Electronic Supplementary Information

Chemical Bridging in 2D/3D Heterojunction via Dual-Anchoring Functionalized Molecules for Efficient, Stable and Flexible Perovskite Solar Cells

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Contents

1. Experimental Section

Materials and Precursor Preparation: Lead iodide (PbI_2, 99.9%, Xi'an Polymer Light Technology Corp), formamidinium iodide (FAI, >99.99%, Great Cell), methylammonium chloride (MACl, >99.99%, Great Cell), cesium iodide (CsI, 99.0%, TCI), methylammonium lead tribromide ($MAPbBr_3$, 99%, Xi'an Yuri Solar Co., Ltd.), Spiro-OMeTAD (99.5%, Xi'an Yuri Solar Co., Ltd.), ethyl acetate (EA, 99.8%, Adamas), 2-pentanol (IPA, 98%, Adamas), acetonitrile (ACN, 99.9%, Sigma Aldrich), N,N-dimethylformamide (DMF, ≥99.8%, Sigma-Aldrich), dimethyl sulfoxide (DMSO, ≥99.9%, Sigma-Aldrich), chlorobenzene (CB, 99%, Sigma-Aldrich), 4-tert-butylpyridine (TBP, 98%, Sigma-Aldrich), 5-Methyltryptamine hydrochloride (Me-TACl, 99.5%, Macklin).

Preparation of perovskite, Spiro-OMeTAD and modification solutions: The perovskite studied in this work was $(Cs_{0.03}FA_{0.97}PbI_3)_{0.975}$ $(MAPbBr_3)_{0.025}$. FAI (233 mg), MACl (33 mg), CsI (11 mg), PbI_2 (705 mg), $MAPbBr_3$ (18 mg) were dissolved in a mixed solvent of DMF and DMSO (8:1 v/v) to achieve the triple-cation perovskite solution. For hole transport material (HTM) solution, 72.3 mg Spiro-OMeTAD was dissolved in 1 mL CB with additives of 17.6 µL LiTFSI solution (520 mg mL−1 in ACN) and 28.8 µL TBP. For the post treatment, 5 mg Me-TACl was dissolved in 1 mL IPA.

Preparation of SnO_2 layer: For rigid PSCs, the chemical bath deposition (CBD) is employed. In detail, the solution was prepared by mixing urea (2.55 g), HCl (2.5 mL), thioglycollic acid (TGA) (110µL), and $SnCl_2{\cdot}2H_2O$ (0.555 g) in DI water (400 mL). Urea was gradually dissolved under continuous stirring. Subsequently, HCl was introduced to stabilize the solution. Afterward, TGA and $SnCl_2{\cdot}2H_2O$ was added in sequence under vigorous stirring. The resulting solution was stirred for an additional 30 min. Fluorine-doped tin oxide (FTO) substrates were immersed into the precursor solution, ensuring full submersion without air bubble adhesion. The reaction vessel with the FTO substrates inside was then heated to 125 °C and stored for 2.5 h. Afterward, the substrates were sequentially rinsed with ultrapure water and isopropanol, prior to annealing at 170 °C for 60 min. For flexible PSCs, the SnO_2 solution was spin-coated onto PEN/ITO substrates at 3000 rpm for 30 s, followed by annealing at 100°C for 1 h.

Device Fabrication: The perovskite solution was spin-coated onto the FTO/SnO_2 substrates (both glass and PEN supports) at 1000 rpm for 10 s and then 3000 rpm for 30 s. For anti-solvent treatment, 150 µL EA was dripped onto perovskite films before the end of the second spin coating step. Afterward, the prepared perovskite films were annealed at 100°C for 40 min. After this step, the Me-TACl solution was spin coated onto the as-prepared perovskite film (5000rpm for 30 s) and then anneal at 85 ℃ for 1 min, followed by a spin coating of Spiro-OMeTAD solution (3000 rpm, 30 s). Finally, 18-nm-thick MoO_3 and 130-nm-thick Ag electrodes were thermally evaporated under vacuum in sequence to complete the PSC fabrication.

Characterizations and Measurements:

The *J-V* sweeps of the photovoltaic devices were obtained using a Keithley 2400 Source Meter under simulated AM 1.5 G illumination (100 mW cm^{-2}) with a solar simulator (EnliTech SS-F5-3A), and the light intensity was calibrated using a reference silicon solar cell, calibrating to 1 sun. The measurements were carried out in a N_2 glove box (<0.1 ppm O_2 and H_2O, temperature: 25℃). The devices were measured both in forward scan (1.2 V → -0.2 V, step 0.02

V, delay 20 ms) and reverse scan (-0.2 V → 1.2 V, step 0.02 V, delay 20 ms). The EQE spectra were measured using a QTEST HIFINITY 5 (Crowntech Inc., USA) at room temperature in air. The light intensity was calibrated using a standard single-crystal Si photovoltaic cell. SEM measurements were carried out on a Hitachi S-4800 electron microscope. UV-vis absorption spectra were measured with a UV/Vis spectrophotometer (U-3900H, Hitachi High-tech Co., Ltd). TRPL and PL measurements were carried out on FLS1000. XPS and UPS measurements were carried out with a Kratos Axis Supra photoelectron spectrometer equipped with a monochromatic source of Al (Ka) (1486.6 eV) X-rays. GIWAXS measurements were performed at beamline BL16B1 of SSRF. The X-ray energy was 10 keV (wavelength λ=1.24 Å). Synchrotron X-ray continuously exposes on substrate with a 0.4° incident angle with 5 s detector exposure time. The detector pixel size is 0.172 mm × 0.172 mm.

2. Supporting Figures

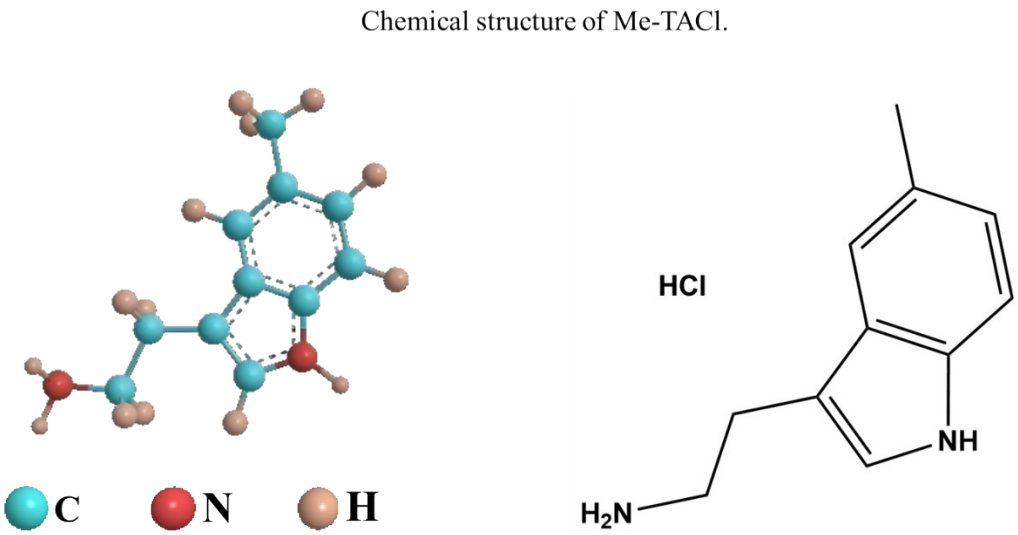

Figure S1. Chemical structure of Me-TACl.

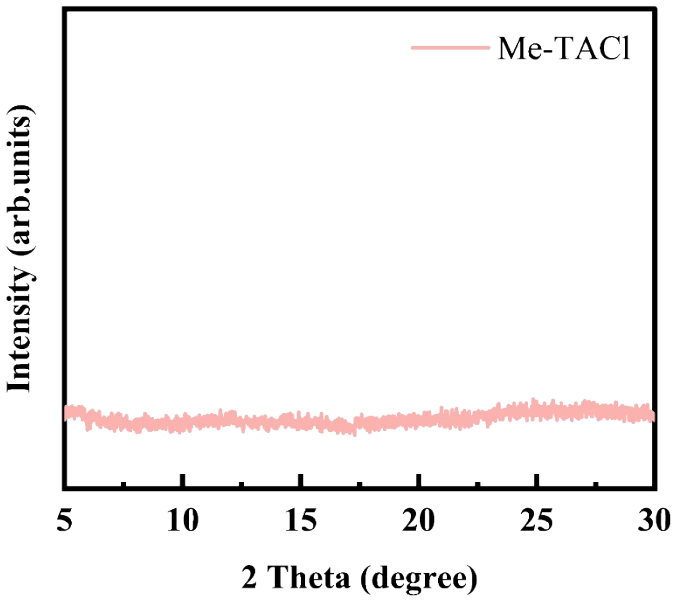

Figure S2. XRD pattern of the pure Me-TACl.

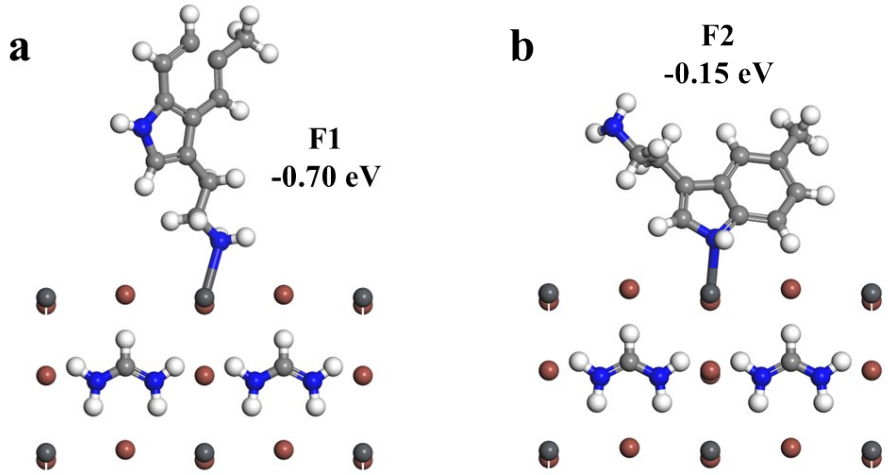

Figure S3. Binding energy between Me-TA^{+} and $[PbI_6]^{4-}$ for (a) F1 and (b) F2 type.

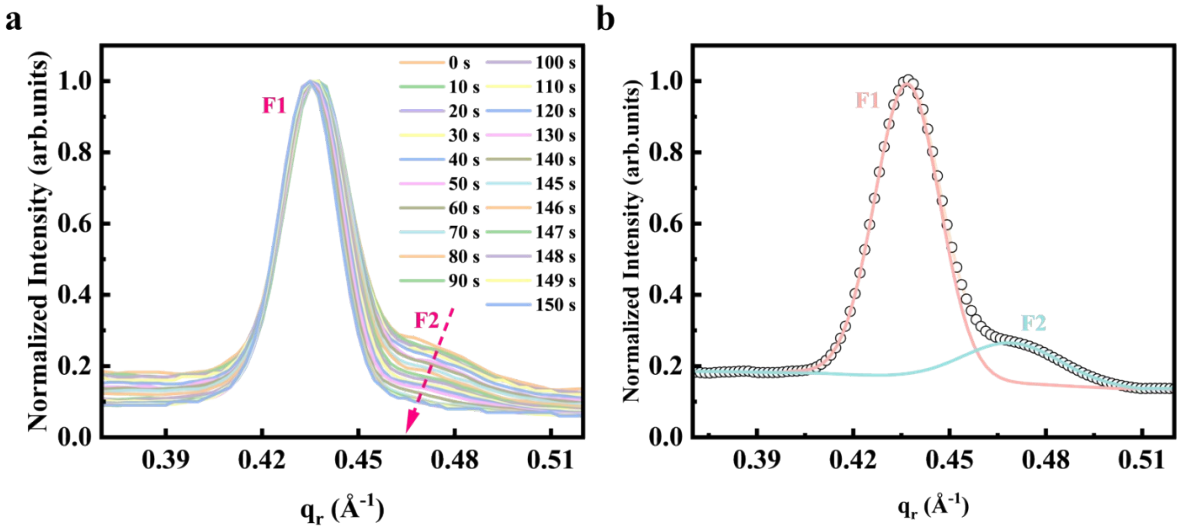

Figure S4. In-situ GIWAXS data of the 2D perovskites.

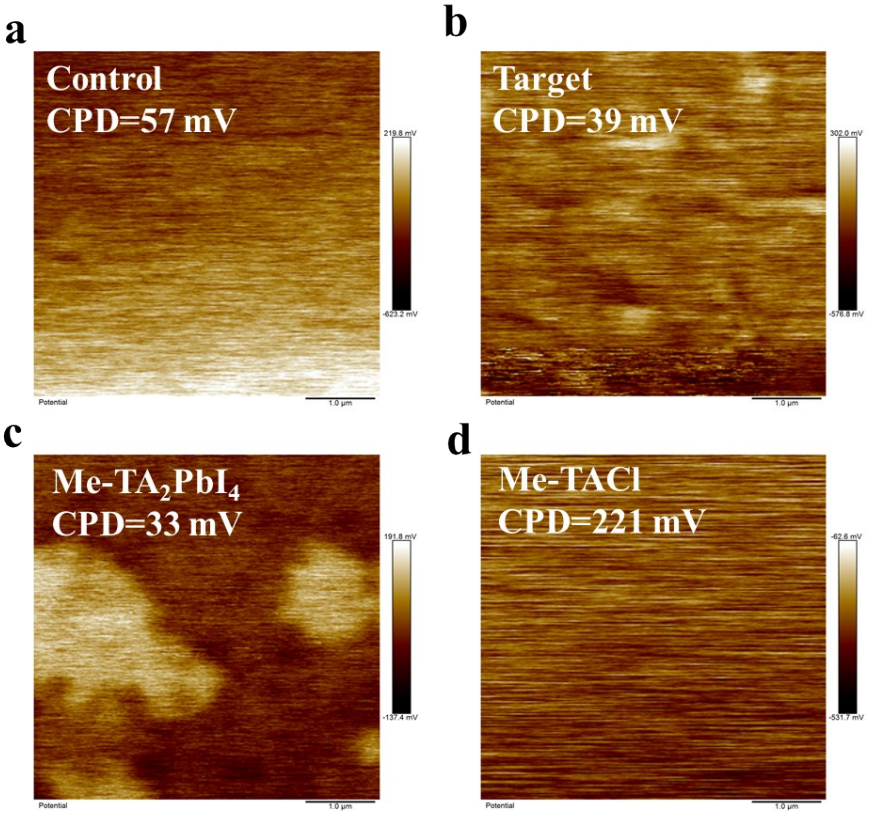

Figure S5. KPFM of (a) the control, (b) target, (c) Me-TA_2PbI_4 (n=1 phase) and (d) pure Me-TACl films.

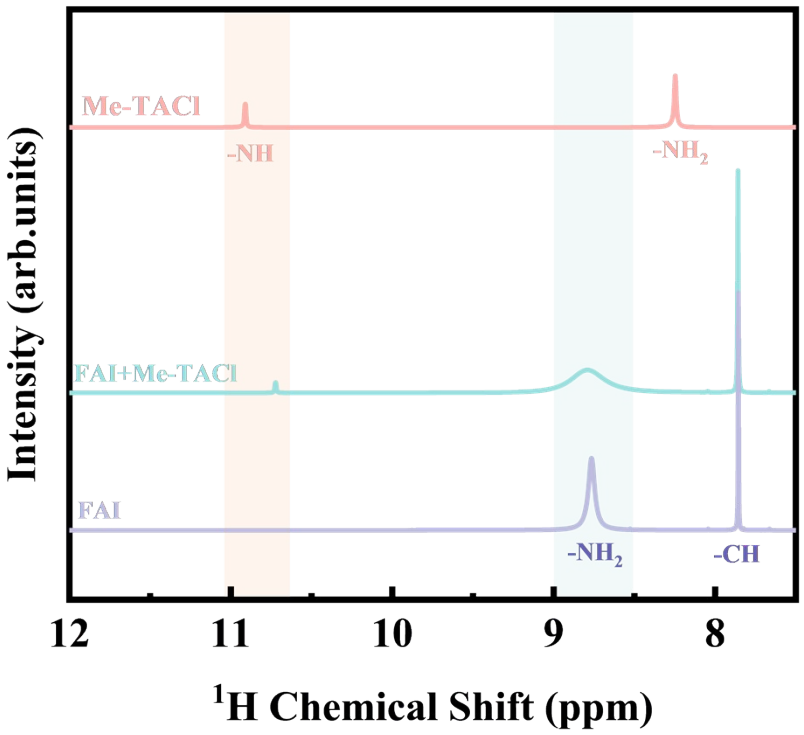

Figure S6. 1H-NMR spectra of Me-TACl, FAI and Me-TACl/FAI dissolved in DMSO-D6 solution.

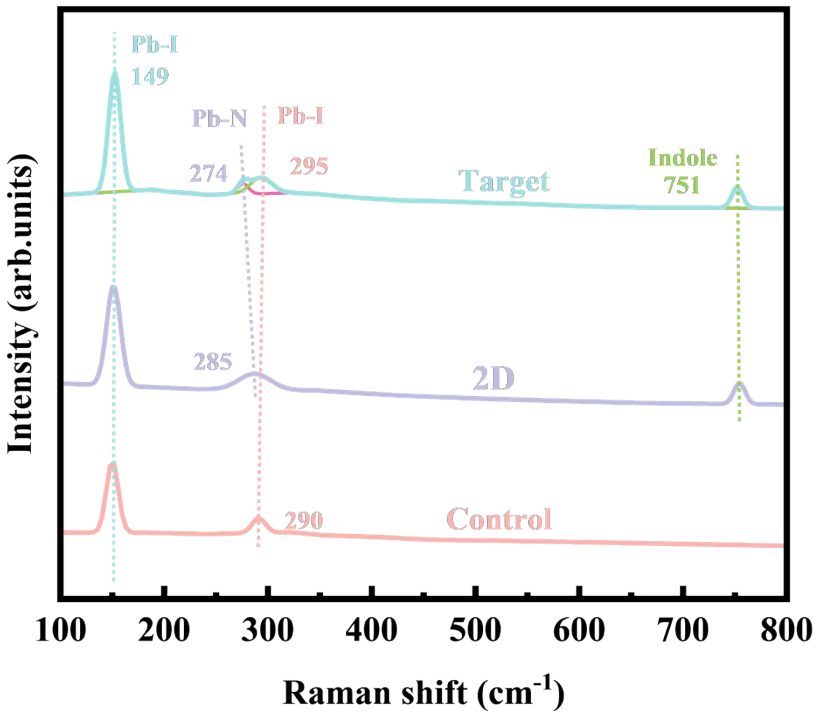

Figure S7. Raman spectra of pure 2D, pure 3D and 2D/3D perovskites.

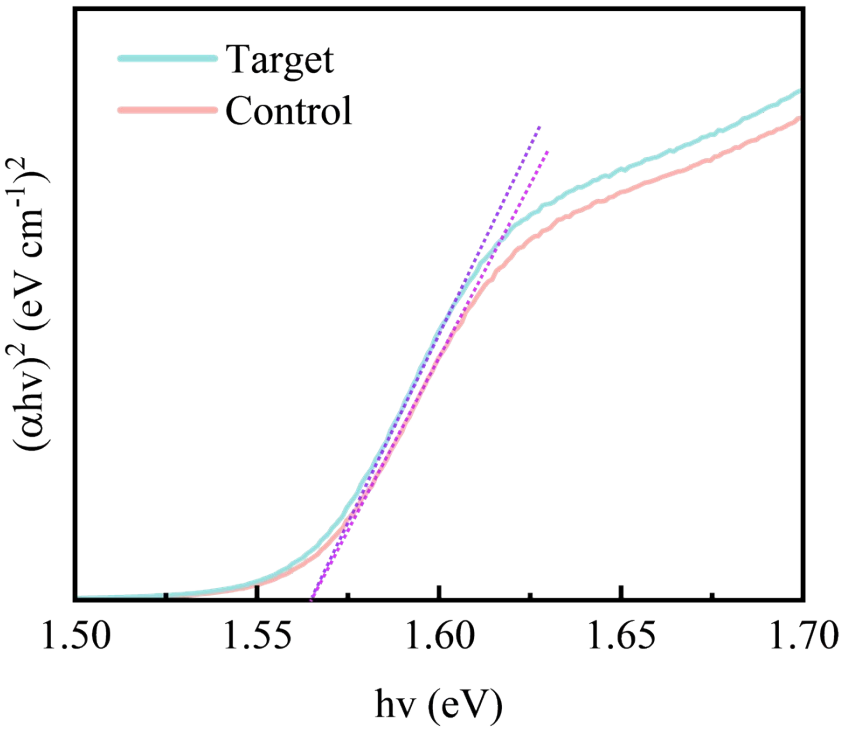

Figure S8. Tauc plots of the control and target films.

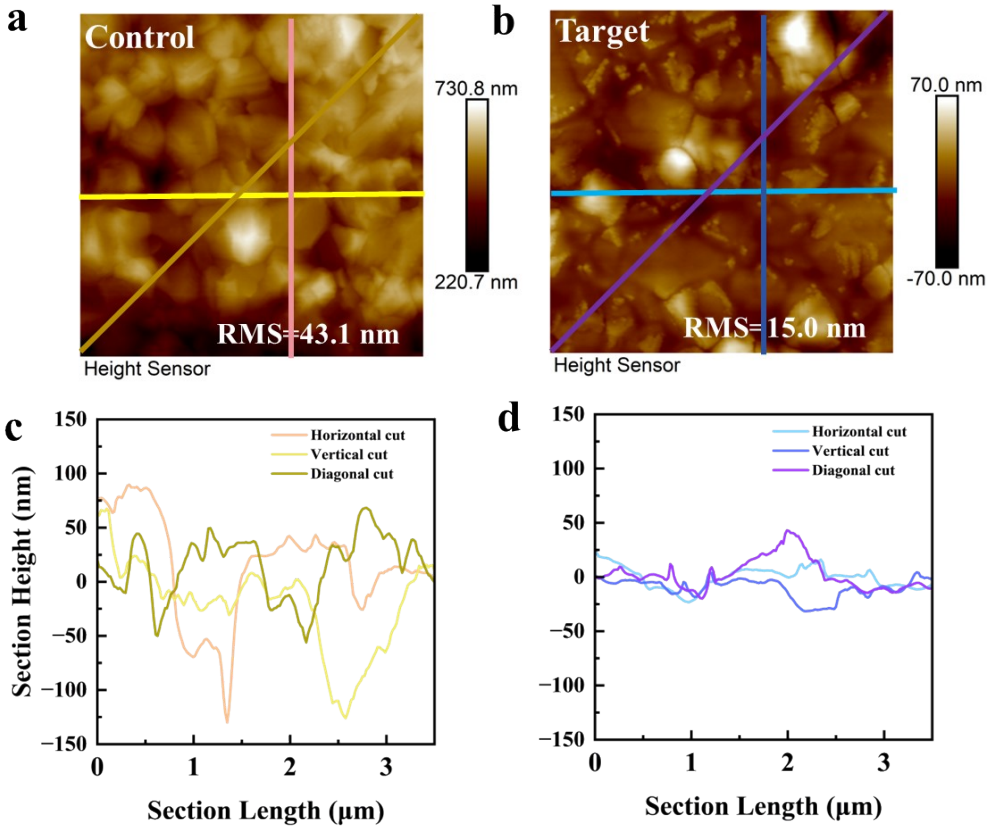

Figure S9. Mean square roughness (RMS) analysis of (a) control and (b) target films. The height profiles of the (c) control film and the (d) target film.

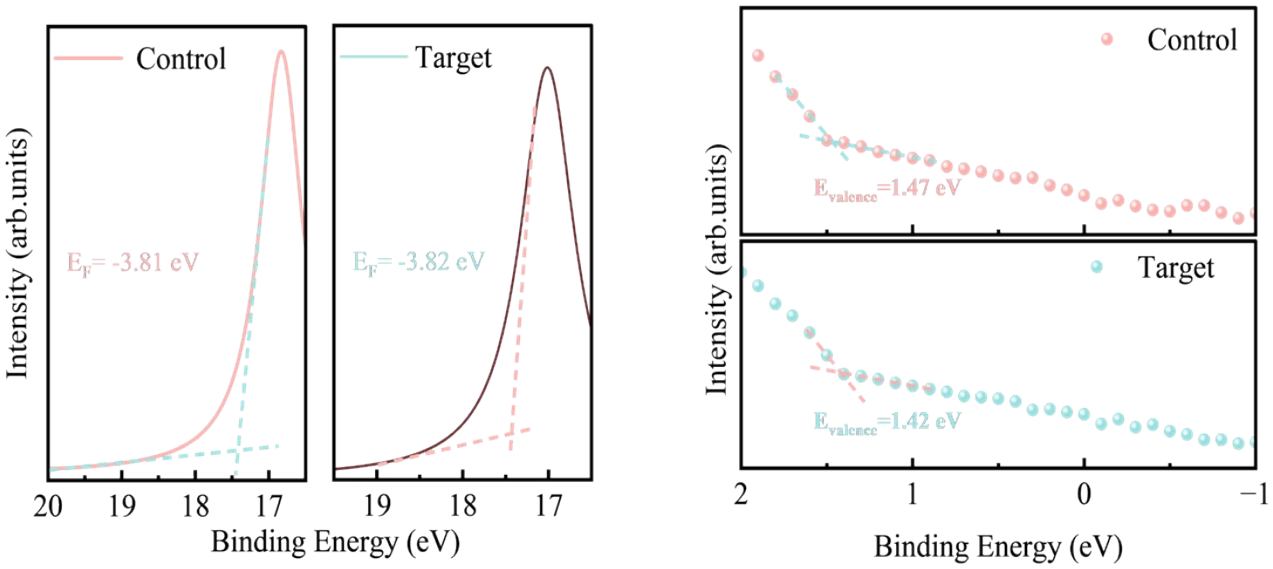

Figure S10. Secondary electron cutoff region and onset region of UPS spectra for the control and target films.

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TESTING
CNAS L2338

TEST REPORT

Report No：PWQC-WT-P24013021-5R

Sample Name	:	Photovoltaic cell
Client	:	Prof. Song Lin's Group, Northwestern Polytechnical University
Client Address	:	No. 127 West Youyi Road, Xi'an, P. R. China
Type of Project	:	Consignation

PHOTOVOLTAIC AND WIND POWER SYSTEMS QUALITY TEST CENTER，IEE, CHINESE ACADEMY OF SCIENCES

October, 24, 2024

PHOTOVOLTAIC AND WIND POWER SYSTEMS QUALITY TEST CENTER, IEE, CHINESE ACADEMY OF SCIENCES

Report No: PWQC-WT-P24013021-5R

Testing information:

Date：January, 31, 2024

Location：No.6 Bei-er-tiao, Zhongguancun, Haidian district, Beijing, China

Environmental conditions：(24.9±2)℃, (31.8±5)%RH

Testing items：

Measurement of photovoltaic current-voltage characteristics

Standards：

IEC 60904-1：2006 Photovoltaic (PV) devices

— Part 1：Measurement of photovoltaic current-voltage characteristics

Equipments：

Name	S/N	Expired date
Solar simulator	LE106-04	2024-10-15
Source Meter	LE177-01	2024-04-09
Reference cell	J-CH04	2024-02-15

Edited by(signatory)：Jiang Feifei

Date：2024.10.24

Approved by(signatory)：

Date：2024.10.24

PHOTOVOLTAIC AND WIND POWER SYSTEMS QUALITY TEST CENTER, IEE, CHINESE ACADEMY OF SCIENCES

Report No: PWQC-WT-P24013021-5R

Sample No.	DC2024a144
Sample S/N	5
Type	Single junction perovskite solar cell
Designated area	0.08713 cm^2 The designated area was certified by National Institute of Metrology, China. Test Report No. CDjc2021-10891.

Items of testing	Measurement of photovoltaic current-voltage characteristics				
Sample No.	DC2024a144				
Results	**Isc** (mA)	**Jsc** (mA/ cm^2)	**Voc** (V)	**Pm** (mW)	**Curve**
	2.296	26.356	1.177	2.240	A2024013116 0248
	Ipm (mA)	**Vpm** (V)	**FF** (%)	**E_{ff}** (%)	
	2.175	1.030	82.89	25.71	

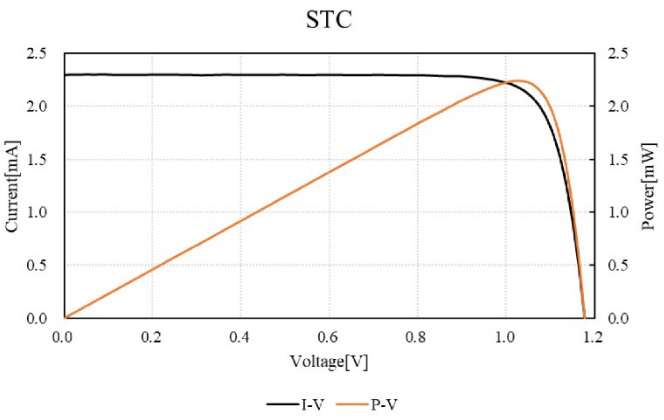
Measurement uncertainty:

$U_{95(Isc)}$=1.9% (k=2)

$U_{95(Voc)}$=1.8% (k=2)

$U_{95(Pm)}$=2.5% (k=2)

Report No: PWQC-WT-P24013021-5R



Type	Single junction perovskite solar cell	
Sample No.	DC2024a144	
Area	0.08713	cm^2
Isc	2.296	mA
Jsc	26.356	mA/cm^2
Voc	1.177	V
FF	82.89	%
Pm	2.240	mW
E_{ff}	25.71	%
Ipm	2.175	mA
Vpm	1.030	V
Voltage Sweep	Reverse	
Sweep time	25.1	s
Temp	25	℃
Irr	100	mW/cm^2
Curve	A20240131160248	

— End of Report —

NOTICE

1. The test result in this report relate only to the sample tested.
2. This report is not available without seal of Photovoltaic and Wind Power Systems Quality Test Center, IEE, Chinese Academy of Sciences (PWQTC). Additionally, Appendix pages are not available without seal of PWQTC.
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Tel： +86-10-82547051 E-mail：pvcenter@mail.iee.ac.cn

Figure S11. Independent PCE testing report by an accredited laboratory of Photovoltaic and Wind Power Systems Quality Test Center (Chinese Academy of Science, China). The measurements were carried out under ambient conditions. The devices were measured in reverse scan (1.25 V→-0.1 V, step 0.02 V) with a total sweep time of 25.1 s.

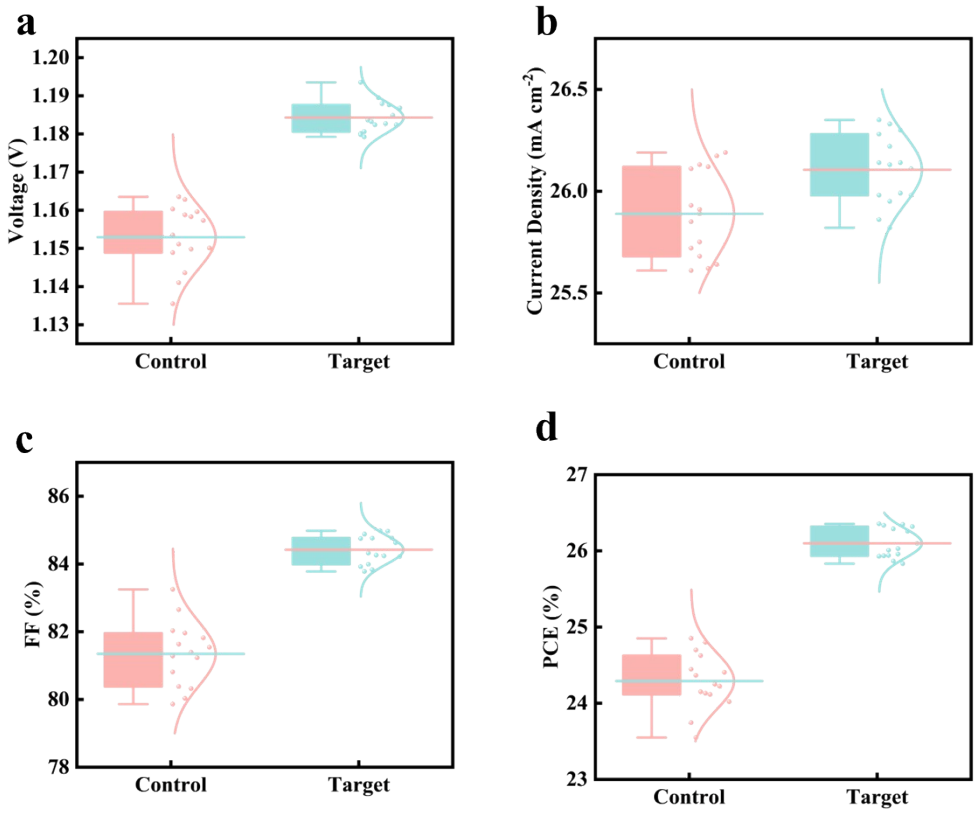

Figure S12. Rigid device photovoltaic parameters of control and target devices. Box plots showing the distribution of the (a) V_{oc}. (b) J_{sc}. (c) FF and (d) PCE of the rigid devices.

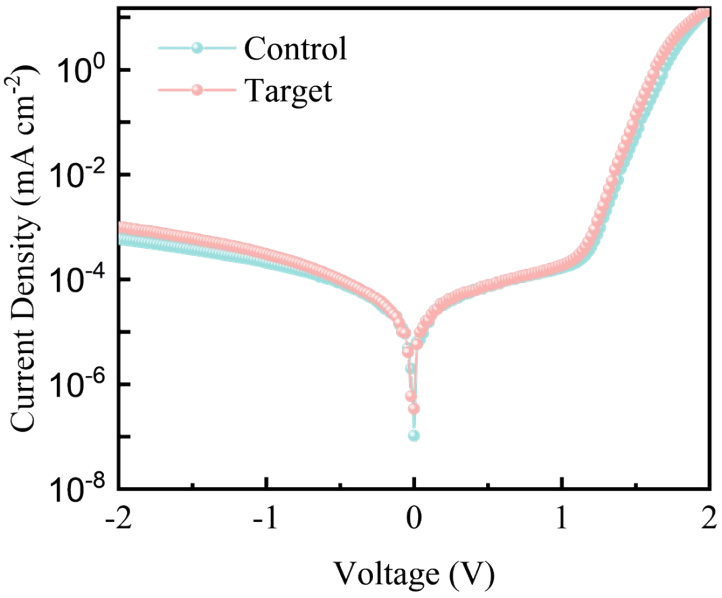

Figure S13. *J-V* curves under the dark condition.

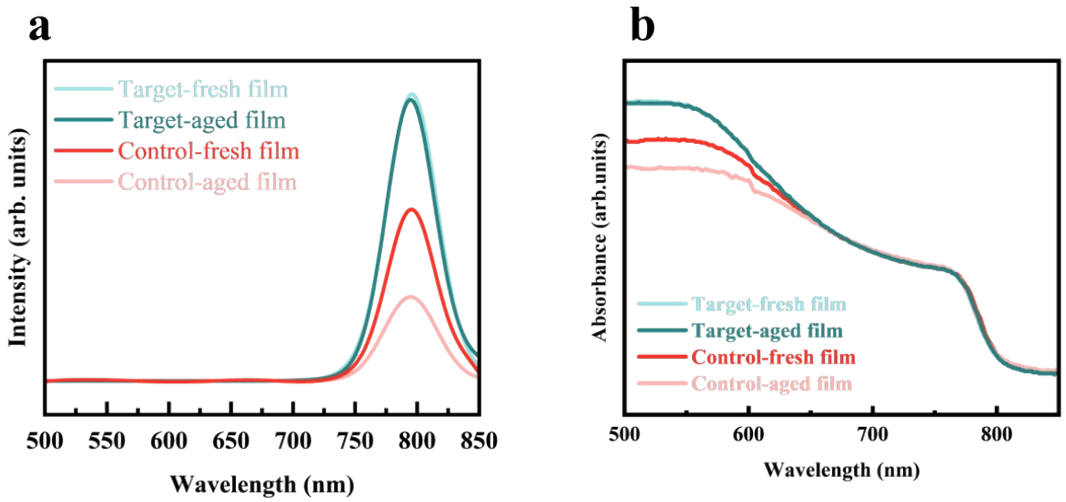

Figure S14. (a) PL and (b)UV-vis curves of the control and target films stored in air (60% RH) for 30 d.

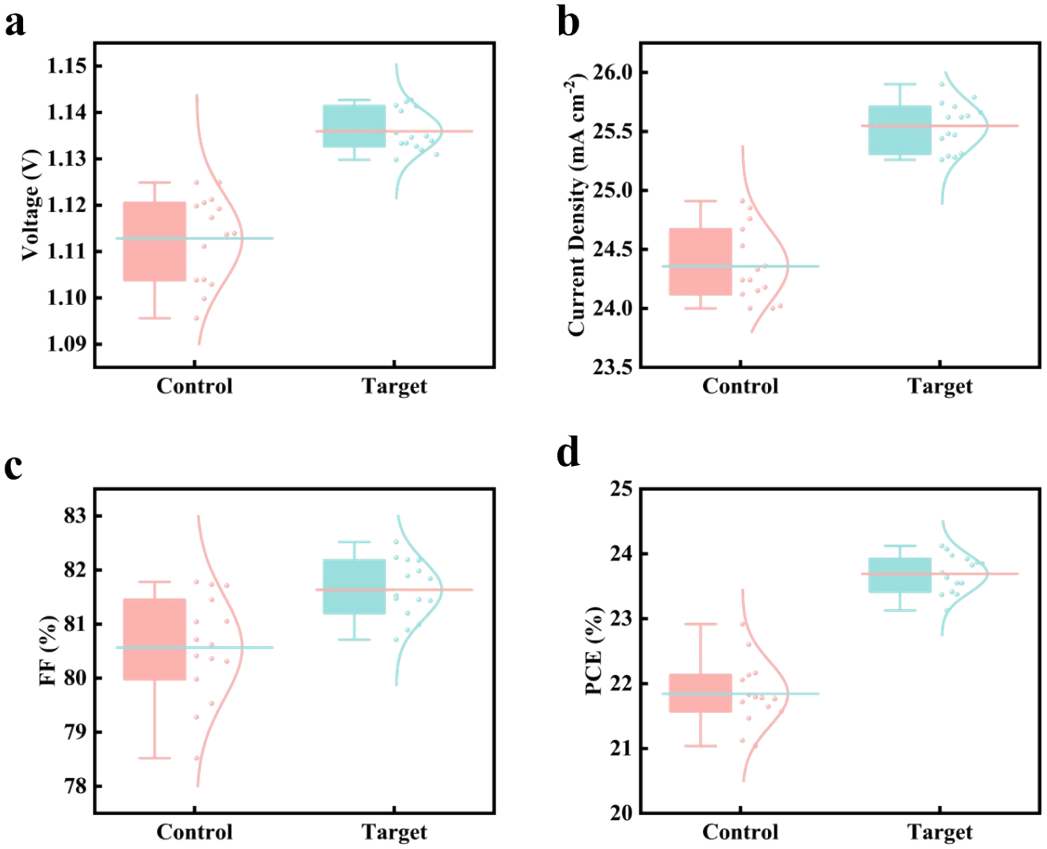

Figure S15. Flexible device photovoltaic parameters of control and target devices. Box plots showing the distribution of the (a) V_{oc}. (b) J_{sc}. (c) FF and (d) PCE of the flexible devices.

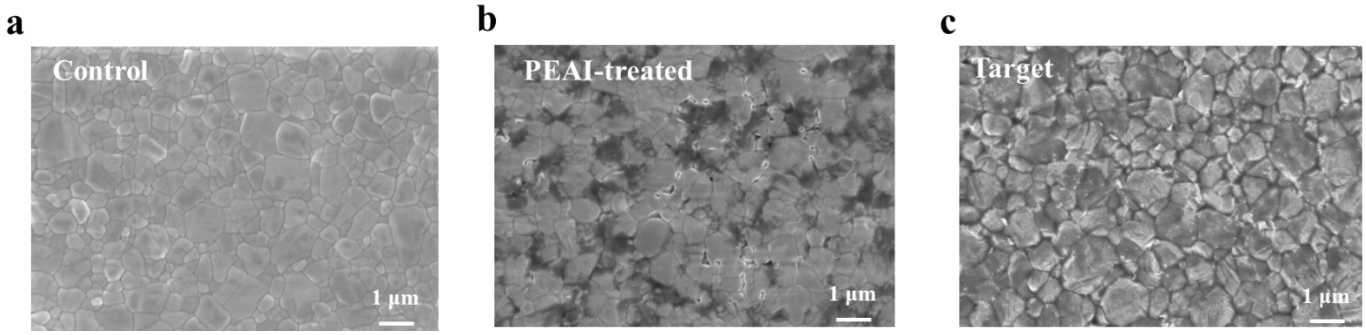

Figure S16. Plan-view SEM images of (a) the control, (b)PEAI-treated and (c) target samples before bending.

3. Supporting Tables

Table S1. TRPL fitting results.

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{ave} (ns)
Control	**0.66**	**20.61**	**0.34**	**180.51**	**151.94**
Target	**0.63**	**1.87**	**0.37**	**32.46**	**29.71**

Device type	Sample	V_{oc} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Rigid [a)]	Control	1.15±0.0089	25.96±0.2437	81.36±0.9644	24.33±0.3788
	Target	1.18±0.0048	26.12±0.1768	84.43±0.3550	26.11±0.1807
Flexible [b)]	Control	1.11±0.0104	24.36±0.3192	81.17±1.2883	21.90±0.6002
	Target	1.14±0.0062	25.54±0.3415	81.77±0.8998	23.75±0.5212

Table S2. Average photovoltaic performance and standard deviation of different devices

1. All efficiency data were obtained from three independent batches (5 control devices and 5 target devices per batch), with hysteresis effects verified by stabilized power output (SPO) measurements (26.20% vs. *J-V* 26.35%). Environmental-induced errors were confirmed to be <±0.3% through controlled experiments.

2. All efficiency data were obtained from five independent batches (3 control devices and 3 target devices per batch), with hysteresis effects verified by stabilized power output (SPO) measurements (24.14% vs. *J-V* 24.21%). Environmental-induced errors were confirmed to be <±0.3% through controlled experiments.

Table S3. Comparison of the method and performance with previously reported 2D/3D heterojunction perovskite solar cells.

Year	Molecule Name	Structure of 2D perovskite	PCE	Ref.
2025	**Me-TACl**	**$(Me\text{-}TA)_2PbI_4$**	**26.35%** **24.21% (flexible)**	**This work**
2025	3-F-4-ClAnI	$(3\text{-}F\text{-}4\text{-}ClAn)_2FAPb_2I_7$	24.74 %	[29]
2025	DPA-PEAI	$(DPA\text{-}PEA)_2PbI_4$	25.70 %	[30]
2024	2F-PD	$(2F\text{-}PD)_2PbI_4$	24.82 %	[31]
2023	4AP	$4APPbI_4$	24.9 % 22.3 % (flexible)	[32]