Supporting Information

Surface passivation with an electron-donating sulfonate group for high-performance and stable perovskite solar cells

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Experimental Section

Materials: Tin oxide (SnO_2) colloidal dispersion (15% in H_2O colloidal dispersion) was purchased from Alfa Aesar. Lead iodide (PbI_2), cesium iodide (CsI), formamidinium iodide (FAI), methylammonium chloride (MACl), lithium bis(trifluoromethanesulfonyl)imide salt (LiTFSI), 4-tert-butylpyridine (tBP), and 2,2',7,7'-tetrakis(N,N-dipmethoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD) were purchased from Xi'an Polymer Light Technology Co., Ltd. 4-Aminophenyl sulfone (APS) was purchased from Adamas Reagent, Ltd. N, N-Dimethylformamide (DMF), dimethyl sulfoxide (DMSO), chlorobenzene (CB), acetonitrile (ACN), and isopropanol (IPA) were purchased from Sigma-Aldrich. All materials and solvents were used directly as received without further purification.

Device Fabrication: we used a two-step spin-coating method to fabricate solar cells. Firstly, SnO_2 colloidal dispersion was spin-coated on ITO at 4000 r.p.m. for 30 s after being treated with UV-Ozone for 15 min to eliminate organic impurities. The prepared ITO/SnO_2 was then annealed at 150 °C for 30 min. Subsequently, a 50 μL PbI_2 solution, prepared by dissolving 691.5 mg PbI_2 and 18 mg CsI in a mixed solvent of DMF and DMSO (volume 9:1), was spin-coated on the SnO_2 layer at 1500 r.p.m. for 30 s, followed by annealing at 70 °C for 1 min. After cooling, 120 μL of FAI Solution, created by dissolving 90 mg FAI and 9 mg MACl in 1 mL IPA, was deposited in the PbI_2 layer quickly and annealed at 150 °C for 15 min under ambient air conditions (RH 30%). It should be emphasized that humidity played a key role in the quality of the perovskite film. Following perovskite formation, the film was transferred to a nitrogen-filled glove box for further processing. For APS modification, an APS solution with a concentration of 3 mg/mL in IPA was spin-coated onto the perovskite surface at 5000 r.p.m. for 30 s and then annealed at 100 °C for 5 min. Subsequently, a 60 μL Spiro solution, comprising 72.3 mg Spiro, 17.5 μL LiTFSI and 28.8 μL tBP in 1 mL CB was spin-coated on top of the APS layer at 3200 r.p.m. for 30 s, Finally, a 100 nm thick Ag film was thermally evaporated as a counter electrode using a shadow mask. After device preparation, it was oxidized in a drying cabinet for several days.

Characterizations

The chemical state of the elements was recorded on X-ray photoelectron spectra (XPS, Thermo Scientific K-Alpha, Al-Ka.1486.6 eV). Fourier transform infrared (FTIR) spectra are recorded by Thermo Scientific (NICOLET6700). X-ray diffraction

(XRD) patterns were collected with an X-ray diffractometer using Cu-Ka radiation (λ=0.154187 nm). The surface morphology of the perovskite films was characterized by scanning electron microscopy (SEM, Nova NanoSEM450) and atomic force microscopy (AFM, Bruker Dimension). The contact angles are measured by dropping a drop of ultrapure water on the surface of the perovskite films using a contact angle measuring instrument (OAC30, Shanghai JMH Science & Technology Co., Ltd.). Ultraviolet photoelectron spectroscopy (Thermo Fisher EscaLab 250Xi) and UV-vis absorption spectroscopy (Shimadzu, UV-2600i) were measured to analyze the band structure of the perovskite films. Excitation-emission-matrix (EEM) spectra are recorded by Duetta-HORIBA. Time-resolved photoluminescence (TRPL) spectra are recorded by Omni 990 (Zolix). The electrochemical impedance spectroscopy (EIS) measurement was carried out on a Zahner Zennium electrochemical workstation in the frequency range from 1 MHz–0.1 Hz. J-V curves of the perovskite solar cells were measured by using the solar simulator (AM 1.5G, Zolix, Sirius-SS150A) and calibrated using standard silicon solar cells. The external quantum efficiency (EOE) data were obtained using the solar cell spectral response measurement system (RE-R, Enlitech). Perovskite devices and films were tested humidity stability in a seal dark environment with a relative humidity of 30% (room temperature) for humidity aging. Perovskite devices and films were continuously heated at 70 °C in N_2 and relatively dry sealed atmosphere for testing the thermal stability.
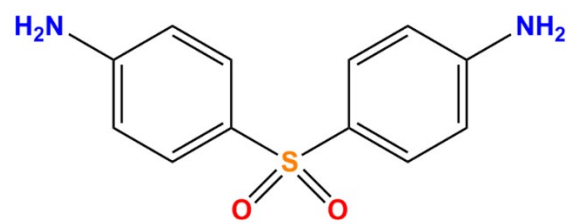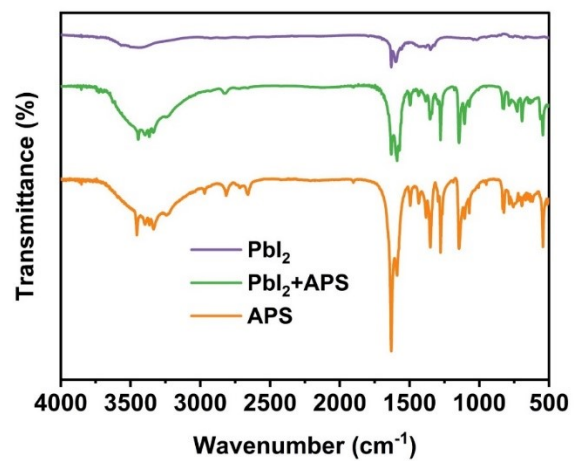
Fig. S1 The chemical structure of APS.

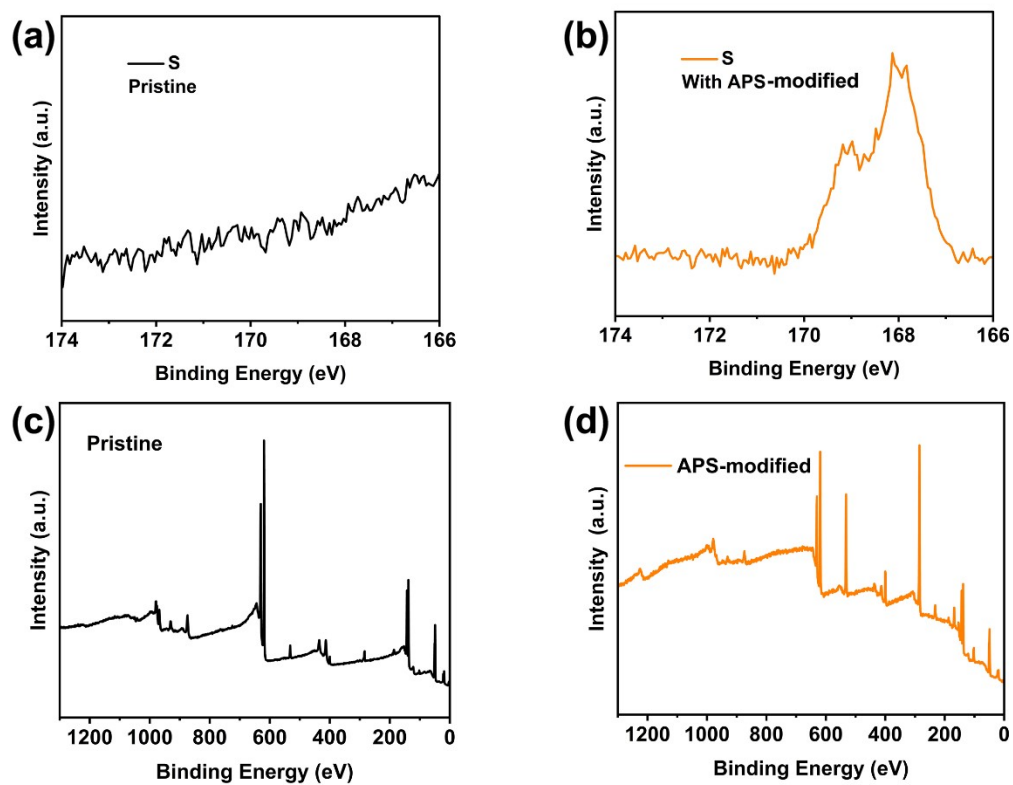**Fig. S2** The FTIR spectra of PbI_2, APS, and APS with PbI_2.

Fig. S3 XPS spectra of the (a, b) S atom core level and (c, d) survey of perovskite films with/without APS modification.
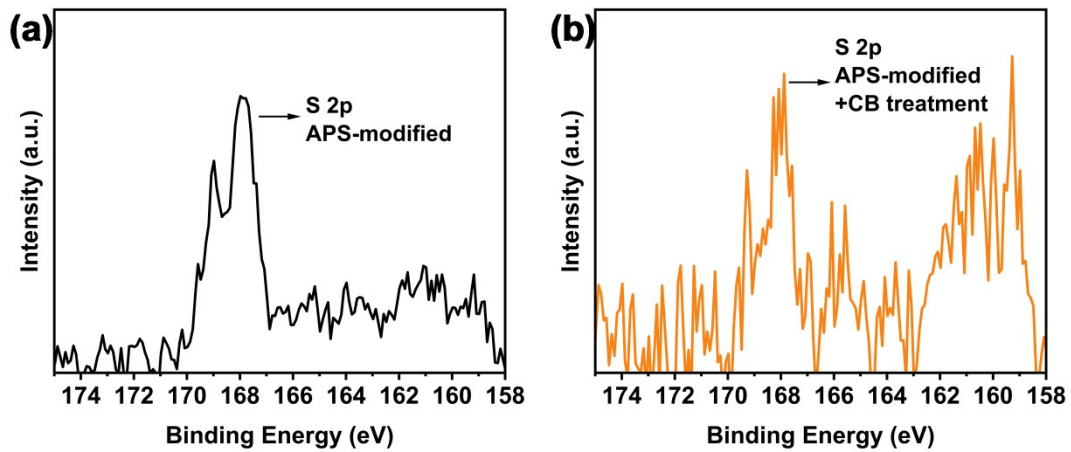
Fig. S4 XPS spectra of S 2p for perovskite films with (a) APS modification, (b) CB treatment after APS modification.
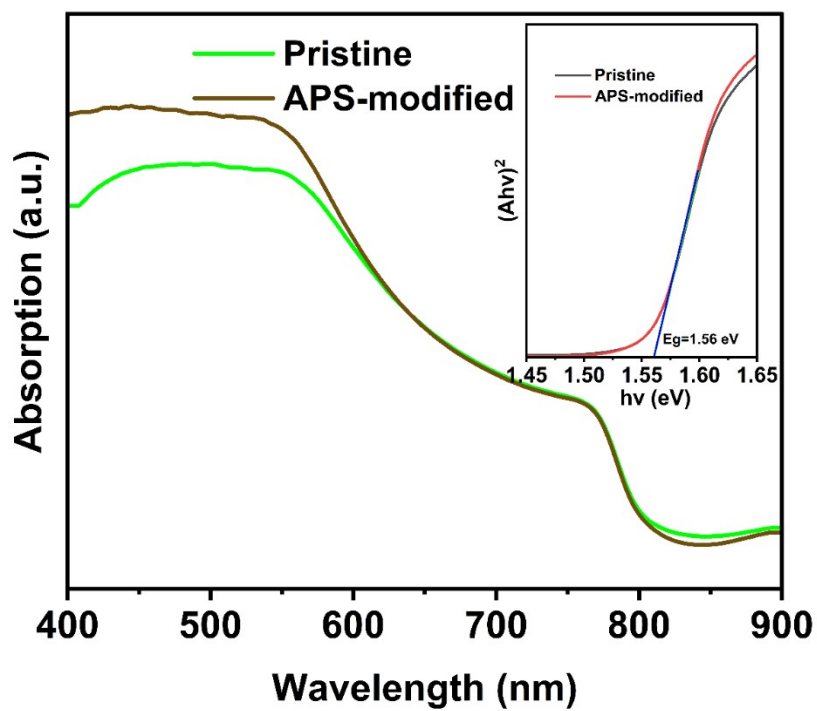
Fig. S5 UV–vis absorption spectra of pristine and APS-modified perovskite films.
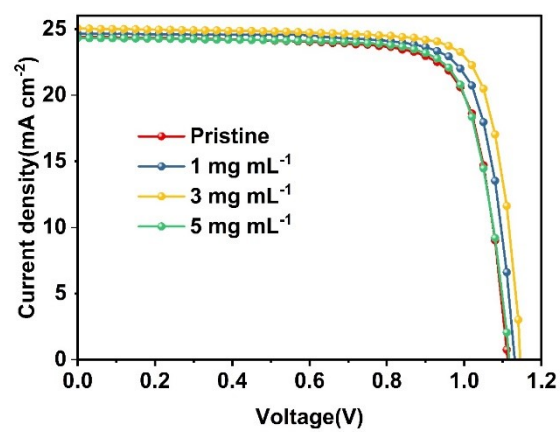
Fig. S6 The J-V curves of the champion devices based on perovskite films modified with different APS concentrations.
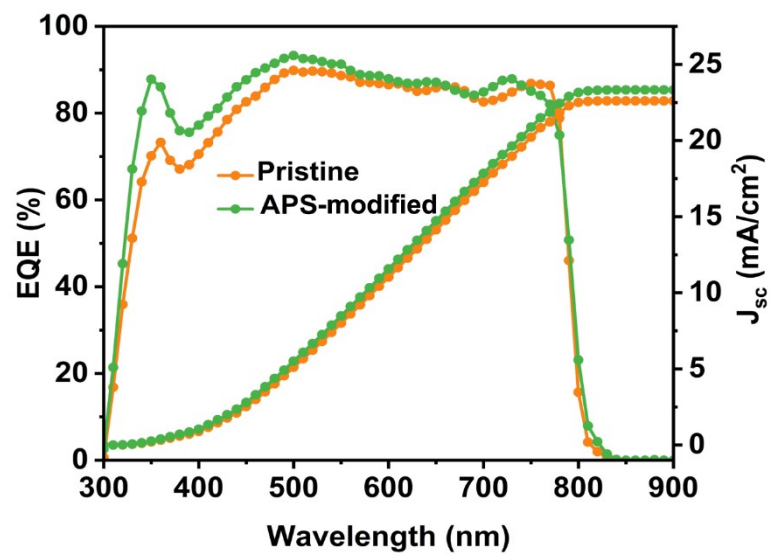
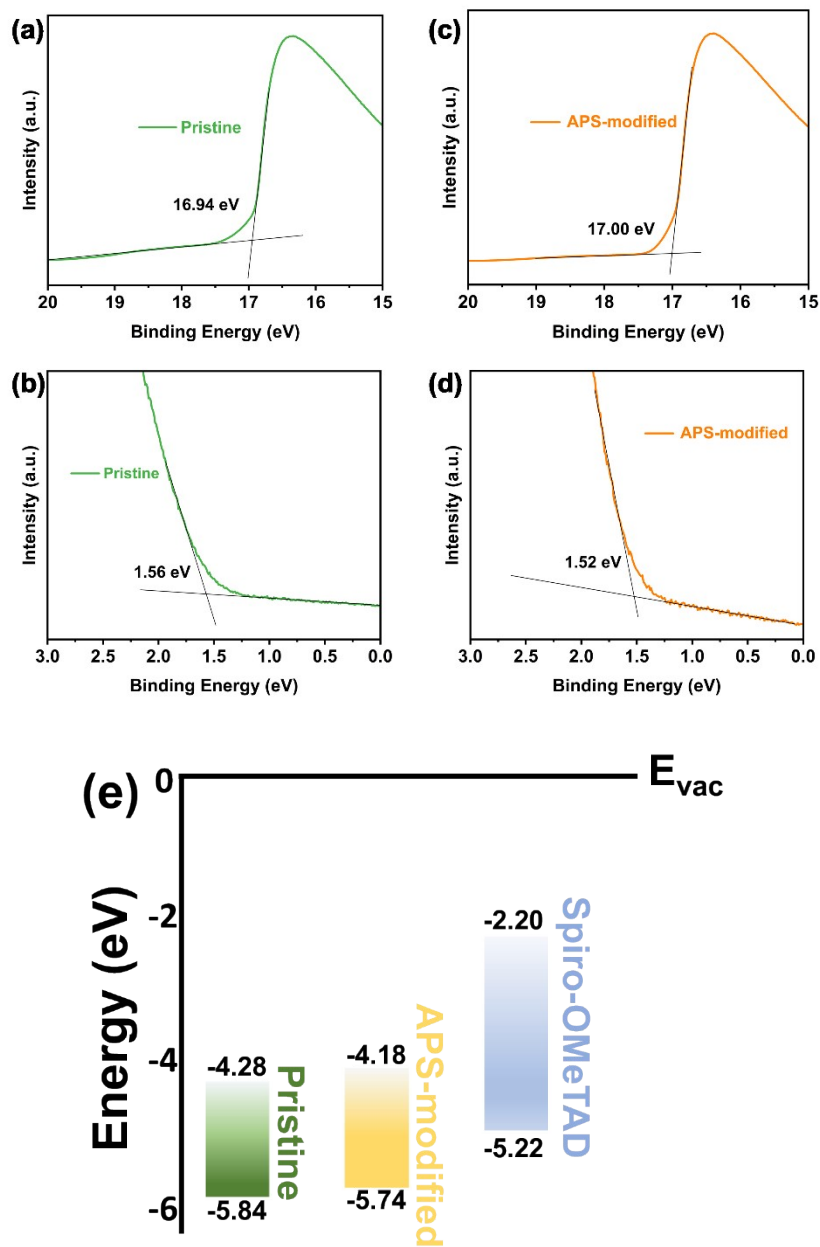**Fig. S7** EQE and the corresponding integrated J_{SC} curves of PSCs.

Fig. S8 UPS spectra and energy level diagrams of pristine and APS-modified perovskite films.
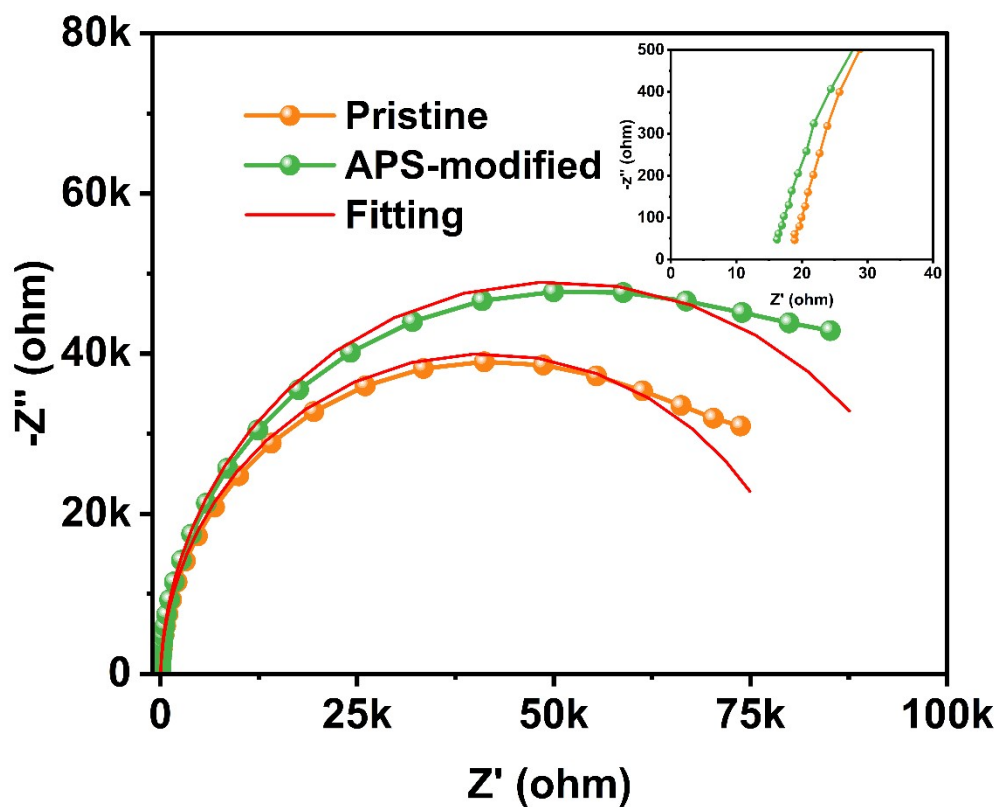
Fig. S9 Nyquist plots of PSCs based on pristine and APS-modified perovskite films under dark conditions. Inset: The equivalent circuit model used for fitting the Nyquist plots of the devices. EIS was conducted in dark and atmospheric environments with a 0.5 V bias voltage.
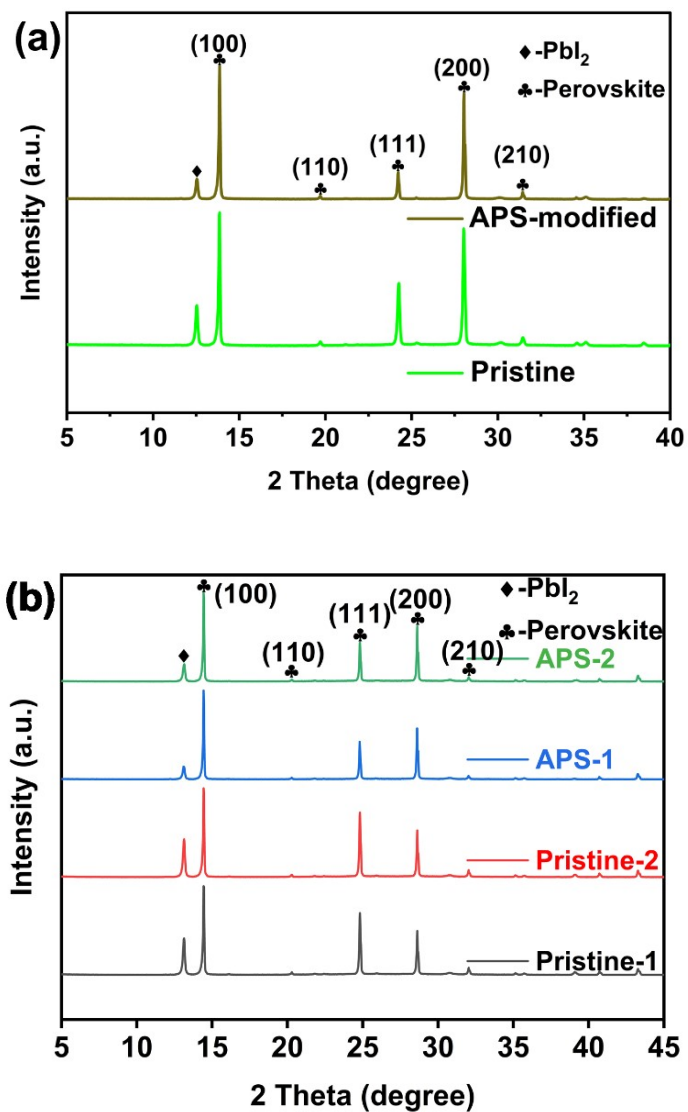
Fig. S10 (a) XRD patterns with long-term stability measurement of pristine and APS-modified perovskite films. (b) XRD patterns of the pristine and APS-modified perovskite films with multiple samples.

Table S1. The fitted results of TRPL for pristine and APS-modified perovskite films

Sample	A_1 (%)	τ_1 (ns)	A_2 (%)	τ_2 (ns)	τ_{avg} (ns)
Pristine	23.70	105.65	73.46	556.39	530.37
APS-modified	28.42	192.40	65.93	1149.91	1085.49

The TRPL lifetime was obtained by fitting the TRPL spectra measured from the perovskite films with a biexponential decay function:

$$I(t) = A_1 exp(-\frac{t}{\tau_1}) + A_2 exp(-\frac{t}{\tau_2}) + A_0$$

where A_1 and A_2 are the decay amplitude, τ_1 and τ_2 are the decay time and A_0 is the decay constant. The average PL decay times (τ_{avg}) are further estimated using the following expression:[2]

$$\tau_{avg} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

Table S2 Photovoltaic parameters of PSCs modified with different APS concentrations

	Sample	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
	0 mg mL^{-1}	24.49	1.111	78.14	21.26
	1 mg mL^{-1}	24.64	1.131	78.98	22.01
APS-modified	3 mg mL^{-1}	25.05	1.145	80.29	23.03
	5 mg mL^{-1}	24.31	1.116	78.11	21.20

Table S3 Photovoltaic parameters of champion PSCs with/without APS modification

Sample	Scan direction	J_{SC} (mA·cm^{-2})	V_{OC} (V)	FF (%)	PCE (%)
Pristine	Reverse	24.49	1.111	78.14	21.26
	Forward	23.99	1.079	72.77	18.83
APS-modified	Reverse	25.05	1.145	80.29	23.03
	Forward	24.83	1.120	76.31	21.22

References

[1] C.-L. Mai, Q. Xiong, X. Li, J.-Y. Chen, J.-Y. Chen, C.-C. Chen, J. Xu, C. Liu, C.-Y. Yeh and P. Gao, Angew. Chem. Int. Ed., 2022, 61, e202209365.

[2] W. Wang, K. Wei, L. Yang, J. Deng, J. Zhang and W. Tang, Mater. Horiz., 2023, 10, 2609-2617.