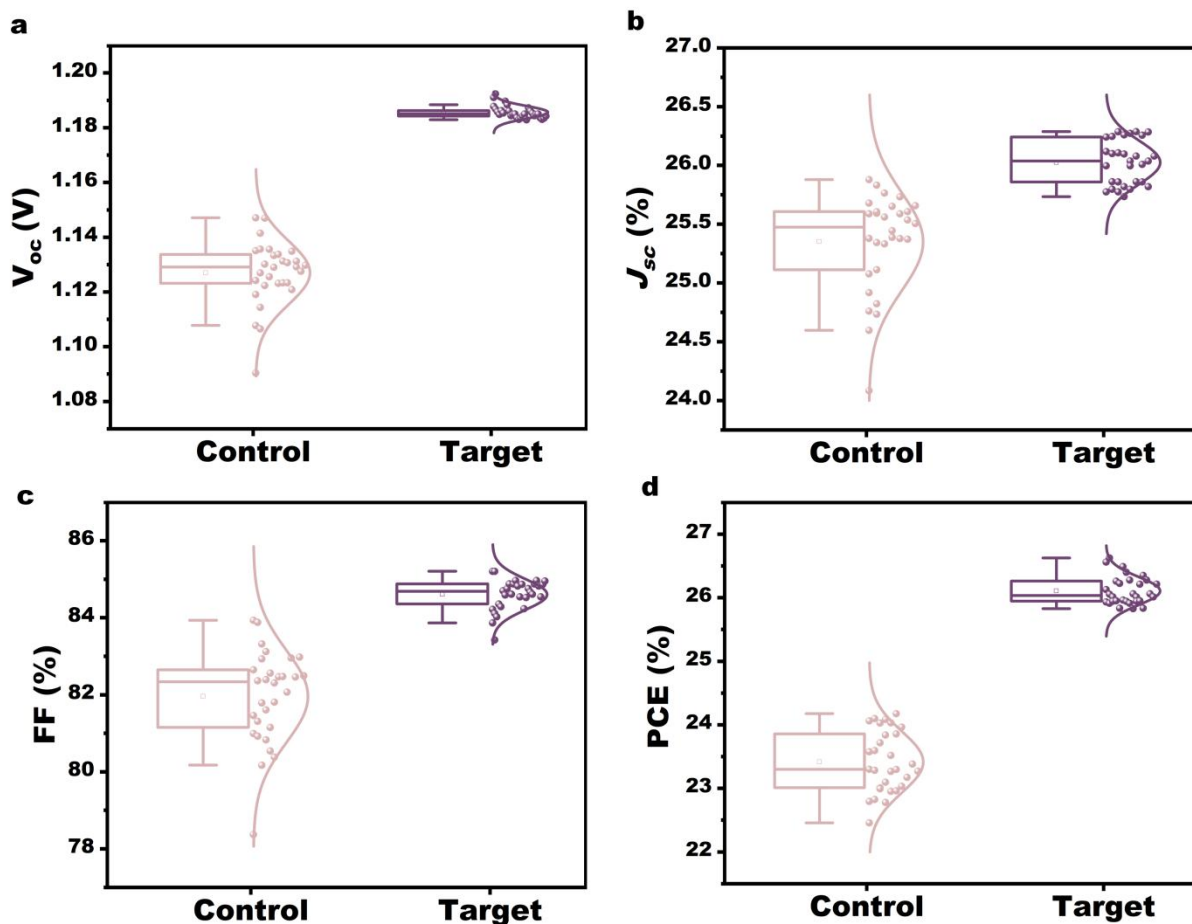


Figure S25. Statistical distribution of photovoltaic parameters from 30 individual rigid devices. (a) V_{oc} normal distribution. (b) J_{sc} normal distribution. (c) FF normal distribution. (d) PCE normal distribution. Each dataset represents 30 independent devices. The box-and-whisker plot shows the distribution of data. The minimum value is indicated by the lower whisker, whereas the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box and the third quartile at the upper edge. The central line of the box plot represents the media, and the open square represents the mean value. Outliers are represented as individual points beyond the whiskers.

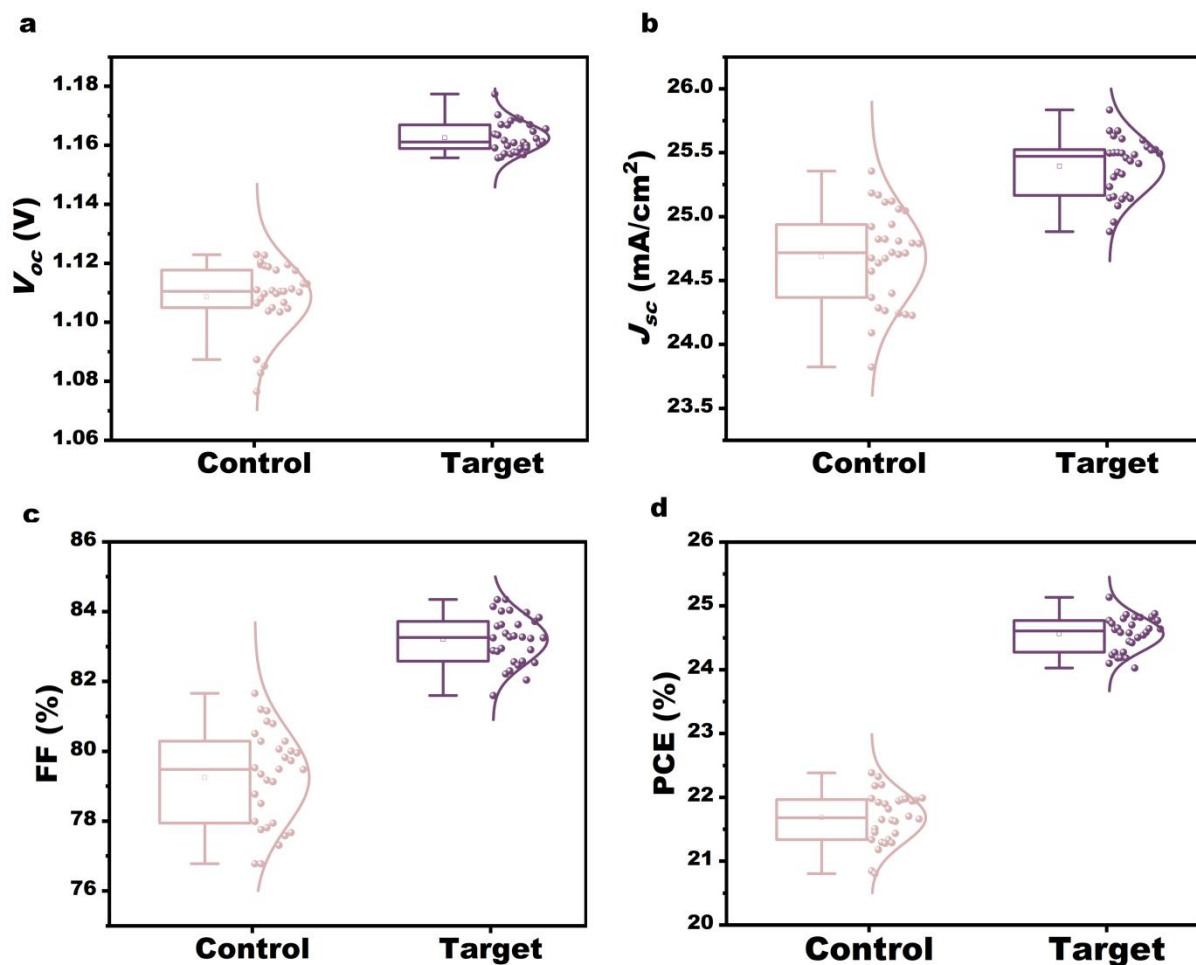


Figure S26. Statistical distribution of photovoltaic parameters from 30 individual flexible devices. (a) V_{oc} normal distribution. (b) J_{sc} normal distribution. (c) FF normal distribution. (d) PCE normal distribution. Each dataset represents 30 independent devices. The box-and-whisker plot shows the distribution of data. The minimum value is indicated by the lower whisker, whereas the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box and the third quartile at the upper edge. The central line of the box plot represents the media, and the open square represents the mean value. Outliers are represented as individual points beyond the whiskers.

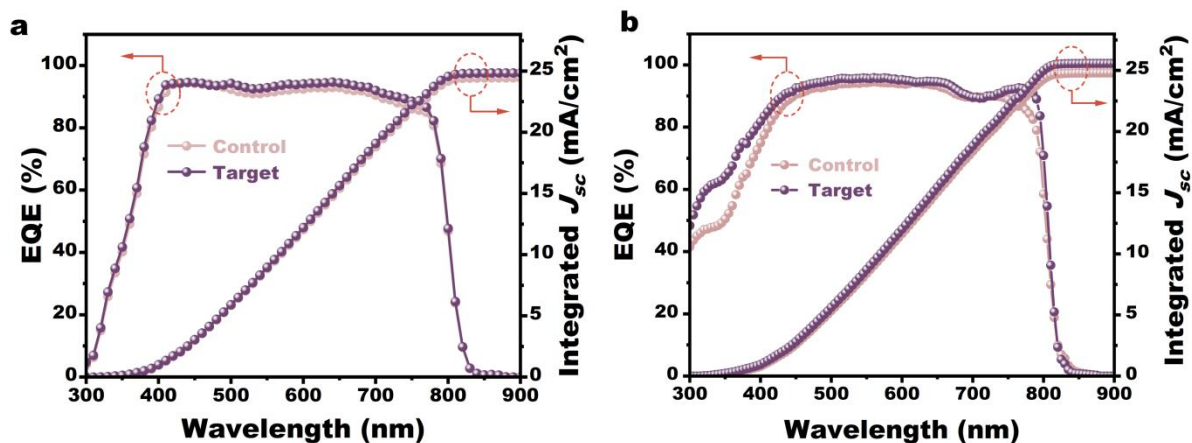


Figure S27. EQE spectra and the corresponding integrated current density of flexible (a) and rigid PSCs (b).

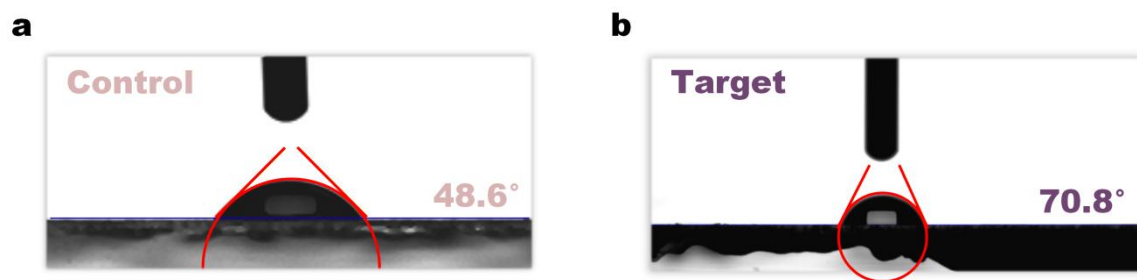


Figure S28. Water contact angles of the corresponding perovskite films.

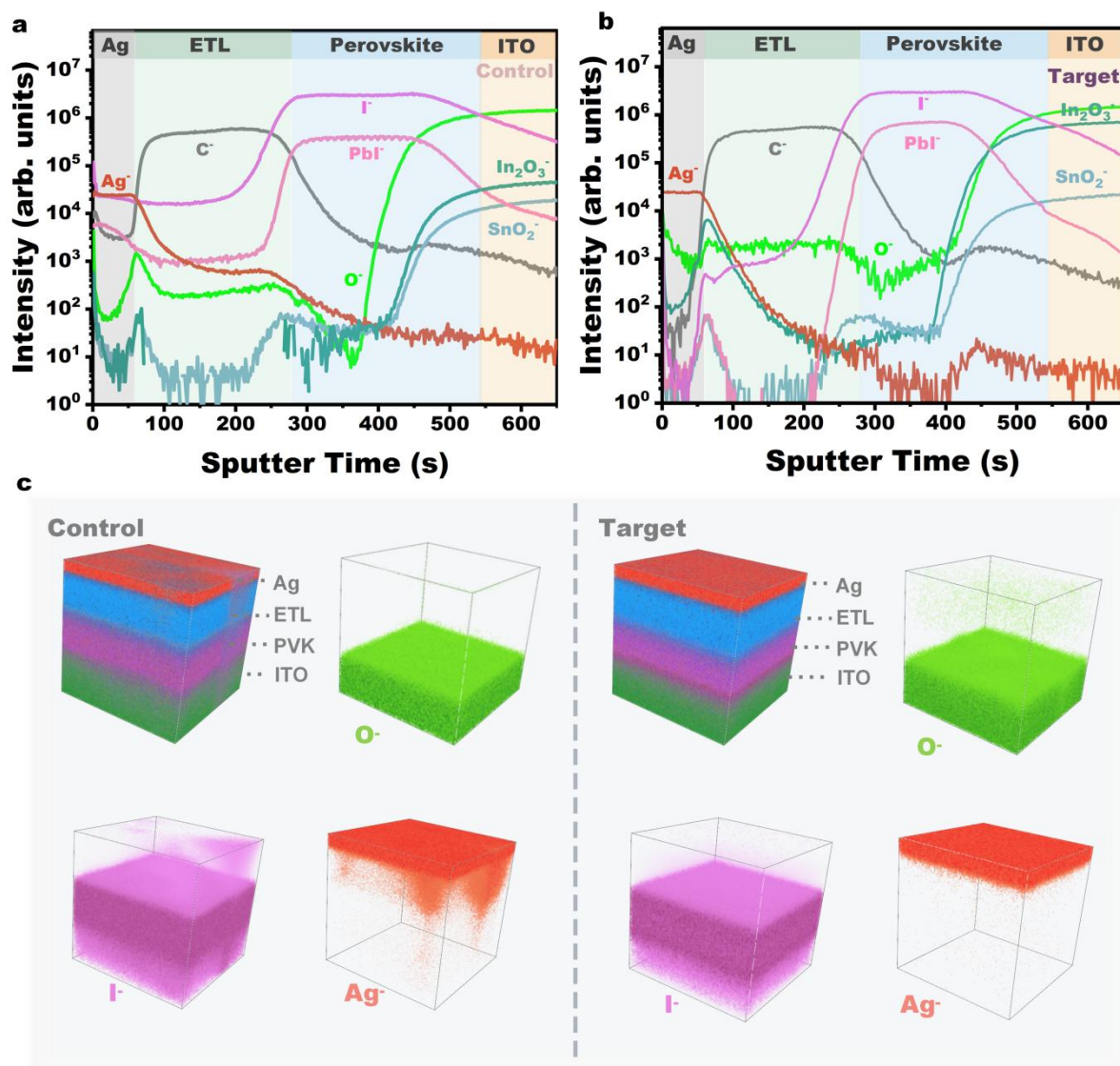


Figure S29. Time-of-light secondary-ion mass spectrometry (ToF-SIMS) depth profiles after 100 hours MPP tracking. (a) Control device. (b) Target device. (c) Corresponding ToF-SIMS 3D tomography results for control and target devices.

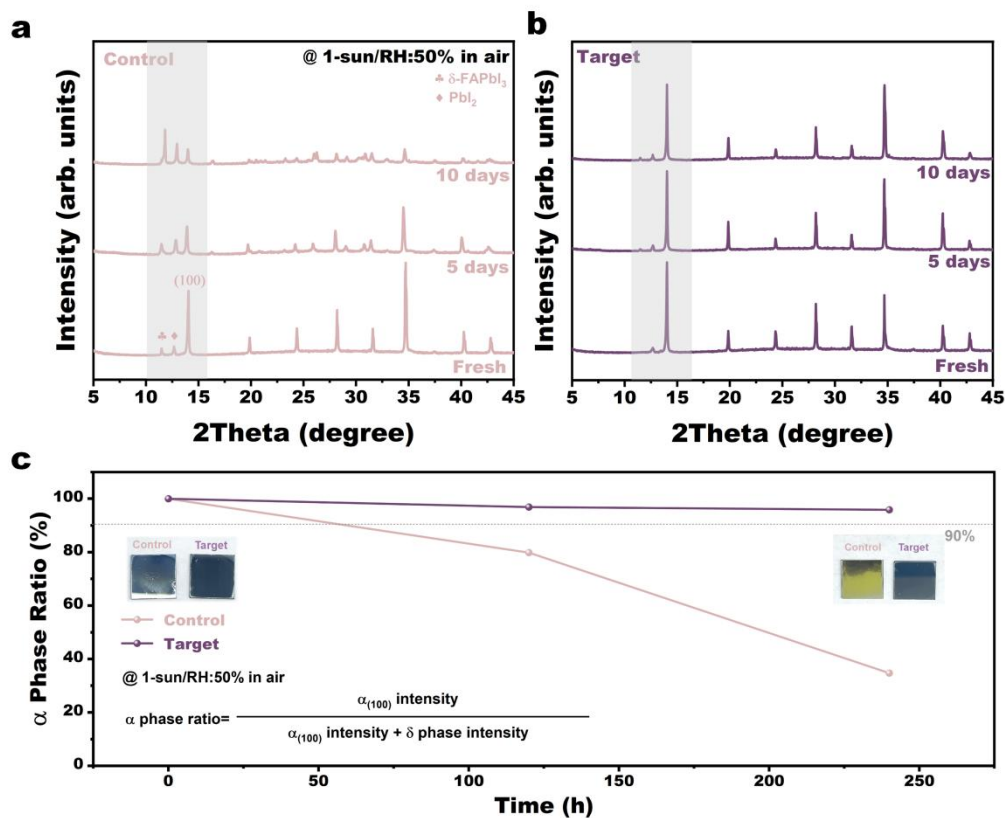


Figure S30. XRD patterns of the perovskite films during the accelerated aging process (air, 1-sun, 50% RH). (a) Control sample. (b) Target sample. (c) The corresponding α -phase (100) intensity ratio estimated by the equation $[\alpha_{(100)}]/[\alpha_{(100)} + \delta\text{-phase}]$, inset: photographs of the control and target perovskite films aged for different times, left (fresh), right(10 days).

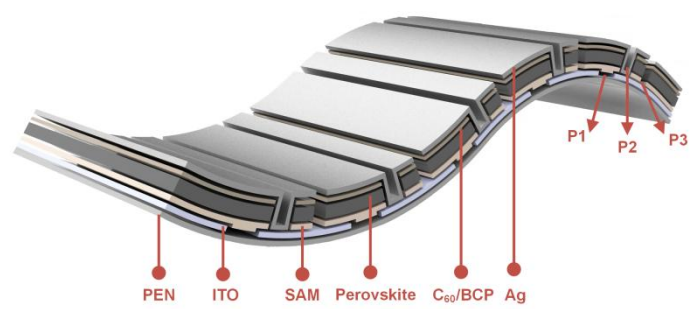


Figure S31. Schematic diagram of the minimodule's structure.

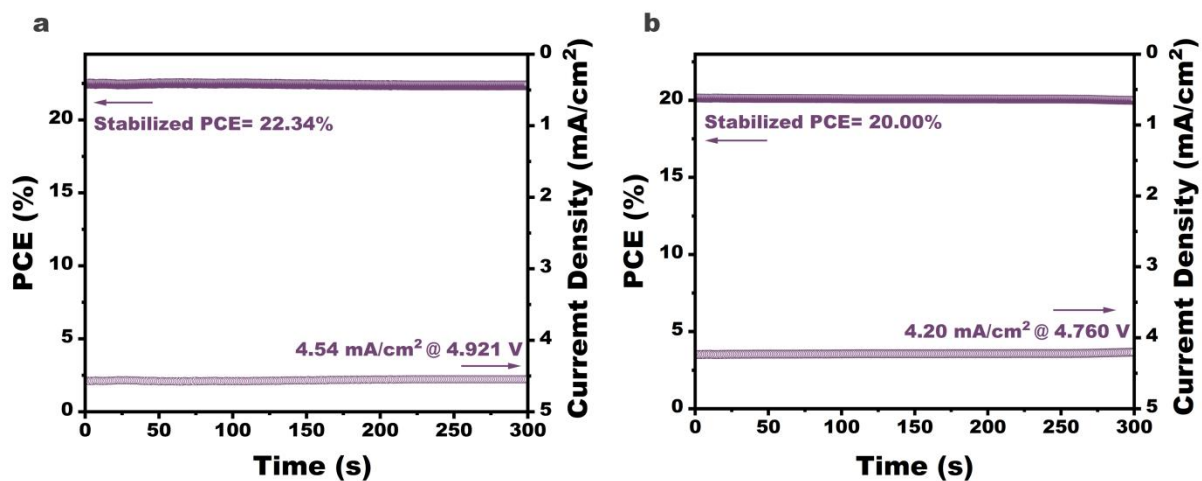


Figure S32. The stable power output and steady-state current density of the best-performance rigid and flexible PSMs.

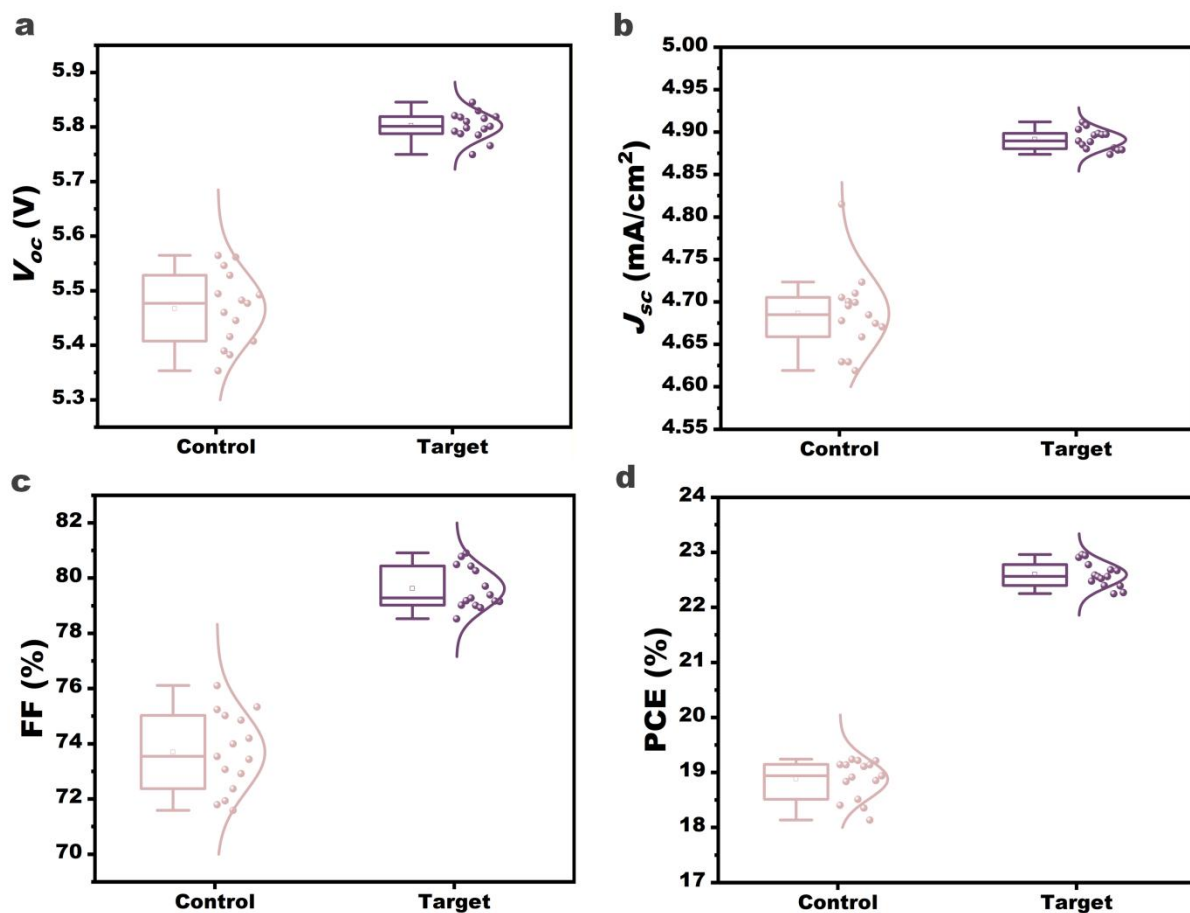


Figure S33. Statistical comparison of control and target-based perovskite mini-module with aperture area 10.24 cm^2 (the statistical results are obtained from 15 rigid mini-modules for each condition). (a) V_{OC} normal distribution. (b) J_{SC} normal distribution. (c) FF normal distribution. (d) PCE normal distribution. The box-and-whisker plot shows the distribution of data. The minimum value is indicated by the lower whisker, whereas the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box and the third quartile at the upper edge. The central line of the box plot represents the media, and the open square represents the mean value. Outliers are represented as individual points beyond the whiskers.

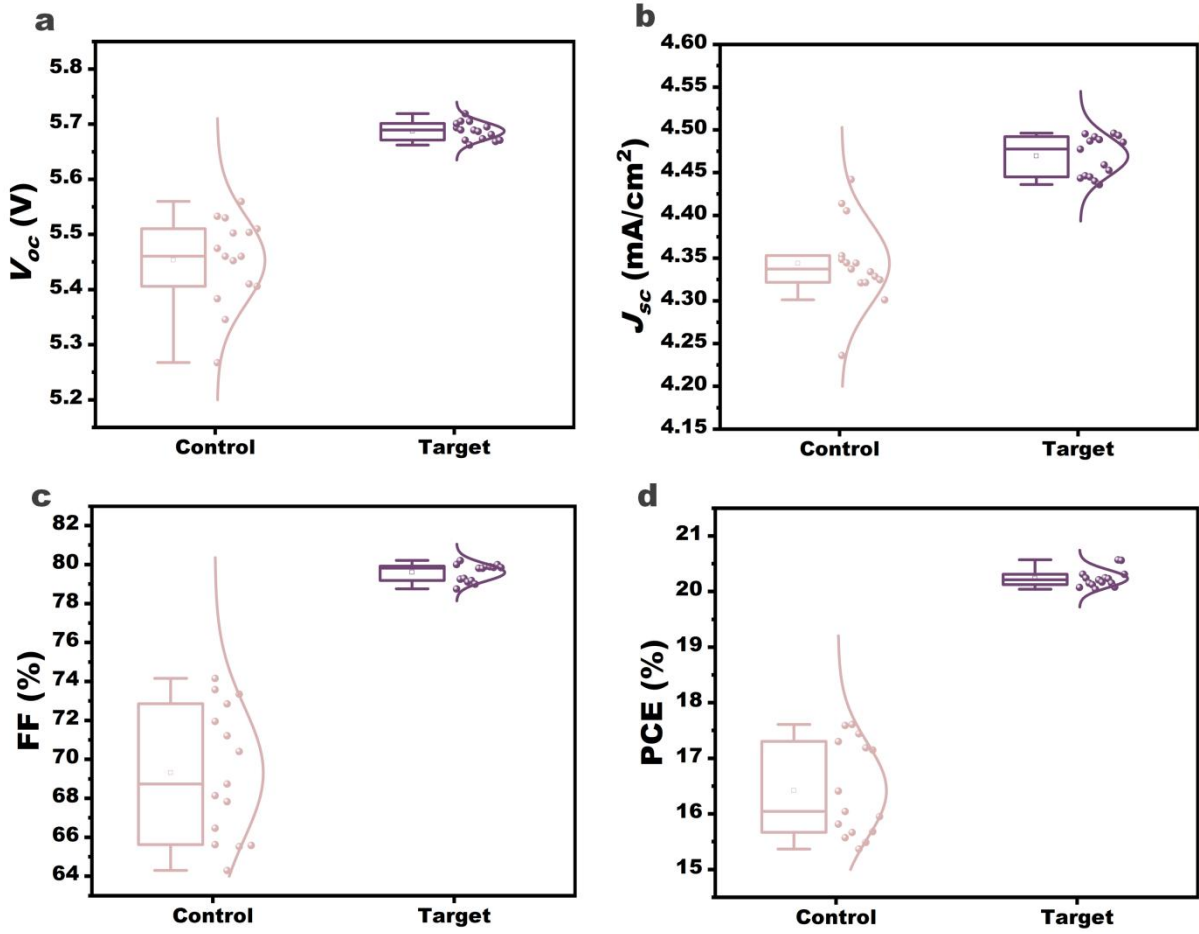


Figure S34. Statistical comparison of control and target-based perovskite mini-module with aperture area 10.24 cm² (the statistical results are obtained from 15 flexible mini-modules for each condition) (a) V_{oc} normal distribution. (b) J_{sc} normal distribution. (c) FF normal distribution. (d) PCE normal distribution. The box-and-whisker plot shows the distribution of data. The minimum value is indicated by the lower whisker, whereas the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box and the third quartile at the upper edge. The central line of the box plot represents the media, and the open square represents the mean value. Outliers are represented as individual points beyond the whiskers.

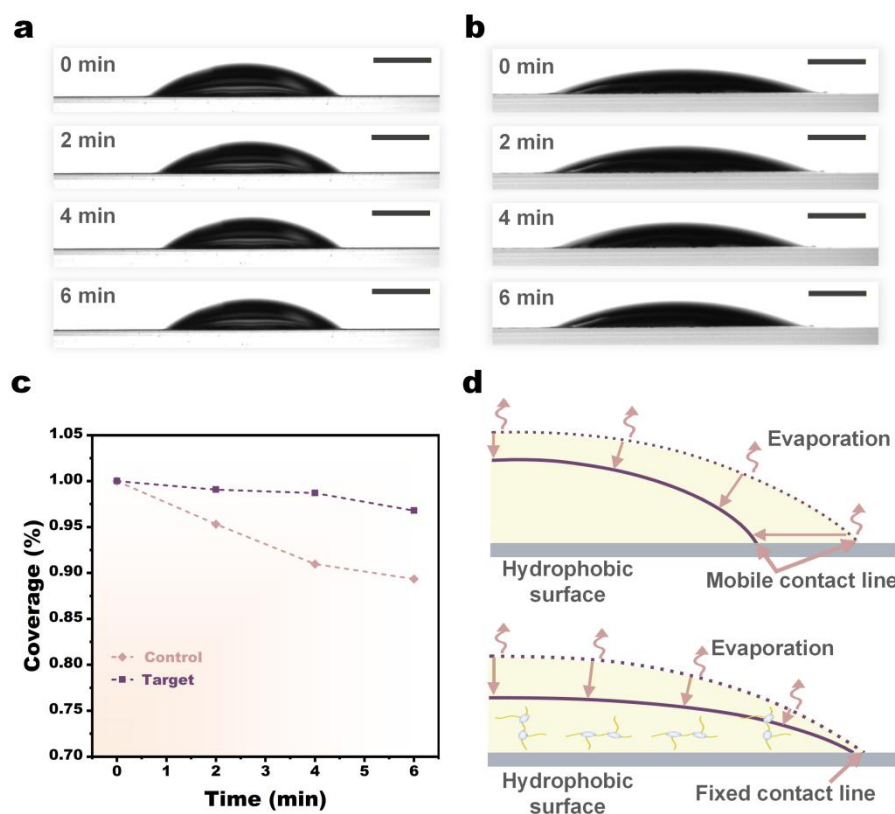


Figure S35. Comparison of droplet drying dynamics and surface coverage on hydrophobic SAM-based substrates. (a, b) Time-lapse optical images capturing the drying process of perovskite ink droplets on hydrophobic 4PADCB-covered substrates under ambient conditions: (a) control, (b) target. (c) Evolution of the normalized surface coverage of perovskite droplets as a function of drying time. (d) Schematic illustration for the shrinkage of the ink droplet drying on a hydrophobic substrate.

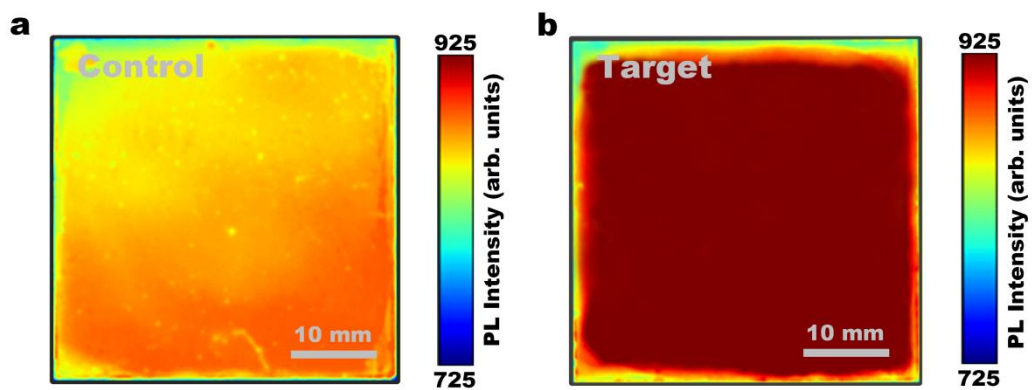


Figure S36. PL mapping images of perovskite films spin-coated on $50 \times 50 \text{ mm}^2$ substrate.

(a) Control sample, (b) Target sample.

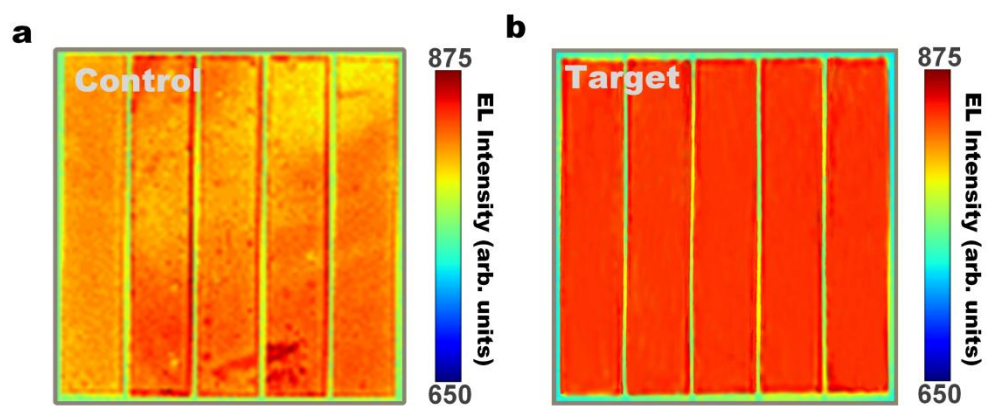


Figure S37. EL imaging of the (a) control and (b) target minimodules.

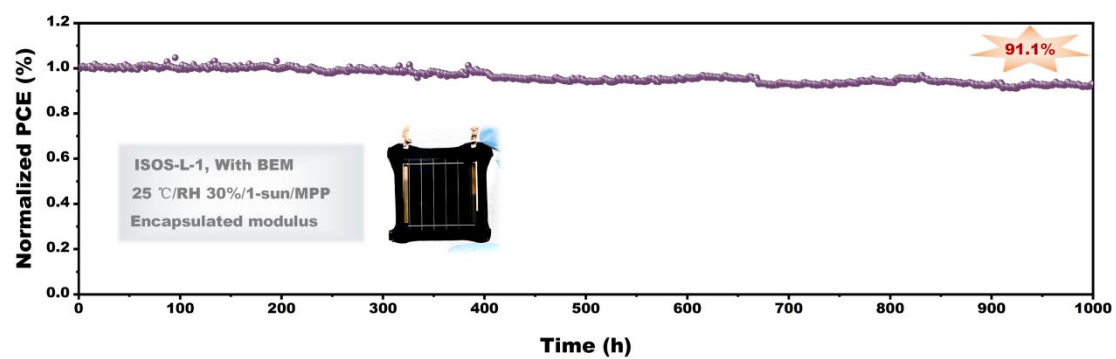


Figure S38. Stability of target module during MPP tracking measurement with 100 mW/cm² LED continuous illumination, inset: the encapsulated module.

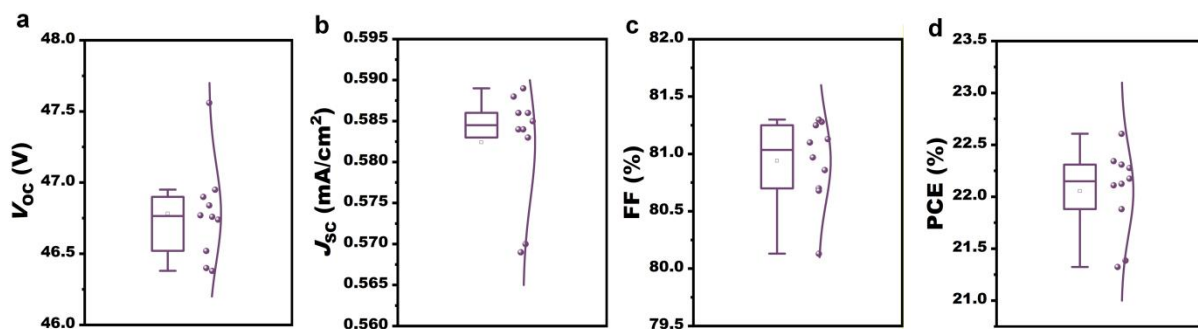


Figure S39. Statistical distribution of photovoltaic parameters for ten independent $30 \times 30 \text{ cm}^2$ target submodules. The box-and-whisker plot shows the distribution of data. The minimum value is indicated by the lower whisker, whereas the maximum value is shown by the upper whisker. The box represents the interquartile range, with the first quartile at the lower edge, the median as the line inside the box and the third quartile at the upper edge. The central line of the box plot represents the media, and the open square represents the mean value. Outliers are represented as individual points beyond the whiskers.

Table S1. Contact angles and surface tension of control and perovskite precursor with BFDGE, IPDA, and BFDGE + IPDA.

	Control	W/BFDGE	W/IPDA	Target
θ (°)	29.5	26.0	23.0	16.2
γ (mN/m)	35.0	33.3	31.9	28.5

Table S2. Fitting carrier lifetimes of perovskite films determined by TRPL.

Sample	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{ave} (ns)
Control	0.41	165.36	0.72	1283.77	1207.50
Target	0.13	201.92	0.89	1929.79	1904.55

Table S3. R_1 and R_2 values from electrochemical impedance spectroscopy (EIS) data of devices.

Sample	$R_1(\Omega)$	$R_2(\Omega)$
Control	43.5	1173
Target	26.3	3377

Table S4. Results derived from electronic-only SCLC

Sample	V_{TFL} (V)	N_t (cm ⁻³)
Control	0.72	1.07×10^{16}
Target	0.42	6.24×10^{15}

Table S5. The dependence of V_{OC} and J_{SC} of the f-PSCs on light intensity

Sample	$n k_B T/q$	α
Control	$1.43 k_B T/q$	0.972
Target	$1.29 k_B T/q$	0.998

Table S6. Statistics of photovoltaic parameters for 30 individual rigid PSCs.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	1.127±0.012	25.35±0.42	81.9±1.19	23.41±0.48
Target	1.186±0.002	26.02±0.19	84.6±0.39	26.10±0.22

Table S7. Statistics of photovoltaic parameters for 30 individual flexible PSCs.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	1.109±0.012	24.69±0.37	79.2±1.37	21.68±0.40
Target	1.163±0.005	25.39±0.23	83.2±0.71	24.56±0.27

Table S8. Photovoltaic parameters of the rigid mini-modules in Figure 6a.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	5.46	4.63	76.1	19.24
Target	5.99	4.92	78.9	23.25

Table S9. Photovoltaic parameters of the flexible mini-modules in Figure 6b.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	5.48	4.34	74.1	17.61
Target	5.72	4.50	80.0	20.59

Table S10. Statistics of photovoltaic parameters for 15 individual rigid PSMs.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	5.46±0.07	4.68±0.05	73.6±1.42	18.87±0.36
Target	5.80±0.02	4.89±0.01	79.6±0.76	22.60±0.23

Table S11. Statistics of photovoltaic parameters for 15 individual flexible PSMs.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Control	5.45±0.08	4.34±0.05	69.3±3.39	16.41±0.86
Target	5.69±0.02	4.47±0.02	79.6±0.45	20.23±0.16

Table S12. Photovoltaic parameters for the champion $30 \times 30 \text{ cm}^2$ submodules.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Target	47.56	0.589	80.7	22.60

Table S13. Summary of photovoltaic parameters of reported high-performance inverted PSMs up to now (active area over 100 cm²)

Device Architecture	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)	Area (cm ²)	Subcell (unit)	Ref.
Glass/FTO/NiO _x /SAM/Al ₂ O ₃ /Perovskite/C60/BCP/Cu	16.13	1.593	78.4	20.14	113	14	¹
Glass/FTO/NiO _x /Perovskite/PCBM/BCP/Ag	20.74	1.143	78.4	18.6	174	20	²
Glass/FTO/NiO _x (Urea)/Perovskite/BzMIMBr/C60/BCP/Cu	19.84	1.16	74.7	17.18	178.4	19	³
Glass/ITO//NiO _x /SAM/Perovskite/NH ₄ F/PC ₆₁ BM/BCP/Ag	21.9	1.02	76.0	18.1	228	20	⁴
Glass/FTO/SAM/Perovskite/Y7-BO/PCBM/BCP/Ag	47.12	6.17	76.8	22.32	400	-	⁵
Glass/FTO/NiO _x /SAM/Perovskite/LiF/C ₆₀ /BCP/Ag	-	-	-	19.25	641.4	-	⁶
Glass/ITO/NiO _x /SAM/Al ₂ O ₃ /Perovskite/PCBM/BCP/Ag	38.25	0.623	77.8	18.54	642	38	⁷
Glass/FTA/NiO _x /Perovskite/PCBM/HDFA/PCBM/SnO ₂ /ITO/Cu/ITO	38.84	0.626	74.8	18.20	642	-	⁸
Glass/ITO/NiO _x /SAM/Perovskite/LiF/C ₆₀ /SnO ₂ /Cu	45.02	0.56	79.5	20.06	651.42	-	⁹
Glass/ITO/NiO _x /PTAA/AlO _x /Perovskite/PCBM/BCP/Ag	37.06	0.679	71.1	17.05	669	-	¹⁰
Glass/ITO/NiO _x /SAM/Perovskite/PCBM/C ₆₀ /SnO ₂ /Cr/Ag	50.1	0.547	77.0	21.1	730	46	¹¹
Glass/ITO/NiO_x/SAM/Perovskite/C₆₀/BCP/Ag	47.56	0.589	80.7	22.60	655.2	42	This work

Table S14. Statistics of photovoltaic parameters for 10 individual $30 \times 30 \text{ cm}^2$ submodules.

Sample	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
Target	46.78 ± 0.34	0.582 ± 0.007	80.94 ± 0.36	20.05 ± 0.41

Supplementary Reference

1. Liu, W. *et al.* Buried Interface Engineering for Scalable Processing of High-Performance Inverted Perovskite Solar Modules. *Adv. Energy Mater.* **15**, 2404374 (2024).
2. Du, M. *et al.* Surface redox engineering of vacuum-deposited NiOx for top-performance perovskite solar cells and modules. *Joule* **6**, 1931-1943 (2022).
3. Li, C. *et al.* Efficient Inverted Perovskite Solar Cells with a Fill Factor Over 86% via Surface Modification of the Nickel Oxide Hole Contact. *Adv. Funct. Mater.* **33**, 2214774 (2023).
4. Zhao, X. *et al.* Operationally stable perovskite solar modules enabled by vapor-phase fluoride treatment. *Science* **385**, 433–438 (2024).
5. Liu, Q. *et al.* Enhancing the Efficiency and Stability of Inverted Perovskite Solar Cells and Modules through Top Interface Modification with N-type Semiconductors. *Angew. Chem. Int. Ed.* **137**, e202416390 (2025).
6. Guo, H. *et al.* Intermolecular interactions triggered crystallization phase transition regulation for efficient and stable perovskite photovoltaics. *Energy Environ. Sci.* **18**, 7114-7123 (2025).
7. Wang, K. *et al.* Amidino-based ligand enables oriented crystallization and boosted carrier extraction for inverted perovskite solar cells and modules. *Joule* **9**, 102044 (2025).
8. Xu, Z. *et al.* Double amidino-mediated multiple hydrogen-bonded Dion–Jacobson perovskites enable oriented crystallization for efficient inverted FAPbI₃ solar cells and modules (642 cm²). *Energy Environ. Sci.* **18**, 8268-8279 (2025).
9. Yang, H. *et al.* Molecular Extrusion Drives Polymer Dynamic Soft Encapsulation to Inhibit Lead Leakage for Efficient Inverted Perovskite Solar Cells and Modules. *Adv. Mater.*, e11855 (2025) doi.org/10.1002/adma.202511855.
10. Gong, C. *et al.* Efficient and stable inverted perovskite solar cells enabled by homogenized PCBM with enhanced electron transport. *Nat. Commun.* **15**, 9154 (2024).
11. Sun, X. *et al.* Vapor-assisted surface reconstruction enables outdoor-stable perovskite solar modules. *Science*, **388**, 957-963 (2025).