Supporting Information

Environmentally Friendly Anti-Solvent Engineering for High-Efficiency Tin-based Perovskite Solar Cells

Yang Su, Jia Yang, Huan Rao, Yang Zhong, Wangping Sheng, Licheng Tan, Yiwang Chen**

Y. Su, J. Yang, H. Rao, Y. Zhong, W. Sheng, L. Tan, Y. Chen

College of Chemistry and Chemical Engineering/Institute of Polymers and Energy Chemistry (IPEC), Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Prof. Y. Chen

National Engineering Research Center for Carbohydrate Synthesis/Key Lab of Fluorine and Silicon for Energy Materials and Chemistry of Ministry of Education, Jiangxi Normal University, 99 Ziyang Avenue, Nanchang 330022, China

Prof. L. Tan, Prof. Y. Chen

Peking University Yangtze Delta Institute of Optoelectronics, 60 Chongzhou Avenue, Nantong 226010, China

E-mail: ywchen@ncu.edu.cn (Y. Chen); tanlicheng@ncu.edu.cn (L. Tan)

Experimental Section

Materials:

Formamidinium iodide (FAI, 99.9%), phenethylammoniumiodide (PEAI), tin(II) iodide (SnI_2, 99.99%), tin(II) fluoride (SnF_2, 99%), Sn powder, N,N-dimethylformamide (DMF) (99.8%), dimethyl sulfoxide (DMSO) (99.9%), bathocuproine (BCP, 99%), and chlorobenzene (CB, 99.8%) were purchased from Sigma-Aldrich. Ethylammonium iodide (EAI, 98%) and ethylenediamine dihydroiodide ($EDAI_2$, 98%) were purchased from Tokyo Chemical Industry Co., Ltd.. Formic acid (AC, 99.9%), Acetic acid (HAc, >99.7%) and propionic acid (PA, >99.9%) were purchased from aladdin. ICBA were purchased from 1-Material. Ag (99.99%), [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) and poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, Clevios VP AI 4083) were acquired from Xi'an Polymer Light Technology Corp.

Solution Preparation:

The $PEA_{0.15}FA_{0.85}SnI_3$ precursor solution was prepared by dissolving 0.85 mM FAI, 0.15 mM PEAI, 1 mM SnI_2, 0.1 mM SnF_2 and 0.1 mM Sn powder in a mixed solvent of 1000 μL of DMF and 250 μL of DMSO. The $(FA_{0.9}EA_{0.1})_{0.98}EDA_{0.01}SnI_3$ precursor solution was prepared by dissolving 0.882 mM FAI, 0.098 mM EAI, 0.01 mM $EDAI_2$, 1 mM SnI_2, 0.1 mM SnF_2 and 0.1 mM Sn powder in a mixed solvent of 1000 μL of DMF and 250 μL of DMSO. The ICBA or $PC_{61}BM$ solution was prepared by dissolving 20 mg $PC_{61}BM$ in 1000 μL CB. The BCP solution was prepared by dissolving 0.5 mg BCP in isopropanol.

Device Fabrication:

The cleaned ITO-coated glasses were placed under UV ozone treatment for 10 min. PEDOT:PSS aqueous solution was spin-coated on ITO substrates at 6000 rpm for 60 s and then annealed at 140 °C for 20 min in air. The precursor was spin-coated at 1000 rpm and 5000 rpm for 10s and 30s, respectively. And 150μL CB was dropped during the second process at 8th second, while the 150μL HAc was dropped during the second process at 22th second. Then, the films were annealed on a hot stage at 70 °C for 15 min. Noted that the precursor solutions, CB and HAc were cooled to close to 18 ℃ before use. Next, ICBA or $PC_{61}BM$ solution was deposited (2000 rpm/30 s) on top and then annealed at 70 °C for 10 min. BCP solution was spin-coated at 4500 rpm for 1 min, followed by annealing at 70 °C for 10 min. Finally,100 nm-thick Ag was deposited on BCP. PEDOT:PSS and precursor solutions need to be filtered before use.

Preparation and detection of SnI_2:

Add appropriate amount of $SnAc_2$ into concentrated hydrochloric acid solution and stir until the solution produces a yellow solid substance. Then, the yellow solid substance is transferred to a glass plate and dried at 50℃. Finally, the solid products are analyzed by XRD.

Characterization of Perovskite Films and Devices:

Then film morphology images were analyzed by scanning electron microscopy (SEM) (JSM-6701F, JEOL Ltd., Japan). Glancing incident angle X-ray diffraction (GIXRD) and X-ray diffraction were performed on a D8-discover 25 diffractometer (Bruker). The photoluminescence (PL) and time-resolved photoluminescence (TRPL) spectra were investigated by the NTAS-TCSPC Fluorescence Lifetime System (HORIBA Scientific).

Ultraviolet-Vis (UV-Vis) measurement was performed on a UV-2600 (SHIMADZU) spectrophotometer. The digital source meter (Keithley 2400) was used to obtain the current density-voltage (*J-V*) and space-charge-limited current (SCLC) data under 100 mW cm^{-2} illumination AM 1.5G irradiation (Enli Tech) via using the QE-R systems (Enli Tech). X-ray photoelectron spectroscopy (XPS) measurement was performed in an ESCALAB 250Xi, Thermo Fisher (by using Al Kα X-ray source) under high vacuum (10-9 mbar). The electrochemical impedance spectra (EIS) of all devices were measured with Zahner electrochemical workstation. The ^{1}H NMR spectra were recorded in deuterated solvents on a Bruker ADVANCE 400 NMR Spectrometer.

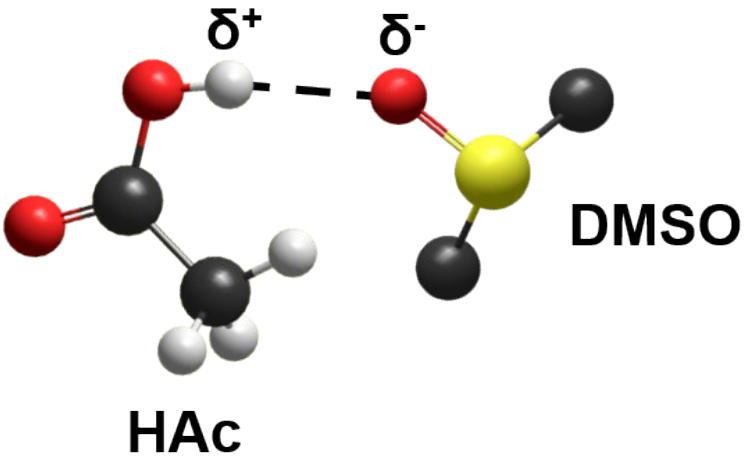

Figure S1. Schematic diagram of hydrogen bonding between DMSO and HAc.

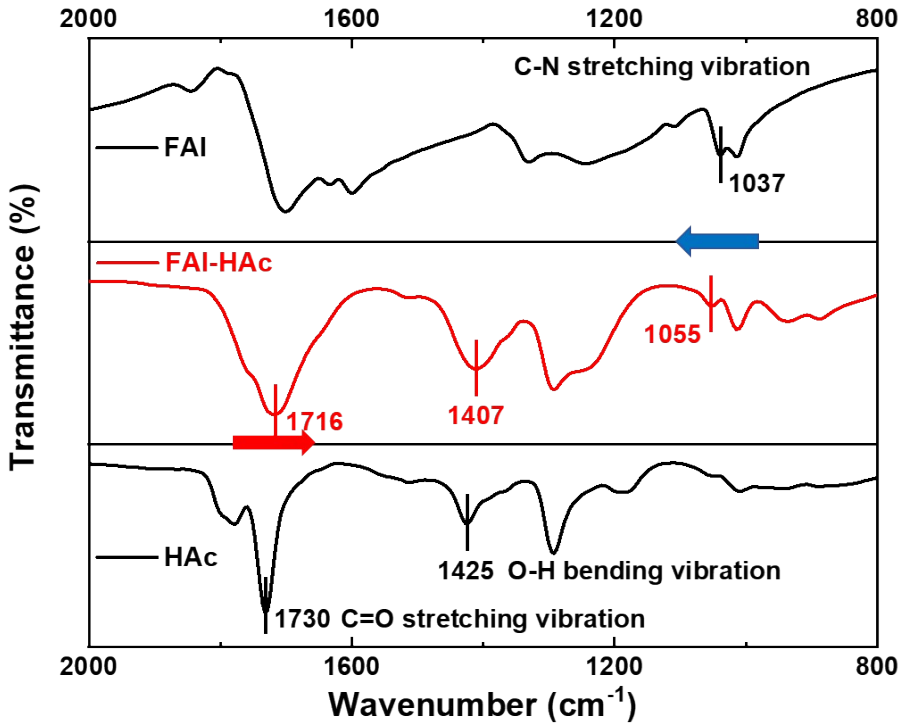

Figure S2. Fourier transform infrared (FTIR) spectroscopy spectra of HAc, HAc-FAI and FAI.

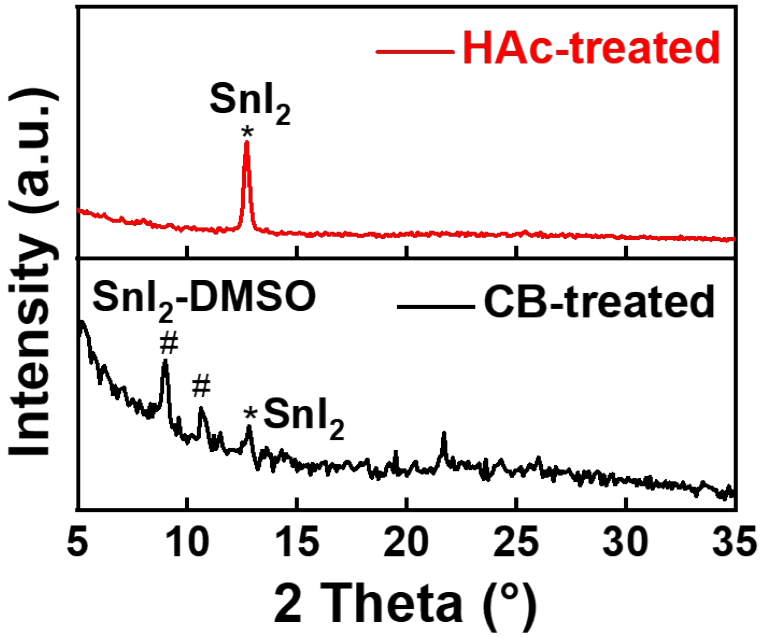

Figure S3. XRD patterns of SnI_2 films prepared by CB and HAc.

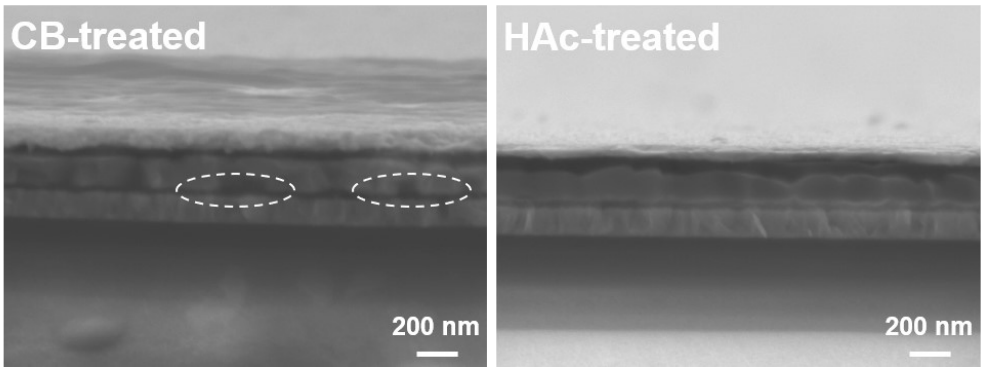

Figure S4. Cross-sectional SEM images of typical devices prepared by CB and HAc.

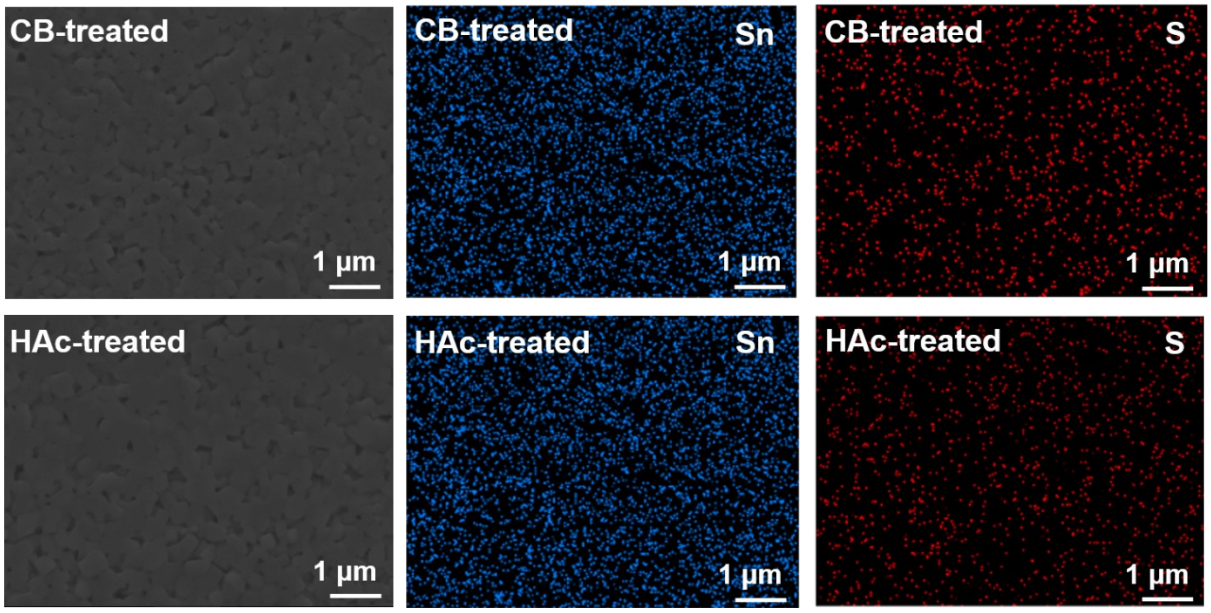

Figure S5. SEM image of perovskite films prepared by CB and HAc and corresponding EDS distribution of Sn and S.

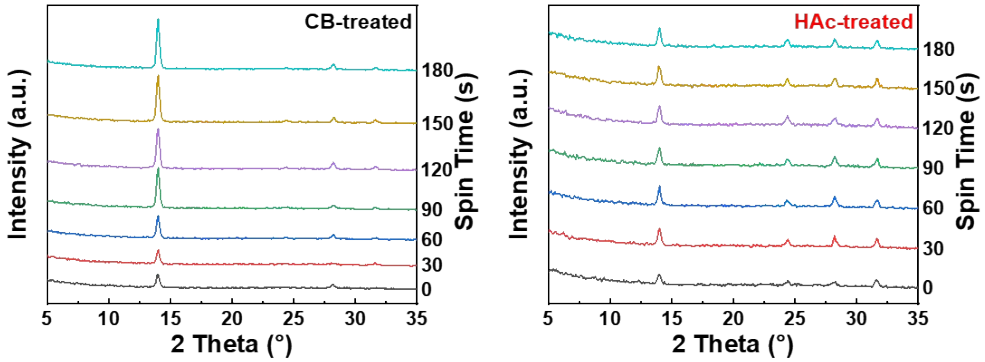

Figure S6. XRD patterns of perovskite films prepared by CB and HAc with different spin times.

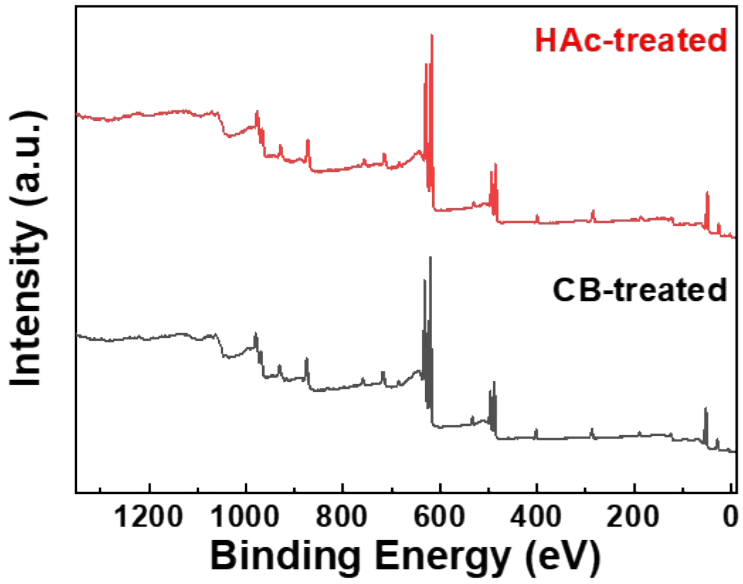

Figure S7. XPS spectrum of perovskite films prepared by CB and HAc.

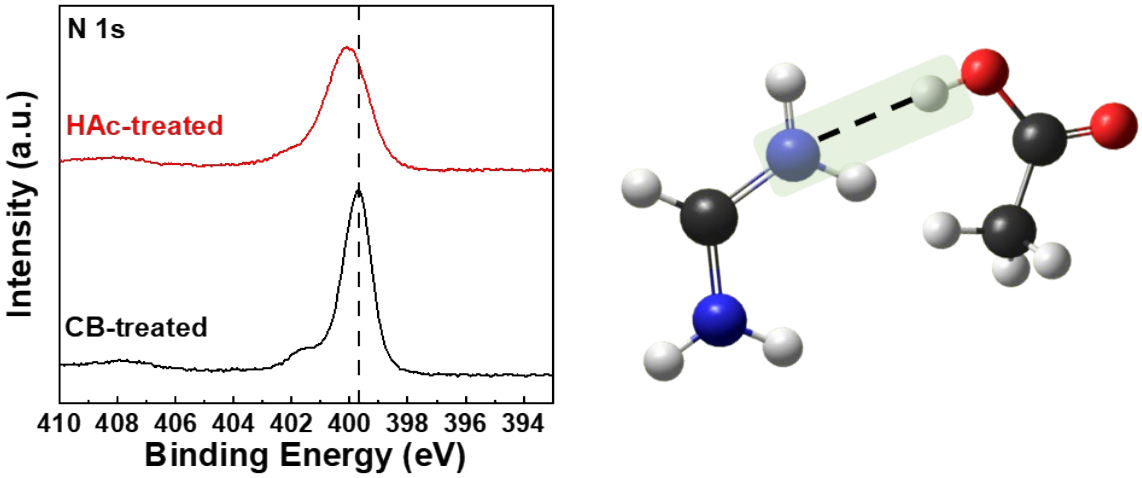

Figure S8. XPS spectra N 1s of perovskite films prepared by CB and HAc and the corresponding schematic diagram of hydrogen bonding between FA^+ and HAc.

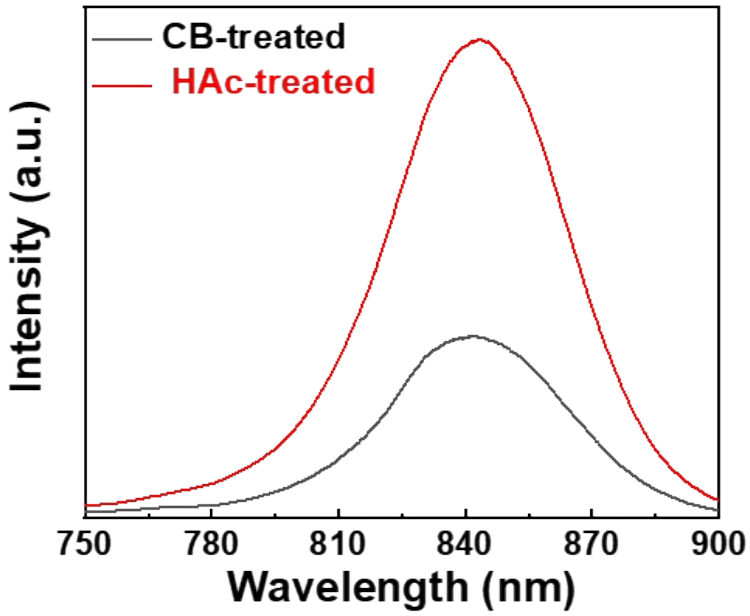

Figure S9. Steady-state PL spectra of perovskite films prepared by CB and HAc.

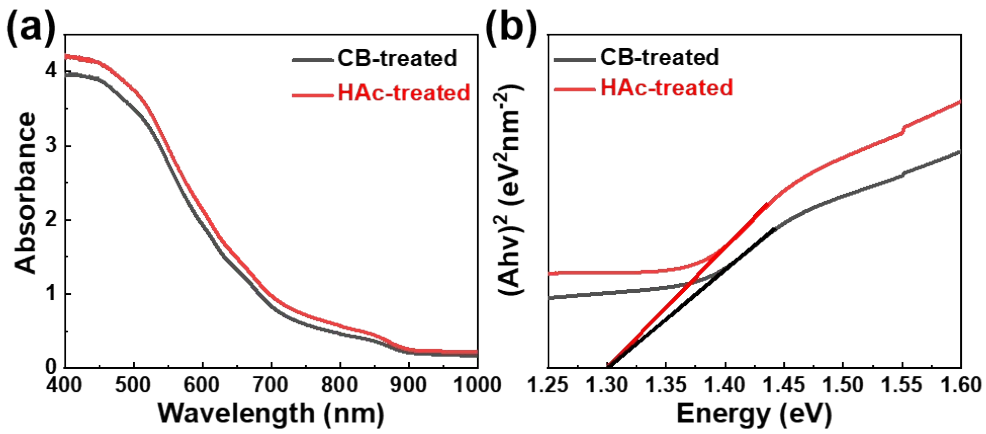

Figure S10. (a) UV-vis absorption spectra and (b) Tauc plots of perovskite films prepared by CB and HAc.

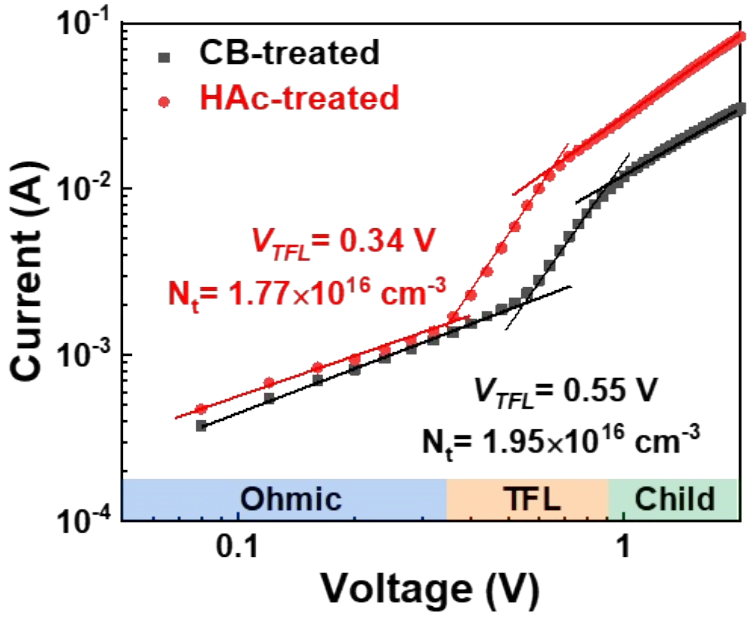

Figure S11. Dark *J-V* curves of the hole-only device with the structure of ITO/PEDOT:PSS/perovskite prepared by CB and HAc/spiro-OMeTAD/Ag based on the space-charge-limited-current (SCLC) model.

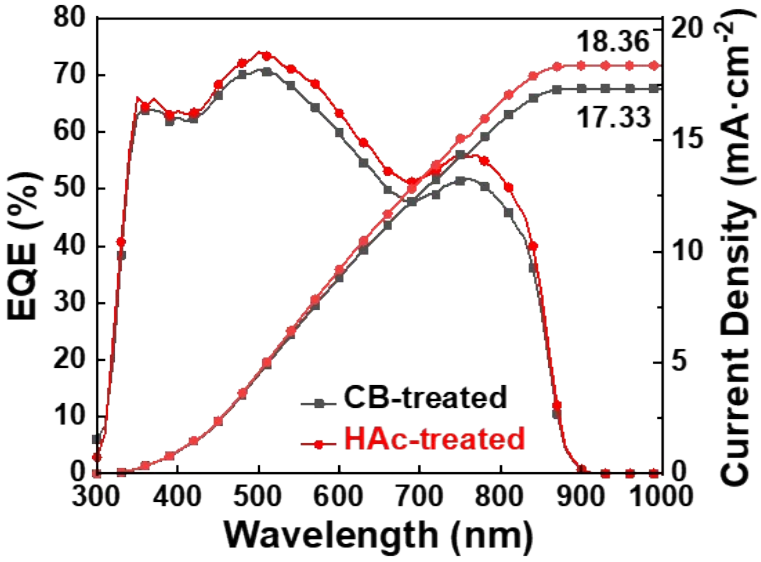

Figure S12. EQE spectra and integrated J_{sc} values for CB-treated and HAc-treated devices, respectively.

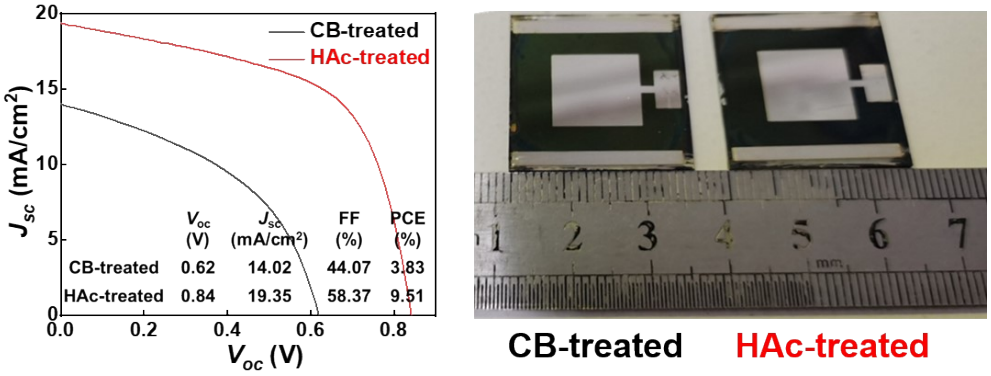

Figure S13. Current density-voltage (J-V) curves and optical photograph of large area devices (1 cm^2) fabricated by CB and HAc.

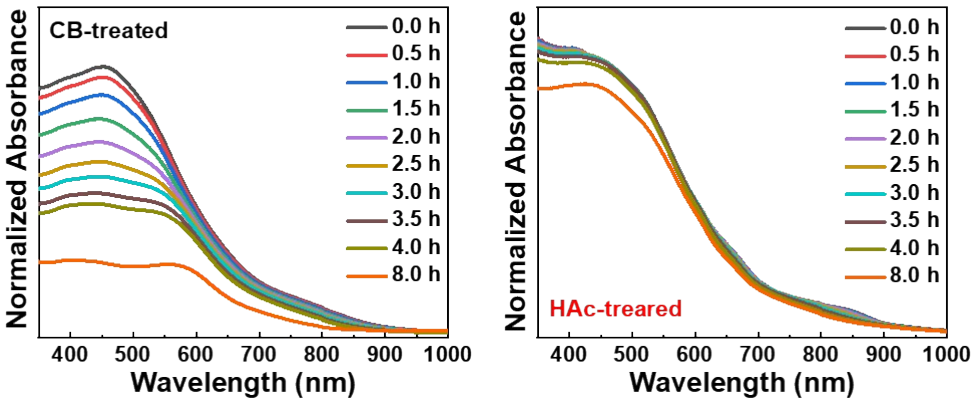

Figure S14. UV-vis absorption spectra of unencapsulated perovskite films prepared by CB and HAc in atmosphere.

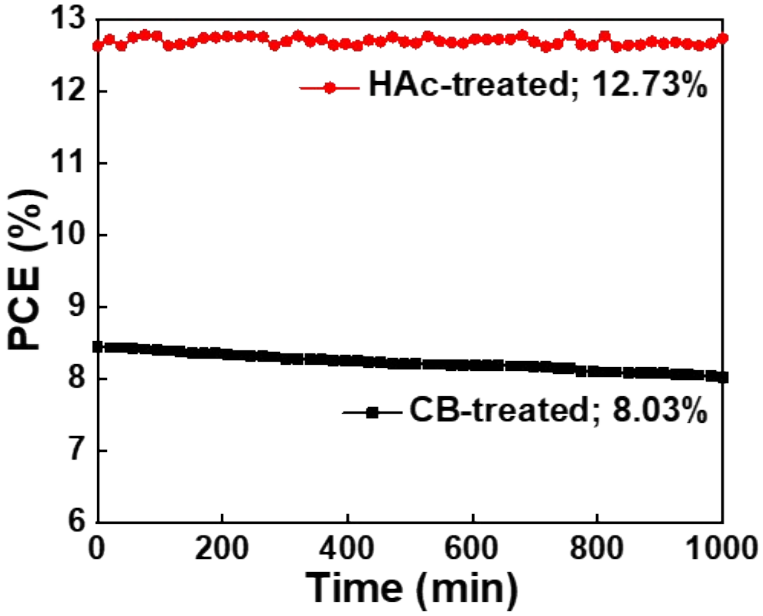

Figure S15. 1000-min continuous output of the devices measured under the maximum power point (MPPT).

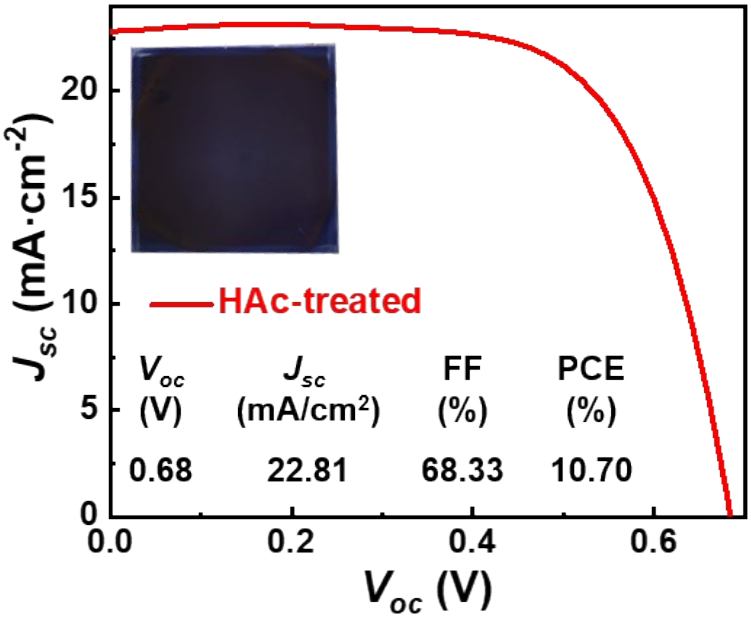

Figure S16. Current density-voltage (*J-V*) curves of the best device (active layer: $(FA_{0.9}EA_{0.1})_{0.98}EDA_{0.01}SnI_3$) prepared by HAc.

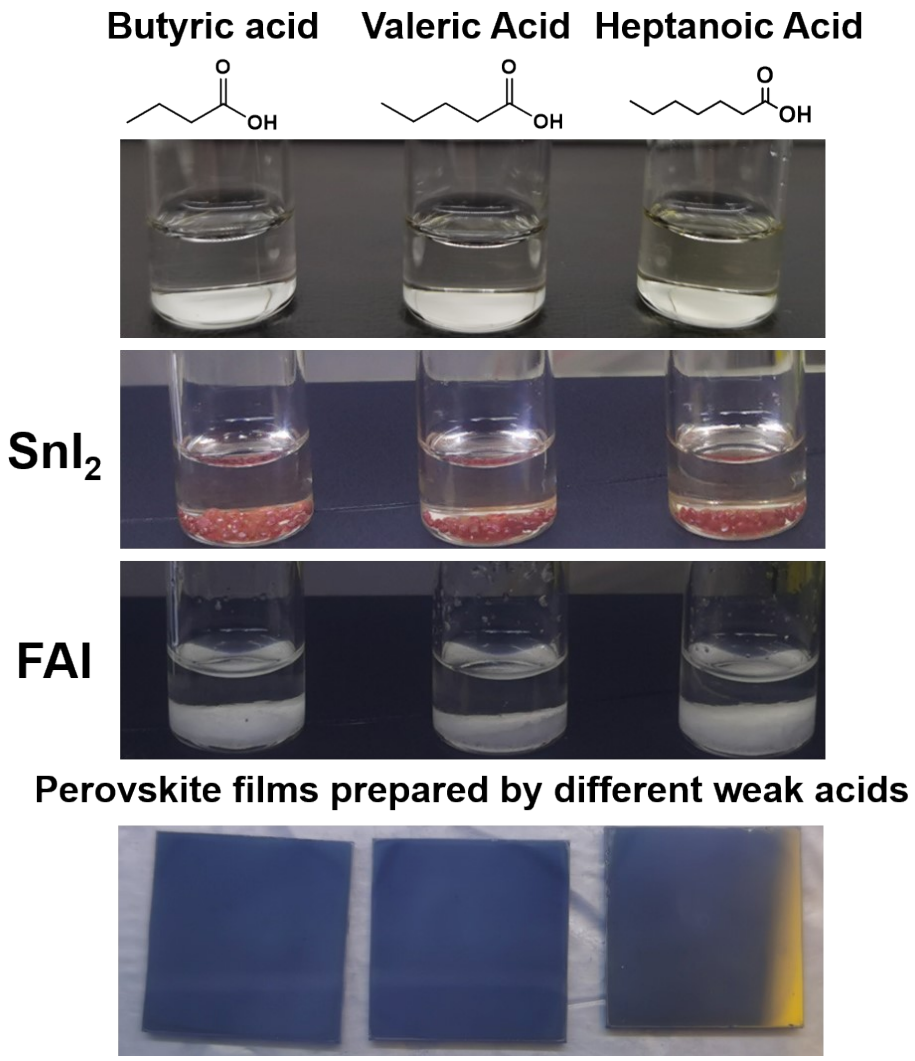

Figure S17. Optical photographs of the perovskite compositions in different weak acids and perovskite film prepared by different weak acids.

Table S1. Contents of S and Sn in chlorobenzene and acetic acid-treated perovskite films characterized by EDS.

element	CB-treated (%)	HAc-treated (%)
S	1.88	0.32
Sn	98.12	99.68

Table S2. Summary of the related works on mixed cationic system (PEA^+ and FA^+).

Perovskite layer	Strategy	Anti-solvents	PCE (%)	Ref.
$PEA_{0.15}FA_{0.85}SnI_3$	$C_{60}Cl_6$	CB	13.3	1
$PEA_{0.15}FA_{0.85}SnI_3$	NH_4SCN	HAc	12.65	This paper
$PEA_{0.15}FA_{0.85}SnI_3$	ICBA	CB	12.4	2
$PEA_{0.1}FA_{0.1}SnI_3$	TU	CB	10.9	3
$PEA_{0.15}FA_{0.85}SnI_3$	NH_4SCN	CB	9.41	4
$PEA_2FA_{n-1}SnnI_{3n+1}$	2D/3D heterojunctions	CB	9.0	5

References

[1] J. Chen, C. Tian, C. Sun, P. Yang, W. Feng, L. Zheng, L. Yang, E. Hou, J. Luo, L. Xie, *Energy Environ. Sci.* **2022**, e12529.

[2] X. Jiang, F. Wang, Q. Wei, H. Li, Y. Shang, W. Zhou, C. Wang, P. Cheng, Q. Chen, L. Chen, *Nat. Commun.* **2020**, 11, 1.

[3] C. Zheng, P. Qiu, S. Zhong, X. Luo, S. Wu, Q. Wang, J. Gao, X. Lu, X. Gao, L. Shui, S. Wu, J.-M. Liu, *Adv. Funct. Mater.* **2023**, 2212106.

[4] F. Wang, X. Y. Jiang, H. Chen, Y. Q. Shang, H. F. Liu, J. L. Wei, W. J. Zhou, H. L. He, W. M. Liu, Z. J. Ning, *Joule* **2018**, 2, 2732-2743.

[5] S. Shao, J. Liu, G. Portale, H. H. Fang, G. R. Blake, G. H. ten Brink, L. J. A. Koster, M. A. Loi, *Adv. Energy Mater.* **2018**, 8, 1702019.

Table S3. The photovoltaic parameters of PVSCs prepared by green anti-solvents.

Anti-solvents	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)	Ref.
HAc	0.91	18.38	75.83	12.65	this paper
Ethyl ether	0.47	22.07	60.67	6.22	1
Ethyl ether	0.49	23.7	55.3	6.39	2
Ethyl ether	0.53	24.1	71	9.0	3

References

[1] W. Q. Liao, D. W. Zhao, Y. Yu, C. Grice, C. L. Wang, A. J. Cimaroli, P. Schulz, W. W. Meng, K. Zhu, R. G. Xiong, Y. F. Yan, *Adv. Mater.*, **2016**, 28, 9333-9340.

[2] X. H. Liu, K. Yan, D. W. Tan, X. Liang, H. M. Zhang, W. Huang, *ACS Energy Lett.*, **2018**, 3, 11, 2701-2707.

[3] S. Y. Shao, J. Liu, G. Portale, H-H. Fang, G. B. Blake, G. Brink, L. J. A. Koster, M. A. Loi, *Adv. Energy Mater.*, **2017**, 8, 1702019.