

Supporting Information

Underlayer Engineering on Grain Strain toward Efficient and Stable Tin Perovskite Solar Cells

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Experimental

Materials. Tin perovskite precursors, Tin iodide (SnI_2 , 99.999%) and Tin fluoride (SnF_2 , 99%) were purchased from Alfa Aesar. Formamidinium iodide (FAI), Ethylenediamine iodine (EDADI), C_{60} , bathocuproine (BCP), and poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), Octylammonium Iodide (OAI), Dodecylammonium Iodide (DDAI) and Octadecylammonium iodide (ODAI) were purchased from Xi'an Polymer Light Technology Corporation (China). Tin powder, Dimethyl sulfoxide (DMSO, anhydrous, 99.9%), Dimethyl formamide (DMF, anhydrous, 99.9%), and Chlorobenzene (CB, anhydrous, 99.8%) were purchased from TCI. All these materials in experiments were used as received without any further purification.

Device fabrication. ITO substrates were first sonic-cleaned by detergent (Decon 90) for 1 hour, and then sequentially sonic-cleaned by deionized water, acetone and ethanol absolute for 15 min, respectively. The clean ITO substrates were treated with UV ozone for 20 min before use. PEDOT:PSS aqueous solution was filtered through a $0.45\ \mu\text{m}$ filter and spin-coated on the ITO surface at 3500 rpm for 60 s, and then annealed at $120\ ^\circ\text{C}$ for 15 min. The alkylamine underlayer ($1.0\ \text{mg mL}^{-1}$ in IPA) was spun onto the PEDOT:PSS layer with a speed of 5,000 rpm for 30 s and annealed at $100\ ^\circ\text{C}$ for 5 min. The tin perovskite (with a composition of $\text{FA}_{0.98}\text{EDA}_{0.01}\text{SnI}_3$) precursor solution was prepared by dissolving SnI_2 , FAI, SnF_2 and EDADI with a molar ratio of 1:0.98:0.1:0.01 in DMSO/DMF (1/4) for a concentration of 0.9 M. A certain amount of tin powder was added to inhibit the oxidation of Sn^{2+} . The solution was stirred at room temperature for 8 hours and was filtered through a $0.45\ \mu\text{m}$ filter before use. The perovskite films were fabricated via spin-coating perovskite precursor solution on substrate at the speed of 1000 rpm for 10 s and 5000 rpm for 40 s. Anti-solvent CB ($150\ \mu\text{L}$) was dripped at 15 s before the end of this process. The freshly deposited films were then annealed at $100\ ^\circ\text{C}$ for 12 min. After cooling to room temperature, C_{60} (40 nm), BCP (6 nm) and silver (120 nm) were sequential thermally evaporated onto the substrates to finish the device fabrication.

Characterization. The surface-view morphologies were characterized by SEM (QUATTROS, Thermal Fisher Scientific). The XPS spectra and the FTIR spectra were characterized by AXIS

Supra XPS system and Thermo Scientific Nicolet iS 50, respectively. Bruker Dimension Kelvin probe force microscopy in Potential Channel equipped with PFQNE-AL probe was used to measure the surface potentials of perovskite films. XRD analysis was conducted by an XPERT-PRO diffractometer system. GIXRD measurements were carried out with 45 kV and 200 mA of X-ray generator, D/teX Ultra 250 detector, continuous scan mode, 0.0001° of resolution, and $2.00^\circ/\text{min}$ of scan speed/duration time. UV-vis absorption was carried out by a UV-vis. spectrometer (PerkinElmer model Lambda 2S). FLS980 was used to obtain steady-state and time-resolved PL spectra with an excitation wavelength of 485 nm. SCLC was performed on hole-only (ITO/PEDOT:PSS/ perovskite/MoO₃/Ag), and measured from 0 to 6 V with a 0.02 V step size under dark conditions using a Keithley 2400 source/meter unit. Under simulated AM 1.5G in N₂ glovebox at room temperature, the J–V curves of perovskite devices were recorded using a Keithley 2400 source meter, and the EQE spectra were carried out by a QE-R EQE system (EnLi Technology, Taiwan). The active area was defined as 0.105 cm² and the light intensity was calibrated using a standard KG2 Si diode.

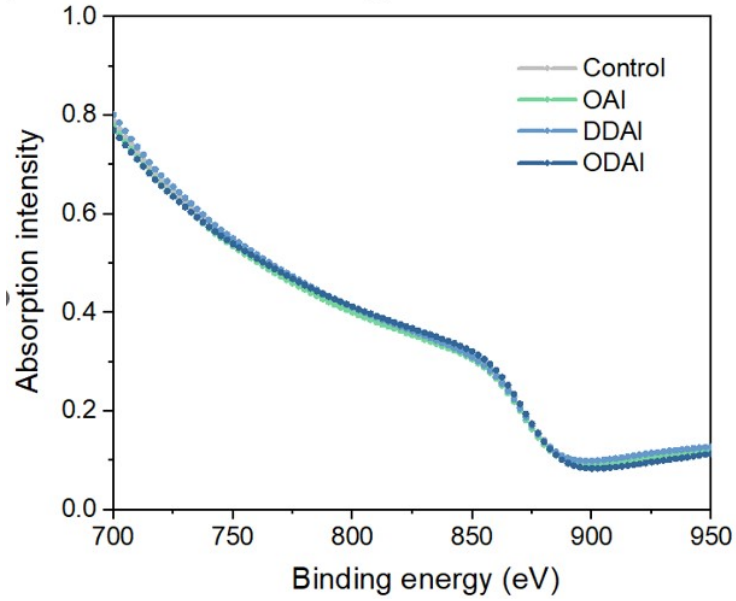


Fig. S1 UV-vis absorption spectra of tin perovskite devices with and without different alkylamine underlayers.

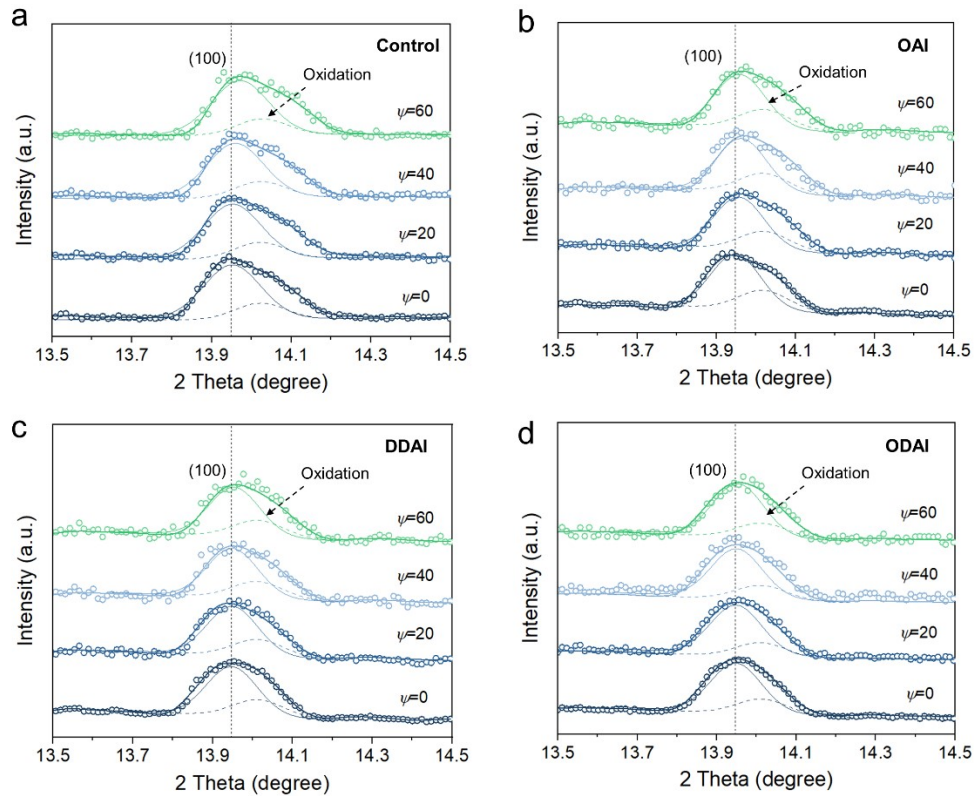


Fig. S2. Fitted GIXRD patterns of tin perovskite with different underlayers. The appearance of two peaks indicates the partial oxidation and decomposition, which are inevitably caused during sample transportation and testing. The plots were fitted through peakfit software.

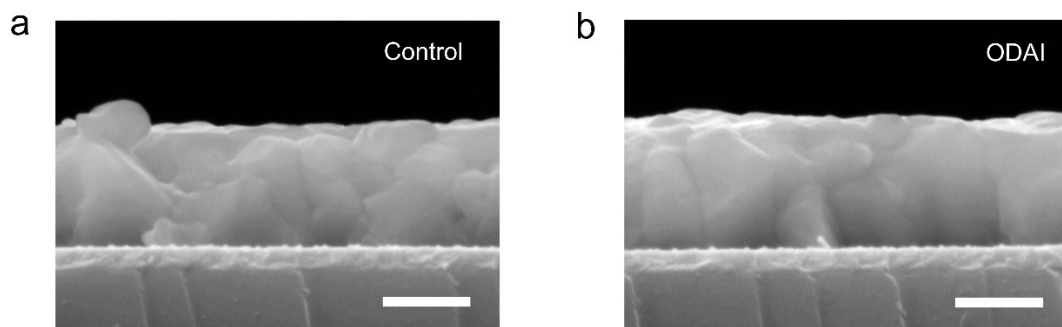


Fig. S3 Cross-section SEM images of control and ODAI underlayer modified tin perovskite films. The scale bar is 200 nm.

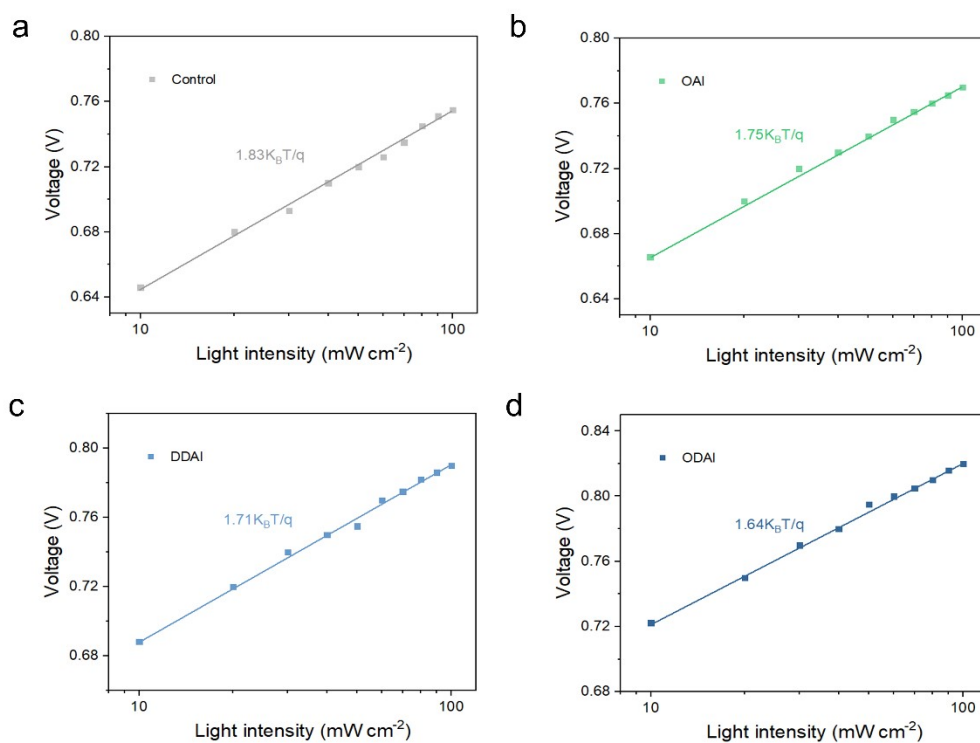


Fig. S4 Light intensity vs open-circuit voltage curves of tin perovskite devices with and without different alkylamine underlayers.

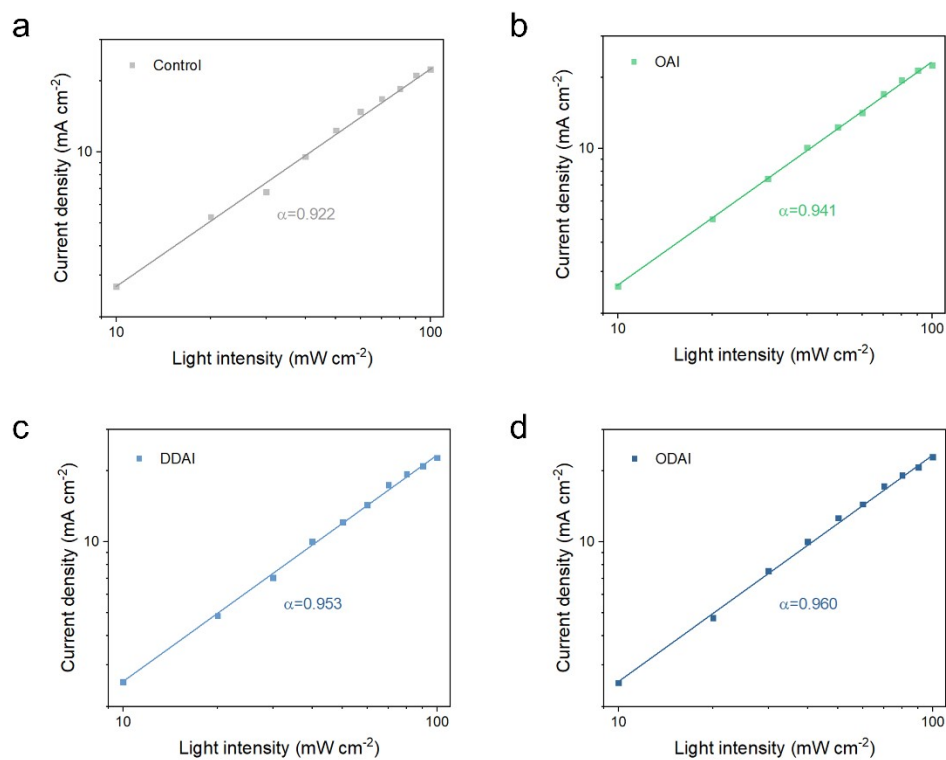


Fig. S5 Light intensity vs short-circuit current density curves of tin perovskite devices with and without different alkylamine underlayers.

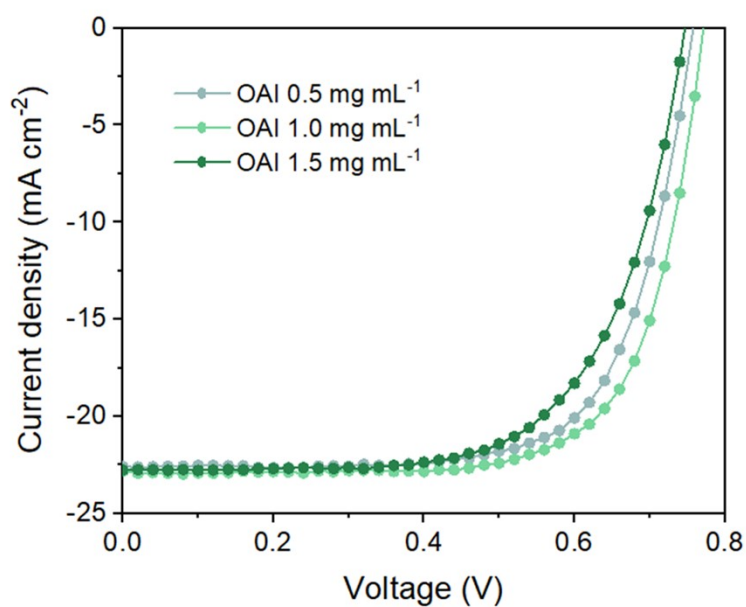


Fig. S6 J-V curves of best-performing TPSC with different OAI treating concentrations.

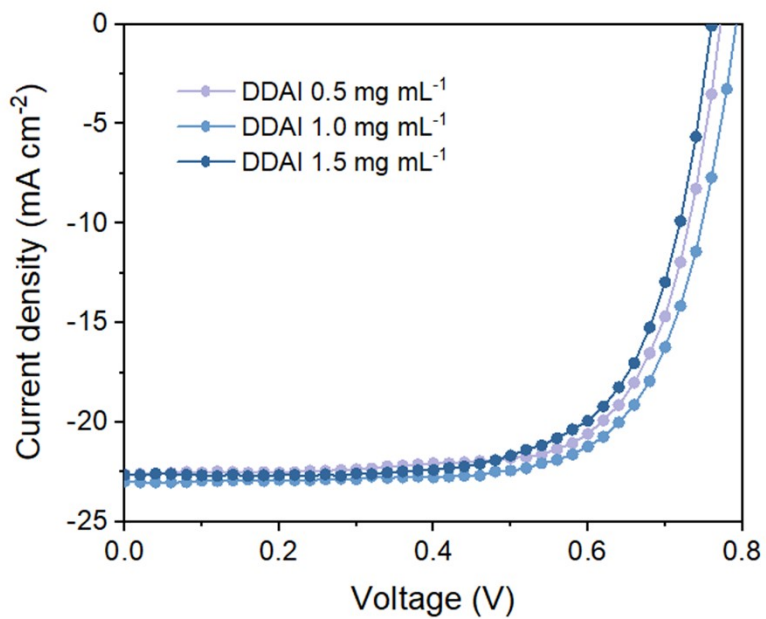


Fig. S7 J-V curves of best-performing TPSC with different DDAI treating concentrations.

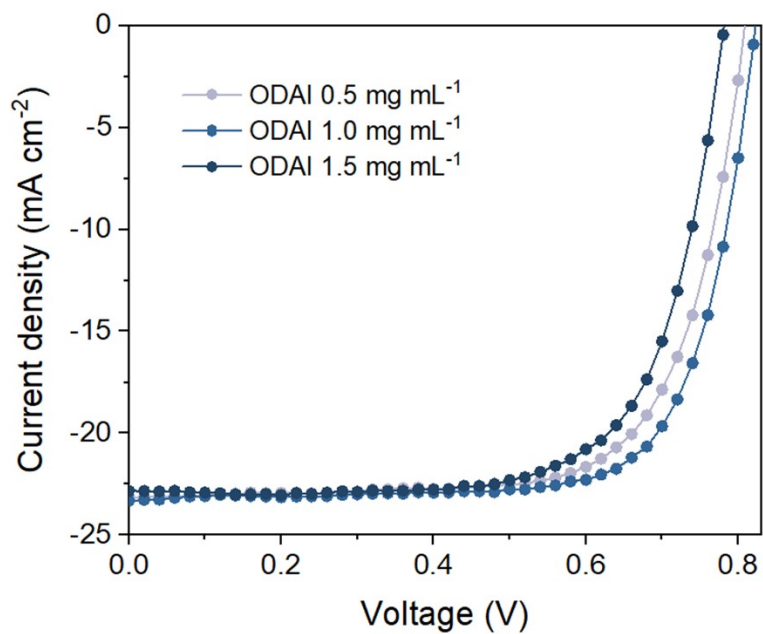


Fig. S8 J-V curves of best-performing TPSC with different ODAI treating concentrations.

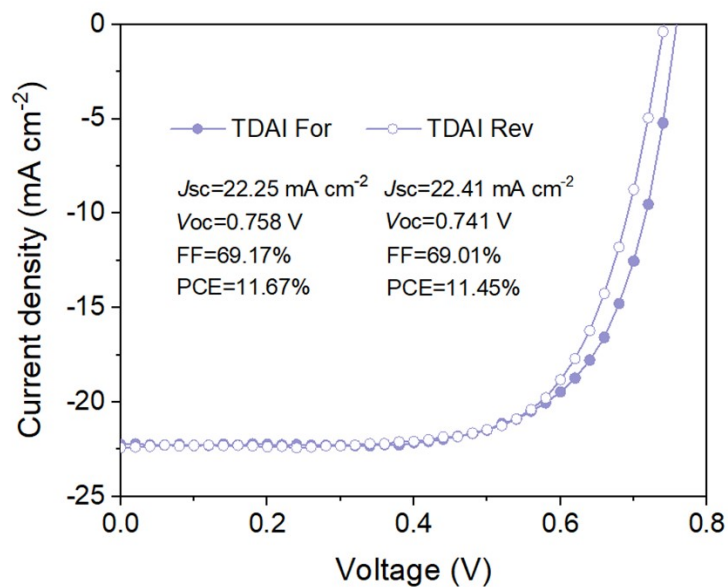


Fig. S9 J-V curves of best-performing TDAI treated TPSC under forward and reverse scans.

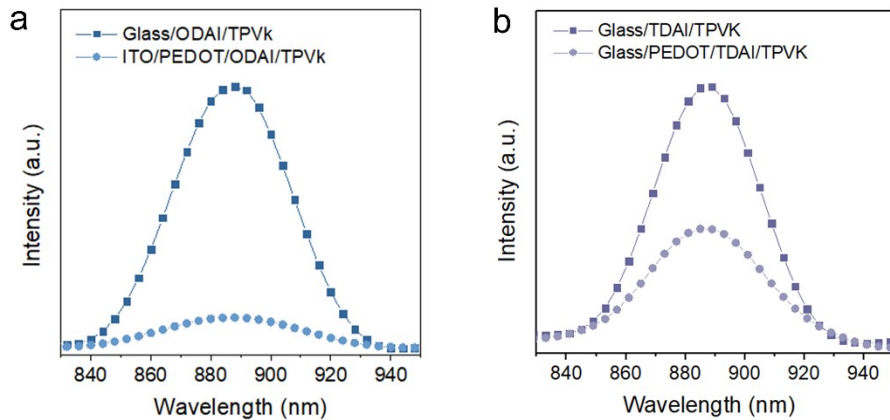


Fig. S10 PL spectra of tin perovskite films with and without HTL for a) ODAI underlayer and b) TDAI underlayer

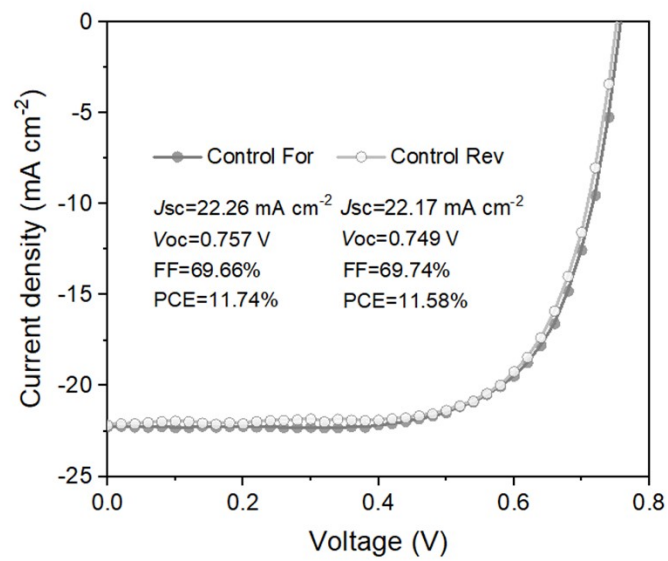


Fig. S11 J-V curves of best-performing control TPSC under forward and reverse scans.

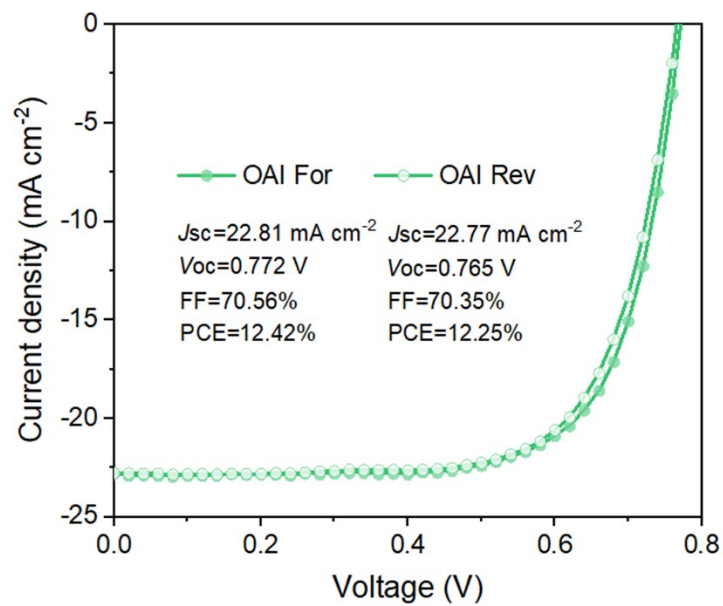


Fig. S12 J-V curves of best-performing OAI treated TPSC under forward and reverse scans.

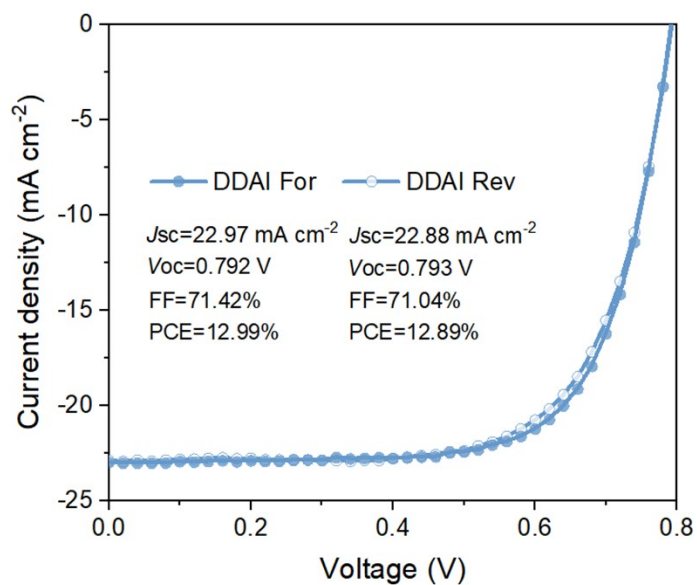


Fig. S13 J-V curves of best-performing DDAI treated TPSC under forward and reverse scans

Table S1 Photovoltaic parameters of champion TPSCs with different interlayer layers

Interlayer	Concentration	Jsc (mA cm ⁻²)	Voc (V)	FF (%)	PCE (%)
OAI	0.5 mg mL ⁻¹	22.58	0.758	69.89	11.96
	1.0 mg mL ⁻¹	22.81	0.772	70.56	12.42
	1.5 mg mL ⁻¹	22.76	0.743	67.81	11.46
DDAI	0.5 mg mL ⁻¹	22.62	0.758	70.72	12.13
	1.0 mg mL ⁻¹	22.97	0.792	71.42	12.99
	1.5 mg mL ⁻¹	22.64	0.770	69.45	12.10
ODAI	0.5 mg mL ⁻¹	23.12	0.807	70.96	13.24
	1.0 mg mL ⁻¹	23.05	0.818	73.31	13.82
	1.5 mg mL ⁻¹	22.83	0.782	70.80	12.64