

Supplementary information

Incorporation of 2D pyreneammonium iodide for enhancing the efficiency and stability of perovskite solar cells

Zhongquan Wan^{1,2*}, Yuanxi Wang¹, Hui Lu², Runmin Wei², Haomiao Yin¹, Huaibiao Zeng², Muhammad Azam¹, Junsheng Luo^{1,2*}, Chunyang Jia^{1,2*}

¹National Key Laboratory of Electronic Films and Integrated Devices, School of Integrated Circuit Science and Engineering, University of Electronic Science and Technology of China, 611731 Chengdu, P. R. China

²Shenzhen Institute for Advanced Study, University of Electronic Science and Technology of China, 518110 Shenzhen, P. R. China

*Correspondence to: zqwan@uestc.edu.cn, luojs@uestc.edu.cn, cyjia@uestc.edu.cn

Materials

Ether, Hydroiodic acid, Dichloromethane and Hydrochloric acid were purchased from Chengdu Kelong Chemical Co., Ltd. Spiro-OMeTAD, tBP, Li-TFSI, PbBr₂, PbI₂, MAI and PEDOT: PSS were purchased from Xi'an Baolaite. Chlorobenzene, Acetonitrile, Dimethyl sulfoxide and N,N-Dimethylformamide were purchased from Sigma-Aldrich. FTO/TiO₂ electrode was purchased from Liaoning YouXuan Technology. Acetone and Ethanol were purchased from Aladdin Reagent. 1,3,6,8-tetra-(p-aminophenyl)-pyrene was purchased from Boehringer Ingelheim Pharmaceuticals. FAI was purchased from Greatcell Solar. All chemicals and solvents were obtained from commercial sources with certified purity and used as received without further purification.

Synthesis of TAPPyI

Dissolve 200 mg of 1,3,6,8-tetra-(p-aminophenyl)-pyrene (TAPPy) in 100 mL of dichloromethane, then add hydrogen iodide (45%, 1 mL) dropwise to the solution. After stirring at room temperature for 4 hours, centrifuge to obtain the precipitate, then wash three times with diethyl ether, and vacuum dry at 60 °C for 24 hours to obtain a black solid product. RMS (ESI, m/z): Calculated for C₄₀H₃₄I₄N₄, 1077.9;

obtained 1100.5 [M+Na]⁺. Elemental analysis: calcd, C 44.55, H 3.18, N 5.20. Found, C 44.62, H 3.26, N 5.24.

Solution Preparation

TAPPyI solution: 1 mg of TAPPyI is dissolved in 1 mL of DMF at room temperature, and then heated and stirred overnight at 60 °C on a magnetic stirrer. The solution is filtered and diluted to concentrations of 0.25 mg/mL, 0.50 mg/mL, and 0.75 mg/mL, respectively.

Perovskite precursor solution: FAI (190.12 mg), MABr (21.84 mg), PbI₂ (548.6 mg), and PbBr₂ (77.07 mg) are sequentially weighed and placed in a reagent bottle. Then, 800 µL of N,N-dimethylformamide (DMF) and 200 µL of dimethyl sulfoxide (DMSO) are added and stirred thoroughly. After that, 34 µL of CsI solution (103.92 mg CsI dissolved in 200 µL DMSO and stirred for 8 hours) is added and stirred overnight. For the experimental group, 1 mL of filtered perovskite precursor solution is taken, and 20 µL of TAPPyI solution is added, followed by stirring for more than 3 hours.

Spiro-OMeTAD solution: Dissolved 72.3 mg of Spiro-OMeTAD in 1 mL of chlorobenzene, then add 28.8 µL of tBP and 17.5 µL of Li-TFSI solution (104 mg of Li-TFSI in 200 µL of acetonitrile) and stirred constantly.

Device Fabrication

Preparation of FTO/TiO₂ electrode: The purchased FTO/TiO₂ electrode was heated at 200 °C on a hot plate for 30 minutes, followed by cleaning with nitrogen gas, and then treated with UV/O₃ for 30 minutes to remove residual hydroxyl groups from the surface.

Preparation of perovskite layer: The perovskite layer was deposited on the treated FTO/TiO₂ electrode by spin-coating filtered perovskite precursor at speeds of 1300 rpm and 4500 rpm for 10 and 45 seconds, respectively. During the last 15 seconds of the latter process, 200 µL of chlorobenzene is rapidly added as an anti-solvent to the center of the film. After spin-coating, the substrate is quickly moved to a hot plate at 110 °C and annealed for 60 minutes.

Preparation of hole transport layer (HTL): The Spiro-OMeTAD solution is spin-

coated dynamically onto the perovskite layer at a speed of 3000 rpm for 30 seconds.

Deposition of gold (Au) electrode: Gold electrode was patterned on the hole transport layer using a vacuum deposition system, completing the fabrication of the entire unencapsulated device. After patterning, the effective area of each device is 0.09 cm².

Characterizations

The surface/cross-sectional morphology of the perovskite film was examined using scanning electron microscopy (SEM) with a JEOL JSM-7600F instrument. Atomic force microscopy (AFM) was utilized to analyze the surface morphology of the film using a Bruker Dimension Icon AFM instrument. UV-visible absorption spectra were acquired using a UV-visible spectrophotometer (Hitachi U-2910). X-ray diffraction (XRD) patterns were obtained with a Rigaku Ultima IV instrument. The water contact angle of the film was determined using a contact angle analyzer (Krüss DSA100). Steady-state photoluminescence (PL) spectra were measured using a Hitachi F-4600 spectrophotometer, while transient photoluminescence (TRPL) spectra were recorded using time-correlated single-photon counting (TCSPC) technique with a modular fluorometer (HORIBA FluoroLog-3). Electrochemical impedance spectroscopy (EIS) and *J-V* curves were obtained in air using an electrochemical workstation (CHI 760E, Shanghai Chenhua) and a solar simulator (Sirius-SS150A-D, Beijing Zolix), respectively, with the incident light intensity calibrated using a standard silicon solar cell. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha instrument. Incident photon-to-electron conversion efficiency (IPCE) spectra were measured using a CROWNTECH, QTest Station 2000 IPCE testing system.

Theoretical calculations

The geometric optimization calculations of relevant molecules were completed using the Materials Studio program, employing the B3LYP/6-311++ G(d, p) basis set. Geometric optimization calculations related to perovskite were conducted using the Dmol3 program with the GGA-PBE functional. Van der Waals interactions were described using DFT-D. Calculations concerning electronic properties utilized the

CASTEP program package, with parameters set to match those in the Dmol3 program. To simplify the calculations, a MAPbBr₃ perovskite (001) surface was simulated to represent the defective states on the perovskite surface, with a vacuum layer thickness of 20 Å and a cutoff energy of 600 eV.

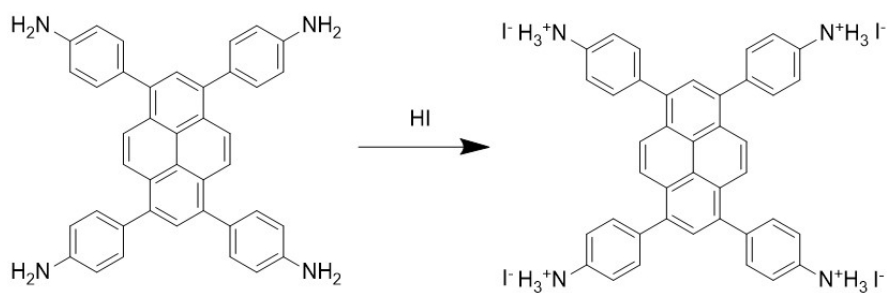


Figure S1. Synthetic routes of TAPPyI.

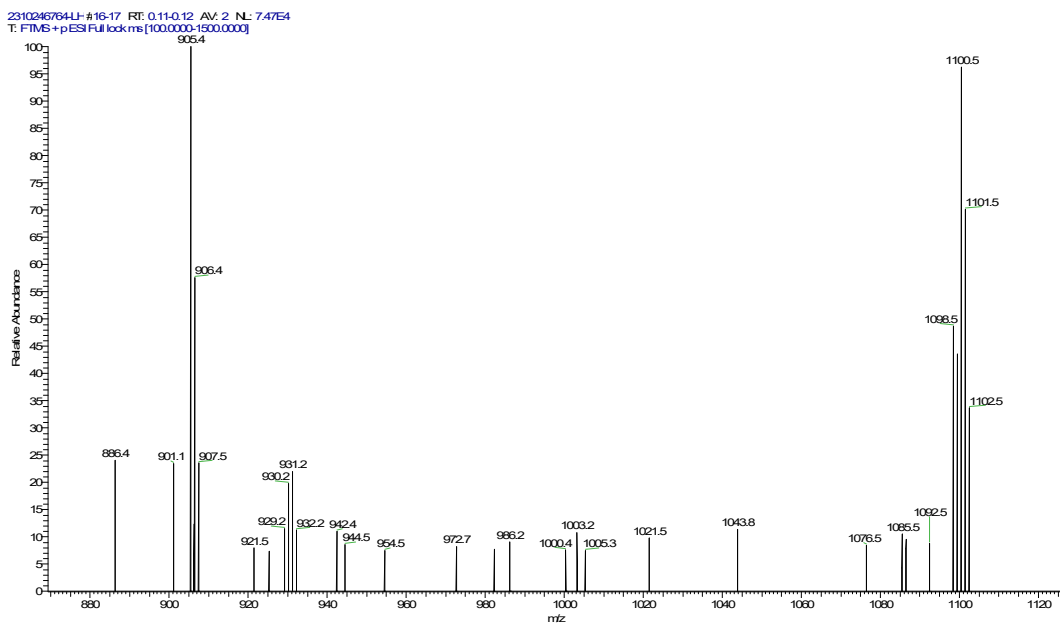


Figure S2. Mass spectrum of TAPPyI.

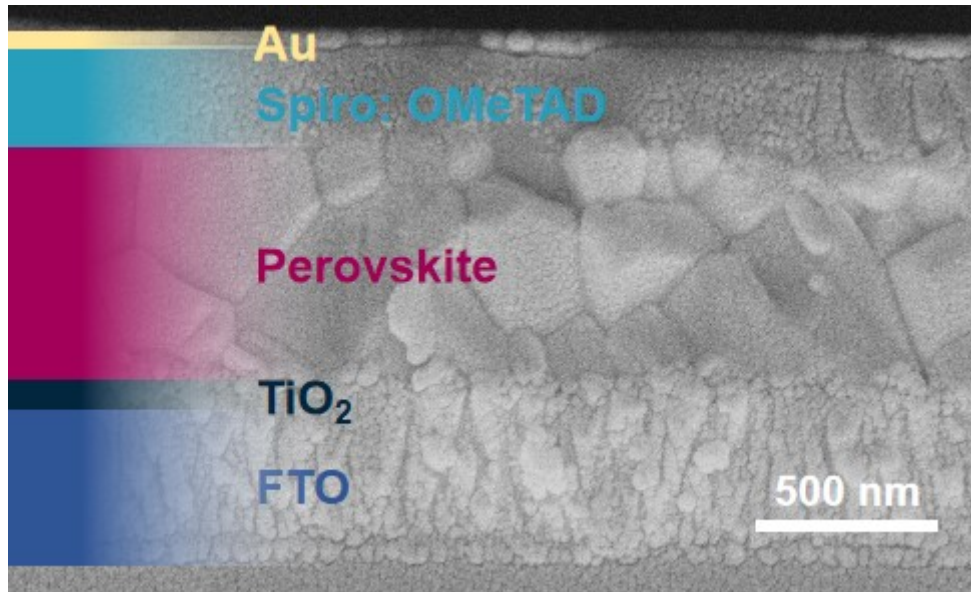


Figure S3. Cross-sectional SEM image of the reference PSC.

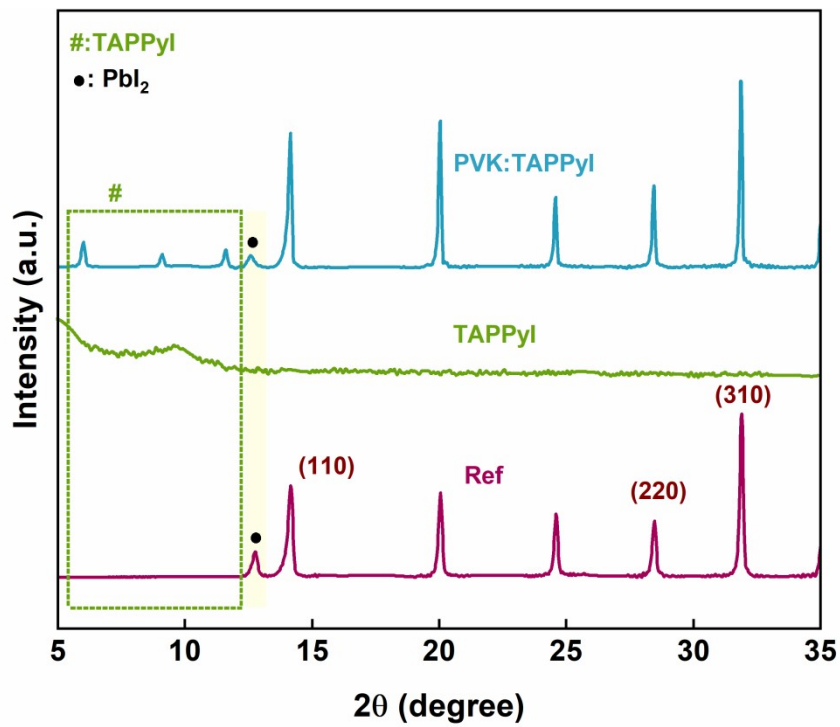


Figure S4. XRD patterns of the perovskite films before and after 0.5mg/mL TAPPyI modification.

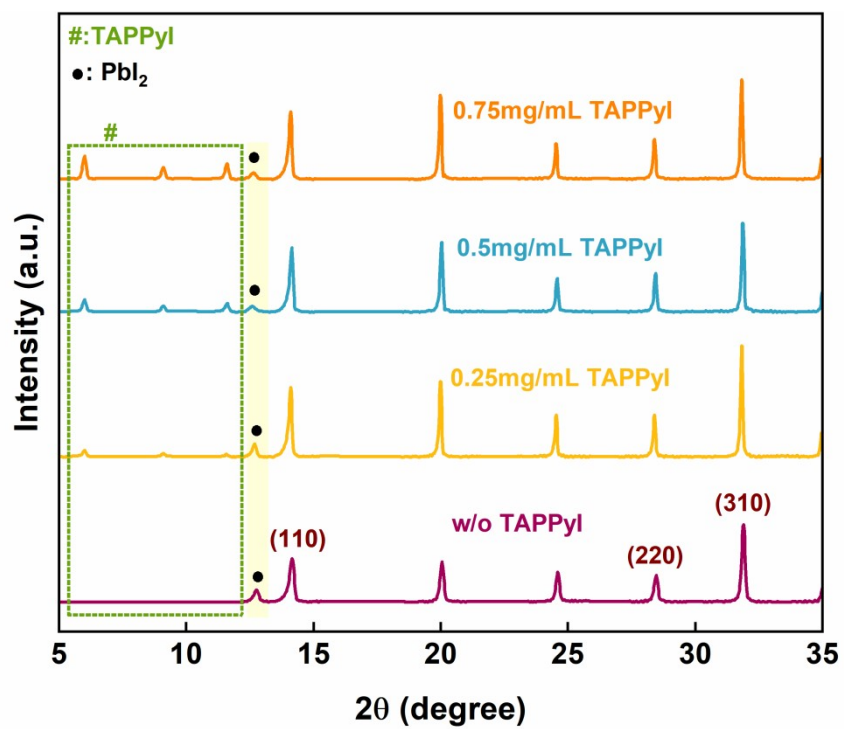


Figure S5. XRD patterns of the perovskite films with different concentrations of TAPPyl.

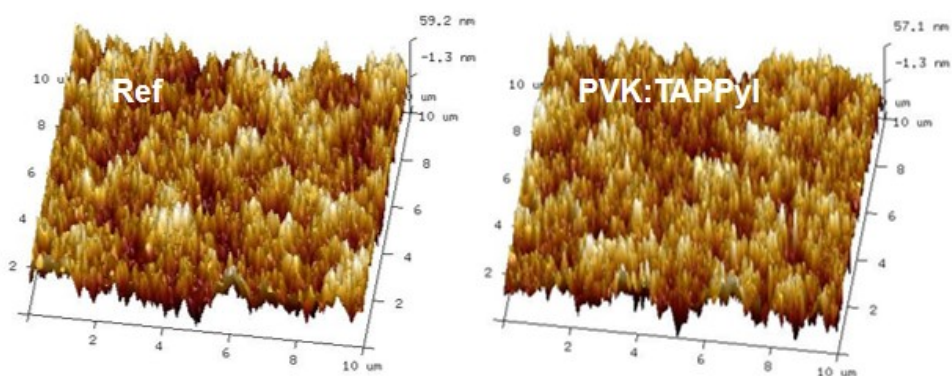


Figure S6. 3D AFM images of the surface of the perovskite films before and after modification.

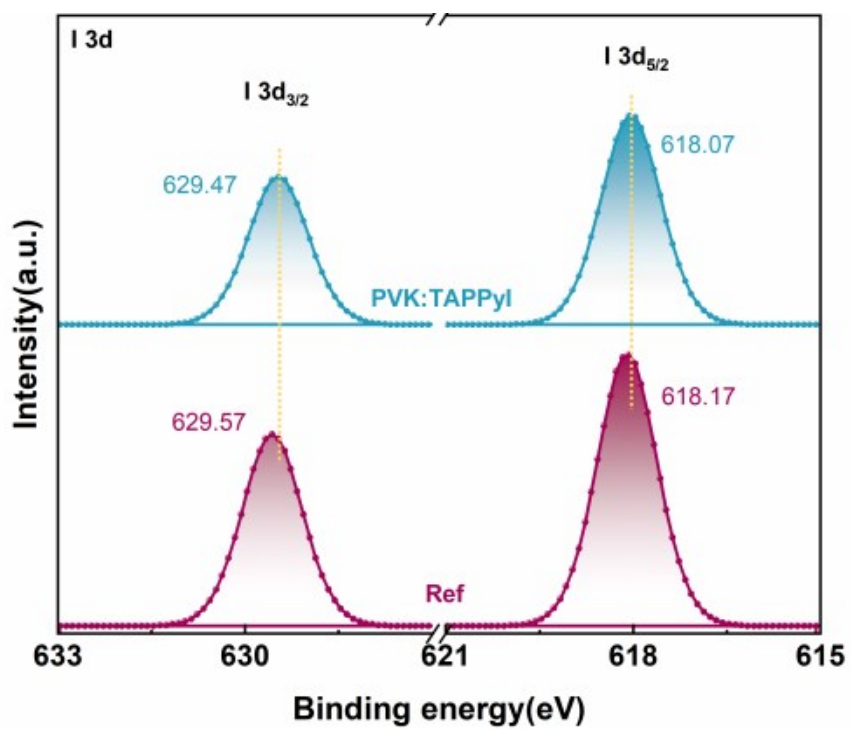


Figure S7. The high-resolution XPS spectra of I 3d.

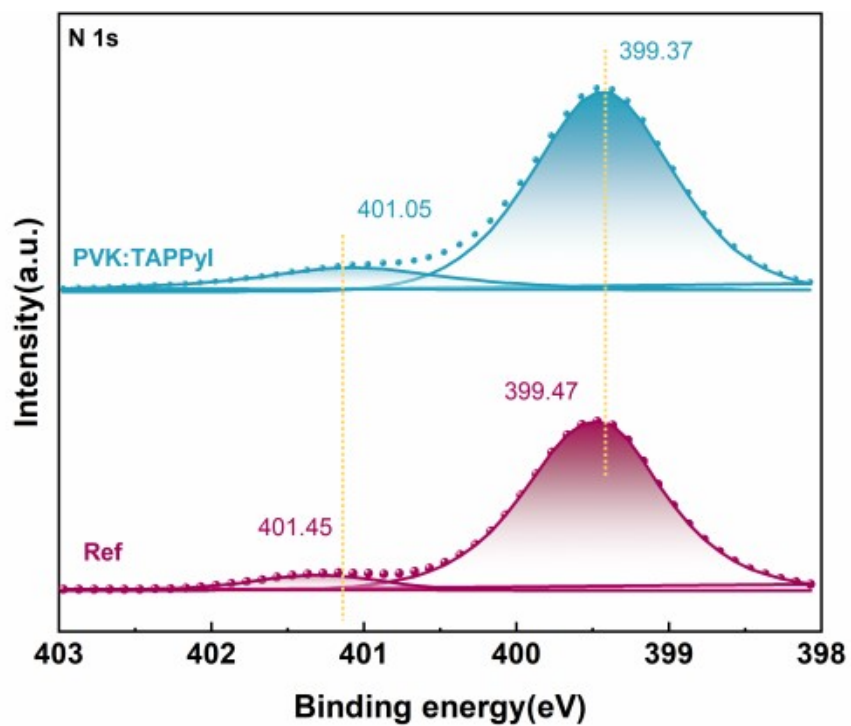


Figure S8. The high-resolution XPS spectra of N 1s.

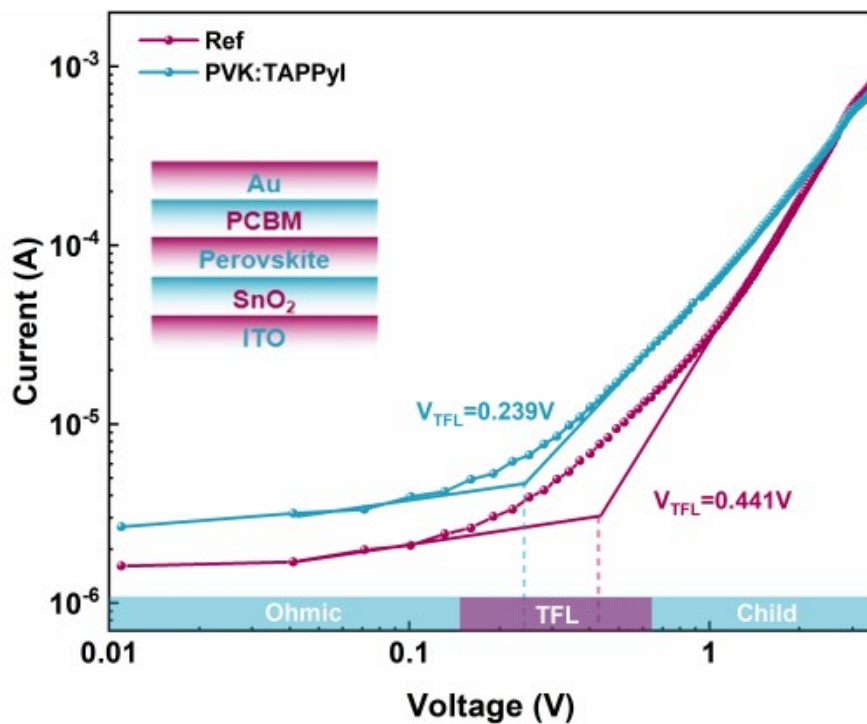


Figure S9. SCLC measurement of defect density in electron-only devices before and after modification.

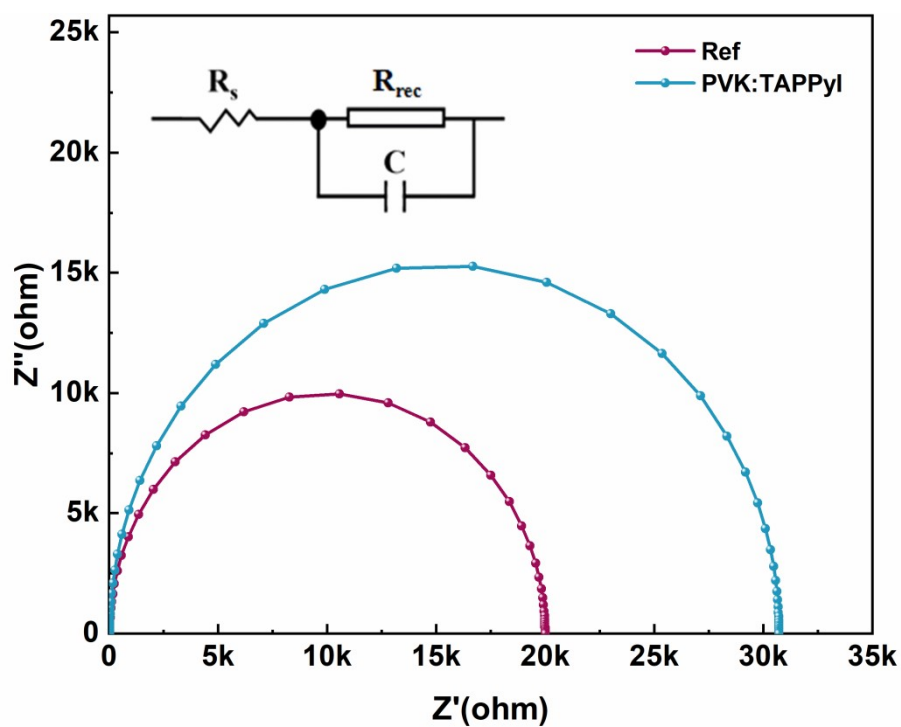


Figure S10. EIS spectra of devices before and after modification under dark conditions.

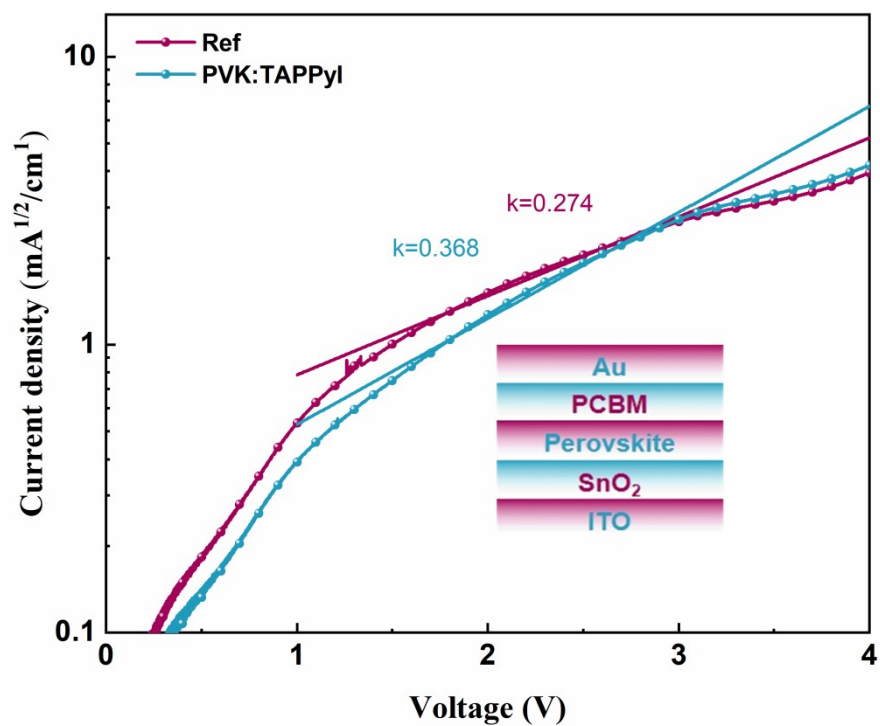


Figure S11. SCLC method for measuring electron mobility before and after modification.



Figure S12. Surface images of the perovskite films before modification (left) and after modification (right) taken 5 seconds after dropping a water droplet simultaneously.

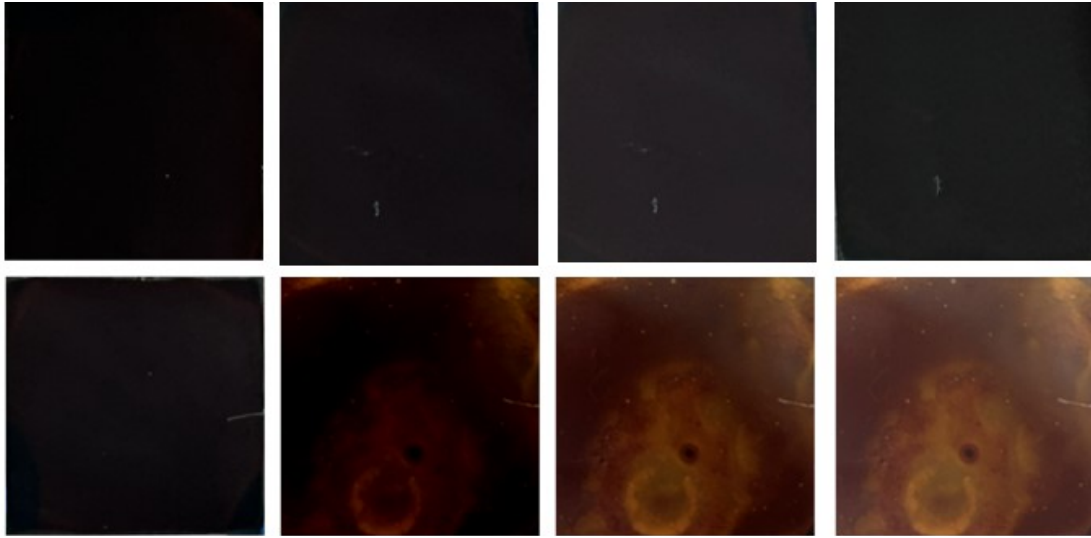


Figure S13. Surface images of the perovskite films before modification (bottom) and after modification (top) under 85°C and N₂ conditions for 360 hours.

Table S1. Bi-exponential decay function parameters fitted on FTO/PVK substrates

Substrate	A ₁	τ ₁ (ns)	A ₂	τ ₂ (ns)	τ _{ave} (ns) ^a
Ref	0.621	7.573	0.508	88.916	81.2
PVK:TAPPyI	0.677	8.706	0.425	259.610	246.9

^aThe formula for calculating the average lifetime is given in formula (2).

Table S2. Photovoltaic parameters of TAPPyI-modified perovskite solar cells

Sample	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	PCE (%)
W/O TAPPyI	1.143	24.32	0.738	20.51
0.25 mg/mL TAPPyI	1.159	24.46	0.761	21.50
0.50 mg/mL TAPPyI	1.194	24.63	0.773	22.73
0.75 mg/mL TAPPyI	1.173	24.44	0.741	21.25