

Improved Crystallization-Front Dynamics Reduce Buried-Interface Defects in Perovskite Solar Cells

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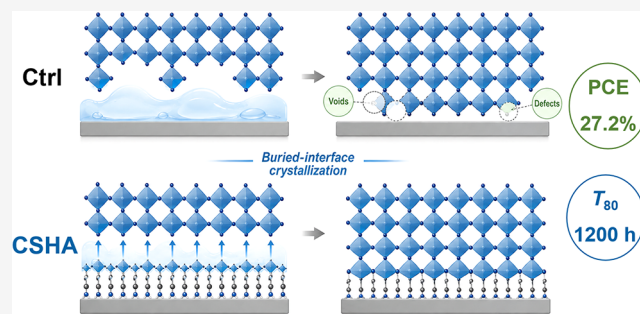


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Supporting Information

ABSTRACT: Inverted perovskite solar cells have achieved substantial efficiency gains owing to advances in surface passivation; as a result, progress is now limited by buried defects at the perovskite/hole transport layer (HTL) interface. During top-down perovskite crystallization, the downward film-closure front eventually reaches precursor-phobic, low-surface-energy HTLs in a regime of severe local solution depletion, leading to interfacial solution cavities that then evolve into defects and voids, an issue that becomes increasingly pronounced with larger device areas. We hypothesize that pre-embedding adhesion-enhancing molecules at the HTL surface could trigger early buried-interface crystallization. This could produce solidification on a precursor-affine, homogeneous perovskite-terminated surface, preventing solution cavities and suppressing void formation. We explore a series of substrate-anchored crystallization accelerators, among which structures featuring isothiuronium templating groups we find to be the most impactful in promoting ionic assembly, strengthening substrate–precursor interactions, and accelerating crystallization at the buried interface, which allows final film coalescence to occur on a precrystallized perovskite surface. The strategy enables a void-suppressed buried interface with 8-fold lower defect density and a 1.5× increase in the yield of radiative recombination, enabling uniform performance across centimeter-scale areas. The resulting devices have certified quasi-steady-state power conversion efficiencies of 26.8% and 25.2% for 0.05 and 1.03 cm² illuminated areas, respectively, and retain 80% of their initial efficiency after 1200 h of operation at 85 °C and 50% relative humidity.



INTRODUCTION

Inverted perovskite solar cells (PSCs) have undergone rapid development owing to their increased operating stability, low-temperature fabrication, and excellent compatibility with tandem architectures.^{1–3} Advances in top-interface passivation have effectively suppressed nonradiative recombination, with PCEs now widely reported to exceed 26%.^{4,5} However, numerous hidden defects and even nanoscale voids remain at the buried perovskite/hole-transport-layer (HTL) interface,^{6,7} and these become more severe as the device area increases, constituting a critical bottleneck for further improvements in efficiency and long-term stability.^{8,9}

To understand the origin of these voids, we revisit the solution-based crystallization process of perovskite films. During typical processing, rapid supersaturation causes nucleation to initiate at the top surface, followed by downward crystal growth.^{10,11} By the time the crystallization front approaches the substrate, extensive solvent evaporation and precursor consumption have already depleted the local solution supply. When this front encounters precursor-phobic,

low-surface-energy, compositionally heterogeneous substrates such as self-assembled monolayers (SAMs) or polymers, incomplete wetting and local dewetting generate solution cavities between the perovskite and the substrate,^{12–14} which cannot be fully filled during solidification and therefore translate directly into voids at the buried interface. Incomplete solution spreading on such substrates may also introduce additional challenges, such as the retention of high-boiling-point solvents including dimethyl sulfoxide (DMSO), which has been reported to further aggravate void formation.^{15,16}

Several strategies have been explored to mitigate these buried-interface imperfections. One approach introduces

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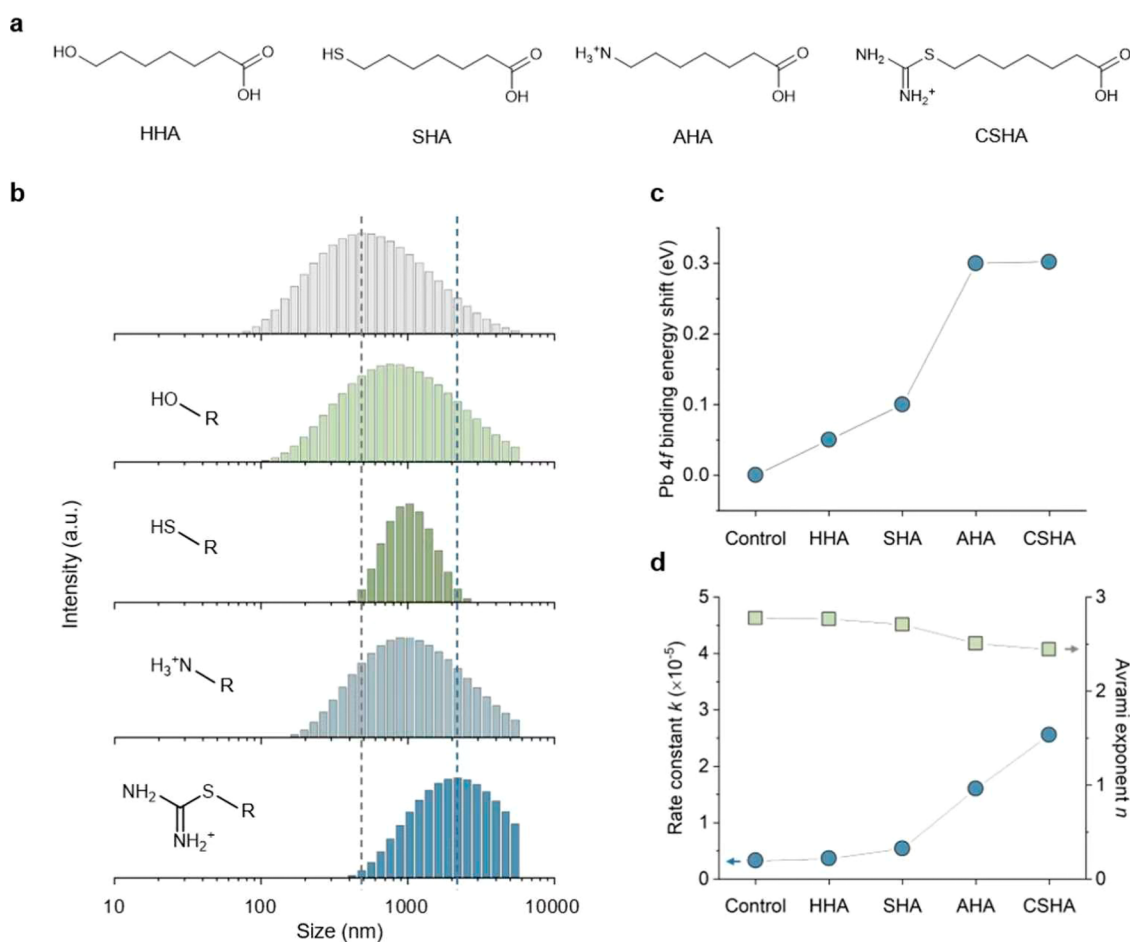


Figure 1. Molecule-precursor interactions and their impact on crystallization kinetics. (a) Molecular structures of HHA, SHA, AHA, and CSHA. (b) DLS analysis of perovskite precursor solutions without additives and with ethanol, ethanethiol, butylammonium bromide, or S-ethylisothiuronium bromide. (c) XPS Pb 4f binding-energy shifts of perovskite films treated with HHA, SHA, AHA, and CSHA. (d) Crystallization kinetic parameters extracted from in situ GIWAXS of perovskite films deposited on HHA-, SHA-, AHA-, and CSHA-based substrates.

micron-sized particles such as Al_2O_3 to improve the macroscopic wetting of the precursor solution.^{17,18} However, because these insulating particles must remain isolated to preserve charge-transport pathways, their coverage is discontinuous and cannot provide the continuous nanoscale regulation required as the crystallization front converges at the interface. Another approach replaces the high-boiling DMSO solvent with solid lead-coordinating additives to avoid solvent-residual-induced interfacial voids.¹⁹ Yet, unlike DMSO, these insulating additives remain in the film, which restricts their permissible concentration and prevents them from exerting full crystallization control without compromising film quality. As a result, device efficiencies achieved with this method have been compromised, and the strategy has not been widely adopted in state-of-the-art architectures. These limitations highlight the need for new strategies that can establish intimate, void-suppressed contact at the buried perovskite/HTL interface while preserving efficient charge transport.

We reason that if the downward-growing crystallization front encounters a substrate with high affinity toward the perovskite precursor solution, ideally a more compositionally homogeneous, perovskite-terminated surface, solution cavities can be avoided and void formation can be suppressed. Achieving this ideal scenario requires triggering perovskite crystallization at the buried interface before the top-down growth front arrives.

Guided by these insights, we hypothesize that pre-embedding molecules capable of strong interactions with perovskite precursors at the substrate will enhance substrate-precursor adhesion, promote early interfacial crystallization, and allow the final coalescence to occur on precrystallized perovskite at the buried interface, thereby minimizing void formation and establishing robust buried interfaces in inverted PSCs.

RESULTS AND DISCUSSION

Molecular Functionalization Modulates Interactions with Perovskite Precursors

We sought to design functional molecules capable of modulating substrate-precursor interactions to trigger early crystallization at the buried interface. We included a carboxylic acid anchoring group to ensure adsorption on the oxide surface, our goal to prevent the molecules from being washed away during the later perovskite solvent-rinsing step (Supporting Figure 1), while also providing structural tunability owing to its synthetic accessibility and chemical compatibility.²⁰ At the opposite end of the molecule, the terminal group was varied to study how this regulates interactions at the substrate/precursor interface: our concept was that it should interact with polar solvents in such a way as to enhance interfacial wettability and preserve the molecule's stability; and that it

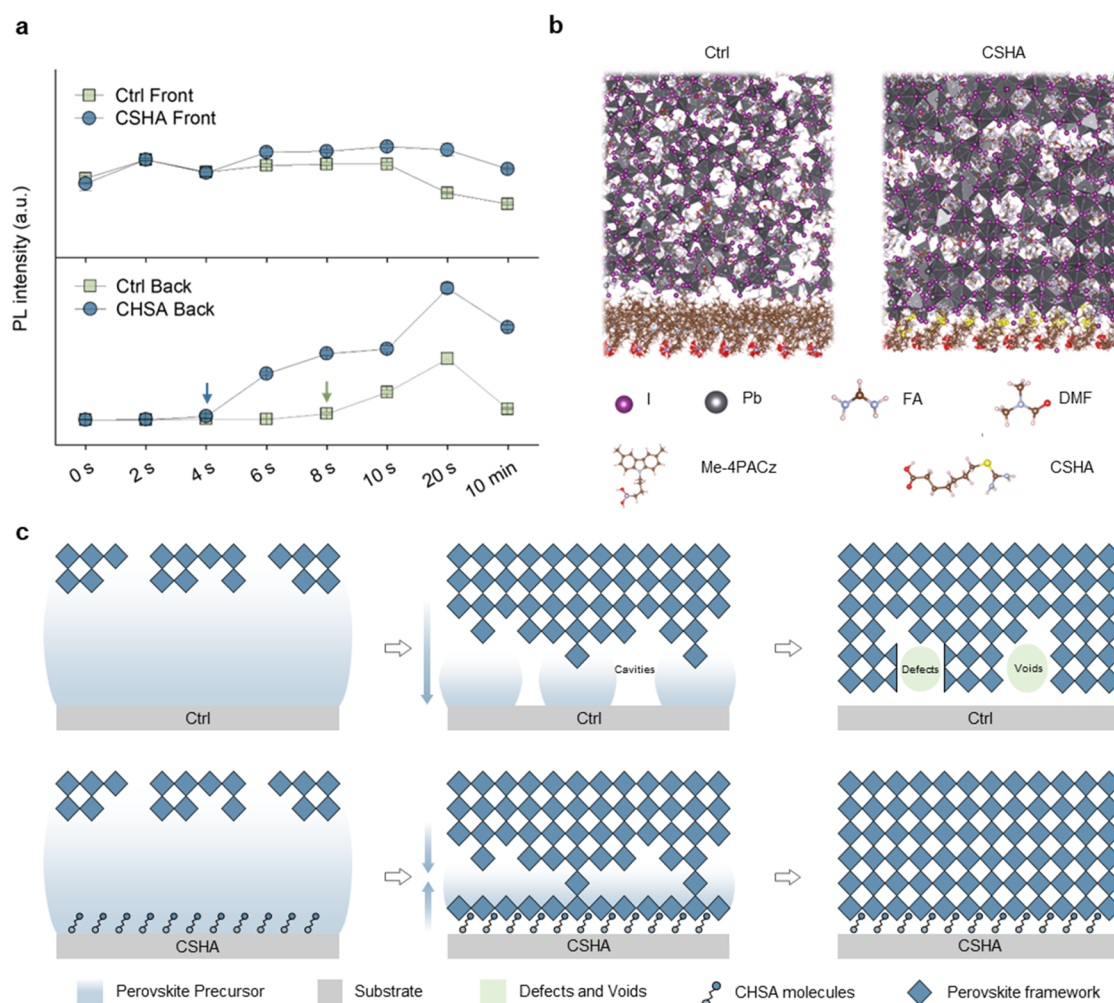


Figure 2. Crystallization kinetics at the buried interface. (a) Time-resolved hyperspectral PL of perovskite films on control and CSHA-based substrates immediately after coating. Using 300 nm excitation (~ 20 nm penetration depth), the 800 nm emission is monitored from both the front and back sides as a function of annealing time. (b) MD simulations depicting the early stage perovskite assembly on Me-4PACz- and CSHA-based substrates. After 500 ns, crystalline perovskite formed on the CSHA layer, in contrast to the Me-4PACz layer, on which perovskite remains amorphous. (c) Schematic illustration of the crystallization pathways of perovskite films on control and CSHA-based substrates.

should also bind sufficiently strongly to perovskite precursors to strengthen substrate-precursor chemical adhesion and facilitate ionic assembly and nucleation at the buried interface.

We explored a series of candidate molecules with the goal of regulating crystallization (Figure 1a), including 7-hydroxyheptanoic acid (HHA), 7-sulfanylheptanoic acid (SHA), 7-ammonium heptanoic acid (AHA), and 7-carbamimidoylsulfanylheptanoic acid (CSHA), which incorporate $-\text{OH}$, $-\text{SH}$, $-\text{NH}_3^+$, and $-\text{S}-\text{C}(\text{NH}_2)_2^+$ terminal groups, respectively. Isothiuronium salts, such as CSHA, have an ionic head that mimics formamidinium, and are obtained through reflux with thiourea (Methods).

We first probed how terminal functionalities affect precursor association, a process closely linked to nucleation and crystallization modulation, by using dynamic light scattering (DLS) to compare the apparent hydrodynamic sizes of scattering species in the precursor solutions. To probe the effects specific to the terminal groups, we studied small-molecule analogs that do not have the $-\text{COOH}$ anchor: ethanol, ethanethiol, butylammonium, and S-ethylisothiuronium were individually introduced into the perovskite precursor solution. Relative to the pristine solution, all

additives increased the colloidal cluster size (Figure 1b). The $-\text{OH}$ group produced slightly larger clusters (~ 800 nm) than the pristine precursor (~ 500 nm). The $-\text{SH}$ and $-\text{NH}_3^+$ groups yielded comparable cluster sizes of ~ 1000 nm. These shifts are consistent with enhanced precursor association through S–Pb coordination and hydrogen-bond-assisted electrostatic interactions, respectively. The most pronounced increase in apparent hydrodynamic size was observed in the case of the $-\text{S}-\text{C}(\text{NH}_2)_2^+$ group, which formed clusters of ~ 2200 nm. We attribute this pronounced size increase to the combined effects of sulfur coordination and the delocalized positive charge of the isothiuronium headgroup, which may facilitate bridging and association between lead-halide complexes.^{21–24}

Spectroscopic analysis sensitive to local coordination environments substantiated these interactions. In ^{207}Pb NMR ($\text{DMSO}-d_6$), the Pb resonance exhibited substantial downfield shifts (~ 84 ppm) upon interaction with $-\text{NH}_3^+$ and $-\text{S}-\text{C}(\text{NH}_2)_2^+$ groups, compared with <5 ppm for $-\text{OH}$ and $-\text{SH}$ (Supporting Figure 2). X-ray photoelectron spectroscopy (XPS) spectra show larger Pb 4f core-level shifts for AHA- and CSHA-treated perovskite (~ 0.3 eV) compared with HHA

and SHA (<0.1 eV), consistent with their stronger modulation of the Pb coordination environment (Supporting Figure 3).

To probe how terminal functionalities influence crystallization at the buried interface, we examined interfacial interactions at two stages of film formation using classical molecular dynamics (MD) simulations and density functional theory (DFT) calculations. Prior to crystallization, we calculated the work of adhesion between the molecular substrate and precursors using MD, our goal to gauge the ability of the molecular layer to confine and stabilize precursor species at the interface, a possible factor in facilitating heterogeneous nucleation. As shown in Supporting Figure 4, the adhesion values for HHA, SHA, AHA, and CSHA are 0.21, 0.23, 0.24, and 0.28 J m⁻², respectively, indicating a progressively enhanced confinement of precursor species.²⁵ Molecules with higher adhesion also exhibit lower contact angles for the perovskite precursor solution on the substrate (Supporting Figure 5). After crystallization, the molecule-perovskite binding energy was calculated to assess interfacial interaction strength using DFT. AHA (−5.33 eV) and CSHA (−5.34 eV) exhibit stronger binding to the perovskite surface than HHA (−1.95 eV) and SHA (−1.34 eV) as shown in Supporting Figure 6.

We then examined the effect of these molecules on crystallization kinetics by performing in situ grazing-incidence wide-angle X-ray scattering (GIWAXS) on fluorine-doped tin oxide (FTO)/NiO_x/SAM with molecule candidates/perovskite materials stacks. Dilute perovskite precursor solutions were used to reduce the film thickness, our purpose to allow the buried interface to exert a more pronounced influence on crystallization kinetics while minimizing the impact of top-surface growth (Figure 1d and Supporting Figures 7 and 8). Time-resolved diffraction profiles were fitted using the Johnson-Mehl-Avrami–Kolmogorov (JMAK) model to compare the relative crystallization kinetics under controlled conditions, where the Avrami exponent (n) describes the nucleation and growth characteristics and the rate constant (k) reflects the crystallization kinetics.²⁶ The analysis shows that n varies little (~2.5–2.8) across all samples, from which we offer that the nucleation mode is only modestly influenced by molecular modification. In contrast, k displays clear dependence on terminal-group chemistry: HHA shows negligible influence relative to the unmodified substrate (control), whereas SHA induces a moderate acceleration, increasing k by approximately 1.7×. Notably, AHA and CSHA lead to pronounced enhancements of ~5× and ~8×, respectively, illustrating the ability of A-site-like cations to promote ionic assembly and support perovskite crystallization, where “A-site-like” refers to cationic motifs that mimic the structural and electronic features of methylammonium (MA⁺)/formamidinium (FA⁺). The highest k value observed for CSHA indicates its most pronounced effect on promoting perovskite crystallization among the examined molecules.

We note that the slower crystallization on AHA than on CSHA arises not only from its less effective intermolecular association of precursor species (Figure 1b), but also from its limited stability once embedded on the substrate. XPS indicates that roughly half of the AHA population undergoes prompt $-\text{NH}_3^+ \rightarrow -\text{NH}_2$ deprotonation upon deposition from protic solvent (Supporting Figure 9), consistent with the lower $\text{p}K_a$ of ammonium groups, thereby diminishing the density of effective cationic templating sites.²⁷ In contrast, the delocalized positive charge of the isothiuronium moiety stabilizes its

protonated state at the interface. Given the pronounced effect of CSHA on perovskite crystallization, we studied its role further, particularly at the buried interface.

Interfacial Templating Accelerates Buried-Interface Crystallization

In an effort to obtain information experimentally on how crystallization proceeds as a function of vertical position within the film, we used hyperspectral photoluminescence (PL) measurements with strongly absorbed (~20 nm penetration depth) $\lambda = 300$ nm excitation, and we monitored the front and back sides of the perovskite films as a function of annealing time (Figure 2a). At the top interface, both control and CSHA-based films show immediate emission after spin coating, followed by a rise in PL intensity that saturates and then decays after ~20 s, reflecting the transition from emissive nanocrystals to coalesced grains accompanied by increasing nonradiative losses.^{28,29} At the buried interface, no emission was detected in the control film until ~8 s, indicating a typical downward crystallization process. By contrast, in the presence of CSHA, emission from the buried interface appeared earlier at ~4 s, corresponding to a 12-fold increase in growth rate and indicating an earlier onset of buried interface nucleation and accelerated local crystallization (Figure 2a), while preserving the overall top-down crystallization sequence. Spatially patterned substrates show that crystallization preferentially initiates in the CSHA-containing region and subsequently propagates into the CSHA-free region (Supporting Figure 10), providing direct spatial evidence that CSHA promotes perovskite crystallization.

Classical MD simulations were carried out to understand the molecular origin of this behavior by tracking the early stages of perovskite assembly on Me-4PACz- and CSHA-based substrates. On the Me-4PACz layer, PbI₂ fragments and FA⁺ ions exhibited a disordered distribution without forming a coherent lattice after 500 ns (Figure 2b), consistent with slow nucleation. In comparison, CSHA rapidly organized both cations and anions, establishing the first few perovskite planes within ~20 ns (Supporting Figure 11). The delocalized cationic motif of the isothiuronium headgroup, featuring multiple hydrogen-bond donors and a spatially uniform electrostatic field,²⁷ facilitates directional binding between iodoplumbate clusters and organic cations. This ionic-assembly behavior was also seen in X-ray diffraction, which shows distinct crystalline features in CSHA-PbI₂ complexes (Supporting Figure 12).

We offer in light of these measurements a mechanistic picture depicted in Figure 2c. In the control, rapid solvent supersaturation drives surface-first nucleation, and the descending crystallization front encounters a precursor-phobic, low-surface-energy substrate at which solvent cavities readily form, hindering film closure and culminating in voids and interfacial defects. With CSHA, accelerated buried-interface crystallization enables perovskite to form before the descending crystallization process reaches completion. Consequently, the final coalescence occurs on a homogeneous, precursor-affinitive perovskite surface rather than on the heterogeneous HTL surface, minimizing solution cavities and suppressing void formation.

Buried-Interface Integrity and Electronic Uniformity

We conducted morphological and photophysical analyses to assess the impact of earlier buried-interface crystallization on perovskite film quality. In an effort to probe the buried

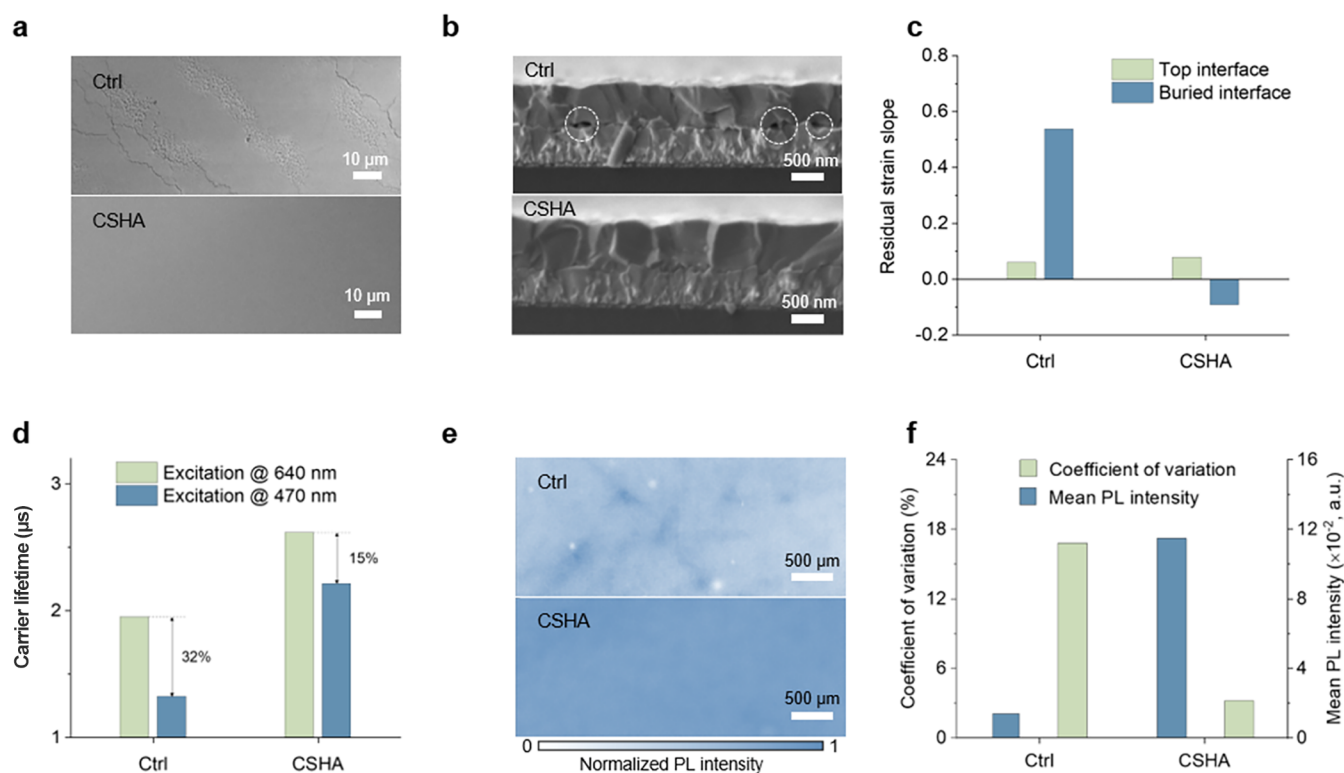


Figure 3. Improved buried-interface integrity and optoelectronic uniformity. (a) Surface SEM images of the buried surfaces of peeled-off perovskite films fabricated on control and CSHA-based substrates. (b) Cross-sectional SEM images of perovskite films on control and CSHA-based substrates. (c) XRD residual strain slopes of control and CSHA-based perovskite films at penetration depths of 50 nm (top interface) and 500 nm (buried interface). (d) TRPL lifetimes extracted using stretched exponential fitting for control and CSHA-based perovskite films excited from the bottom side with 640 and 470 nm wavelengths. (e) Hyperspectral PL mapping of the buried interface in control and CSHA-based perovskite films. (f) Extracted coefficient of variation and mean PL intensity measured from the back side of the perovskite films.

interface, we peeled the perovskite films from the substrates and examined them with the aid of scanning electron microscopy (SEM). From large-area SEM imaging we see that the control film contains irregular, band-like regions with incomplete coverage and visible cracking (Figure 3a and Supporting Figure 13). Cross-sectional SEM shows pronounced interfacial voids at the control substrate side, indicative of poor bottom-side consolidation (Figure 3b). Although HHA, SHA, and AHA exhibit weaker crystallization-regulating capability (Figure 1d), slight improvements in interfacial morphology are observed (Supporting Figure 14), potentially arising in part from enhanced wettability (Supporting Figure 5); however, interfacial voids remain evident, indicating that improved wetting alone is insufficient to substantially suppress buried-interface defects. In comparison, films grown on CSHA-based substrates exhibit a continuous and smooth buried interface with intact substrate contact, indicating improved interfacial integrity and uniform coverage.

The structural state of the perovskite films was further assessed through depth-resolved residual strain analysis using X-ray diffraction (Figure 3c and Supporting Figure 15). Both the control and CSHA-based samples exhibit negligible surface strain, whereas the control film shows pronounced compressive strain accumulation at the buried interface (strain slope = +0.54). CSHA incorporation markedly reduces the interfacial strain magnitude to a near-zero value (−0.093), alleviating lattice distortion and suppressing strain-driven defect formation.

Kelvin probe force microscopy (KPFM) measurements indicate the relatively uniform interfacial distribution of CSHA without apparent spatial heterogeneity (Supporting Figure 16). Drive-level capacitance profiling measurements show that defects in the control devices are predominantly concentrated at the buried interface, with a peak density of $\sim 3 \times 10^{17} \text{ cm}^{-3}$, whereas CSHA-based devices exhibit a shallower defect profile and a substantially lower maximum density of $\sim 4 \times 10^{16} \text{ cm}^{-3}$ (Supporting Figure 17). Back-side photoluminescence quantum yield (PLQY) measurements corroborate this interface improvement, showing a 50% enhancement relative to the control, indicating reduced nonradiative recombination losses specifically at the buried interface (Supporting Figure 18).

Time-resolved photoluminescence (TRPL) measurements were further conducted using 470 and 640 nm pulsed diode laser excitation from the bottom side of the films to assess the quality of the buried interface and bulk regions (Figure 3d and Supporting Figure 19). The control film shows much shorter buried-interface lifetimes (1.3 μs) than the bulk (1.9 μs), whereas CSHA-based films exhibit prolonged interfacial lifetimes (2.2 μs) with a smaller difference relative to the bulk (2.6 μs), confirming reduced recombination at the buried interface.

Hyperspectral PL mapping measured from the back side further visualizes the spatial distribution of optoelectronic uniformity across millimeter-scale regions. CSHA-based films exhibit emission intensities up to 8-fold higher than the control, together with reduced spatial variation ($\sim 3\%$ deviation across the scanned area), reflecting excellent spatial homoge-

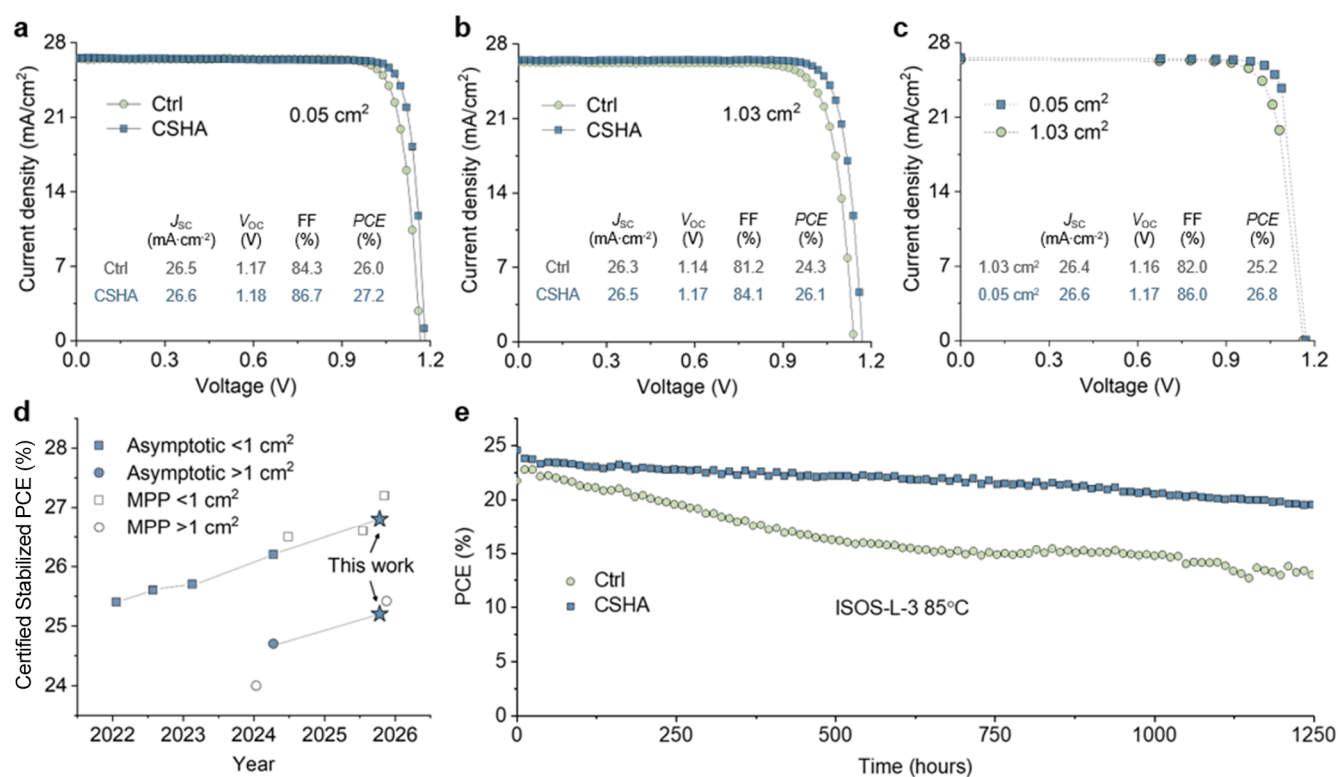


Figure 4. Photovoltaic performance. (a) J – V characteristics (reverse scan) of the champion control and CSHA-based devices with an active area of 0.05 cm². (b) J – V characteristics (reverse scan) of devices with an active area of 1.03 cm². (c) Quasi-steady-state (QSS) J – V curves of representative CSHA-based devices (0.05 and 1.03 cm²) certified at Newport under the strict asymptotic protocol. (d) Statistics of certified stabilized PCEs of PSCs reported in recent years. (e) Maximum power point tracking of control and CSHA-based devices measured at 85 °C under continuous 1-sun (100 mW cm^{−2}) illumination at ~50% relative humidity.

neity. In comparison, control films display pronounced intensity fluctuations exceeding 16%, along with dark, irregular regions indicative of nonradiative recombination sites and interfacial voids (Figure 3e,f). These observations indicate that CSHA promotes defect-suppressed crystallization, enabling perovskite films with uniform optoelectronic quality across device-relevant length scales.

Device Performance and Stability

We fabricated inverted PSCs and optimized the molecular geometry of the crystallization accelerator by varying the alkyl-chain length in CSHA analogs. A mixed SAM incorporating [2-(9*H*-Carbazol-9-yl)ethyl]phosphonic acid (2PACz), Me-4PACz, and CSHA (mass ratio of CSHA:2PACz:Me-4PACz = 3:2:4) was employed as the HTL. The six-carbon spacer yielded the best device performance, balancing conformational flexibility and molecular packing while matching the length scale of widely used SAMs such as Me-4PACz and 4PADCB (Supporting Figures 20 and 21).

CSHA modification increases the average PCE to 26.8%, compared with 25.7% for the control devices, primarily through improvements in open-circuit voltage (V_{oc}) and fill factor (FF) (Supporting Figures 22 and 23). The best-performing CSHA-based device delivers a PCE of 27.2%, with a V_{oc} of 1.182 V, FF of 86.7% and short-circuit current density (J_{sc}) of 26.6 mA/cm² (Figure 4a and Supporting Figure 24a). We attribute these enhancements to improved interfacial interactions, reduced trap density, and faster charge extraction in CSHA-based PSCs (Supporting Figure 25), rather than to concomitant changes in bulk crystallinity or surface morphology (Supporting Figures 26 and 27). These benefits become

even more pronounced in 1 cm² devices, where buried-interface quality and film uniformity are critical, with the PCE increasing from 24.3% to 26.1% (Figure 4b and Supporting Figure 24b). This strategy can also be extended to other perovskite compositions (Supporting Figure 28).

We sent both 0.05 and 1 cm² devices to Newport, an independent photovoltaic calibration laboratory accredited by the National Renewable Energy Laboratory (NREL), for certified measurements. Under the asymptotic protocol, the devices achieved certified quasi-steady state (QSS) PCEs of 26.8 and 25.2%, respectively (Figure 4c and Supporting Figures 29–31). These values represent the highest certified performance to date for PSCs evaluated under the same protocol for both small- and large-area devices (Figure 4d and Supporting Tables 1 and 2).^{2,4,18,30–35}

Device operating stability was evaluated following the ISOS-L-3 protocol (ISOS: International Summit on Organic Photovoltaic Stability), with encapsulated devices operated at the maximum power point (MPP) under continuous 1-sun equivalent illumination from a white light emitting diode at ~50% relative humidity and 85 °C (Figure 4e). CSHA-based PSCs retained 80% of their initial efficiency after 1200 h of continuous MPP tracking, whereas control devices degraded by 40% over the same period, underscoring the improved thermal and operating stability imparted by the consolidated, void-suppressed buried interface.

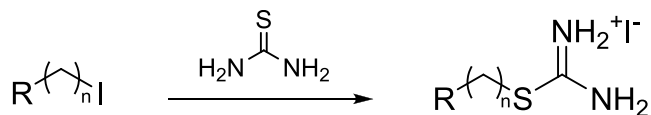
MATERIALS AND METHODS

NiO_x was synthesized by our previously reported method.^{3,36} [2-(9*H*-Carbazol-9-yl)ethyl]phosphonic acid (2PACz), [4-(3,6-Dimethyl-9*H*-

carbazol-9-yl)butyl]phosphonic acid (Me-4PACz), CsI (99.99%), PbI₂ (99.99%), PbCl₂ (99.99%) were purchased from TCI America. Formamidinium iodide (FAI), methylammonium iodide (MAI), methylammonium chloride (MACl), and phenethylammonium iodide (PEAI) were purchased from Greatcell Solar Materials. Ethanol (anhydrous, 99.5%), *N,N*-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.9%), isopropanol (IPA, anhydrous, 99.5%), anisole (anhydrous, 99.7%), ethanethiol, butylammonium bromide (98%), and *S*-ethylisothiuronium bromide (98%) were purchased from Millipore Sigma. 3-(methylthio)-propylamine hydroiodide (3MTPAI), C₆₀ and piperazinium iodide were purchased from Xi'an Yuri Solar Co., Ltd. Tetrakis-(dimethylamino) tin(IV) (99.9999%) was purchased from Strem. 7-hydroxyheptanoic acid (HHA), 7-sulfanyloctanoic acid (SHA), and 7-ammonium heptanoic acid hydrochloride (AHACl) were purchased from Ambeed. All the materials were used as received without any purification.

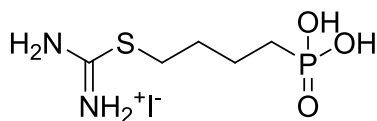
Chemicals required for the synthesis were purchased from Sigma-Aldrich Co., Ltd., Tokyo Chemical Industry Co., Ltd. Europe, BLD Pharmatech, Ltd., and Fluorochem Ltd. and used as received without additional purification. ¹H NMR spectra were recorded at 400 MHz on a Bruker Avance III spectrometer with a 5 mm double resonance broadband BBO z-gradient room temperature probe, ¹³C NMR spectra were collected using the same instrument at 101 MHz. The chemical shifts are expressed in ppm. All the NMR experiments were performed at 25 °C. Reactions were monitored by thin-layer chromatography on ALUGRAM SIL G/UV254 plates and visualized under UV light. MS were recorded on Waters SQ Detector 2 Spectrometer using the electrospray ionization (ESI) technique.

General Procedure for Isothiuronium Iodide Salt Preparation by Alkylation of Thiourea



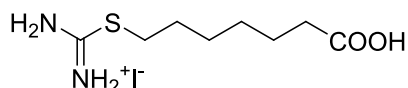
$$n = 4-10; R = \text{PO}(\text{OH})_2, \text{COOH}$$

Thiourea (1.1 mmol) is dissolved in isopropanol (10 mL), and 1 mmol of the corresponding phosphonic or carboxylic acid alkyl iodide is added. The reaction mixture is stirred at 80–85 °C overnight. After cooling the reaction mixture, the solvent is distilled off under reduced pressure. The resulting crystals were dissolved in methanol and precipitated in diethyl ether. The precipitate is filtered, washed with diethyl ether, and dried to obtain isothiuronium iodide salts.



2-(4-phosphonobutyl)isothiuronium iodide (4C)

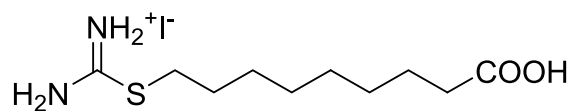
Yield: 80%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.96 (d, *J* = 80.0 Hz, 4H), 3.14 (t, *J* = 7.2 Hz, 2H), 1.69 (t, 2H), 1.56 (t, *J* = 10.3 Hz, 4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 169.82, 29.55, 27.26, 25.90, 21.67 (d_{C-P}, *J* = 4.4 Hz). *m/z* M⁺ calculated 213.05; *m/z* found 212.88.



2-(6-carboxyhexyl)isothiuronium iodide (6C, CSHA iodide salt)

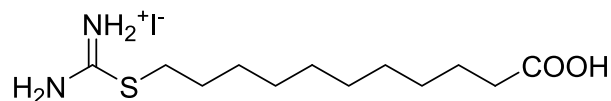
Yield: 83%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 12.00 (s, 1H), 8.94 (d, *J* = 42.1 Hz, 4H), 3.12 (t, *J* = 7.3 Hz, 2H), 2.19 (t, *J* = 7.3 Hz, 2H), 1.58 (p, *J* = 7.3 Hz, 2H), 1.48 (p, *J* = 7.3 Hz, 2H), 1.40–1.21 (m,

4H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 174.47, 169.82, 33.53, 30.07, 28.24, 27.88, 27.52, 24.28. *m/z* M⁺ calculated 205.10; *m/z* found 205.02.



2-(8-carboxyoctyl)isothiuronium iodide (8C)

Yield: 53%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 9.00 (s, 4H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.64–1.53 (m, 2H), 1.51–1.44 (m, 2H), 1.38–1.30 (m, 2H), 1.31–1.18 (m, 6H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 174.53, 169.81, 33.67, 30.11, 28.56, 28.45, 28.29, 28.22, 27.73, 24.46. *m/z* M⁺ calculated 233.13; *m/z* found 233.03.



2-(10-carboxydecyl)isothiuronium iodide (10C)

Yield: 48%. ¹H NMR (400 MHz, DMSO-*d*₆) δ 11.95 (s, 1H), 8.94 (s, 4H), 3.12 (t, *J* = 7.1 Hz, 2H), 2.18 (t, *J* = 7.2 Hz, 2H), 1.64–1.53 (m, 2H), 1.47 (s, 2H), 1.34 (s, 2H), 1.24 (s, 10H). ¹³C NMR (101 MHz, DMSO-*d*₆) δ 174.52, 169.82, 33.66, 30.12, 28.80, 28.70, 28.54, 28.32, 27.76, 24.48. *m/z* M⁺ calculated 261.16; *m/z* found 260.95.

Device Fabrication

Fluorine-doped tin oxide (FTO) glasses were cleaned using acetone and isopropanol each for 15 min in an ultrasonic bath, followed by ultraviolet ozone treatment for 30 min. The hole transport layer (HTL) was NiO_x/2PACz and Me-4PACz. The synthesized NiO_x was dispersed in a 3:1 v/v mixture of deionized water and isopropanol at a concentration of 5 mg/mL and spin-coated onto the substrates at 3000 r.p.m. for 30 s. The mixed 2PACz/Me-4PACz ethanol solution (0.2 mg mL^{−1} 2PACz and 0.4 mg mL^{−1} Me-4PACz) was then spin-coated onto the substrates in nitrogen at 4,000 r.p.m. for 30 s, followed by annealing at 120 °C for 10 min. The substrates were then rinsed with ethanol to remove weakly bound molecules and annealed at 120 °C for 5 min. For molecule-modified substrates, an ethanol solution of HHA, SHA, AHA, or CSHA (0.6 mg mL^{−1}) was mixed with the above 2PACz/Me-4PACz solution at a volume ratio of 1:2. The resulting mixture was spin-coated under identical conditions, followed by annealing at 120 °C for 10 min and the same ethanol rinsing step. 1.67 M FA_{0.95}CS_{0.05}PbI₃ perovskite precursors were dissolved in a mixed DMF/DMSO solvent (4:1 v/v), to which 18 mol % MACl and 8 mol % PbI₂ were added as crystallization additives. The perovskite solution was spin-coated at 1000 r.p.m. for 10 s (acceleration rate 200 r.p.m./s) and then at 5000 r.p.m. for 35 s (acceleration: 1000 r.p.m./s). During the final 15 s of the second step, 130 μL of anisole was dispensed as the antisolvent. The resulting films were then annealed at 120 °C for 10 min. For the passivation treatment, a filtered isopropanol solution containing 0.5 mg/mL piperazinium iodide and 1 mg/mL 3MTPAI was spin-coated onto the perovskite films at 4000 rpm for 25 s, followed by annealing at 100 °C for 5 min. Next, a 30 nm C₆₀ layer was thermally evaporated onto the perovskite films under a high vacuum (~10^{−7} Torr). The films were then transferred to an atomic layer deposition (ALD) system (Savannah) for deposition of a 20 nm SnO₂ layer at 90 °C using tetrakis(dimethylamino) tin(IV) and H₂O as precursors. Finally, a 100 nm Au electrode was thermally evaporated under a high vacuum (~10^{−7} Torr).

Characterization

Scanning Electron Microscope (SEM). SEM images were collected by JEOL JSM-7900FLV microscope using 15 keV beam

energy. For buried interface SEM, FTO substrates were replaced with single crystal sapphire (α -Al₂O₃) due to its low surface roughness and its ability, similar to transparent conducting oxides, to support SAM binding through an analogous chemisorption mechanism.

Current Density–Voltage (*J*–*V*) Characteristics. The *J*–*V* curves were recorded in a nitrogen environment at room temperature using a Keithley 2401 source meter coupled to an Enlitech SS-X100R Class AAA solar simulator (AM 1.5G). Prior to testing, the illumination intensity was adjusted with a calibrated silicon reference cell (SRC2020). No preconditioning of the device was applied before the measurement. Devices were scanned at 100 mV s^{−1} with a voltage step of 20 mV. The active device areas, 0.05 cm² for small cells and 1.03 cm² for large cells, were defined using an opaque metal aperture. Antireflection films (NanoEcoWay Co. Ltd.) were used on the substrates to reduce light reflection.

Stability Test. The operating stability test was performed on encapsulated devices in ambient air (~50% relative humidity) under 1-sun equivalent illumination provided by white light-emitting diodes (LEDs) at 85 °C. Encapsulation was achieved using CYTOP (Bellex International Corporation) and a capping glass slide, which was sealed with ultraviolet-curable epoxy (Lumtec LT-U001). A two-dimensional perovskite passivation layer was used for both control and CSHA-based devices to further enhance their stability.^{36,37} The precursor solution containing PEAI (1 mg/mL) and FAI (0.5 mg/mL) in mixed IPA and DMF (IPA:DMF = 200:1, v/v) solution was deposited on perovskite films at 4000 rpm for 30 s, followed by annealing at 100 °C for 5 min.

Photoluminescence Measurements. The Photoluminescence quantum yield (PLQY) was measured by a LuQY Pro System (Quantum Yield Berlin) under the excitation of 532 nm laser (100 mW). Spatially resolved PL maps were acquired using a HERA hyperspectral camera, which records a full hyperspectral data cube under 300 nm excitation and reconstructs pixel-level PL spectra via Fourier transformation. TRPL was measured using a PicoQuant PicoHarp 300 TCSPC system with excitation sources of 470 and 640 nm pulsed diode lasers. The excitation intensity of different lasers is adjusted to yield the same absorbed photon flux of $\sim 5.2 \times 10^{16}$ photons/cm²/s in the perovskite.

Grazing-Incidence Wide-Angle X-ray Scattering (GIWAXS). GIWAXS was conducted at beamline BL19B2 of SPring-8 synchrotron radiation facility with a photon energy of 12.39 keV (1 Å) and an incident angle of 2°. The samples were heated from room temperature (25 °C) to 120 °C at a rate of 20 °C min^{−1} under a dry N₂ atmosphere. Dilute perovskite precursor solutions with a concentration of 0.2 M were used for the measurement.

Depth-Resolved Residual Stress Analysis. The crystalline structure and depth-dependent lattice strain of the perovskite films were analyzed using a high-resolution X-ray diffractometer (Rigaku SmartLab) with a Cu rotating anode operating at 45 kV and 160 mA and equipped with a parabolic multilayer mirror to select out Cu K α radiation (λ = 1.5418 Å). The receiving arm was equipped with 0.5° (vertical) and a 5° (horizontal) Soler slits. To investigate the strain gradient, we employed depth-resolved residual stress analysis technique with residual strain package, targeting two specific penetration depths: ~ 50 nm (surface) and ~ 500 nm (buried interface). The lattice strain was determined by measuring the shift in the diffraction angle (θ) as a function of the tilt angle (ψ) between the surface and the crystal-plane normals. The perovskite (012) reflection was scanned around 31° at various ψ angles. To ensure that the X-ray probing depth remained constant during the tilting process, the incidence angle (α) was adjusted at each ψ step based on the X-ray absorption coefficient (μ) of material composition and the target depth, as described previously.^{38,39} The lattice strain was then evaluated by analyzing the slope of the linear plot of the diffraction peak positions 2θ versus $\sin^2 \psi$.

Other Characterization. X-ray diffraction (XRD) was performed by Rigaku Miniflex diffractometer (Cu K α radiation). Drive-level capacitance profiling (DLCP) was conducted by the Fluxim PAIOS system at various frequencies, with a driving voltage ranging from 20 mV to 200 mV in increments of 20 mV. The spatial profiles from 5

and 500 kHz are used to separate trap densities from free carrier contributions. X-ray photoelectron spectroscopy (XPS) was performed using Thermo Scientific Nexsa G2 with an X-ray spot size of 400 μ m. Dynamic light scattering (DLS) measurements were performed on 0.5 M precursor solutions containing 5 mol % of the corresponding molecules using Malvern Zetasizer Ultra instrument. All solutions were filtered through a PTFE syringe filter and measured after standing for ~ 2 h, similar to the precursor preparation used for device fabrication. The reported particle size distributions are based on intensity-weighted analysis. Despite the increased hydrodynamic size observed in solution, no apparent deterioration in film uniformity was observed, as confirmed by surface morphology and PL mapping (Supporting Figure 27 and Figure 3e).

DFT Calculations

We performed the binding energy calculations using density functional theory (DFT) implemented in the Vienna Ab initio Simulation Package (VASP).⁴⁰ The generalized gradient approximation of Perdew–Burke–Ernzerhof (PBE)⁴¹ exchange–correlation functional and the projector augmented wave (PAW)⁴² pseudopotentials were employed. van der Waals corrections were accounted for using the DFT-D3⁴³ method. The perovskite was modeled by a four-layer 2×4 supercell, separated by a vacuum region of 20 Å along the *z*-direction. Prior to the binding energy calculations, all atomic positions were optimized, with the bottom perovskite layer fixed and the other atoms allowed to relax. A plane-wave energy cutoff of 400 eV was used. The energy and force convergence criteria were set to 10^{−5} eV and 0.02 eV Å^{−1}, respectively. The Brillouin zone was sampled with a Γ -centered *k*-mesh at a density of $2\pi \times 0.02$ Å^{−1}. The binding energy (*E*_b) between the molecule and the perovskite surface was calculated as $E_b = E_{\text{mol+pvsk}} - E_{\text{pvsk}} - E_{\text{mol}}$, where *E*_{mol+pvsk}, *E*_{pvsk}, and *E*_{mol} are the total energies of the system, the pure perovskite surface and the molecule, respectively. For all the molecules, we compared their binding energy in different possible configurations on the perovskite surface, including (i) insertion of the molecular tail into the lattice with FA⁺ substituted, (ii) insertion of the molecular tail into the lattice with FA⁺ and I[−] substituted, and (iii) adsorption on the perovskite surface.

Molecular Dynamics Simulations

All the classical molecular dynamics (MD) simulations were performed by using the LAMMPS package⁴⁴ with a time step of 1 fs. We carried out the MD simulations in the canonical ensemble (NVT). The temperature of the system was controlled by the Nose–Hoover thermostat with a time constant of 100 fs. The simulation box consisted of a layer of interfacial molecules and a slab of randomly distributed perovskite precursors. The lengths of *x*–*y* directions of the simulation box were set to be integer times of the lattice of perovskite, avoiding the possible strain induced by crystallized perovskite. Specifically, the simulation box was set to be 50.89 Å $\times$ 50.89 Å $\times$ 96.64 Å with a 20 Å-vacuum region in *z*-direction, and we placed one interfacial molecule at each lattice center in accordance with the perovskite lattice. Periodic boundary conditions were applied in *xyz*-directions, whereas the carbon atoms in the anchoring group are fixed. We used the GAFF2 force fields⁴⁵ for organic molecules (including DMF and interfacial molecules), and a transferable force field⁴⁶ for the perovskite. The interactions between molecules and perovskites were described as Lennard–Jones potential by combining their force-field parameters using geometric mixing rules. The atomic charges for the GAFF2 force field used the restrained electrostatic potential charges, computed at the B3LYP/def2-TZVP+D3 level, using the ORCA 5.0.0 package.⁴⁷

Using the system settings, we performed MD simulations to monitor the perovskite crystallization process on the surfaces of Me-4PACz (control) and CSHA. Before starting simulations, the PbI₂ and FAI in addition to $\sim 6\%$ of DMF were randomly distributed. The temperature of the simulations was controlled at 400 K. For both systems, we performed more than 500 ns of simulations.

We calculated the work of adhesion for a layer of molecules with perovskite precursors. All the calculations were performed before perovskite crystallized and the temperature was controlled at 300 K.

We leveraged the dry-surface method,⁴⁸ which reversibly switches the molecule-precursor interactions from realistic to fully off, and it obtains the work of molecule-precursor adhesion via thermodynamic integration. We chose a reversible path, where $\lambda = 0$ indicates fully turning-off the molecule-precursor interactions, while $\lambda = 1$ represents the original systems for which we want to obtain the work of adhesion.^{49,50} Therefore, the work of adhesion can be obtained via $W_{\text{ad}} = \int_0^1 \langle \frac{\partial u}{\partial \lambda} \rangle d\lambda$, where λ is an arbitrary coupling parameter and $u = \frac{\Phi}{A}$ is the total molecule-precursor potential energy per unit area, A is the area of the molecular layer (i.e., xy cross-section).

■ ASSOCIATED CONTENT

Data Availability Statement

All data are available in the main text or the [Supporting Information](#).

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c11350>.

Figures and tables, additional characterization of molecular interactions, crystallization kinetics, buried-interface defects, photovoltaic performance, and supporting computational analyses ([PDF](#))

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Notes

The authors declare the following competing financial interest(s): Y.Y., Cheng L., B.C., K.R., V.G., M.G.K. and E.H.S. are filing a patent based on this work. The remaining authors declare no competing interests.

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REFERENCES

- (1) Lin, R.; Gao, H.; Lou, J.; et al. All-perovskite tandem solar cells with dipolar passivation. *Nature* **2025**, *648*, 600–606.
- (2) Xiong, Z.; Zhang, Q.; Cai, K.; et al. Homogenized chlorine distribution for > 27% power conversion efficiency in perovskite solar cells. *Science* **2025**, *390*, 638–642.
- (3) Liu, C.; Yang, Y.; Chen, H.; et al. Bimolecularly passivated interface enables efficient and stable inverted perovskite solar cells. *Science* **2023**, *382*, 810–815.
- (4) Chen, H.; Liu, C.; Xu, J.; et al. Improved charge extraction in inverted perovskite solar cells with dual-site-binding ligands. *Science* **2024**, *384*, 189–193.
- (5) You, S.; Zhu, H.; Shen, Z.; et al. C₆₀-based ionic salt electron shuttle for high-performance inverted perovskite solar modules. *Science* **2025**, *388*, 964–968.
- (6) Jiang, Q.; Zhu, K. Rapid advances enabling high-performance inverted perovskite solar cells. *Nat. Rev. Materials* **2024**, *9*, 399–419.
- (7) Chen, J.; Wang, X.; Wang, T.; et al. Determining the bonding–degradation trade-off at heterointerfaces for increased efficiency and stability of perovskite solar cells. *Nat. Energy* **2025**, *10*, 181–190.
- (8) Yan, N.; Fang, Z.; Dai, Z.; Feng, J.; Liu, S. Buried Interface-The Key Issues for High Performance Inverted Perovskite Solar Cells. *Adv. Funct. Mater.* **2024**, *34*, No. 2314039.
- (9) Gao, H.; Xiao, K.; Lin, R.; et al. Homogeneous crystallization and buried interface passivation for perovskite tandem solar modules. *Science* **2024**, *383*, 855–859.
- (10) Hoffman, J. M.; Strzalka, J.; Flanders, N. C.; et al. In Situ Grazing-Incidence Wide-Angle Scattering Reveals Mechanisms for Phase Distribution and Disorientation in 2D Halide Perovskite Films. *Adv. Mater.* **2020**, *32*, No. 2002812.
- (11) Chen, S.; Xiao, X.; Chen, B.; et al. Crystallization in one-step solution deposition of perovskite films: Upward or downward? *Sci. Adv.* **2021**, *7*, No. eabb2412.
- (12) Kargupta, K.; Konnur, R.; Sharma, A. Spontaneous Dewetting and Ordered Patterns in Evaporating Thin Liquid Films on Homogeneous and Heterogeneous Substrates. *Langmuir* **2001**, *17*, 1294–1305.
- (13) Deng, W.; Wan, F.; Peng, X.; et al. Super hydrophilic, ultra bubble repellent substrate for pinhole free Dion-Jacobson perovskite solar cells. *Appl. Phys. Lett.* **2022**, *121*, No. 233902.
- (14) Lee, S. M.; Tsou, J. Y.; Evans, M.; et al. Elucidating and Mitigating Instabilities of Poly(vinyl alcohol) Thin Films in Aqueous Environments. *Langmuir* **2025**, *41*, 28119–28128.
- (15) Mo, K.; Zhu, X.; Yang, M.; et al. Minimizing DMSO Residues in Perovskite Films for Efficient and Long-Term Stable Solar Cells. *Adv. Energy Mater.* **2025**, *15*, No. 2404538.
- (16) Wang, Y.; Lu, C.; Liu, M.; et al. Solvent-assisted reaction for spontaneous defect passivation in perovskite solar cells. *Nat. Photonics* **2025**, *19*, 985–991.
- (17) Peng, W.; Mao, K.; Cai, F.; et al. Reducing nonradiative recombination in perovskite solar cells with a porous insulator contact. *Science* **2023**, *379*, 683–690.
- (18) Li, J.; Liang, H.; Xiao, C.; et al. Enhancing the efficiency and longevity of inverted perovskite solar cells with antimony-doped tin oxides. *Nat. Energy* **2024**, *9*, 308–315.
- (19) Chen, S.; Dai, X.; Xu, S.; et al. Stabilizing perovskite-substrate interfaces for high-performance perovskite modules. *Science* **2021**, *373*, 902–907.
- (20) Li, M.; Liu, M.; Qi, F.; Lin, F. R.; Jen, A. K. Y. Self-Assembled Monolayers for Interfacial Engineering in Solution-Processed Thin-Film Electronic Devices: Design, Fabrication, and Applications. *Chem. Rev.* **2024**, *124*, 2138–2204.
- (21) Warshawsky, A. Integrated Ion Exchange and Liquid-Liquid Extraction Process for the Separation of Platinum Group Metals (PGM). *Sep. Purif. Methods* **1982**, *11*, 95–130.
- (22) Warshawsky, A.; Fieberg, M. M. B.; Mihalik, P.; Murphy, T. G.; Ras, Y. B. The Separation of Platinum Group Metals (PGM) in Chloride Media by Isothiouonium Resins. *Sep. Purif. Methods* **1980**, *9*, 209–265.
- (23) Jones, M. D. Process for Removing Iodide Compounds From Carboxylic Acids And/or Their Anhydrides. EP Patent EP0482787B1, 1995.
- (24) Zhang, Y.; Wang, Y.; Yang, X.; et al. Mechanochemistry Advances High-Performance Perovskite Solar Cells. *Adv. Mater.* **2022**, *34*, No. 2107420.
- (25) Ebnesaajad, S. *Surface Treatment of Materials for Adhesive Bonding*, 2nd ed.; William Andrew Publishing, 2014; pp 7–24.
- (26) Shirzad, K.; Viney, C. A critical review on applications of the Avrami equation beyond materials science. *J. R. Soc. Interface* **2023**, *20*, No. 20230242.

- (27) Yang, Y.; Chen, H.; Liu, C.; et al. Amidation of ligands for chemical and field-effect passivation stabilizes perovskite solar cells. *Science* **2024**, 386, 898–902.
- (28) Liu, M.; Zhang, J.; Qin, S.; et al. Efficient and Stable p–i–n Perovskite Solar Cells Enabled by In Situ Functional Group Conversion. *J. Am. Chem. Soc.* **2024**, 146, 32105–32116.
- (29) An, Y.; Zhang, N.; Zeng, Z.; et al. Optimizing Crystallization in Wide-Bandgap Mixed Halide Perovskites for High-Efficiency Solar Cells. *Adv. Mater.* **2024**, 36, No. 2306568.
- (30) Liu, S.; Li, J.; Xiao, W.; et al. Buried interface molecular hybrid for inverted perovskite solar cells. *Nature* **2024**, 632, 536–542.
- (31) Li, Y.; Zheng, Z.; Zheng, X.; et al. Mutual stabilization of hybrid and inorganic perovskites for photovoltaics. *eScience* **2026**, 6, No. 100449.
- (32) Kim, M.; Jeong, J.; Lu, H.; et al. Conformal quantum dot-SnO₂ layers as electron transporters for efficient perovskite solar cells. *Science* **2022**, 375, 302–306.
- (33) Zhao, Y.; Ma, F.; Qu, Z.; et al. Inactive (PbI₂)₂RbCl stabilizes perovskite films for efficient solar cells. *Science* **2022**, 377, 531–534.
- (34) Park, J.; Kim, J.; Yun, H. S.; et al. Controlled growth of perovskite layers with volatile alkylammonium chlorides. *Nature* **2023**, 616, 724–730.
- (35) Wang, P.; Sun, R.; Sun, X.; et al. Electrostatically Enhanced Self-Assembled Monolayers Anchoring for Scalable and Stable Inverted Perovskite Solar Cells. *Adv. Mater.* **2026**, 38, No. e14735.
- (36) Chen, H.; Teale, S.; Chen, B.; et al. Quantum-size-tuned heterostructures enable efficient and stable inverted perovskite solar cells. *Nat. Photonics* **2022**, 16, 352–358.
- (37) Teale, S.; Degani, M.; Chen, B.; Sargent, E. H.; Grancini, G. Molecular cation and low-dimensional perovskite surface passivation in perovskite solar cells. *Nat. Energy* **2024**, 9, 779–792.
- (38) Benediktovitch, A.; Ulyanenkova, T.; Keckes, J.; Ulyanenko, A. Sample tilt-free characterization of residual stress gradients in thin coatings using an in-plane arm-equipped laboratory X-ray diffractometer. *J. Appl. Crystallogr.* **2014**, 47, 1931–1938.
- (39) Zhu, C.; Niu, X.; Fu, Y.; et al. Strain engineering in perovskite solar cells and its impacts on carrier dynamics. *Nat. Commun.* **2019**, 10, No. 815.
- (40) Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B* **1996**, 54, 11169–11186.
- (41) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.
- (42) Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B* **1994**, 50, 17953–17979.
- (43) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H–Pu. *J. Chem. Phys.* **2010**, 132, No. 154104, DOI: 10.1063/1.3382344.
- (44) Thompson, A. P.; Aktulga, H. M.; Berger, R.; et al. LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.* **2022**, 271, No. 108171.
- (45) Bayly, C. I.; Cieplak, P.; Cornell, W.; Kollman, P. A. A well-behaved electrostatic potential based method using charge restraints for deriving atomic charges: the RESP model. *J. Phys. Chem.* **1993**, 97, 10269–10280.
- (46) Seijas-Bellido, J. A.; Samanta, B.; Valadez-Villalobos, K.; et al. Transferable Classical Force Field for Pure and Mixed Metal Halide Perovskites Parameterized from First-Principles. *J. Chem. Inf. Model.* **2022**, 62, 6423–6435.
- (47) Neese, F. The ORCA program system. *WIREs Comput. Mol. Sci.* **2012**, 2, 73–78.
- (48) Leroy, F.; Müller-Plathe, F. Dry-Surface Simulation Method for the Determination of the Work of Adhesion of Solid–Liquid Interfaces. *Langmuir* **2015**, 31, 8335–8345.
- (49) Surblys, D.; Leroy, F.; Yamaguchi, Y.; Müller-Plathe, F. Molecular dynamics analysis of the influence of Coulomb and van der Waals interactions on the work of adhesion at the solid-liquid interface. *J. Chem. Phys.* **2018**, 148, No. 134707, DOI: 10.1063/1.5019185.
- (50) Surblys, D.; Müller-Plathe, F.; Ohara, T. Computing the Work of Solid–Liquid Adhesion in Systems with Damped Coulomb Interactions via Molecular Dynamics: Approaches and Insights. *J. Phys. Chem. A* **2022**, 126, 5506–5516.