Supporting Information

Dual-site passivation by heterocycle functionalized amidinium cations toward high-performance inverted perovskite solar cells and modules

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Materials and Methods

Materials

Formamidine iodide (FAI), methylammonium iodide (MAI), methylamine hydrochloride (MACl), and methylammonium bromide (MABr) were purchased from Greatcell Solar Materials. Lead chloride ($PbCl_2$, 99.5%) was purchased from Xi'an Bright Optoelectronics Technology Co., Ltd. Lead iodide (PbI_2, 99.999%), cesium iodide (CsI, 99.99%) and lead bromide ($PbBr_2$, 99.999%) were purchased from Chengdu Alpha Metal Materials Co., Ltd.. N, N-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.9%) and 1-methy-2-pyrrolidinone (NMP, 99.9%), Isopropanol (IPA, 99.7%) were purchased from Alfa Aesar. [2-(9H-Carbazol-9-yl)ethyl]phosphonic acid (2PACz, >98.0% HPLC) and [4-(3,6-Dimethyl-9H-carbazol-9-yl)butyl]phosphonic Acid (Me-4PACz, >99.0% HPLC) were purchased from TCI. BCP, $PC_{61}BM$, and C_{60} were purchased from Advanced Election Technology. 4-Amidinopyridinium chloride (APCl, 99.9%), benzamidine hydrochloride (phFACl, 99.9%), and 2-thiazolecarboxamidine hydrochloride (TFACl, 99.9%) were obtained from MACKLIN. Nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) was purchased from Sigma-Aldrich for synthesizing the NiO_x nanoparticles. DMSO-D6 for nuclear magnetic analysis was purchased from energy-chemical. All chemicals were used without further purification. ITO glass (Huaming 01-AR, 8 Ω sq^{-1}) was bought from Beijing Huamin New Materials Technology Co., Ltd.

NiO_x nanoparticles were synthesized as follows: Firstly, 3 g of $Ni(NO_3)_2 \cdot 6H_2O$ was dissolved in 50 mL of deionized (DI) water. The solution was stirred at room temperature for 30 min. Subsequently, a 1.0 M NaOH solution was slowly added with continuous magnetic stirring until the pH reached approximately 10. After additional one hour of stirring, a green precipitate was obtained via centrifugation at 9000 rpm for 6 min. The precipitate was washed three times with DI water. The collected green solid was frozen for 3 h, then freeze-dried at 5 Pa for 15 hours, and finally calcined at 270 °C for 2 hours to produce NiO_x nanoparticles. Prior to use, the NiO_x was dispersed in

DI water by sonication for 10 min at a concentration of 30 mg/mL.

Preparation of perovskite precursor solutions and perovskite films

1.53 eV $Cs_{0.05}FA_{0.95}PbI_3$ for small-area devices. For the composition $Cs_{0.05}FA_{0.95}PbI_3$, 1.5 M perovskite precursor solution was prepared by dissolving CsI, FAI and PbI_2 in DMF:DMSO = 4:1 (vol/vol) mixed solvents according to the stochiometric ratio. 3 mol% PbI_2 and 10 mol% MACl were additionally added to the precursor for better crystallization and perovskite phase transformation. The perovskite films were deposited by spin-coating the perovskite precursor solution on glass/ITO/NiO_x/Me-4PACz substrate at 1000 rpm for 10 s and 5000 rpm for 30 s. The wet perovskite film was quickly put into a sample chamber connected to vacuum-pumping instrumentation (Internal space is 12 cm × 12 cm × 2.1 cm). By opening the valve connecting the specimen chamber to the pump system, the perovskite film was immediately exposed to low pressure maintained at 10 Pa for 30 s, followed by full pressurization by admitting ambient air into the specimen chamber. Subsequently, the perovskite film was annealed at 100 °C for 15 min in the air (RH = 30±10%, Temperature = 25±5 ^{o}C) for full crystallization. It needs to be noted that the perovskite films were prepared in ambient air with a RH of 30±10% and at 25±5 ^{o}C.

1.56 eV $Cs_{0.05}MA_{0.05}FA_{0.9}PbI_3$ for large-area modules. The stoichiometric $Cs_{0.05}MA_{0.05}FA_{0.9}PbI_3$ precursor solution was prepared by dissolving 20.78 mg of CsI, 247.68 mg of FAI, 12.72 mg of MAI, 15 mg of MACl, 11.12 mg of $PbCl_2$, and 785.55 mg of PbI_2 in a mixed solvents of DMF/DMSO (8:2, by volume). The perovskite films were deposited by spin-coating the perovskite precursor solution on glass/ITO/NiO_x/Me-4PACz substrate at 1000 rpm for 10 s and 5000 rpm for 30 s. The wet perovskite film was quickly put into a sample chamber connected to vacuum-pumping instrumentation (Internal space is 12 cm × 12 cm × 2.1 cm). By opening the valve connecting the specimen chamber to the pump system, the perovskite film was immediately exposed to low pressure maintained at 10 Pa for 30 s, followed by full pressurization by admitting ambient air into the specimen chamber. Subsequently, the perovskite film was annealed at 100 °C for 15 min in the air (RH = 30±10%, Temperature = 25±5 °C) for full crystallization. It needs to be noted that the perovskite films were prepared in ambient air with a RH of 30±10% and at 25±5 ^{o}C.

Device fabrication

Small-area PSCs fabrication. First, the ITO glass substrate was etched by laser etching technology. Ultrasonic cleaning of ITO glass was carried out with glass cleaning agent, deionized water, and ethanol in sequence, and each step took 15 min. The wettability of the ITO substrate was enhanced by UV-ozone treatment for 15 min. Then, the water-based ink of NiO_x nanoparticles (30 mg NiO_x nanoparticles dispersed into 1 ml deionized water) was coated on ITO glass at 4000 rpm for 30 s and annealed at 150 °C for 10 min. After annealing, the ITO/NiO_x substrate was quickly transferred into an N_2-filled glove box for subsequent preparation. Me-4PACz solution (0.5 mg/ml dissolved in IPA, ultrasonic bath for 10 min) was coated on ITO/NiO_x substrate at 4000 rpm for 20 s and then annealed at 150 °C for 10 min. The perovskite films based on different perovskite compositions of $Cs_{0.05}FA_{0.95}PbI_3$ and $Cs_{0.05}MA_{0.05}FA_{0.9}PbI_3$ were fabricated as described above. For modulated perovskite films, different concentrations of phFACl, APCl or TFACl solutions in IPA of (0.5, 0.1 and 0.5 mg/mL) were spin-coated on the as-prepared perovskite film at 5000 rpm for 30 s, and the modulated perovskite films were annealed at 100 °C for 5 min. And then, about 30 nm C_{60} were thermally evaporated on the perovskite films under a high vacuum 8×10^{-4} Pa. Subsequently, BCP solution was spin-coated on C_{60} layer at a speed of 5000 rpm for 30 s. Finally, the 80 nm Cu or Ag electrode is thermally evaporated on C_{60}. It should be stressed that the Cu electrode is thermally evaporated for long-term stability measurements. For sealing the devices for MPP stability testing, a UV-curable adhesive (Eversolar AB-341, Everlight Chemical) was applied over the active area of the perovskite solar cells, followed by the placement of a highly transparent glass panel. The device was then compressed and cured under ultraviolet light for 3 minutes.

Large-area PSC modules fabrication. The fabrication process for 1.53 eV

$Cs_{0.05}MA_{0.05}FA_{0.9}PbI_3$ perovskite-based large-area modules closely mirrors that of smaller devices. The procedure began by evenly dispersing 1 mL of the $Cs_{0.05}MA_{0.05}FA_{0.9}PbI_3$ precursor solution across an ITO substrate. After allowing the solution to rest for 10 seconds to facilitate even distribution, spin-coating is performed at 2500 rpm for 20 s. The assembly of subcells of the modules utilized a three-stage laser etching technique (P1, P2, P3) on a 6 × 10 cm^2 ITO substrate, forming 11 subcells. The first etching step, P1, targets the ITO substrate, achieving a track width of 30 ± 3 µm using a 1064 nm, nanosecond laser. This step ensures that the insulation resistance between adjacent conductive layers exceeds 10 MΩ, without leaving residual TCO film in the etched tracks or damaging the underlying glass. The second etching step, P2, processed the ITO/NiO_X/Me-4PACz/Perovskite/C_{60}/BCP layers, using a 532 nm, picosecond laser to achieve a width of 50 ± 5 µm. Care is taken to avoid penetrating the bottom TCO layer, maintaining a 30 µm gap between the P1 and P2 etchings. The final stage, P3, involved etching the Ag electrodes with the same width specification as P1 (30 ± 3 µm) using a 532 nm, picosecond laser. Like the P2 process, P3 ensures that the bottom TCO layer remains intact, preserving a 30 µm interval between the P2 and P3 etchings.

Characterizations of perovskite films and devices

The *J–V* characteristics were obtained using a Keithley 2400 source meter in a controlled environment simulating AM 1.5 solar irradiance (100 mW cm^{-2}), facilitated by a standard xenon lamp solar simulator (7ISO503A, SOFN INSTRUMENTS). These measurements were conducted in a forward scan ranging from -0.1 V to 1.4 V, or a reverse scan from 1.4 V to -0.1 V. The *J-V* measurements for the solar cells were conducted in ambient air conditions. The active area of PSCs was defined to be 0.052 cm^2 by black metal mask. The external quantum efficiency (EQE) was measured using an EQE measurement system from Enli Tech, Taiwan. All assessments were performed at room temperature in an ambient atmosphere, and the solar cells were not encapsulated during these measurements. SEM measurement was carried out by JEOL

JSM7610F SEM. The scanning voltage is 3 kV. X-ray diffraction (XRD) patterns were measured on the Rigaku SmartLab X-ray diffractometer using Cu Ka target radiation (λ=1.5405 A) (measurement power of 2 kW, scan rate of 8° min^{-1}). Field-emission SEM (JEOL 7610F) was used to investigate the surface morphology of the film at 3 kV. The SSPL and TRPL were measured by a fluorescence spectrometer (FLS1000, Edinburgh Instruments). The ultraviolet-visible absorption spectra of the films were measured by Shimazu UV-1900 spectrophotometer. The Asylum Research MFP-3D was used to measure AFM and KPFM in tapping mode. XPS and UPS spectra were collected through Thermo ESCALAB XI+. Fourier transform infrared (FTIR) spectroscopy was recorded using the FTIR-805 spectrometer of Tianjin Gangdong SCI.&TECH. CO,.LTD. The Mott-Schottky measurements were performed using the AMETEK VersSTAT 3F electrochemical workstation at a fixed frequency of 1k Hz. The applied bias voltage range is 0~1.5 V. EIS measurements are made in the dark, with frequencies ranging from 0.1 Hz to 1,000,000 Hz, using the same instruments as the Mott-Schottky measuring instruments. TPC/TPV was tested by PD-RS of ENLITECH, Taiwan. The long-term stability was conducted in ambient conditions at a relative humidity (RH) of 35±5% and a temperature of 25±5°C. LBIC mapping measurements were tested by LSD4 of ENLITECH.

MPPT of devices

The operational MPPT stability of the encapsulated devices was assessed under continuous one-sun conditions using a white LED lamp without a UV filter in a 99.99% nitrogen environment. These tests were conducted using an MPP tracking system (YH-VMPP-16, Yanghua, Suzhou). Specifically, 16 solar cell samples were simultaneously placed in aging equipment. The environment around solar cells is maintained at around 25°C through a refrigeration system. Aging equipment is tracked and tested by Continuously scanning and analyzing the maximum power point of the device. The interval between each test is 8.01h. White LED light sources have a light intensity energy of approximately 100 mW cm^{-2}.

Cyclic *J-V* test of devices

Cyclic *J-V* testing is conducted every hour to test the *J-V* data of scanning devices. The specific testing conditions are White LED illumination (Intensity ≈ 100 mW cm^{-2}), Stored in 99.99% nitrogen environment, T ≈ 25 ± 5 ^{o}C.

Certification of device PCE

The PSC devices were sent to the Tianjin Institute of Metrological Supervision and Testing, China, for official certification. Specifically, we fill the prepared solar cell samples for certification testing with nitrogen, then store them with a vacuum sealer and always place them in a dark sealed box. During the certification test, the certification agency recalibrates the effective active area of our solar cells to ensure accurate evaluation of data such as photocurrent density. The test environment and test methods are recorded in the certification data in **figs. S9-14.**

Theoretical calculation

The DFT calculations were performed based on the projector-augmented-wave (PAW) pseudopotentials. The electron exchange and correlation interactions were described by the Perdew-Burke-Ernzerhof (PBE) functional within the framework of the Generalized Gradient Approximation (GGA). An energy cutoff of 400 eV was employed for the plane-wave basis-set expansion. The perovskite surface was modeled using a slab consisting of five atomic layers, with a vaccum gap of 40 Å. The atomic positions within the top three layers were relaxed until the force acting on each atom converged to within 0.03 eV/Å, while the bottom two atomic layers were fixed to mimic the bulk structure. The binding energy of ligand with the perovskite surface containing vacancy defects was defined as $E_b = E(\text{perovskite@ligand}) - E(\text{perovskite}) - E(\text{ligand})$. Here, E(perovskite@ligand) represents the energy of the system where the perovskite slab interacts with the ligand, while E(perovskite) and E(ligand) denote the energies of the isolated perovskite slab and the ligand, respectively.

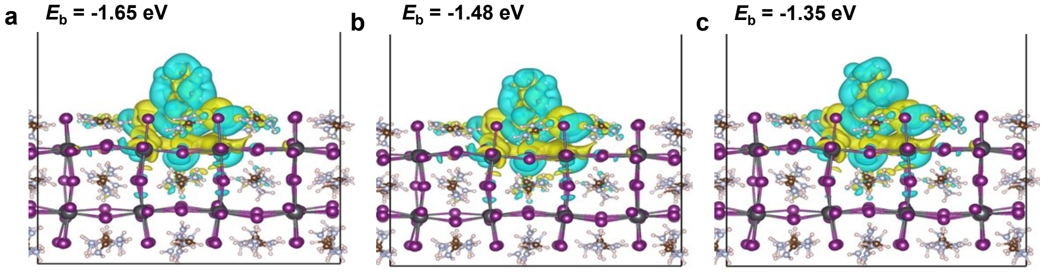

Fig. S1. The binding energy of $phFA^+$, AP^+, and TFA^+ with $FAPbI_3$ containing V_I and V_{FA} defects in vertical configuration.

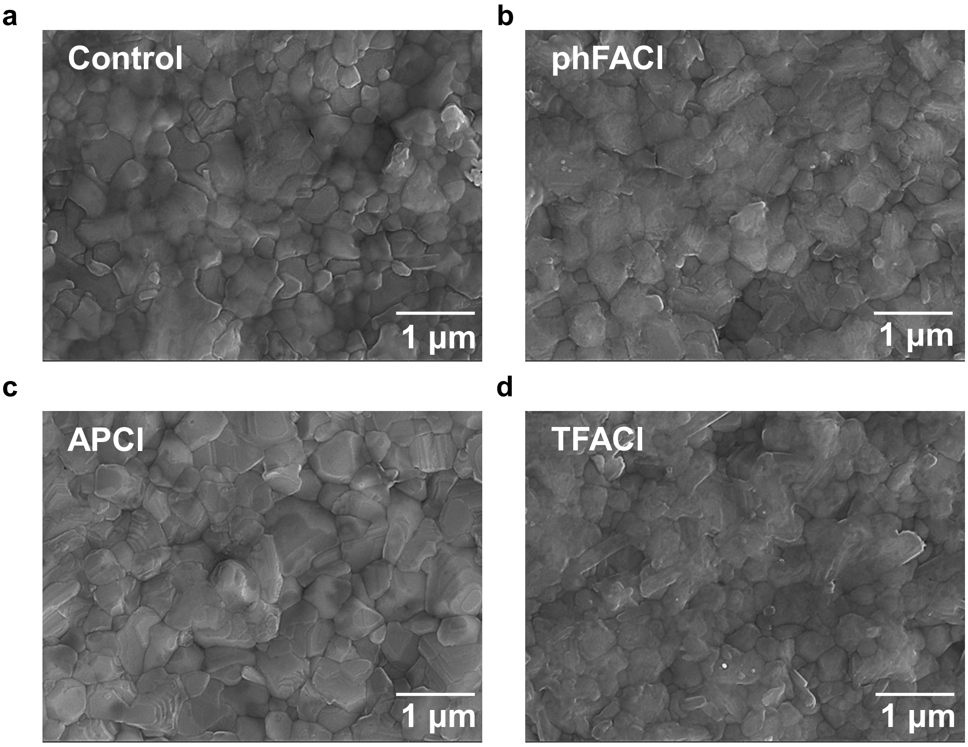

Fig. S2. SEM images for the (**a**) Control, (**b**) phFACl, (**c**) APCl and (**d**) TFACl-modulated perovskite films.

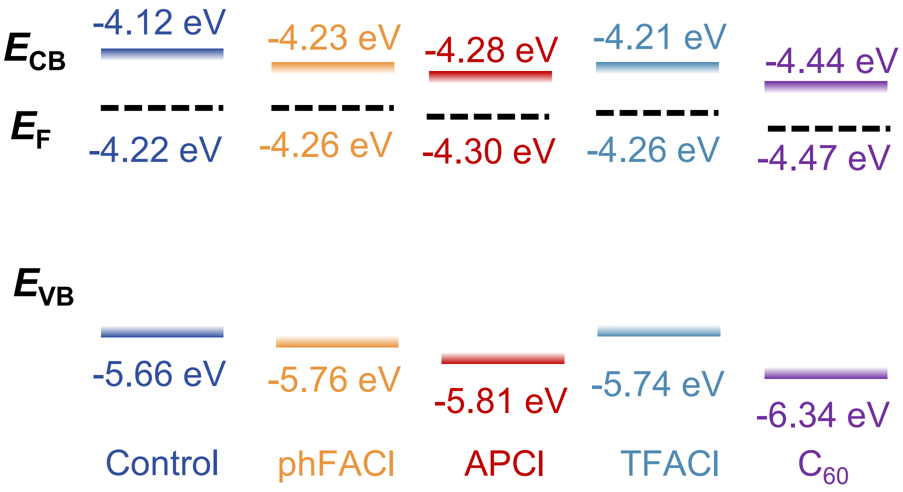

Fig. S3. Energy-level diagram of the control, phFACl, APCl, and TFACl modulated perovskite films as well as C_{60}.

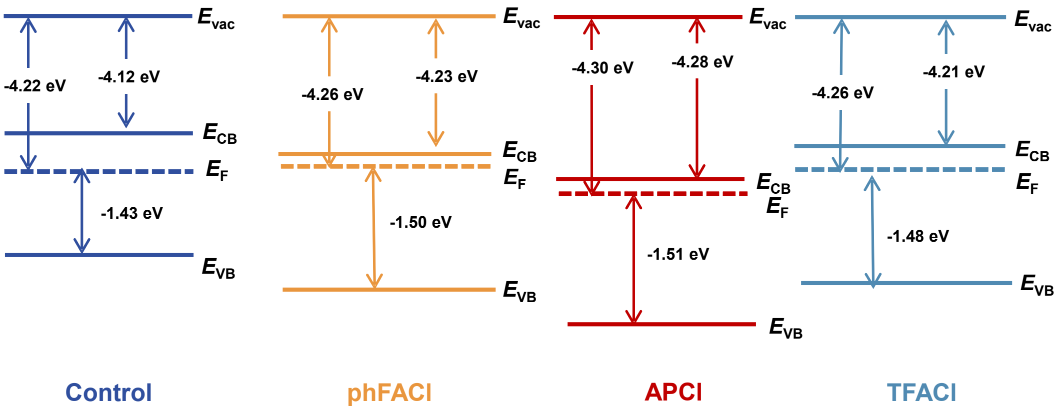

Fig. S4. Energy-level diagram of the control, phFACl, APCl, TFACl modulated perovskite films.

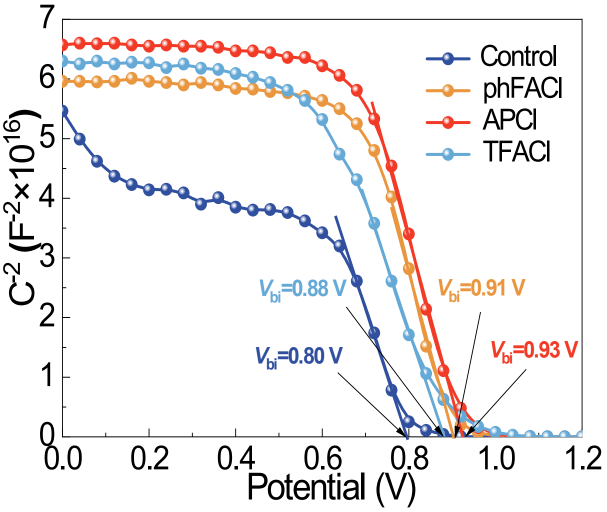

Fig. S5. Mott−Schottky plots of the control and phFACl, APCl, TFACl-modulated PSCs.

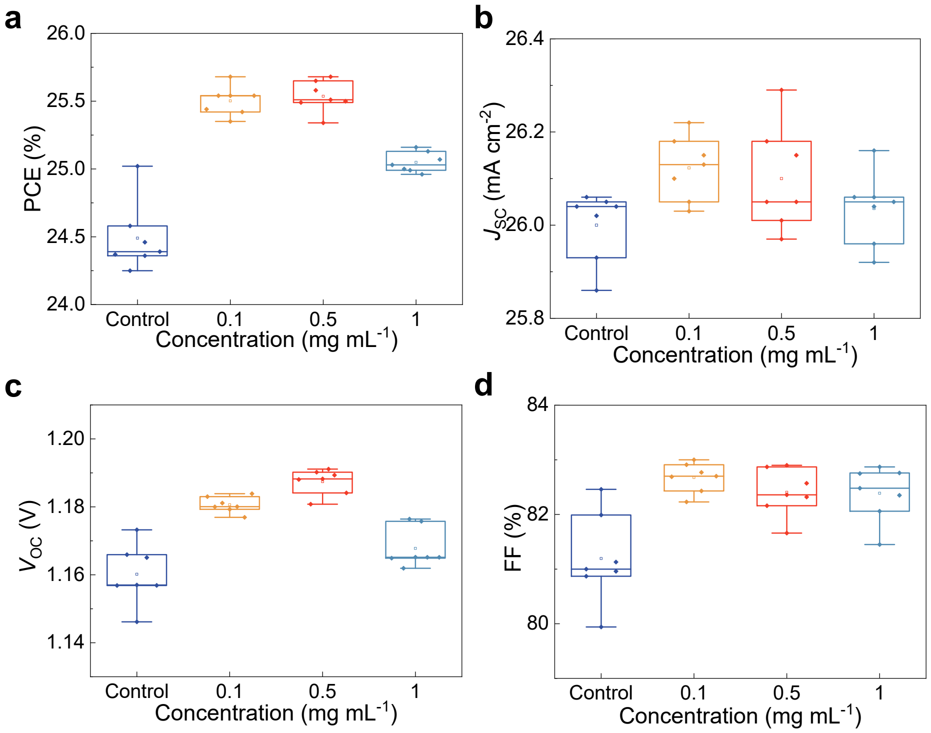

Fig. S6. Statistics of V_{OC}, FF, PCE and J_{SC} of the PSCs modulated by different concentrations of phFACl. The statistic data were obtained from individual 7 devices for each kind of PSCs.

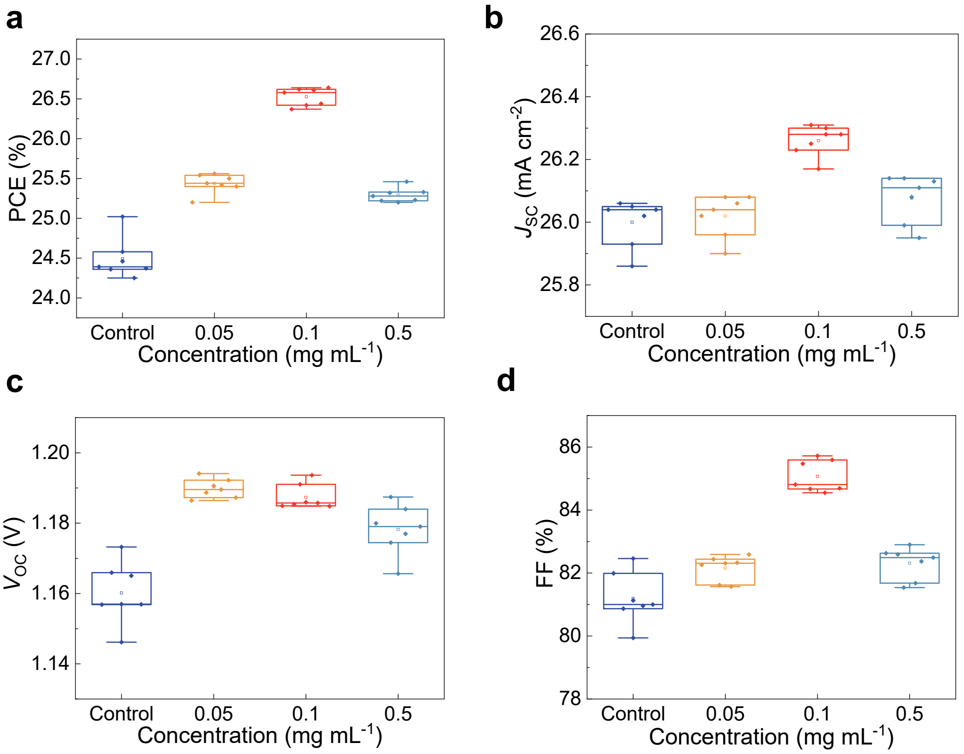

Fig. S7. Statistics of V_{OC}, FF, PCE and J_{SC} of the PSCs modulated by different concentrations of APCl. The statistic data were obtained from individual 7 devices for each kind of PSCs.

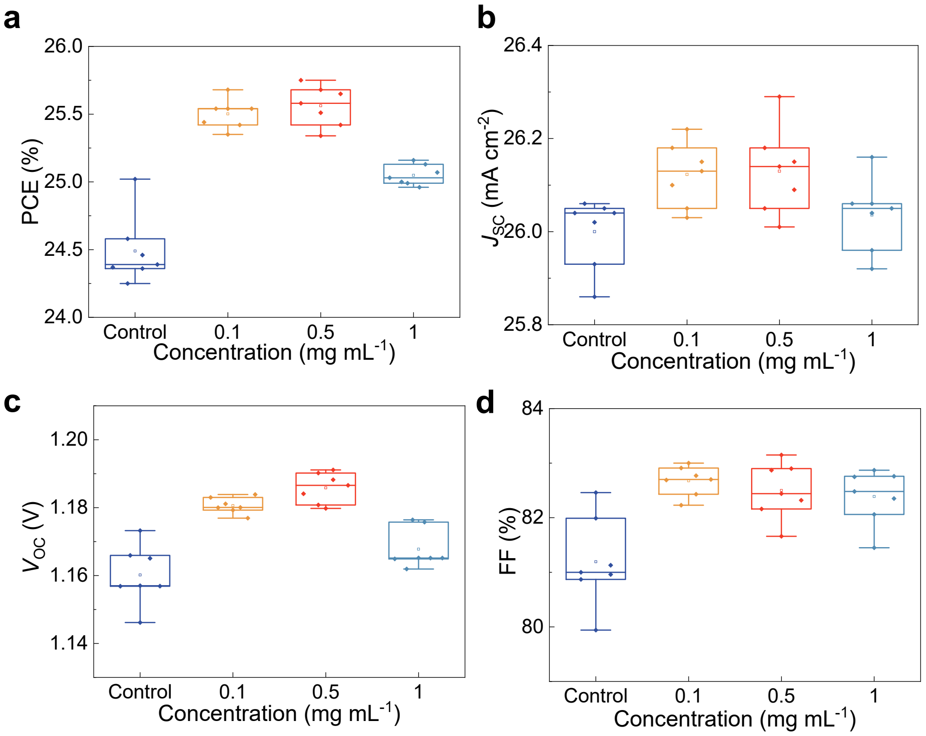

Fig. S8. Statistics of V_{OC}, FF, PCE and J_{SC} of the PSCs modulated by different concentrations of TFACl. The statistic data were obtained from individual 7 devices for each kind of PSCs.

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检 测 报 告

Test Report

报告编号：
Report No. JLY20241823W

样品名称 Sample Name	河北工大陈聪课题组钙钛矿太阳能电池
委托单位 Name of Client	河北工业大学 Hebei University of Technology
生产单位 Manufacturer	ChencongGroup-2024

天津市计量监督检测科学研究院
Tianjin Institute of Metrological Supervision and Testing

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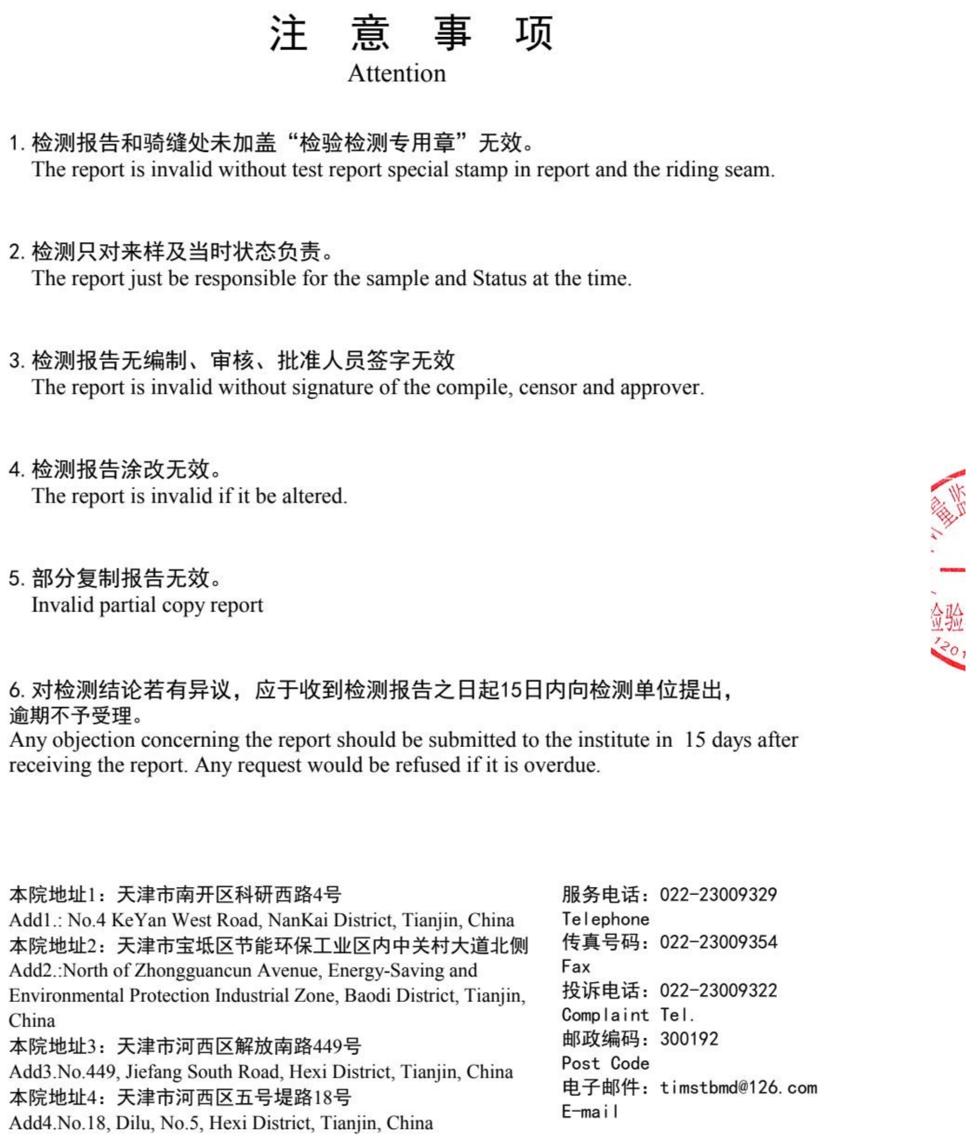
Fig. S9. PSCs certification report.



注意事项
Attention

1. 检测报告和骑缝处未加盖“检验检测专用章”无效。
The report is invalid without test report special stamp in report and the riding seam.

2. 检测只对来样及当时状态负责。
The report just be responsible for the sample and Status at the time.

3. 检测报告无编制、审核、批准人员签字无效
The report is invalid without signature of the compile, censor and approver.

4. 检测报告涂改无效。
The report is invalid if it be altered.

5. 部分复制报告无效。
Invalid partial copy report

6. 对检测结论若有异议，应于收到检测报告之日起15日内向检测单位提出，逾期不予受理。
Any objection concerning the report should be submitted to the institute in 15 days after receiving the report. Any request would be refused if it is overdue.

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Fig. S10. PSCs certification report, attention of the report.

天津市计量监督检测科学研究院

Tianjin Institute of Metrological Supervision and Testing

检测报告

Test Report

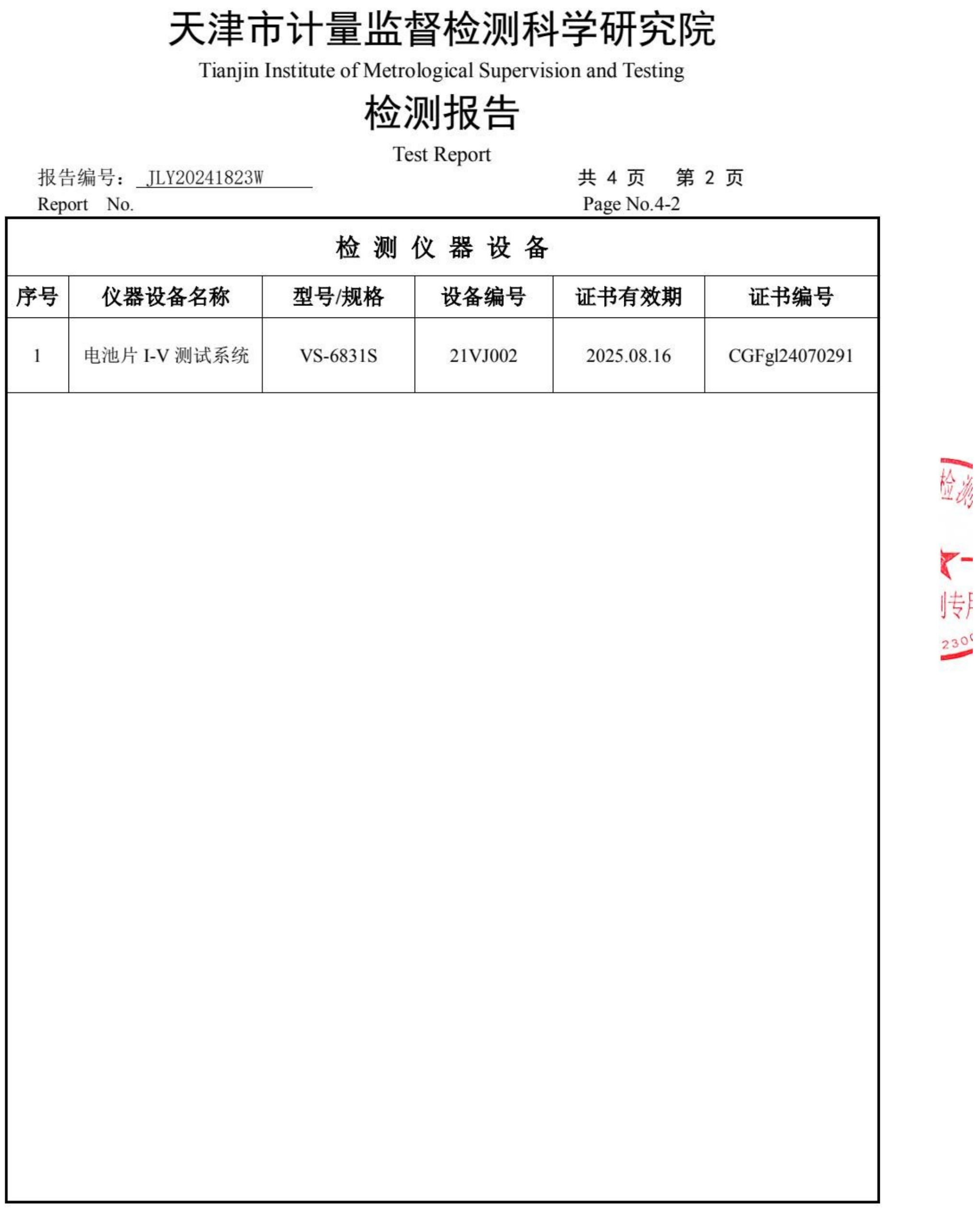
报告编号：JLY20241823W　　　　共 4 页 第 1 页

Report No.　　　　Page No. 4-1

样品名称 Sample Name	河北工大陈聪课题组钙钛矿太阳能电池				
规格型号 Specification Type	HEBUT-PSCs-1129	**商标/出厂编号** Brand/Serial Number	HEBUT-ChenCong-PSCs #202411-1-262 - P_{max}	**生产日期/批号** Produce Date/ Serial Number	2024-11-29
样品等级 Sample Grade	单节/single-junction	**样品描述** Sample Description	外观良好，无明显可见缺陷	**样品接收时间** Sample receive time	2024-12-03
委托日期 Delivery Date	2024-12-03	**送样人员** Delivered by	陈聪	**样品数量** Sample Quantity	1块
委托单位名称及联系电话 Name of Client	河北工业大学 Hebei University of Technology/18743093695				
生产单位名称 Manufacturer	ChencongGroup-2024				
检测时间 Test Time	2024-12-03	**检测地点** Test Location	本院五号堤路院区光伏产业计量部106室	**检测环境** Test Condition	温度：25.1℃ 相对湿度：25.3%
检测依据 Test Standard	IEC 60904-1:2020《光伏器件 第1部分：光伏电流-电压特性的测量》				
检测结论 Test Conclusion	/ 检验检测专用章 （Stamp of Test Institution） 签发日期：2024-12-10 Issue Date: Y M D				
备注 Remark	/				

编制： Compiled by　　**审核：** Checked by 柳云秀　　**批准：** Approved by

Fig. S11. PSCs certification report, Page #1.



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Tianjin Institute of Metrological Supervision and Testing

检测报告

Test Report

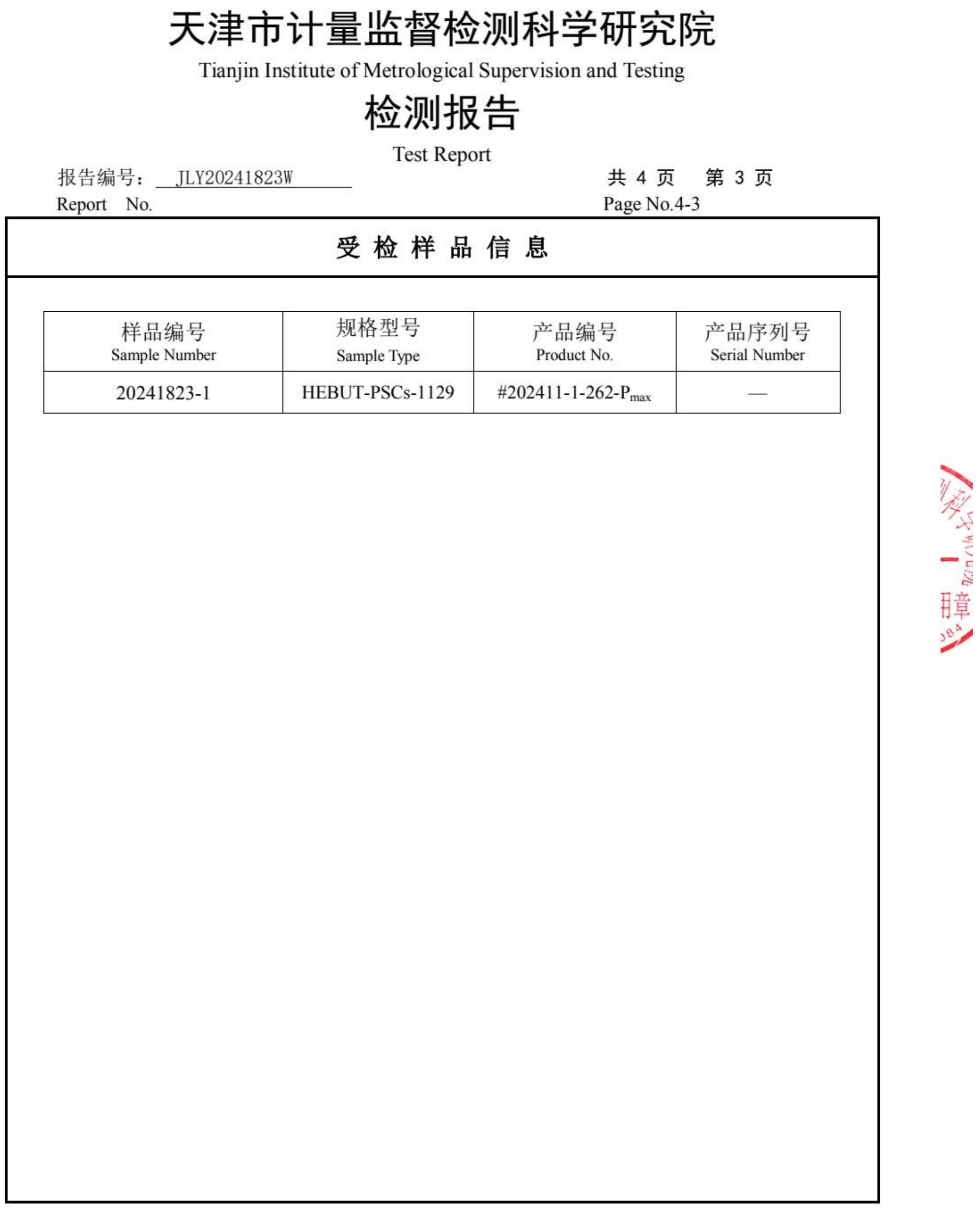
报告编号：JLY20241823W　　　　共 4 页　第 2 页

Report No.　　　　Page No.4-2

检测仪器设备

序号	仪器设备名称	型号/规格	设备编号	证书有效期	证书编号
1	电池片 I-V 测试系统	VS-6831S	21VJ002	2025.08.16	CGFgl24070291

Fig. S12. PSCs certification report, Page #2.



天津市计量监督检测科学研究院
Tianjin Institute of Metrological Supervision and Testing

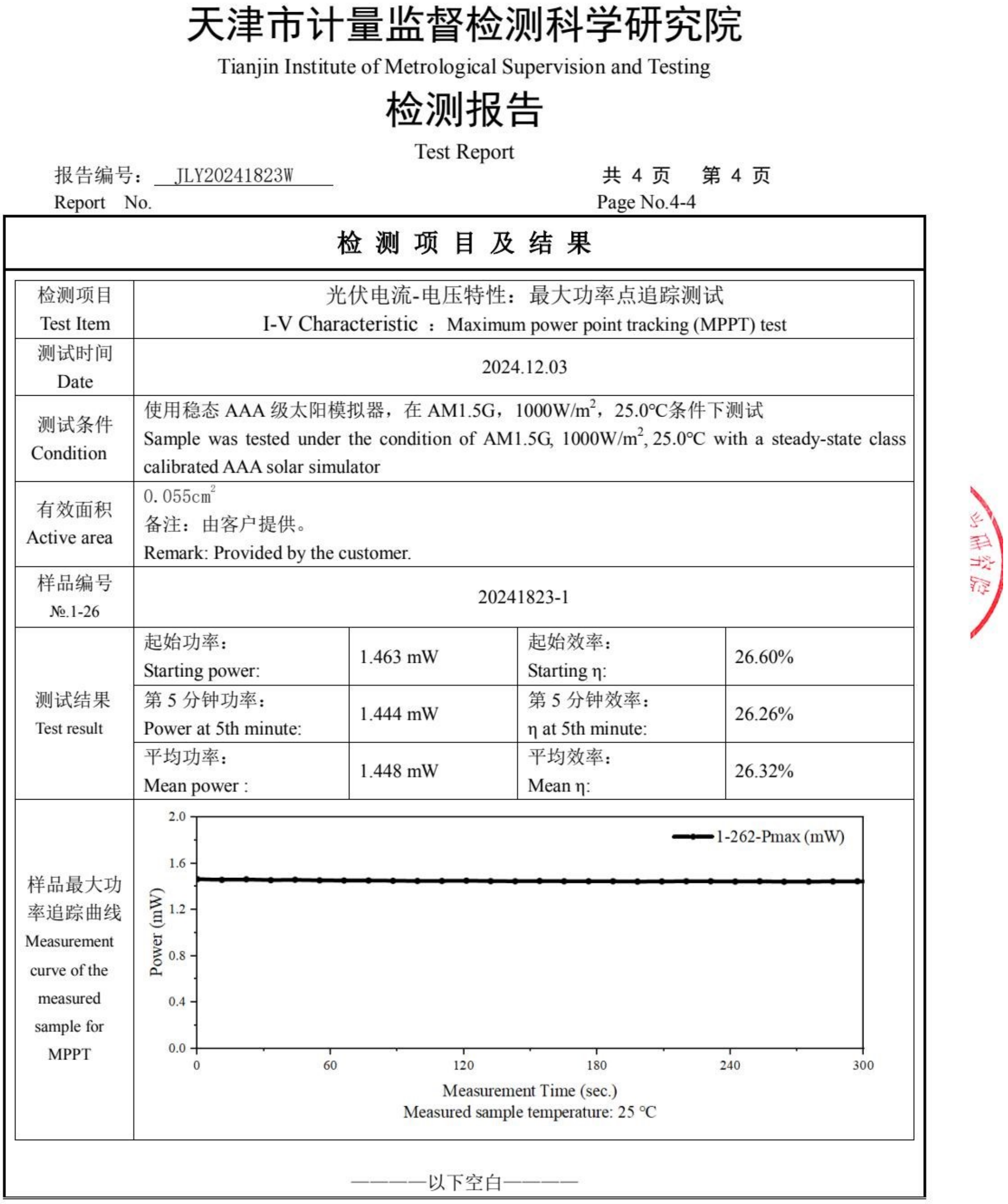
检测报告
Test Report

报告编号： JLY20241823W　　　　共 4 页　第 3 页
Report No.　　　　Page No.4-3

受检样品信息

样品编号 Sample Number	规格型号 Sample Type	产品编号 Product No.	产品序列号 Serial Number
20241823-1	HEBUT-PSCs-1129	#202411-1-262-P_{max}	—

Fig. S13. PSCs certification report, Page #3.



天津市计量监督检测科学研究院
Tianjin Institute of Metrological Supervision and Testing

检测报告
Test Report

报告编号：JLY20241823W　　　　共 4 页　第 4 页
Report No.　　　　Page No.4-4

检 测 项 目 及 结 果

检测项目 Test Item	光伏电流-电压特性：最大功率点追踪测试 I-V Characteristic ：Maximum power point tracking (MPPT) test			
测试时间 Date	2024.12.03			
测试条件 Condition	使用稳态 AAA 级太阳模拟器，在 AM1.5G，1000W/m^2，25.0℃条件下测试 Sample was tested under the condition of AM1.5G, 1000W/m^2, 25.0°C with a steady-state class calibrated AAA solar simulator			
有效面积 Active area	0.055cm^2 备注：由客户提供。 Remark: Provided by the customer.			
样品编号 №.1-26	20241823-1			
测试结果 Test result	起始功率： Starting power:	1.463 mW	起始效率： Starting η:	26.60%
	第 5 分钟功率： Power at 5th minute:	1.444 mW	第 5 分钟效率： η at 5th minute:	26.26%
	平均功率： Mean power :	1.448 mW	平均效率： Mean η:	26.32%
样品最大功率追踪曲线 Measurement curve of the measured sample for MPPT				

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Fig. S14. PSCs certification report, Page #4.

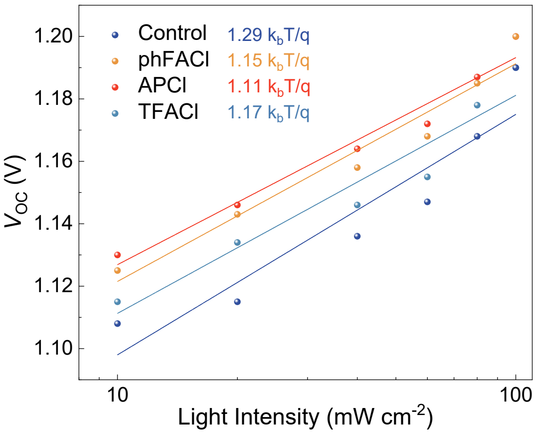

Fig. S15. V_{OC} as a function of light intensities for the control and phFACl, APCl and TFACl modulated PSCs.

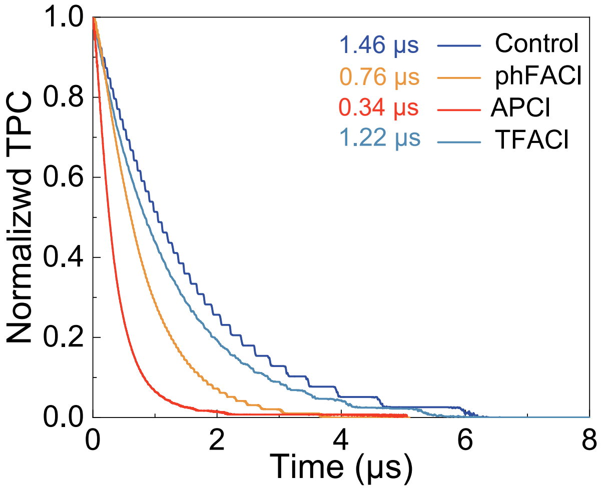

Fig. S16. TPC curves for the control and phFACl, APCl and TFACl-modulated devices.

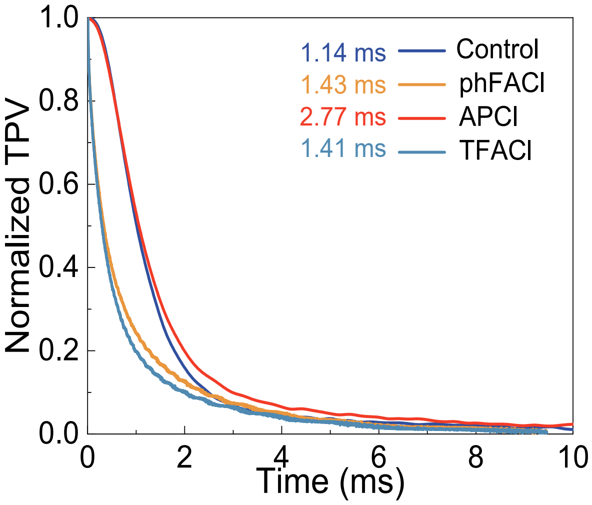

Fig. S17. TPV curves for the control and phFACl, APCl and TFACl-modulated devices.

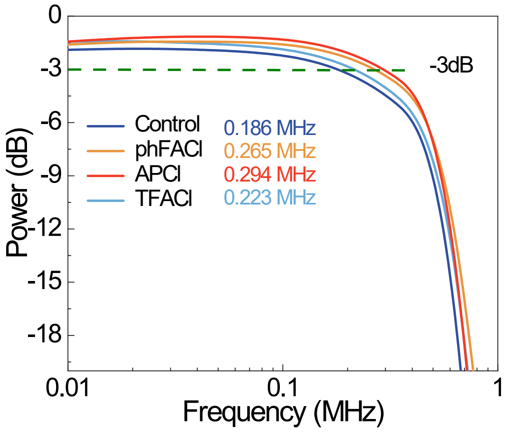

Fig. S18. The frequency response of the control and phFACl, APCl and TFACl-modulated devices.

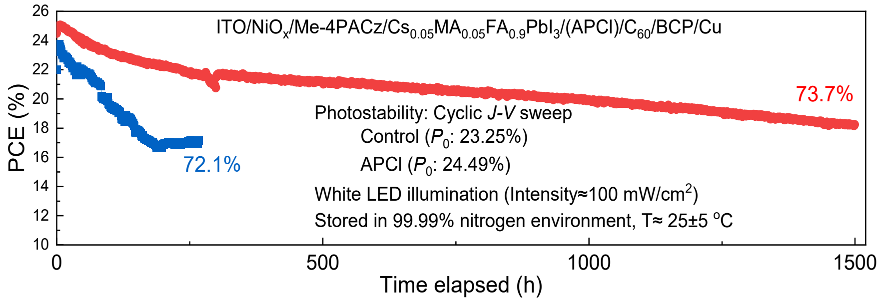

Fig. S19. PCE output changing from cyclic *J*-*V* scanning measurement of the control and APCl-modulated PSCs.

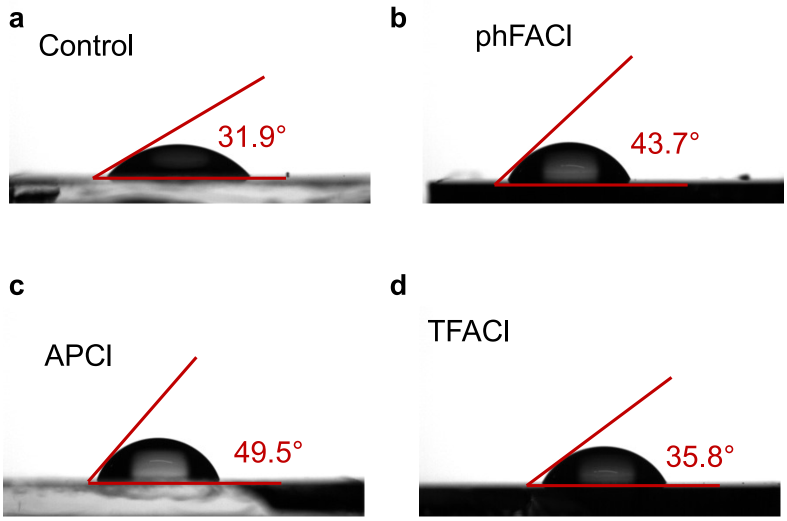

Fig. S20. The contact angle of the control, phFACl, APCl, and TFACl-modified perovskite films.

Table S1. Fitting data of TRPL curves in **Fig. 4d** based on double exponential function.

Condition	τ_1 (μs)	A_1 (%)	τ_2 (μs)	A_2 (%)	τ_{avg} (μs)
Control	0.30	63.17	1.26	36.83	0.99
phFACl	0.28	53.36	2.17	46.64	1.93
APCl	0.26	13.78	2.09	86.22	2.05
TFACl	0.08	13.76	1.77	86.24	1.76

Table S2. Photovoltaic parameters of the champion control and phFACl, APCl, and TFACl modulated devices.

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)	HI (%）
Control RS	1.165	26.04	82.45	25.02	4.0
Control FS	1.165	25.90	79.66	24.02	
phFACl RS	1.191	26.01	82.90	25.68	2.1
phFACl FS	1.187	26.01	81.43	25.14	
APCl RS	1.194	26.36	85.27	26.83	0.5
APCl FS	1.194	26.36	85.27	26.70	
TFACl RS	1.189	26.20	85.76	25.31	3.0
TFACl FS	1.175	26.03	80.28	24.55	

Table S3. Photovoltaic parameters of control and APCl modulated wide-bandgap devices.

	V_{OC} (V)	J_{SC} (mA cm^{-2})	FF (%)	PCE (%)
Control RS	1.235	21.70	76.09	20.40
Control FS	1.233	21.65	76.04	20.31
APCl RS	1.256	21.90	80.55	22.16
APCl FS	1.250	21.72	80.32	21.82