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Mitigating tin ion migration and reinforcing buried interface via synergistic polymer-modified tin oxide

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Abstract

The buried interface between charge transport layer and the overlying perovskite absorber is critical yet difficult to probe in perovskite solar cells. Because light enters through the transparent substrate and is predominantly absorbed near this region, photo-induced degradation processes are most likely initiated at hidden buried interface. Here, we reveal that instability at the buried SnO₂/perovskite interface triggers structural and chemical decomposition of the perovskite layer. To address this issue, we introduce polymeric interlayers that simultaneously reinforce interfacial bonding and suppress tin-ion migration. Poly(1-ethenylpyrrolidine-2,5-dione) (PED) forms the most robust and chemically compatible interface, yielding enhanced phase purity, reduced defect density, and significantly mitigated tin diffusion. These findings identify the buried interface as the primary origin of perovskite degradation and highlight interfacial polymer design as an effective strategy for achieving intrinsically stable perovskite photovoltaics.

Main

Perovskite solar cells (PSCs) have rapidly emerged as one of the most promising next-generation photovoltaic technologies, achieving power conversion efficiencies (PCEs) that now rival those of crystalline silicon^{1,2}. Despite this remarkable progress, their operational stability remains a major obstacle to commercialization^{3,4}. Among the multiple interfaces within the device architecture, the buried interface between the charge transport layer (CTL) and the perovskite absorber plays a particularly crucial yet remain relatively underexplored^{5,6}. Unlike the readily accessible top surface, this bottom interface is physically enclosed and challenging to probe, resulting in its frequent neglect in both mechanistic studies and materials optimization.

Furthermore, the top and bottom surfaces of a perovskite film exhibit intrinsic asymmetry^{7,8}, the factor that has been largely overlooked. Differences in nucleation kinetics, substrate interactions, and illumination exposure produce variations in morphology and defect density between the two surfaces. This structural disparity implies that treating the perovskite layer as a homogeneous bulk material oversimplifies its degradation behavior and limits the effectiveness of conventional stabilization strategies. Understanding and stabilizing this “hidden” interface is therefore essential for achieving intrinsically durable perovskite photovoltaics.

In the conventional n-i-p device configuration, light enters through the transparent conductive substrate and is predominantly absorbed near the buried electron transport layer (ETL)/interface, particularly for high energy photons, owing to the exceptionally high optical absorption coefficient of metal halide perovskites (**Supplementary Fig.3**). Consequently, this region experiences the highest photon flux, carrier density, and thus possible local heating, forming

a hotspot where photochemical and electrochemical reactions are likely to initiate^{9,10}. Growing evidence indicates that degradation of perovskite films often originates from this buried interface rather than from the exposed top surface, as interfacial defects^{11,12}, trapped charges^{13,14}, and ion migration^{5,15,16} collectively accelerate structural decomposition and chemical instability. Previous efforts to improve the buried interface have explored self-assembled monolayers^{17,18}, fullerene derivatives¹⁹, two-dimensional perovskite passivation layers^{20,21}, and post-treatments such as plasma or molecular doping^{22,23}. While these methods have yielded partial improvements in charge extraction and surface passivation, they often suffer from limited chemical robustness, non-uniform coverage, or instability under prolonged illumination and thermal stress. Moreover, few strategies have directly addressed the issue of tin-ion migration from the SnO₂ ETL, a subtle but critical degradation pathway that compromises both the electronic and structural integrity of the perovskite layer.

Here, we introduce a series of polymeric interlayers designed to simultaneously strengthen interfacial bonding, improve perovskite film morphology, and suppress tin-ion diffusion across the SnO₂/perovskite boundary. Among them, poly(1-ethenylpyrrolidine-2,5-dione) (PED) forms an exceptionally stable and chemically compatible interface, leading to markedly enhanced efficiency and long-term operational stability. This work identifies the buried interface as the true origin of perovskite degradation and establishes interfacial polymer engineering as an effective strategy for realizing intrinsically stable, high-performance perovskite solar cells.

Optimized perovskite quality at bottom interface

Polymeric interlayers including poly(1-ethenylpyrrolidine-2,5-dione) (PED), poly(1-ethenyl-3-methylpyrrolidin-2-one) (PEM) and polyvinylpyrrolidone (PVP) were introduced between the SnO₂ ETL and the perovskite absorber, and their effects were compared with control samples without interlayers (**Fig.1a**). To evaluate the influence of these polymers on perovskite crystallinity, the perovskite films were peeled from the substrates using epoxy (**Supplementary Fig.27**), and X-ray diffraction (XRD) measurements were performed from the bottom side on as-fabricated samples. The XRD results revealed that the intensity ratio between the (001) α -FAPbI₃ and (001) PbI₂ diffraction peaks increased substantially upon incorporation of the polymeric interlayers. Among them, the PED-modified film exhibited the highest ratio, indicating enhanced perovskite phase purity and crystallinity (PED : PEM : PVP : REF = 3.18 : 1.20 : 1.20 : 0.87 (**Fig.1b**, **Supplementary Fig.4, Table.1**)). Cross-sectional scanning electron microscopy (SEM) images of

the bottom interface (**Fig.1c to f**) revealed that the reference perovskite films contained numerous voids and grooves along grain boundaries. These morphological defects serve as pathways for oxygen and moisture ingress, promote ion migration, and induce localized electric fields, all of which accelerate phase segregation and non-radiative recombination^{24,25}. In contrast, perovskite films incorporating polymeric interlayers exhibited denser microstructures with significantly reduced grain boundary grooves, confirming that the polymers effectively suppress interfacial void formation and improve film compactness.

The improved interface quality was further reflected in the optoelectronic properties of the perovskite films. Time-resolved photoluminescence (TRPL) decay profiles (**Fig.1g**), fitted using a bi-exponential model, revealed prolonged carrier lifetimes of 1.43 μ s (PED), 1.10 μ s (PEM), and 0.96 μ s (PVP), compared to 0.52 μ s for the control. Steady-state photoluminescence (PL) spectra (**Fig.1h**) showed that polymer-treated samples exhibited markedly higher PL intensity than the reference film. In addition, trap density analysis based on total density of states (tDOS) measurements (**Fig.1i**) demonstrated a reduced density of in-gap states in polymer-modified films, indicating suppressed trap-assisted recombination and improved charge carrier dynamics. These results suggest improved perovskite film quality at the bottom interface by introducing the polymeric interlayers.

Degradation behavior and interfacial stabilization

To verify the difference in degradation rates between the top and bottom regions of the perovskite layer, perovskite films identical to those used in PSC devices were deposited on glass substrates using a two-step deposition process. The films were continuously illuminated under xenon light in ambient air at a relative humidity (RH) of 40% for 24 hours without encapsulation. Optical microscopy (OM) images revealed that the bottom interface exhibited a more rapid color change than the top surface (**Supplementary Fig.5**), indicating accelerated degradation at the buried side. These results confirm that, compared to the top surface, the bottom interface is markedly more susceptible to light-induced decomposition.

To further evaluate the effect of polymeric interlayers on the stability of this buried interface, we conducted a series of characterizations on aged films extracted from devices with the structure: substrate /ITO/ETL (SnO_2)/(polymeric interlayer)/perovskite/HTL/Au. The perovskite layer exhibited a bandgap of 1.56 eV (**Supplementary Fig.6**). The perovskite layers were peeled off after operation under maximum power point tracking (MPPT) for 200 hours. SEM analysis

(**Fig.2a**) showed that the aged perovskite bottom surfaces of reference devices developed pronounced grain boundary grooves and voids, consistent with structural degradation. In contrast, films incorporating polymeric interlayers exhibited smoother, denser morphologies, as further confirmed by atomic force microscopy (AFM) (**Supplementary Fig.7**). X-ray photoelectron spectroscopy (XPS) provided additional insights into the chemical stability of the buried interfaces (**Fig.2b**). In fresh samples, the Pb 4f core-level spectra confirmed the expected oxidation state of Pb^{2+} . After aging, however, the reference sample displayed peak broadening and an evident positive binding energy shift (0.81 eV), signifying oxidation and the formation of lead-containing degradation species. The incorporation of polymeric interlayers did not significantly affect the chemical state of fresh samples. After aging, the PED-modified sample retained much smaller binding energy shift of Pb 4f (0.15 eV) and line shapes, demonstrating outstanding resistance to oxidative degradation. Although PVP- and PEM-treated samples also exhibited improved interfacial stability compared to the control, PED provided the most effective suppression of chemical deterioration.

To further examine phase evolution upon aging, perovskite films were subjected to simultaneous light and thermal stress under one-sun illumination at 65 °C. As shown in **Figure 2c**, XRD patterns of the reference film revealed an increased PbI_2 peak intensity and the emergence of the δ -FAPbI₃ phase, both indicative of decomposition and phase transformation. In contrast, the PED-treated film retained a stable α -FAPbI₃ diffraction pattern with negligible PbI_2 formation and no detectable δ -phase, evidencing superior phase stability. While PVP and PEM interlayers also mitigated phase degradation to some extent, PED proved the most effective in maintaining crystallinity and suppressing structural transition (**Supplementary Fig.8, Table.2**).

To elucidate the distinct interfacial behaviors of the three polymers, molecular dynamics (MD) simulations were performed to investigate their interactions with the perovskite surface. As illustrated in **Figures 2d to f** and **Supplementary Figures 9, 10, 11**, PED molecules exhibited strong adhesion and close packing at the perovskite interface, forming a compact and robust interfacial configuration. In contrast, a significant fraction of PEM and PVP molecules detached from the surface, suggesting weaker interfacial interactions and a higher tendency for nonuniform coverage. In practical device structures, such weak adhesion may promote polymer aggregation and result in incomplete interlayer formation, thereby reducing passivation effectiveness and allowing morphological defects to persist²⁶.

Mitigation of tin ion migration

Cross-sectional scanning transmission electron microscopy (STEM) images of reference devices operated under MPPT for 2000 hours revealed clear evidence of perovskite degradation initiating from the bottom interface (**Fig.3a, Supplementary Fig.12**)^{27,28}. Energy-dispersive X-ray spectroscopy (EDS) elemental maps confirmed that tin ions originating from the SnO₂ ETL infiltrated into the lower region of the perovskite film, triggering early-stage interfacial decomposition. These observations demonstrate that tin migration from the SnO₂ ETL into the perovskite active layer constitutes a significant yet often overlooked degradation pathway, posing a critical threat to device efficiency and operational lifetime. In contrast, devices incorporating a PED interlayer between the SnO₂ and perovskite layers (**Fig.3b, Supplementary Fig.13**) exhibited minimal interfacial degradation and no discernible Sn penetration into the absorber, highlighting the effectiveness of the polymeric barrier in mitigating ion diffusion.

To elucidate the underlying mechanisms of Sn-ion suppression, density functional theory (DFT) calculations were performed to examine the interaction between tin ions and the three polymeric interlayers. All polymers introduced additional energy barriers that impeded tin migration (**Fig.3c**). Among them, PED produced the highest migration barrier of 0.54 eV, followed by PVP (0.35 eV) and PEM (0.25 eV). Further investigations for overall ion migrations, including halide and oxygen ions, were conducted through temperature-dependent conductivity measurements on devices with the structure of FTO/SnO₂/perovskite/Au (**Supplementary Fig. 14**). The activation energy (E_a) for ion migration values was extracted from linear fits to the Nernst-Einstein relation²⁹:

$$\sigma(T) = \frac{\sigma_0}{T} \exp\left(\frac{-E_a}{k_b T}\right)$$

where $\sigma(T)$ is the temperature-dependent conductivity, σ_0 is a pre-exponential constant, and k_b is the Boltzmann constant. The extracted activation energies for PED-, PEM-, and PVP-modified films were 0.402 eV, 0.295 eV, and 0.320 eV, respectively, significantly higher than that of the reference film (0.262 eV) (**Fig.3d**). The experimental trend in E_a values was consistent with the DFT results for Sn-ion in **Figure 3c**, confirming the enhanced energy barrier to effectively suppress ion migration by PED.

Resistive-switching tests were further conducted to assess ion mobility under an applied electric field (**Fig.3e, Supplementary Fig.15, 16, 17**). The transition from high resistance state

(HRS) to low resistance state (LRS) is mainly determined by conductive filament formation via mobile ion migrations (**Supplementary Fig.15**). Under the applied electric field, the reference device exhibited abrupt increase in current (set transitions) below 1 V, indicative of rapid conductive filament formation between top and bottom electrodes driven by mobile ions (**Fig.3e**). In contrast, devices with polymer interlayer, particularly those incorporating PED, showed a markedly enhanced threshold voltage of ~ 5 V for the transition from HRS to LRS (**Fig.3e** and **Supplementary Fig.16**). Notably, the device with only PED without SnO_2 demonstrated relatively lower threshold voltage compared to that for REF device (**Supplementary Fig.17**). These results imply that the synergetic effects between SnO_2 and PED can effectively suppress the mobile ion migrations in PED treated devices. Collectively, both computational and experimental analyses confirm that polymeric interlayers, especially PED, play a vital role in retarding migration of mobile ions including tin ions and stabilizing the buried interface.

Tin ion migration becomes more pronounced under external stresses such as prolonged illumination and elevated temperature. To quantify tin diffusion and evaluate the barrier efficacy of PED, inductively coupled plasma atomic emission spectrometry (ICP-AES) was performed on perovskite films that were dissolved from the substrate after MPPT operation (**Fig.3f**). After 100 hours of MPPT operation, the tin content in the reference device increased from 0.83 at% to 2.03 at%, whereas the PED-modified device showed only a minimal increase from 0.34 at% to 0.41 at%. XPS corroborated these findings, revealing a detectable Sn signal (0.25 at%) on the bottom surface of aged reference devices but no measurable Sn in polymer-interlayer-treated samples (**Supplementary Fig.18, 19, Table.3**). These results confirm the strong barrier capability of PED against tin diffusion, consistent with STEM/EDS observations.

To further probe the chemical state of migrated tin species, X-ray absorption near-edge structure (XANES) spectroscopy was performed on aged devices (**Fig.3g, Supplementary Fig.20**). The Sn K-edge spectra revealed that the oxidation state of diffused tin lies between that of SnI_2 and SnO_2 , indicating partial oxidation within the perovskite matrix. This intermediate oxidation state suggests that tin migration introduces chemical perturbations that alter the local electronic structure and promote defect formation, unintentional doping, and interfacial recombination^{30,31}. The inability of migrated tin to revert to its original oxidation state implies irreversible modification of the perovskite environment, with long-term consequences for both device stability and efficiency. These findings underscore the importance of suppressing not only tin migration

but also its subsequent oxidation, providing a mechanistic basis for the exceptional durability achieved through PED-based interfacial engineering.

Enhanced photovoltaic performance and long-term operational stability

The photovoltaic performance of devices incorporating different polymeric interlayers was systematically evaluated. The introduction of a PED interlayer resulted in a pronounced enhancement in average PCE, increasing from 23.43% for the reference device to 26.74%. Devices incorporating PEM and PVP interlayers also exhibited improved performance, with average PCEs of 25.23% and 25.12%, respectively. The addition of polymeric interlayers led to simultaneous increases in open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), and fill factor (FF), reflecting enhanced charge extraction and reduced interfacial recombination (**Fig.4a** and **Supplementary Fig.23, Table.4**). A certified PCE was achieved by PED-modified device achieved the highest PCE of 26.58 %, with a V_{oc} of 1.194 V, J_{sc} of 25.187 mA cm⁻², and FF of 86.06% (**Supplementary Fig.21**). The stabilized PCE values also improved markedly, from 21.3% in the reference device to 26.2%, 24.4%, and 23.8% for PED-, PEM-, and PVP-modified devices, respectively (**Fig.4b**). External quantum efficiency (EQE) spectra (**Fig.4c**) confirmed these results, showing excellent agreement between the integrated J_{sc} and values obtained from J - V measurements, with less than 5% deviation for the PED-treated device (integrated J_{sc} = 25.2 mA cm⁻²). While the EQE spectra displayed negligible differences above 500 nm, the PED-modified device exhibited a distinctly higher EQE in the 350-400 nm region, indicating improved photocarrier generation and extraction near the bottom interface. These results demonstrate that polymeric interlayers effectively enhance interfacial charge transport and overall photovoltaic performance, with PED yielding the most significant improvement. Building on the improvements observed in small-area devices, we further examined the scalability of the polymer-interlayer strategy by fabricating large-area perovskite modules with an active area of 21.54 cm². The PED-interlayer-based module achieved a certified power conversion efficiency of 24.17% (**Fig.4d**, **Supplementary Fig.22**), demonstrating that the interfacial advantages introduced by the PED interlayer are well preserved during scale-up. These results underscore the effectiveness of polymeric interlayers in enabling high-efficiency, large-area perovskite modules.

To gain further insight into the origin of the improved device efficiency, the interfacial energy level alignment was examined using ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe force microscopy (KPFM). As shown in **Supplementary Figures 24, 25** and **Table**

5, the PED-modified SnO₂ exhibited a shallower work function compared to the pristine SnO₂, while its valence band maximum (VBM) remained nearly unchanged. This upward shift of the Fermi level indicates enhanced n-type character and improved energy alignment with the perovskite conduction band, facilitating electron extraction and suppressing interfacial recombination. The KPFM mapping also revealed a more homogeneous surface potential distribution for the PED-treated film, implying reduced surface trap density and a more uniform interface.

The operational stability of the solar cell devices was further examined under MPPT using continuous 1-sun-equivalent white-light LED illumination at 65 °C (**Fig.4e**). The PED-treated device exhibited exceptional stability, maintaining 96 % of its initial PCE after 2000 hours of continuous operation, whereas the reference device degraded completely. Devices with PEM and PVP interlayers also showed improved retention of performance over time. To assess thermal-light cycling durability, unencapsulated devices were further tested under accelerated ISOS-L-2I conditions at 85 °C and 1-sun-equivalent illumination in a nitrogen-filled glovebox (**Fig.4f**). After 2400 hours, the reference device exhibited complete degradation, while devices containing PED, PEM, and PVP interlayers retained 90.5 %, 63.7 %, and 41.5 % of their initial PCEs, respectively. Furthermore, the perovskite film incorporating the PED interlayer exhibited significantly enhanced stability under 40% relative humidity and continuous light illumination compared to the reference sample (**Supplementary Fig.26**). Collectively, these results underscore the critical role of polymeric interlayers in stabilizing the buried interface and suppressing ion migration, thereby enabling substantial improvements in both efficiency and long-term operational durability of perovskite solar cells.

Discussion

This work identifies the buried interface between the SnO₂ electron transport layer and the perovskite absorber as one of the primary origins of performance degradation in perovskite solar cells. Owing to its high photon flux and carrier density, this hidden interface is particularly vulnerable to light-induced decomposition and tin-ion migration. By introducing polymeric interlayers, we strengthened interfacial bonding, improved film morphology, and effectively suppressed tin diffusion. Among the investigated polymers, PED exhibited the strongest adhesion and chemical stability, leading to enhanced crystallinity, higher activation barriers for ion migration, and suppressed phase transformation under stress. Consequently, PED-modified

devices achieved a power conversion efficiency of 26.58% and retained 96% of their initial performance after 2000 hours of operation. These findings highlight interfacial polymer engineering as an effective approach to achieving intrinsically stable and high-efficiency perovskite photovoltaics.

Materials and Methods

Dimethylsulfoxide (DMSO, 99.7%), isopropanol (IPA, 99.7%), dimethylformamide (DMF, 99.8%), acetone (99.9%), chlorobenzene (99.8%), acetonitrile (99.8%), 4-*tert*-butyl pyridine (98%) and lithium bis(trifluoromethanesulfonyl)imide (99.95%) were all purchased from Sigma-Aldrich. Lead iodide beads (PbI_2 , 99.999%) and SnO_2 colloidal solution (15% in water) were purchased from Alfa Aesar. Formamidinium iodide (FAI) and methylammonium iodide (MAI) were purchased from GreatCell Solar. Spiro-MeOTAD (99.8%) and methylammonium chloride (MACl) were purchased from Xi'an Polymer Light Technology. All the materials were used without further purification. ICP-AES tuning solution and chloric acid (trace metal grade) were from Alfa Aesar and Fisher Chemical, respectively. Standard element solution was purchased from the National Center of Analysis and Testing for Nonferrous and Electronic Materials. The standard solution was diluted into 1,000.0, 500.0, 200.0, 100.0 and 20.0 ppb with 1% HCl for the calibration curve. Milli-Q water (18.2 M Ω) was used in all experiments.

ITO glass slides were sequentially cleaned with detergent, deionized water, acetone, and IPA for 30 minutes each. Then, the ITO substrates were dried with a nitrogen gun and treated by UV-ozone for 20 minutes to remove organic residue from the surface. Some 0.2 ml of SnO_2 colloidal solution was diluted in 1.2 ml of deionized water and dropped on the pre-cleaned ITO glass slides at a rate of 3,000 r.p.m. for 30 s, followed by annealing at 150 °C for 30 minutes in air. After cooling to room temperature, the substrates were treated by UV-ozone for another 10 minutes and transferred into the glove box for the following steps. For the polymer interlayers, PED was dissolved in chloroform with a concentration of 1mg/ml. PEM and PVP were dissolved in chlorobenzene with a concentration of 1mg/ml. The solutions were spin-coated at a speed of 3000 r.p.m. for 30 s and annealed at 75°C for 1 minute. For the fabrication of perovskite films, a typical two-step method was employed: 1.5 M PbI_2 in DMF and DMSO (volume ratio, 9.5:0.5) was spin-coated onto the SnO_2 films at a rate of 1,500 r.p.m. for 30 s and annealed at 80 °C for 30 seconds. Organic salts of FAI/MABr/MACl (70 mg:10 mg:4 mg in 1 ml IPA) were spin-coated on PbI_2 films at a rate of 1,800 r.p.m. for 30 s, followed with thermal annealing at 150 °C for 13 min in ambient air with a controlled humidity (30–40%). The actual composition can be closer to that of FAPbI_3 due to the volatility of MACl during the annealing process. After being cooled to room temperature, the perovskite films were transferred into a glove box for spiro-MeOTAD deposition. The spiro-MeOTAD solution consisted of 72.3 mg spiro-MeOTAD, 28.8 μl of 4-*tert*-butyl

pyridine and 17.5 μl of lithium bis(trifluoromethanesulfonyl) imide solution (520 mg lithium bis(trifluoromethanesulfonyl) imide in 1 ml acetonitrile) in 1 ml of chlorobenzene. Some 40 μl of the spiro-MeOTAD solution was spin-coated on perovskite films at a rate of 3,000 r.p.m. for 30 s. For the stability test devices, we employed poly(bis(4-phenyl)(2,4,6-trimethylphenyl)amine) doped with 4-isopropyl-4'-methyldiphenyliodonium tetrakis (pentafluorophenyl) borate as the hole-transporting layer. Finally, 80 nm of Ag or Au was thermally evaporated as the electrode under high vacuum ($<5.0 \times 10^{-6}$ Pa).

Module Fabrication

Perovskite solar modules, consisting of nine sub-cells connected in series, were fabricated on FTO glass substrates with dimensions of $6 \times 6 \text{ cm}^2$. The series interconnection of the module was achieved by patterning P1, P2, and P3 lines using a laser scribing system with a wavelength of 1064 nm and a power output of 20 W. The FTO substrate was pre-patterned for P1 (20 μm width) utilizing 40% laser power at a speed of 500 mm/s, a frequency of 200 kHz, and a pulse width of 50 ns. The subsequent processes for preparing SnO_2 substrates were identical to those used for small-area devices. Similarly, the deposition procedure for the perovskite precursor mirrored that of small-scale solar cells, with the notable variation being the concentration of the perovskite precursor. Specifically, a 1.55 M perovskite precursor solution was employed for the perovskite layer using the spin-coating method, with the antisolvent addition duration matching that of the small-scale cells. After cooling to room temperature, the deposition procedures for the passivation layer and the Spiro-OMeTAD layer followed a methodology similar to that used for smaller-scale devices.

The P2 lines (80 μm width) were etched prior to the Au evaporation step, using an average laser power of 33%, a speed of 500 mm/s, a frequency of 50 kHz, and a pulse duration of 50 ns. The distance between P1 and P2 was approximately 60 μm . Following the deposition of a 100 nm thick gold layer, the P3 line (10 μm width) was fabricated under the same scribing conditions as the P2 line. The distance between P1 and P3 was approximately 180 μm , and the geometric fill factor (GFF) was around 96.5%. Additionally, laser edge cleaning was applied to the perovskite components, resulting in a light-receiving area of 21.54 cm^2 for the perovskite component. And the certified test was conducted using a Mask with an aperture area of 21.5 cm^2 .

Material characterization

Resistivity switching tests were measured using voltage sweep mode (CC=1 mA) on Keithley 4200 SCS under vacuum around 10^{-2} torr.

XPS measurements were carried out on an XPS AXIS Ultra DLD (Kratos Analytical). An Al K α (1,486.6 eV) X-ray was used as the excitation source. UPS measurements were carried out using a helium discharge lamp, emitting ultraviolet energy at 21.2 eV. All UPS measurements were performed using standard procedures with a -9V bias applied between the samples and the detectors.

PL spectroscopy was performed with a Horiba Jobin Yvon system, with a 532-nm xenon lamp or a 640-nm monochromatic laser excitation source. Time-resolved PL spectra were measured using a Picoharp 300 with time-correlated single-photon counting capabilities (PLD 800B, PicoQuant) with a repetition frequency of 100 kHz.

X-ray absorption spectroscopy measurements were performed at the QAS (7-BM) beamline of National Synchrotron Light Source – II at Brookhaven National Laboratory. The measurements were performed in fluorescence mode and up to 50 scans for each sample were merged to improve the signal to noise ratio.

SEM (Nova Nano 230) was used to characterize the morphology of the perovskite films. X-ray diffraction measurement was carried out by an X-ray diffractometer (PANalytical) with Cu K α radiation at a scan rate of 4° min^{-1} .

J–V characterizations of the solar cells were carried out with a Keithley 2401 source meter, under simulated one-sun illumination (AM 1.5G, 100 mW cm^{-2} ; Oriel Sol3A with class AAA solar simulator, Newport). The intensity calibration of the light was done by a National Renewable Energy Laboratory (NREL)-certified Si photodiode with a KG-5 filter. For each condition, at least eight devices were fabricated and measured for statistical analysis. The steady-state power output of the solar cells was calculated from the photocurrent, measured under constant bias voltage operation, that corresponds to a maximum power output. The IPCE measurement was carried out using a specially designed system (Enli Tech) in a.c. mode (chopping frequency, 210 Hz) without bias light.

Cross sectional TEM samples were prepared using Tescan Gaia3 Dual Beam FIB. STEM and EDS experiments were carried out by using a JEOL JEM-2800 S/TEM operated at 200 kV with dual 100 mm^2 silicon drift detector X-ray detectors.

AFM/KPFM was performed on Dimension Icon Scanning Probe Microscope (Bruker Nano, Inc.).

Molecular dynamics

All Molecular Dynamics (MD) simulations were carried out using the GPU-accelerated version of AMBER24³². For molecular mechanics parameters, the General AMBER Force Field (GAFF) were used for PED, PEM and PVP and FA⁺, following a standard protocol described in previous studies³³. For the remaining ions, force-field parameters designated within AMBER24 code were selected. A large 10nm x 10nm FAPbI₃ perovskite slab, and a polymer layer on top with or without free Sn ions, were first generated. Initial geometries of the polymers (having few monomer units) were prepared by randomly placing 12 polymers on the surface using the PACKMOL code³⁴, ensuring a minimum intermolecular distance of 2 Å. Partial charges were generated via the Merz-Singh-Kollman scheme using HF/6-31G(d) as implemented in Gaussian09³⁵ and incorporated as restrained electrostatic potential (RESP) charges^{36,37}. Periodic boundary conditions were imposed. The whole structure was initially energy-minimized over 1000 MD steps, with positional restraints applied to all heavy atoms. Each system was then heated and equilibrated at 300 K for 4 ns, during which the temperature was controlled using a Langevin thermostat (collision frequency of 5.0 ps⁻¹). This was followed by an additional 2 ns of relaxation using a Berendsen barostat to equilibrate the system at a pressure of 1 atm. Lastly, all restraints are removed and a production run of 40 ns was performed, maintaining the system at a constant temperature of 300 K and a time-averaged pressure of 1 atm.

Density Functional Theory Calculations

We calculated the energy barrier of tin migration through polymer materials on the perovskite surface with density functional theory (DFT). All simulations were performed in VASP (Vienna Ab initio Simulation Package) with a plane-wave basis and the projector-augmented wave (PAW) method^{38,39}. We used the Perdew–Burke–Ernzerhof (PBE) generalized-gradient functional for both the self-consistent field steps and the geometry optimizations. For the optimizations, we used a Γ -centered $2 \times 2 \times 1$ k-point mesh and a 400eV plane-wave cutoff. Atoms and cell parameters were relaxed with a conjugate-gradient algorithm until the residual forces were below 0.02 eV/Å. To avoid spurious interactions between periodic images, we added a 10–15 Å vacuum layer along the z direction. We placed the polymer atop the perovskite slab and made it laterally periodic so its repeat matches the perovskite lattice.

We evaluated tin migration barriers by tracking how the energy changes as the tin ion moves along its migration pathway. First, we optimized the initial and final structures; tin ion above the polymer and tin at the polymer-perovskite interface. We then generated intermediate geometries by linearly interpolating between them and mapped the pathway with the nudged elastic band (NEB) method and constrained minimization, using 16 images in total. The energy barrier height was taken as the energy difference between a minimum-energy state and the saddle point along the path.

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Author contributions: W.Y. and Y.Z. conceived the idea, designed and conducted the experiments, and prepared the manuscript under the supervision of Y.Y.. Z.-Y. S. conducted the small-area device and module efficiency certification experiments under the guidance of J. C. Y.L synthesized the polymeric materials and provided helpful guidance. I.Y. performed the DFT and MD calculations. M.W. collected cross section SEM , EQE and stability test data. W.H. helped with XANES tests under the supervision of A.I.F.. J.-G.Z performed STEM/EDS tests. M.X. also help with the STEM/EDS tests under the supervision of X.P.. J.-H.L. helped performed resistive switching test under the supervision of J.-W.L.. Y.Z. and T.-A.Y. performed KPFM/AFM tests. D.M., R.Z., Y. Z. and H. D. provided helpful discussion during the project. All the authors discussed the results and commented on the manuscript.

Competing interests: Authors declare no competing interests.

Data and materials availability: All data are available in the main text or the supplementary materials.

Supplementary Materials:

Supplementary Text 1-2

Figs. 1-27

Tables 1-5

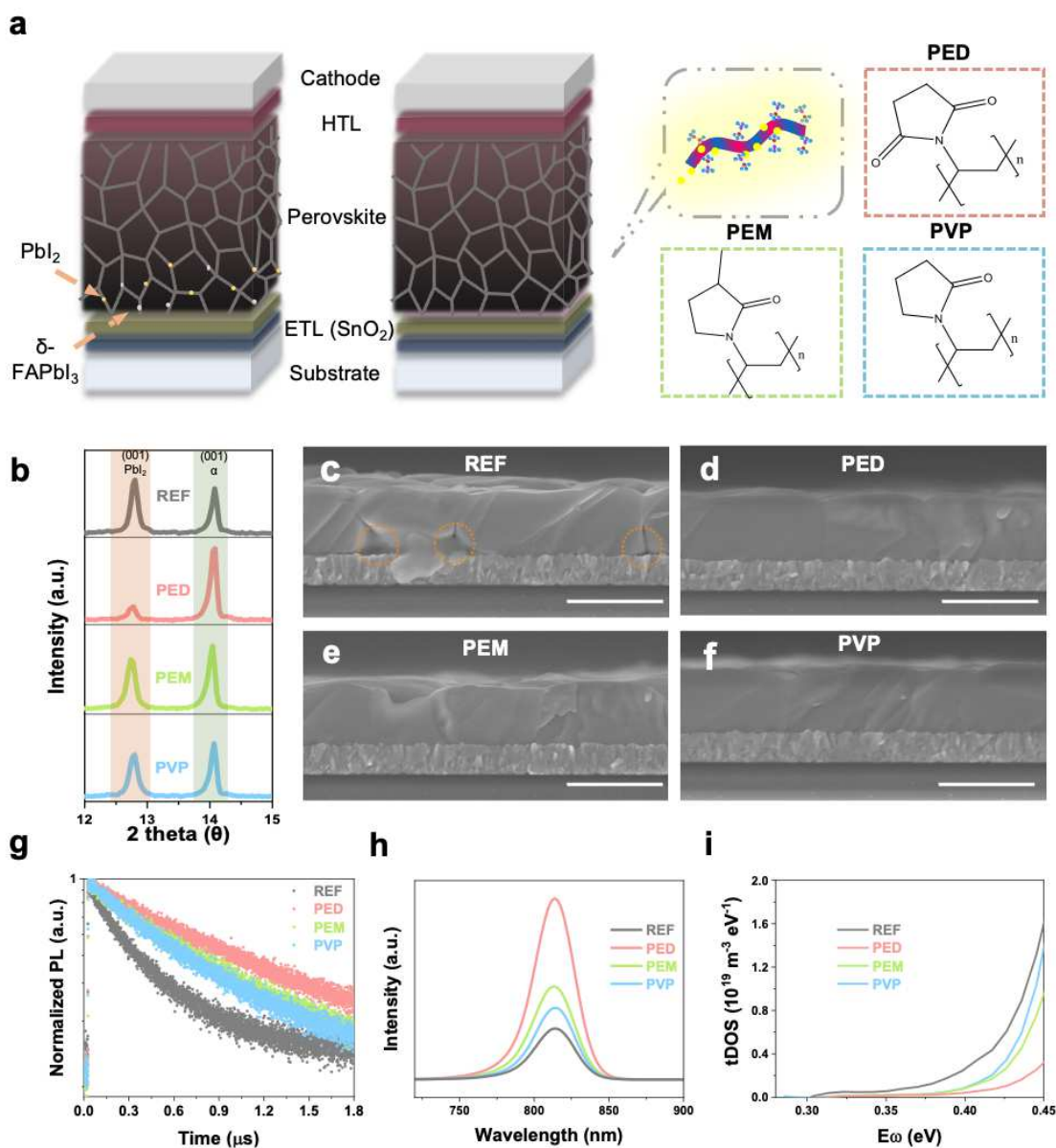


Fig. 1 | **(a)** Device illustration and polymers structures. **(b)** XRD spectra of bottom perovskite interface with and without polymeric interlayers. Cross-section SEM (scale bar: 1 μm) images of the fresh perovskite film: **(c)** without polymeric interlayer treatment; **(d)** with PED; **(e)** with PEM; **(f)** with PVP. **(g)** TRPL spectra without or with the polymeric interlayers. (The testing structure follows a Glass/ITO/SnO₂/perovskite) **(h)** steady-state spectra. **(i)** tDOS in perovskite solar cells with or without polymeric interlayers.

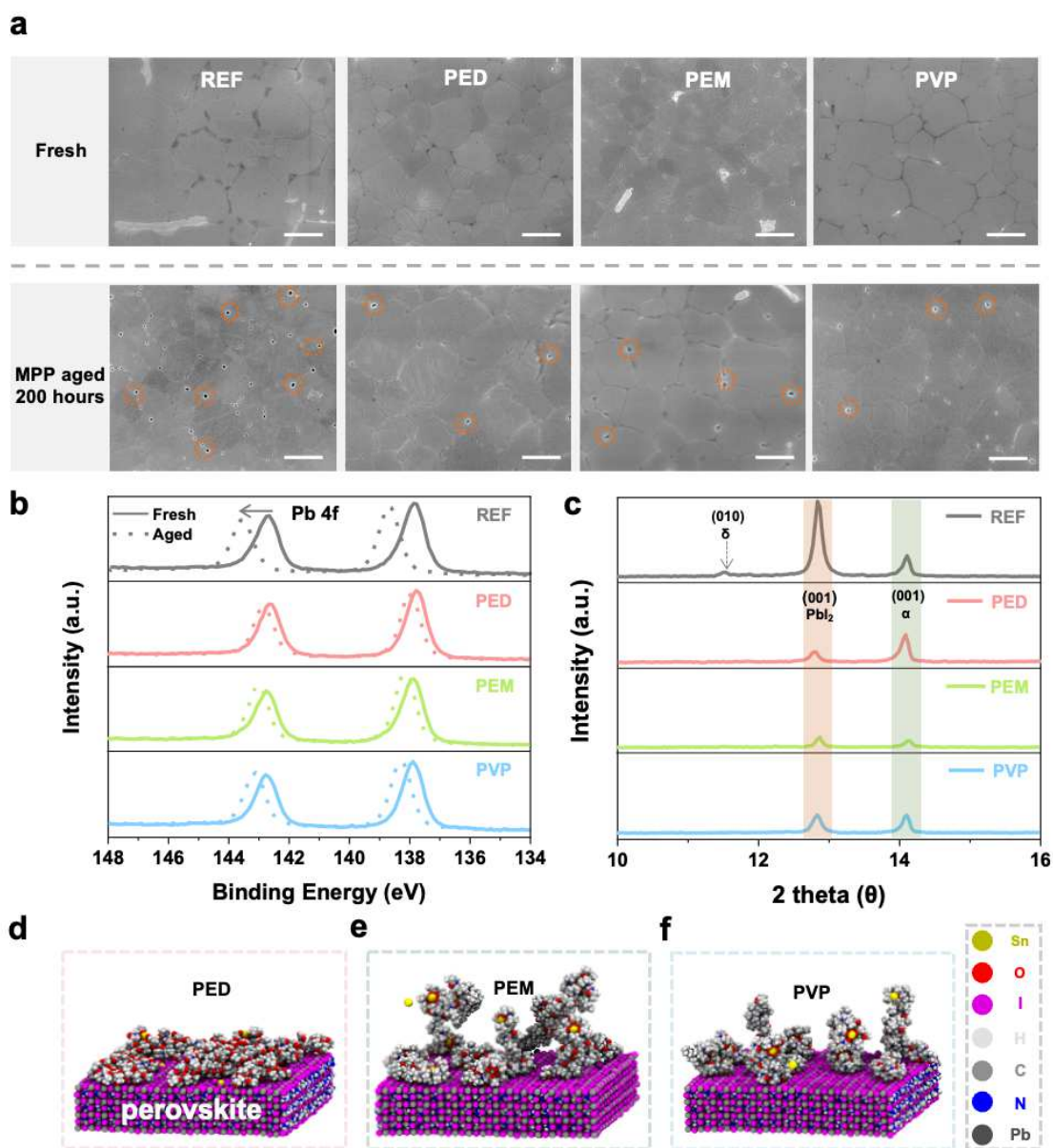


Fig. 2 | **(a)** SEM images (scale bar: 1 μm) of the bottom surface with and without polymeric interlayers. **(b)** XPS spectra of Pb 4f with and without polymeric interlayers before and after operation. **(c)** XRD spectra of bottom perovskite surface after operation. MD simulation of **(d)** PED; **(e)** PEM; **(f)** PVP on the perovskite surface.

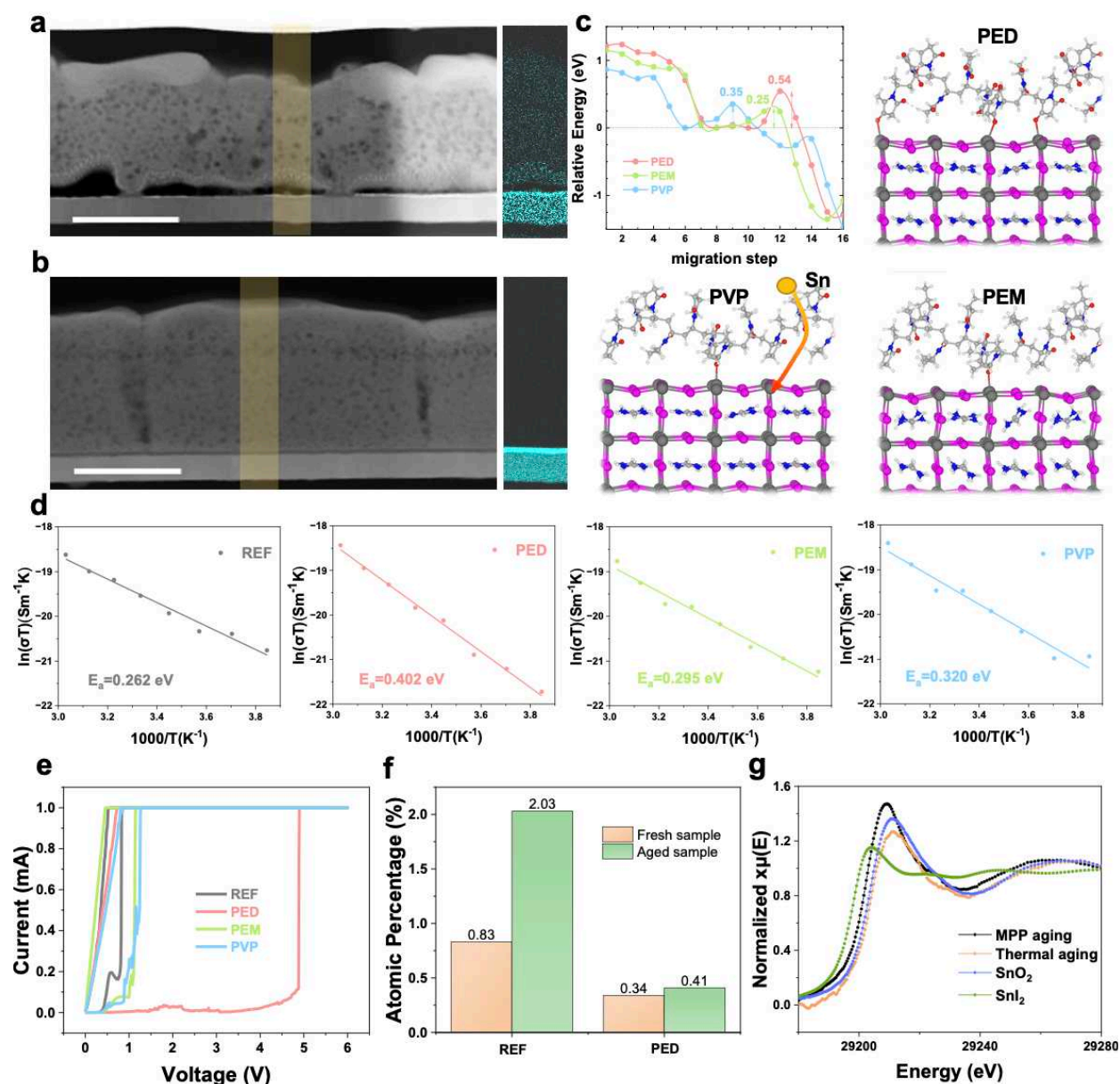


Fig. 3 | **(a)** cross-sectional STEM image (scale bar: 500 nm) and tin EDS elemental map of the highlighted area in the reference sample after MPPT aging. **(b)** cross-sectional STEM image and tin EDS elemental map of the highlighted area in the PED-treated sample after MPPT aging. **(c)** DFT calculation of tin ions near polymeric materials. **(d)** Temperature-dependent conductivity of devices with PED, PEM and PVP polymeric interlayer. Filled circles are measured data while dashed lines are fitted lines. **(e)** Resistivity switching tests of perovskite solar cells with or without polymeric interlayers. **(f)** ICP-AES results of tin content in aged and fresh samples. **(g)** Sn K-edge

X-ray absorption near-edge spectra showing intermediate charge state (between those of SnI_2 and SnO_2) for the aging sample.

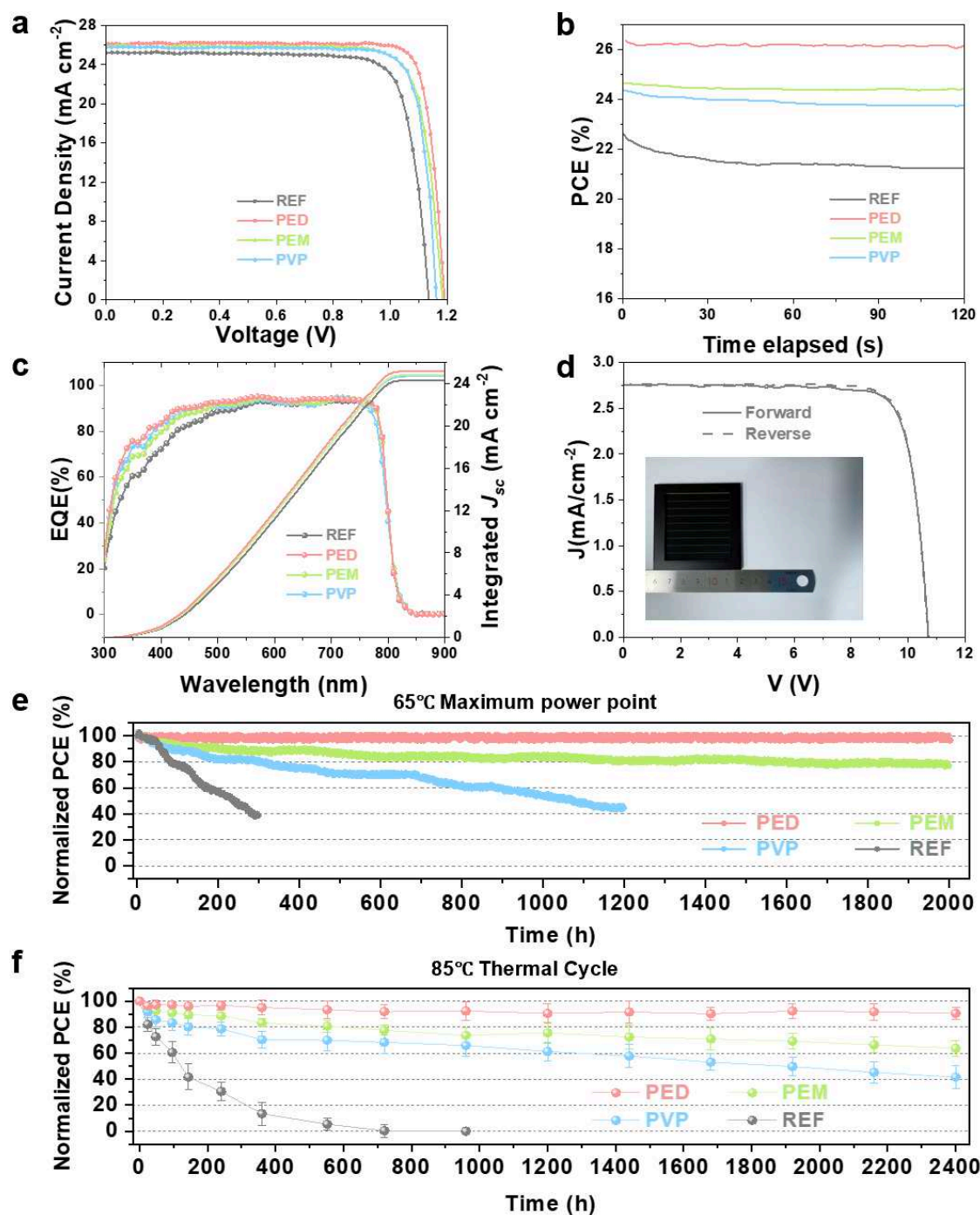


Fig. 4 | (a) J - V curves of devices with and without polymeric interlayers. (b) Stabilized PCE measurement. (c) EQE spectra and Integrated J_{sc} of the best-performing devices. (d) Forward and reverse J - V curves of module device with PED interlayer (e) MPPT stability test under one-sun illumination without or with the polymeric interlayers. (f) Thermal-light stability test under one-sun illumination without or with the polymeric interlayers.

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