

Supporting Information

Suppressing Self-Aggregation of Self-Assembled Monolayers for High-Efficiency Inverted Perovskite Solar Cells

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Experimental section

Materials

All chemicals and solvents were used as received without further purification. MeO-2PACz was purchased from Tixiai (Shanghai) Chemical Industry Development Co., Ltd. Isopropanol (IPA, 99.5%), Chlorobenzene (99.8%) and acetonitrile (99.95%) were purchased from Sigma-Aldrich. Nhydrous dimethyl sulfoxide (DMSO, 99.8%) and N, N-dimethylformamide (DMF, 99.8%) were purchased from Thermo Scientific. Lead iodide (PbI₂, 99.99%) and Cesium iodide (CsI, 99.99%) were purchased from Xi'an Yuri Solar Co., Ltd. BCP (99.99%) and Spiro-OMeTAD (99.5%) were purchased from Xi'an Polymer Light Technology Co., Ltd. MACl (99.99%) and FAI (99.99) were purchased from GreatCell Solar Materials Pty Ltd. PC61BM was purchased from Advanced Election Technology Co., Ltd. Ethanol (99.7%) and thiourea (TU, 99%) were purchased from Aladdin.

Device fabrication

FA_{0.97}Cs_{0.03}PbI₃ PSCs fabrication: ITO substrates were sequentially cleaned with detergent, deionized water and ethyl alcohol. The cleaned ITO substrates were dried with high-pressure N₂ gas flow, and then plasma modified for 3 min and transferred into a N₂-filled glovebox. 0.23 mg of TU powder was weighed and added to a 1 mgmL⁻¹ MeO-2PACz solution, followed by vortexing until fully dissolved. MeO-2PACz was spin-coated at 3000 rpm for 30 s, followed by annealing at 100 °C for 10 min. PbI₂ layers (1.5 M PbI₂ with 3% CsI in VDMF:VDMSO = 9:1) were deposited via spin-coating at 2300 rpm for 30 s and annealed at 70 °C for 1 min. A solution of formamidinium iodide (FAI, 90 mg), methylammonium chloride (MACl, 10 mg) in IPA (1 mL) was spin-coated onto PbI₂ films at 2900 rpm for 30 s and annealed at 150 °C for 15 min in air (30-40% humidity). Finally, phenyl-C61-butyric acid methyl ester (PCBM, 20 mg mL⁻¹ in chlorobenzene) and bathocuproine (BCP, 0.5 mg mL⁻¹ in IPA) were sequentially spin-coated at 2000 rpm for 30 s and annealed at 100 °C for 3 min, followed by thermal evaporation of a 100 nm copper electrode to complete the PSC fabrication.

Characterizations

Top-view scanning electron microscopy (SEM) images were captured with a field emission SEM (Hitachi SU8020). Kelvin probe force microscopy (KPFM) images were obtained using a Kelvin probe force microscopy system (AFM, Asylum Co. MFP-3D-SA-DV-OQ). X-ray photoelectron spectroscopy (XPS) patterns were obtained using a X-ray photoelectron spectroscopy instrument (Thermo ESCALAB 250Xi). Dynamic light scattering (DLS) measurements for nanoparticle size and Zeta potential were conducted using a Malvern Zetasizer Nano ZS90 analyzer. Time-resolved photoluminescence (TRPL) measurements were conducted at an excitation wavelength of 510 nm, and steady state photoluminescence (PL) spectra were obtained at 510 nm using the Horiba spectrofluorometer and FLS920 spectrofluorometer, respectively. PL mapping images were obtained using a confocal fluorescence microscope (ISS Q2 FLIM/FFS, ISS Inc.). ICP was measured through inductively coupled plasma mass spectrometer (Rigaku SmartLab SE). SEPhotocurrent density-voltage ($J-V$) curves of various devices were measured using a sourcemeter (Keithley 2450) under simulated sunlight (AM 1.5, 100 mW cm⁻², calibrated with a standard silicon solar cell, Newport, Oriel Class A, 91195 A) at a voltage range of 0-1.2 V. External quantum efficiency (EQE) spectra were obtained using a monochromatic incident photon-to-electron conversion efficiency (IPCE) kit from Enli Technology Co., Ltd, with a standard Si crystalline solar cell serving as a reference. Steady power output curves at the maximum power point (MPP) were recorded using an electrochemical workstation (CHI660E) at the bias voltage at the maximal power output point. The trap density of PVK films for electron-only and hole-only devices was characterized using a space charge limited current (SCLC) model within the voltage range of 0-3 V under dark conditions. Capacitance-voltage ($C-V$) curves were measured at a frequency of 5 kHz with an amplitude of 5 mV under dark. Dark $J-V$ curves and electrochemical impedance spectroscopy (EIS) of PSCs were measured on a CHI660E electrochemical workstation.

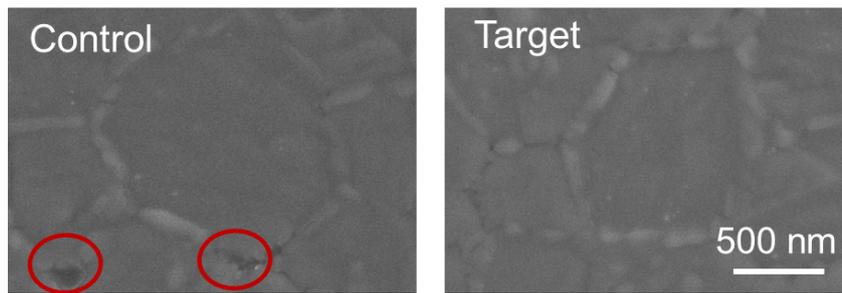


Fig.S1. SEM images of the buried interface of perovskite films.

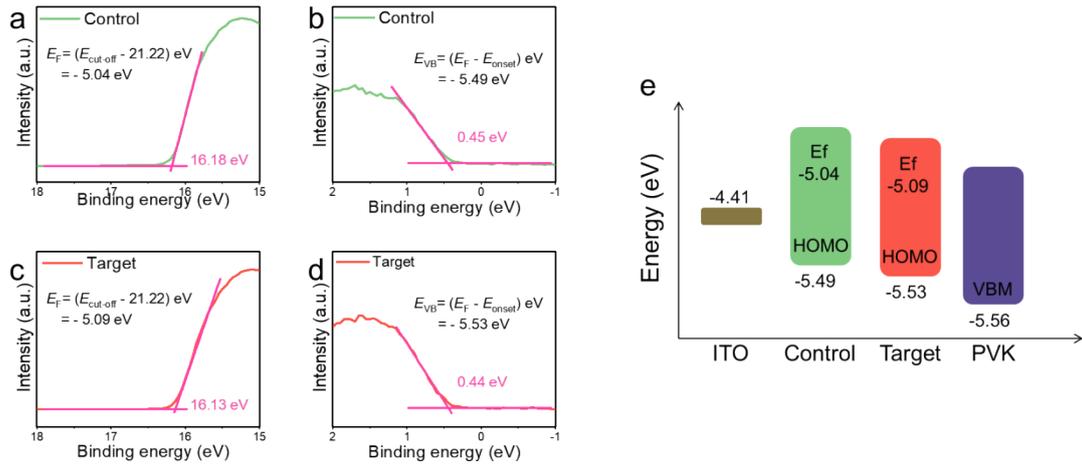


Fig.S2. (a-d) UPS spectra of control and target SAM films, (e) Energy level diagrams of the FA_{0.97}Cs_{0.03}PbI₃ PSCs.

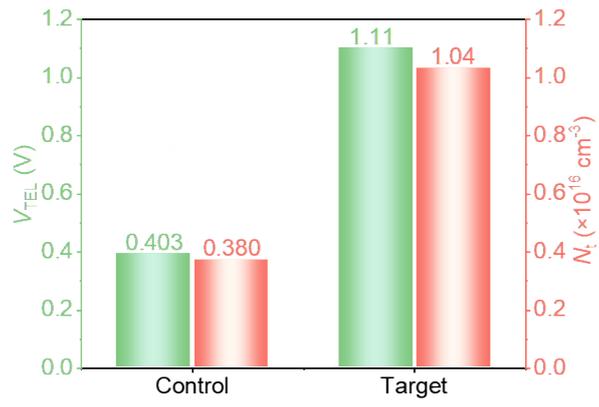


Fig.S3. Nyquist EIS spectrum in the dark.

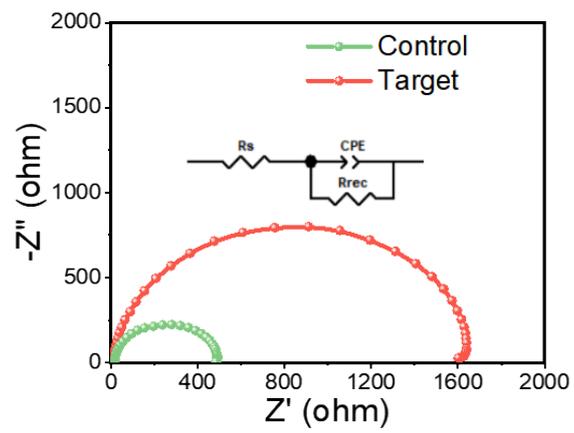


Fig.S4. Nyquist EIS spectrum in the dark.

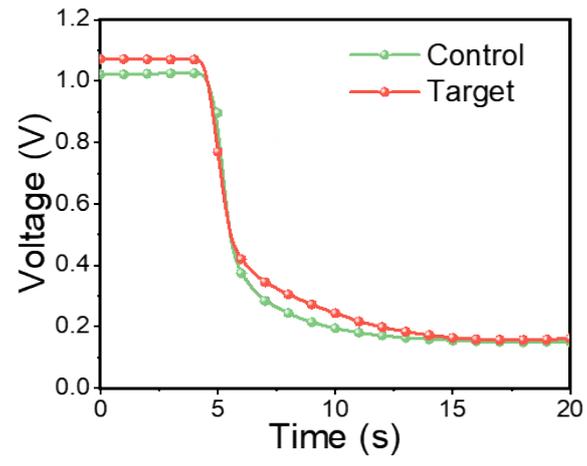


Fig.S5. V_{oc} decay curves.

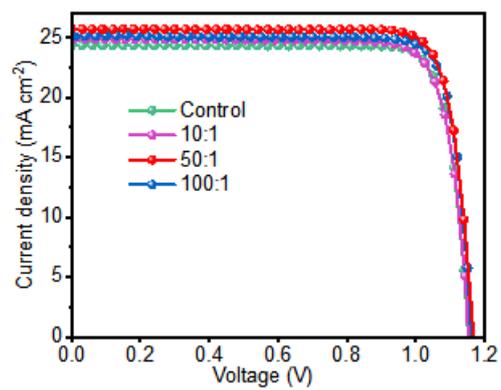


Fig. S6. J - V curves of devices based on different concentrations of TU additive in SAMs solution.

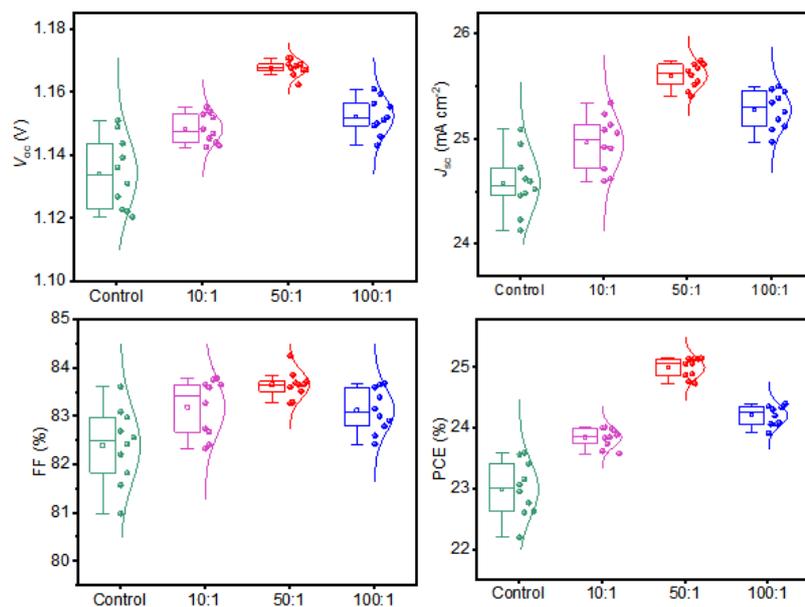


Fig. S7. The statistics of photovoltaic parameters derived from the J - V characteristic curves of devices based on different concentrations of TU additive in SAMs solution.

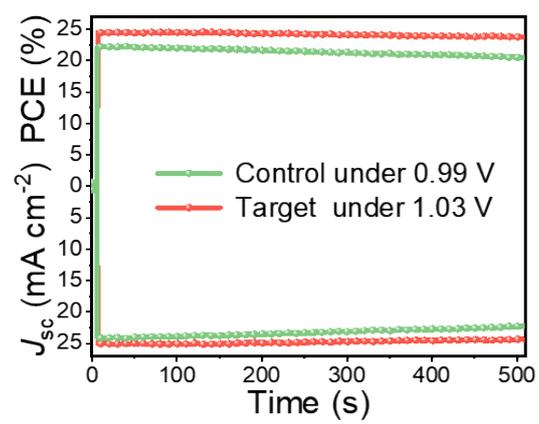


Fig.S8. PPE curves of FA_{0.97}Cs_{0.03}PbI₃ PSCs based on TU.

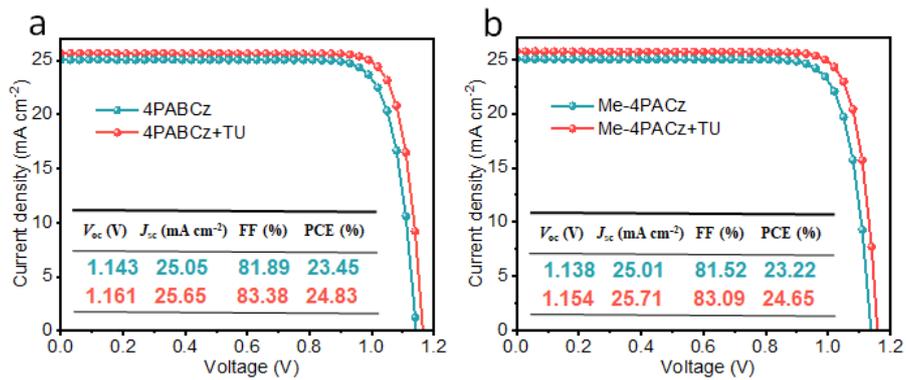


Fig. S9. J - V curves of champion devices based on extended SAMs molecular systems:

(a) 4PABCz and (b) Me-4PACz, with and without TU modification.

Table S1. The V_{TFL} and N_{t} value of hole-only devices for control and target.

| Samples | V_{TFL} (V) | N_{t} (cm^{-3}) |
|---------|----------------------|---------------------------------------|
| Control | 0.403 V | $1.11 \times 10^{16} \text{ cm}^{-3}$ |
| Target | 0.380 V | $1.04 \times 10^{16} \text{ cm}^{-3}$ |

The trap density (N_{t}) was calculated using the following equation: $N_{\text{t}} = 2\varepsilon_{\text{t}}\varepsilon_0 V_{\text{TFL}}/qL^2$, where $\varepsilon_{\text{t}} = 62.23$ is the relative dielectric constant of $\text{FA}_{0.97}\text{Cs}_{0.03}\text{PbI}_3$, $\varepsilon_0 = 8.85 \times 10^{-12} \text{ F m}^{-1}$ is the vacuum permittivity, q is the electron charge, $L = 500 \text{ nm}$ is the thickness of perovskite film, and V_{TFL} is the onset voltage of the trap-filled limit region, which provides a measure of the trap states density.

Table S2. Photovoltaic performance of FA_{0.97}CS_{0.03}PbI₃ PSCs with different concentrations of TU.

| | V_{oc} (V) | J_{sc} (mA cm ⁻²) | FF (%) | PCE (%) |
|---------|--------------|---------------------------------|--------|---------|
| Control | 1.151 | 24.52 | 83.61 | 23.59 |
| 10:1 | 1.152 | 24.91 | 83.65 | 24.01 |
| 50:1 | 1.167 | 25.71 | 83.72 | 25.15 |
| 100:1 | 1.161 | 25.12 | 83.68 | 24.40 |