

RESEARCH ARTICLE

SOLAR CELLS

Stabilized hole-selective layer for high-performance inverted p-i-n perovskite solar cells

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P-i-n geometry perovskite solar cells (PSCs) offer simplified fabrication, greater amenability to charge extraction layers, and low-temperature processing over n-i-p counterparts. Self-assembled monolayers (SAMs) can enhance the performance of p-i-n PSCs but ultrathin SAMs can be thermally unstable. We report a thermally robust hole-selective layer comprised of nickel oxide (NiO₂) nanoparticle film with a surface-anchored (4-(3,11-dimethoxy-7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (MeO-4PADBC) SAM that can improve and stabilize the NiO_x/perovskite interface. The energetic alignment and favorable contact and binding between NiO_x/MeO-4PADBC and perovskite reduced the voltage deficit of PSCs with various perovskite compositions and led to strong interface toughening effects under thermal stress. The resulting 1.53-electronvolt devices achieved 25.6% certified power conversion efficiency and maintained >90% of their initial efficiency after continuously operating at 65 degrees Celsius for 1200 hours under 1-sun illumination.

hosphonic acid self-assembled monolayers (SAMs) with a carbazole core have enabled performance advances in perovskite solar cells (PSCs), for both singlejunction (1-4) and perovskite-based tandem solar cells (5-9), because of their high hole selectivity, fast hole transfer rate, and low interfacial trap state density (10-13). However, compared with conventional polymeric and metal oxide hole transporting materials, SAMbased PSCs have exhibited poorer thermal stability (14–18). The investigation of the device's operational stability, with electrical bias under maximum power point (MPP) operation or at open-circuit voltage ($V_{\rm OC}$), under elevated temperatures (65° to 85°C) is critical to improve the confidence in their stability and to meet the qualification of international stability standards (i.e., International Summit on Organic Photovoltic Stability (ISOS) and International Electrotechnical Commission 61215 standards) (19). Whereas most studies on the SAM-based PSCs have reported the operational stability at room temperature or enhanced the device's durability under thermal stress by stabilizing perovskite surface and bulk (20, 21), the degradation effect of SAM-forming molecules under elevated tem-

perature (>65°C) have rarely been discussed (fig. S1 and table S1). The thermal stability of SAM-forming molecules depends largely on their bonding to the selected substrates, as the bond between the anchoring group and the spacer of the molecule can be broken through temperature-induced desorption (22-25).

We report a new SAM, (4-(3,11-dimethoxy-7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (MeO-4PADBC), which we anchored to the NiO_x film to fabricate inverted p-i-n PSCs (fig. S2). The $NiO_x/MeO-4PADBC$ exhibited an optimal dipole moment and amenable surface for favorable contact with perovskite that resulted in an ideal energetic alignment, fast hole extraction, and low defect density. Such an interface configuration also immobilized the SAM molecules at the NiO_x/perovskite interface and produced a robust hole-selective layer (HSL) for thermally stable PSCs that had thermal-degradation activation energy ~3 times greater than that for ITO/MeO-4PADBC. These synergetic effects enabled 1.53-electron volt (eV) p-i-n PSCs $V_{\rm OC}$ of 1.19 V (95% of calculated potential) and a verified power conversion efficiency (PCE) of 25.6%, 1.68- and 1.80-eVwide bandgap perovskite composition devices also showed encouraging PCEs of 22.7 and 20.1%, respectively. Moreover, 1.53-eV PSCs using NiO_x/MeO-4PADBC HSL maintained >90% of initial efficiency in long-term operational stability tests under 65°C for 1200 hours, and extrapolation of the Arrhenius energy indicates that the solar cells should maintain 80% of initial efficiency for more than 10 months at 25°C.

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SAM design and synthesis

Modulating the terminal functional group is an effective way to tune the interfacial interactions between SAMs and perovskite. For example, the introduction of two methoxy groups (OMe) into [2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz) enabled a new SAM, [2-(3,6dimethoxy-9H-carbazol-9-vl)ethyl]phosphonic acid (MeO-2PACz), which improved the interfacial contact and enabled a higher efficiency of p-i-n PSC compared with 2PACz (10). Nonetheless, the OMe substitution on the carbazole core also caused a decrease in dipole moment from ~2.0 D of 2PACz to ~0.2 D of MeO-2PACz. which in turn led to the offset between the highest occupied molecular orbital (HOMO) of the SAM molecule and the valence band maximum (VBM) of the perovskite (10, 26). This phenomenon can be ascribed to high planarity and symmetry of the carbazole structure; the incorporation of two OMe groups with opposite directions of dipole moment resulted in a net molecular dipole moment of MeO-2PACz close to zero (Fig. 1A). We addressed this issue by using a non-coplanar screw-shaped dibenzo[c,g]carbazole (DBC) unit as the core to reduce the negative effect on the dipole moment when introducing OMe groups, affording a new SAM of MeO-4PADBC (Fig. 1B). Density functional theory (DFT) calculations verified that MeO-4PADBC only has a slightly decreased dipole moment (2.4 D) compared with that of (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (4PADBC) (2.9 D), which is quite different from those obtained for carbazole-based SAMs (figs. S3 and S4).

The synthetic route of MeO-4PADBC is shown in fig. S5, along with structural characterizations presented in figs. S6 to S9. The calculated HOMO and lowest unoccupied molecular orbital distributions are shown in fig. S10, with values of -4.91 and -1.15 eV, respectively. To gain a deeper insight of the SAM molecule structure, we grew a single crystal of 3,11-dimethoxy-7H-dibenzo[c,g] carbazole (MeO-DBC, CCDC number: 2279245), which lacks the anchoring group that would disrupt intermolecular interactions. As shown in fig. S11, A and B, two naphthalene rings are located on different sides of the pyrrole ring and exhibit a dihedral angle of 12.44°, which greatly reduces the planarity and symmetry of the skeleton structure to enable a negligible effect on the dipole moment when introducing OMe groups. Moreover, the MeO-DBC core had a slipped π -stacked packing motif with strong C-H··· π (2.72 Å) and π - π (3.79 Å) interactions (fig. S11C), which could induce a highly ordered one-dimensional assembly that favors a dense, tilted, highly ordered monolayer on the substrate (fig. S11D) (9, 27, 28).

We then calculated the interfacial binding energies between SAMs and perovskite, showing that MeO-4PADBC has a stronger binding with perovskite with a total binding energy (E_b) of -7.19 eV, compared with that of -5.27 eV for MeO-2PACz (fig. S12). The main electrostatic interaction of the calculated SAMs is the O atoms from OMe groups with the Pb from

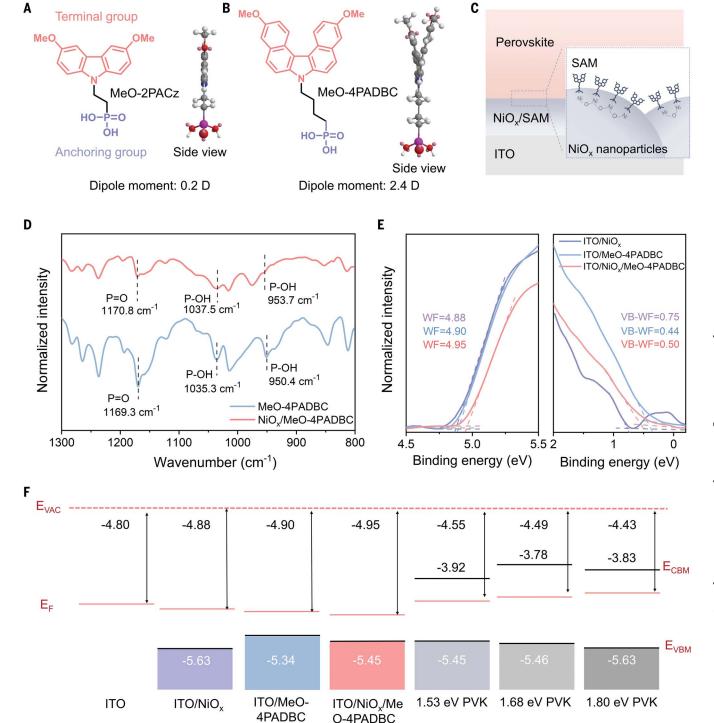


Fig. 1. Molecular structure and electrical properties of HSLs. Molecular structure and side view of **(A)** MeO-2PACz and **(B)** MeO-4PADBC. **(C)** Schematic illustration of MeO-4PADBC anchoring on NiO $_{\rm x}$ nanoparticle as the HSL in PSC. **(D)** FTIR spectra of MeO-4PADBC and NiO $_{\rm x}$ /MeO-4PADBC. **(E)** UPS spectra of ITO substrates covered by NiO $_{\rm x}$. MeO-4PADBC, and NiO $_{\rm x}$ /MeO-4PADBC. (Left) UPS spectra around the secondary electron cutoff (WF, work function);

(right) UPS spectra in the valence band (VB) region. (\mathbf{F}) Schematic representation of the band edge positions of the studied HSLs based on values from UPS measurements, referenced to the vacuum level. E_F and E_{VAC} represent Fermi and vacuum levels, respectively. E_{VBM} and E_{CBM} represent the energy of valence band maximum and conduction band minimum, respectively.

perovskite, however MeO-4PADBC has a more energetically favorable contact with perovskite compared with MeO-2PACz, which can be ascribed to the more concentrated electron distribution of the coordinated OMe group on MeO-4PADBC than that on MeO-2PACz (fig. S13). Moreover, Bader charge analysis also suggests a stronger Pb-O interaction between MeO-4PADBC and perovskite with a shorter calculated interaction length of 4.7 Å than that of MeO-2PACz of 4.9 Å (fig. S14), which can be further confirmed by the results

of ¹H NMR spectra of the SAMs in DMSO- d_6 with or without mixing with PbI₂ (fig. S15).

Hole-selective layer applications

We compared MeO-4PADBC SAM and NiOx/ MeO-4PADBC as the HSLs for p-i-n PSCs (Fig. 1C). Fourier-transform infrared (FTIR) spectra were then collected by scraping the MeO-4PADBC and NiO_x/MeO-4PADBC films off the substrates to amplify the signal, in which the P=O (1169 cm⁻¹) and P-OH (1035 and 950 cm⁻¹) absorption peaks show a clear shift (Fig. 1D), indicating the formation of a chemical bond (29). This can be further confirmed by the changes of the Ni 2p core level of NiO_x and NiO_x/MeO-4PADBC films deposited on the indium tin oxide (ITO) substrates obtained by x-ray photoelectron spectroscopy (XPS) spectra (fig. S16). The crystal structure and absorbance of representative perovskite film with a composition of $Cs_{0.05}FA_{0.85}MA_{0.1}PbI_3$ on both substrates remained unchanged (figs. S17 and S18). However, the perovskite deposited on ITO/NiOx/MeO-4PADBC substrate had larger crystal domains than those on control substrates (fig. S19). This is because of the denser anchoring of SAM molecules onto the ITO/NiO_x substrate through more robust tridentate binding absorption, which can not only reduce the surface roughness of ITO/NiO_x substrate (30-32) (figs. S20 and S21), but also lead to a more hydrophobic surface (fig. S22) and stronger interaction between perovskite and SAM molecules (33-35). These synergetic effects contribute to facilitating the perovskite crystal nucleation and growth, thus enhancing the perovskite crystallization.

We further used ultraviolet photoelectron spectroscopy (UPS) to assess the energetic alignment of different substrates relative to perovskite absorbers with different bandgaps (1.53, 1.68, and 1.8 eV, see Fig. 1E and fig. S23), and the results are summarized in Fig. 1F. The HOMO energy levels are -5.34 eV for ITO/MeO-4PADBC and -5.45 eV ITO/NiO_x/MeO-4PADBC, respectively, and the work function (Φ) of the latter substrate is deeper than that of the former one (-4.95 versus -4.90 eV), indicative of better energetic alignment with different perovskite absorbers. However, upon application of the carbazole-based SAM molecules onto the ITO/ NiO_x surface, the ITO/NiO_x/MeO-2PACz system exhibited an upward shift of the Φ , in contrast to the ITO/NiO_x/2PACz substrate (26, 36) (fig. S24). This phenomenon can be attributed to the incorporation of OMe groups on 2PACz, which considerably reduced the dipole moment. This reduction can be explained by the highly planar carbazole motif, as discussed earlier. Timeresolved photoluminescence (TRPL) decay data showed a decreased carrier lifetime from 925.5 ns for the perovskite on ITO to 42.9 and 32.3 ns for the perovskite on ITO/MeO-4PADBC and ITO/NiO_v/MeO-4PADBC, respectively, indicating a more facilitated hole extraction resulted by the $\rm ITO/NiO_x/MeO\text{-}4PADBC$ substrate (fig. S25 and table S2).

Solar cell performance and characterization

We further evaluated the photovoltaic performance of PSCs with a p-i-n device configuration: glass/ITO/HSL/perovskite/two-dimensional (2D) passivation layer/C₆₀/bathocuproine (BCP)/ Ag (Fig. 2A). The 2D passivation layer was a mixture of 4-trifluorophenylethylammonium iodide (CF3-PEAI) and methylammonium iodide (MAI) with an optimal volume ratio of 3:1 (4). The cross-section scanning electron microscopy (SEM) images of the PSC (1.53 eV) showed a thickness of ~715 nm for the perovskite films (fig. S26). The device with NiO₂/MeO-4PADBC as the HSL (1.53 eV) showed negligible hysteresis and had a high verified PCE of 25.6% for a mask area of 0.0414 cm² (figs. S27 and S28), with a $V_{\rm OC}$ of 1.19 V, a short-circuit current density (J_{SC}) of 25.4 mA cm⁻², and a fill factor (FF) of 84.6%, which outperformed the MeO-4PADBC-based device (PCE = 24.2% with $V_{\rm OC}$ = 1.16 V, $J_{\rm SC}$ = 25.4 mA cm⁻², and FF = 82.1%). The NiOx control device without a SAM only showed a PCE of 21.6%, attributed to a mismatch of energetic alignment and high surface defect density on NiO_x film (37, 38) (Fig. 2B). Moreover, we have also conducted HSL engineering by applying carbazole-based SAM anchoring on NiO_x. The V_{OC} of the NiO_x/MeO-2PACz-based device (1.15 V) is lower than that of the device with NiO_x/2PACz (1.17 V) (figs. S29, A and B). This issue was addressed by replacing the carbazole motif with a nonplanar DBC core in SAM molecules (fig. S29, C and D). To better understand the mechanism of the improved $V_{\rm OC}$ and FF with the use of NiO_x/ MeO-4PADBC as HSL, we further conducted the FF loss (supplementary text and fig. S30) and $V_{\rm OC}$ loss calculations (supplementary text, fig. S31, and table S3). We observed that the improved V_{OC} and FF of NiO_x/MeO-4PADBC were mainly attributed to the suppressed nonradiative recombination loss, indicating reduced trap state density at the HSL/perovskite interface.

Our NiOx/MeO-4PADBC strategy also worked effectively for 1.68- and 1.80-eV PSCs, resulting in PCEs of 22.7 and 20.1%, respectively (Fig. 2C, fig. S32, and table S4). Steady-state power output (SPO) confirmed the reliability of three bandgap devices, with stabilized PCEs of 25.5, 22.3, and 19.5% for 1.53-, 1.68- and 1.80-eV, respectively (Fig. 2D). Additionally, the calculated $J_{\rm SC}$ values from external quantum efficiency (EQE) of the champion devices were consistent with those extracted from the current density-voltage (J-V) measurements (fig. S33), and the derivatives of EQE spectra can further confirm the perovskite bandgaps applied here (fig. S34). We further presented the EQE with internal quantum efficiency (IQE) results of representative 1.53-eV device with HSLs of NiO_x, MeO-4PADBC, and NiO_x/MeO-

4PADBC in fig. S35. The IQE between 550 nm to 700 nm is spectrally flat and approaches nearly 100% for both of MeO-4PADBC and $\rm NiO_x/MeO-4PADBC$ -based devices, indicating efficient charge collection and transfer at the perovskite interface achieved by the incorporation of SAM (12, 39).

The defect density profiles were then studied to identify enhanced photovoltaic performance through the space charge limit current (SCLC) method (fig. S36). The hole-only devices with NiO_x/MeO-4PADBC showed the lowest defect density of 1.96×10¹⁵ cm⁻³, compared with those with MeO-4PADBC (2.91×1015 cm-3) and NiO_x (3.81×10¹⁵ cm⁻³). In addition, the decreased slope of the light intensity dependence $V_{\rm OC}$ plot for NiO_x/MeO-4PADBC-based devices supported a reduced interfacial trap density at the HSL/perovskite interface (40) (fig. S37). We note that PSCs based on NiO_x/ MeO-4PADBC further demonstrated a lower leakage current than those on other HSLs (fig. S38), which we attributed to the compact NiO_v layer preventing the perovskite from contacting ITO through the pinholes in the ultrathin SAM layer. These results demonstrated that the NiO_x/MeO-4PADBC HSL effectively increased the $V_{\rm OC}$ of the PSCs.

To quantify the interface losses, quasi-Fermi level splitting (QFLS) analysis for partial cell stacks was conducted. A laser wavelength of 375 nm was used to illuminate a PSC with 1-sun equivalent intensity by accommodating the generated current near J_{SC} under a standard solar simulator (41, 42) (supplementary text, fig. S39). As shown in Fig. 2E, the QFLS of ITO/NiO_x/MeO-4PADBC/perovskite stack was comparable to the glass/perovskite stack, with implied $V_{\rm OC}$ of 1.17 V versus 1.18 V for 1.53-eV perovskite film, 1.26 V versus 1.27 V for 1.68-eV perovskite film, and 1.35 V versus 1.36 V for 1.80-eV perovskite film, respectively. These results indicated a low voltage loss on the interface between NiOx/MeO-4PADBC and perovskites.

We further performed the QFLS measurements on the ITO/HSL/perovskite/passivation layer/electron-transporting layer (ETL) stacks (Fig. 2F), with the $V_{\rm OC}$ s of the PSCs listed as a comparison. The differences between the QFLS of PSCs on ITO/NiOx/MeO-4PADBC and the $V_{\rm OC}$ extracted from related J-V measurements were comparable, demonstrating spatially flat Fermi levels throughout the device and low energy offset on the HSL for carrier extraction (27, 28). It is noteworthy that the $V_{\rm OC}$ of our 1.53-eV devices (1.19 V) reached 95% of their calculated potential and the $V_{\rm OC}$ of our 1.68-eV (1.25 V) and 1.80-eV (1.34 V) devices also approached 90% of the calculated potential (Fig. 2G).

PSC stability studies

Previous reports have demonstrated that SAMs desorb under thermal stress from the anchored

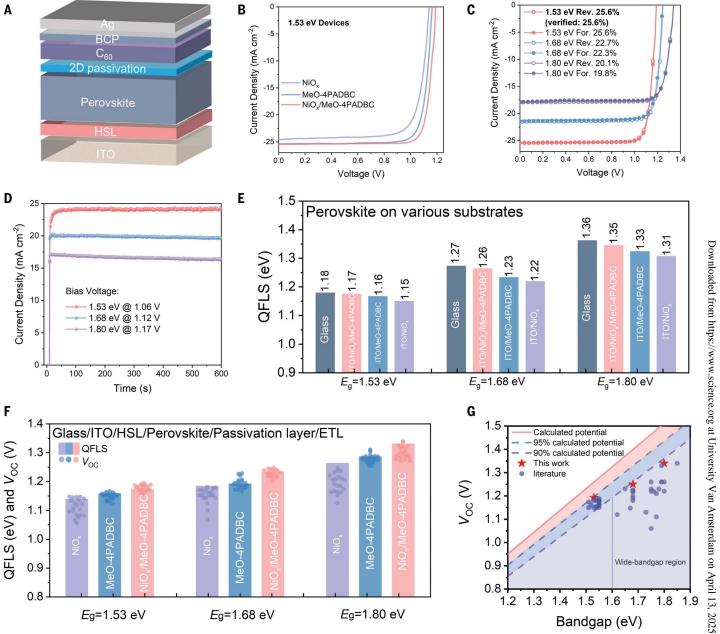


Fig. 2. Photovoltaic performance of PSCs with different HSLs. (A) Schematic illustration of p-i-n PSC. (B) J-V curves of the best-performing 1.53 eV devices with NiO_x, MeO-4PADBC, and NiO_x/MeO-4PADBC as HSL. (C) J-V curves of the bestperforming NiO_x/MeO-4PADBC-based devices with bandgaps of 1.53, 1.68, and 1.80 eV (Rev., reverse scan; For., forward scan). (D) SPO at the MPP for the bestperforming NiO_x/MeO-4PADBC-based PSCs with three bandgaps of perovskite

absorbers. (E) QFLS in the case of three bandgaps of perovskite with different HSLs. (F) Comparison of the $V_{\rm OC}$ of actual PSCs with the corresponding QFLS of representative layer stacks. (**G**) Comparison of the $V_{\rm OC}$ with different bandgaps of devices from the literature to our work. The line represents the $V_{\rm OC}$ extracted from calculated potential. The wide-bandgap region refers to 1.6 to 1.9 eV in the figure.

substrate (29, 30), but few effective solutions to this problem have been explored. To estimate the thermal stability of the ITO/NiO_x/MeO-4PADBC substrate, we applied Kelvin probe force microscopy (KPFM) to record the surface potential evolution of the SAM under heat treatment by taking pristine ITO/MeO-4PADBC as a reference. Before thermal aging, the ITO/ MeO-4PADBC and ITO/NiOx/MeO-4PADBC substrates both exhibited relatively uniform sur-

face potential with a narrow contact potential distribution (CPD) of ~40 mV, indicating that the SAM molecules were densely packed onto both of ITO and NiO_x surfaces (Fig. 3, A and B). After aging on a hotplate at 65°C for 1200 hours, the NiOx/MeO-4PADBC substrate displayed negligible CPD changes, whereas the ITO/MeO-4PADBC CPD value increased to ~70 mV (Fig. 3, C and D). We propose that the fluctuations of CPD for the ITO/MeO-4PADBC substrate could be attributed to desorption, morphological changes under thermal stress, or both.

To further explore the binding ability of SAM to the substrate under heating, DFT simulations were conducted to investigate the binding energies between MeO-4PADBC and ITO or NiO_x substrate at 300 K (~27°C) and 340 K (~67°C) (Fig. 3, E and F). MeO-4PADBC had a higher binding energy with NiO_x (-22.4 eV) than with ITO (-16.7 eV) at 300 K, suggesting

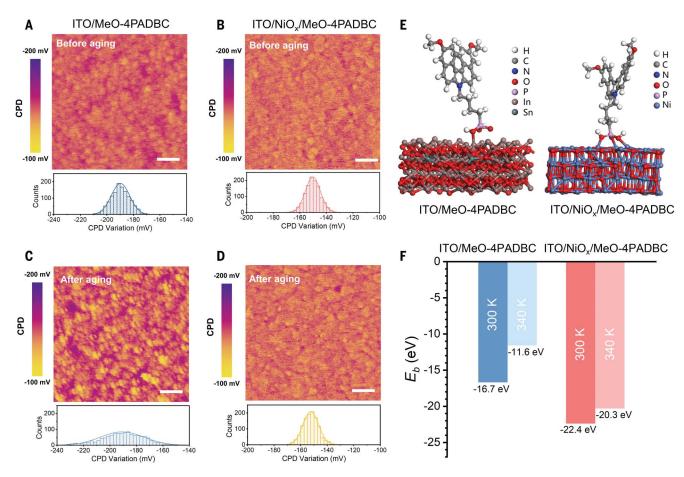


Fig. 3. Analysis of the degradation mechanism of PSCs. (A to **D**) Surface potential images obtained by scanning Kelvin probe microscopy (scale bar 500 nm) of the HSLs before and after aging at 65°C for 1200 hours. At the bottom of the figure are the statistical potential distributions of film surfaces. (**E**) DFT calculation of the binding energy of MeO-4PADBC with ITO and NiO_x. (**F**) Binding energies (E_b) of MeO-4PADBC with ITO and with NiO_x at the temperatures of 300 and 340 K.

a stronger bonding strength on the NiO_x film. This difference was attributed to the higher density of hydroxyl groups on the NiO_x surface than on the ITO, which is critical to the chemisorption of SAM on the metal oxide (43, 44). The tridentate binding between SAM and NiO_x was stronger than the bidentate binding between SAM and ITO (29, 45). At 340 K, the binding energy between SAM and ITO decreased from -16.7 to -11.6 eV, but that between MeO-4PADBC and NiO_x film showed minor changes (-20.3 eV). These results indicated that MeO-4PADBC on the NiO_x film is more robust against thermal stress compared with MeO-4PADBC on bare ITO.

Thermal accelerated aging measurements were conducted to evaluate the reliability of SAM-based PSCs. To avoid the influence of the 2D capping layer, the encapsulated devices without top passivation were prepared for stability testing. The initial *J-V* curves and photographs of the encapsulated devices are shown in fig. S40 and S41, respectively. The PSCs were operated under constant 1-sun illumination at fixed resistance loads near the MPP with the temperature ranging from

25° to 100°C, following the ISOS-L-2I procedure (19). The MeO-4PADBC-based devices degraded to 85 and 65% of starting PCEs after 1200 hours at 25°C and 65°C, respectively (Fig. 4A). When the aging temperature increased to 85°C, only 47% of its initial PCE was retained after 800 hours. The NiOx devices retained 85 and 65% of initial PCEs at 65° and 85°C, respectively, after 1200 hours (Fig. 4B). However, the NiO_x/MeO-4PADBC-based devices retained 90 and 74% of initial PCEs after 1200 hours at 65° and 85°C, respectively (Fig. 4C), which was consistent with the degradation analysis in Fig. 3. Both devices based on NiO_x, MeO-4PADBC, or NiO_x/MeO-4PADBC as HSL showed a more obvious downward trend when the aging temperature was raised to 100°C. For a more comprehensive evaluation of the thermal stability of our NiO_v/MeO-4PADBC strategy, we further applied the PSCs with top passivation to conduct the operational stability at 65°C for 500 hours (fig. S42). The devices presented a slightly improved stability compared with the device without passivation at the same time stage, which maintained 96% of its initial PCE. This may be due to the higher hydrophobic surface brought by the CF₃-PEAI passivation (46).

We then determined the activation energy (E_a) of the temperature-dependent degradation of our PSCs with different HSLs according to a previously reported method (supplementary text) (47). The E_a value of NiO_x/MeO-4PADBC-based devices (0.389 \pm 0.022 eV) was almost three times higher than that of MeO-4PADBC-based devices (0.150 \pm 0.017 eV). The lifetime acceleration factor (AF) of each temperature can be obtained from E_a (Fig. 4D), from which it can be estimated that PSCs with NiO_x/MeO-4PADBC HSL could retained 80% of its initial PCE at room temperature after 7567 hours operation, without top passivation treatment.

Conclusions

We have demonstrated an efficient and stabilized HSL with greatly improved thermal stability for high efficiency SAM-containing inverted p-i-n PSCs. Rational molecular structure design of MeO-4PADBC and in-depth analysis revealed that optimal dipole moment and favorable contact with perovskite are the

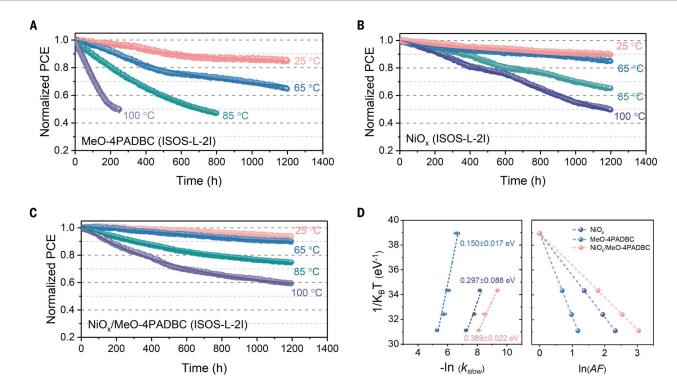


Fig. 4. Long-term stability assessment of PSCs under different temperatures. (A to C) Operational stability of PSCs with HSL of (A) MeO-4PADBC. (B) NiO_x, and (C) NiO_x/MeO-4PADBC at temperatures of 25°, 65°, 85°, and 100°C, respectively. (**D**) Natural logarithm of slow degradation rate (k_{slow}) versus $1/k_BT$

obtained from biexponential fits, where k_B is Boltzmann's constant and T is aging temperature. The dashed line comes from the linear fits to extract the E_a from each exponential (left); and natural logarithm of AF versus 1/k_BT. Standard operating condition for AF value calculation refers to 1-sun illumination at 25°C (right).

keys to ideal energy alignment and fast hole extraction to improve the device efficiency and stability. Moreover, the anchoring of MeO-4PADBC SAM molecules on the NiOx film can form a stronger tridentate bond with NiOx, which effectively reduces the voltage loss and further maintains a strong fixation effect under thermal stress. Our study provides theoretical guidance for the design of efficient and stable HSL and paves the path for facile access to commercially available inverted p-i-n PSCs.

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