

Sterically gated Lewis acid and base pairs enable orthogonal defect passivation in perovskite solar cells

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Charged point defects cause efficiency loss and instability in perovskite solar cells. Although Lewis acids and Lewis bases individually passivate anionic and cationic defects, they are known to react with one another. As a result, introducing different combinations to solar cells forms quenching adducts that fail to provide the necessary passivation. Here we report chemically orthogonal Lewis acid and Lewis base families that enable concurrent passivation of targeted ionic defects by weakening mutual interactions. We found that bulky sp^3 -phosphine bases, which fail to react with fluorinated aromatic acids, can suppress Lewis acid–base orbital overlap. This strategy is effective because surface defect sites are more sterically accessible to each passivator than the two passivators are to one another. Spectroscopic and defect-profiling measurements support the additive suppression of traps, resulting in devices with power conversion efficiencies up to 27.4% (certified steady state of 25.8%).

Perovskite solar cells (PSCs) are promising next-generation photovoltaics, offering high power conversion efficiencies (PCEs) and compatibility with scalable and cost-effective manufacturing. Among device architectures, the inverted (p–i–n) configuration has received particular attention for its stability and ready integration into tandems^{1–6}. Despite these advances, further improvement requires suppression of non-radiative recombination at the perovskite/transport-layer interface^{7,8}, where a chemically diverse range of ionic defects, vacancies, undercoordinated metal ions and antisite substitutions act as trap states and limit carrier lifetimes^{9–13}.

To tackle these interfacial losses, diverse passivation strategies have been developed, including ones based on polymers^{14–17}, organic ammonium salts^{18–21} and inorganic ions^{22–26}. Ionic passivators can neutralize charged defects, but they often lack chemical specificity and interfere with charge transport, and in some cases, they compromise film crystallinity^{27–30}.

Lewis acid (LA) and Lewis base (LB) passivation approaches^{17,31–34} enable chemically selective coordination to specific surface defects without inducing significant lattice disruption. LBs such as pyridine and thiourea bind selectively to undercoordinated Pb^{2+} sites^{35,36}; while

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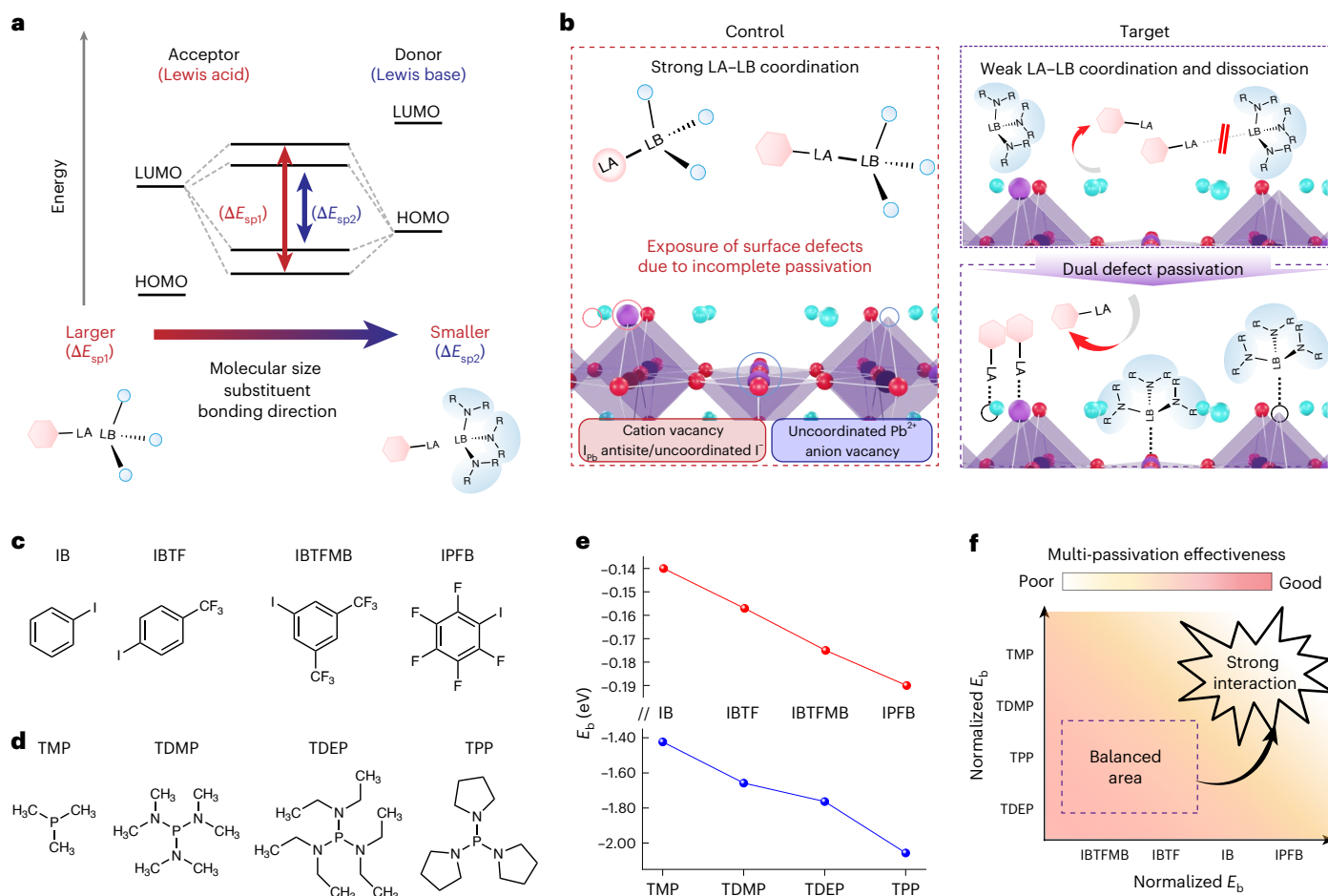


Fig. 1 | Design principles and molecular interactions in orthogonal LA-LB passivation. **a**, An energy diagram of LA-LB orbital interaction strength, highlighting steric- and geometry-dependent ΔE_{sp1} , ΔE_{sp2} and ΔE_{sp3} represent the stabilization energies of unhindered, and sterically and geometrically gated acid-base pairs, respectively. **b**, Schematics of chemical interactions between

LAs, LBs and perovskite surface defects. **c, d**, Chemical structures of LAs (**c**) and LBs (**d**). **e**, DFT calculations of the binding energies of LA and LB molecules with representative ionic defects (I_{pb} antisite and uncoordinated Pb^{2+}). **f**, A conceptual diagram highlighting the orthogonal molecular design strategy enabling decoupled defect targeting in dual-passivation systems.

LAs such as phenyl-C61-butyric acid methyl ester (PCBM) and halogenated aromatics address antisite defects and electron-rich species via halogen and electron-accepting mechanisms^{35–38}. These selective interactions reduce trap densities, improve film quality and enhance both efficiency and stability^{39–42}.

However, molecules possessing a single functional group for ionic passivation often fail to address the chemically diverse defects in perovskites. To overcome this limitation, multifunctional molecules such as zwitterionic ligands have been introduced, which are designed to interact with both cationic and anionic defects through internal charge separation^{43–45}. While these compounds demonstrate the potential of multisite passivation, their rigid charge structures limit molecular mobility and directional binding, resulting in uneven surface coverage and inconsistent performance^{46–49}.

Alternatively, bimolecular approaches have coupled either LA or LB molecules with an additional component that modulates interfacial field effects^{34,42}. This cooperative design enhances both defect passivation and charge transport, demonstrating that multimolecular combinations can be effective when chemical interference is minimized. However, these systems still address only one defect polarity (either positive or negative), as introducing both acids and bases together typically leads to strong acid-base complexation, which precludes independent defect coordination⁵⁰.

Here, a modular multimolecular passivation (MMP) strategy is introduced that enables simultaneous passivation of both cationic and

anionic defects by enforcing chemical orthogonality among the passivating species. We define chemical orthogonality as the condition in which the mutual LA-LB interaction energy is substantially weaker than the binding energy of each passivator to its respective target defect, such that solution-phase association between the two passivators is weak and reversible, enabling each to remain independently reactive towards its target defect site upon film deposition. This is achieved through a steric-electronic gating design. The electronic nature of the gating originates from the highly directional σ -hole potential of the fluorinated aromatics, which necessitates a precise linear alignment for orbital overlap. This specific geometric requirement is obstructed by the steric bulk of the phosphine substituents. These complementary factors suppress acid-base complexation while permitting coordination to the sterically accessible surface defects. As a result, the LA and LB remain weakly and reversibly associated in solution but bind strongly and selectively upon approaching their respective defect sites. This chemically decoupled design enables additive suppression of trap states and produces PSCs with a PCE of 27.4% and >90% retention after 1,030 h under continuous one-sun operation at 85 °C.

Results

Molecular design for chemically decoupled passivation pairs

Owing to the tendency of LAs and LBs to form acid-base complexes, the frontier-orbital energy levels of selected LAs (iodobenzene (IB), 4-iodobenzotrifluoride (IBTF), 1-iodo-3,5-bis(trifluoromethyl)

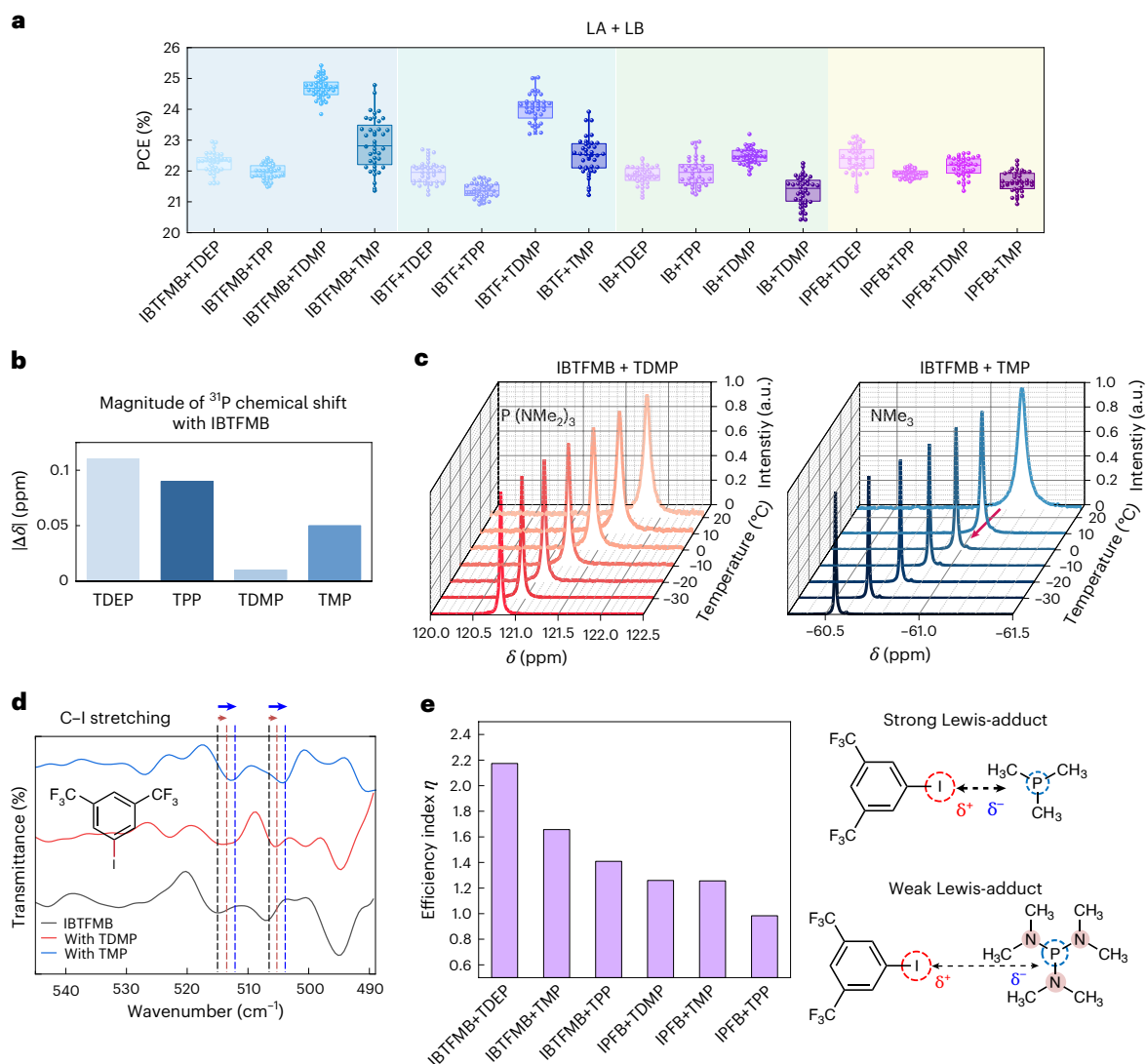


Fig. 2 | Effect and proposed mechanism of dynamic molecular interactions in LA-LB dual-passivation. **a**, PCE comparisons of devices treated with a combination of LA and LB passivators at a fixed molar ratio of LA:LB of 1:1 ($n = 40$ independent devices per condition across LA-LB combinations). Background shading distinguishes the four LA groups; left to right: IBTFMB, IBTF, IB and IPFB. Box plots: centre line, median; bounds, 25th/75th percentiles; whiskers, $1.5 \times \text{IQR}$; and outliers shown as points. **b**, ^{31}P NMR chemical shifts of phosphine-based LBs upon addition of IBTFMB, indicating varying degrees of electronic perturbation

from acid-base interactions. **c**, VT ^{31}P NMR spectra of TDMP-IBTFMB and TMP-IBTFMB mixtures, highlighting differences in interaction strength and dynamics. The red arrow marks the emergence of a new peak, characteristic of a slow-exchange regime. **d**, FTIR spectra showing shifts in the C-I stretching region for IBTFMB-TDMP and IBTFMB-TMP. **e**, Left: the empirical efficiency index quantifying competitive binding trends, which determines the strength of Lewis-adduct binding. Right: illustration of strong/weak Lewis-adducts.

benzene (IBTFMB) and iodopentafluorobenzene (IPFB)) and LBs (tris(diethylamino)phosphine (TDEP), tris(1-pyrrolidinyl)phosphine (TPP), tris(dimethylamino)phosphine (TDMP) and trimethylphosphine (TMP)) were investigated (Supplementary Figs. 1 and 2). These energy levels were used as initial electronic descriptors to infer the relative donor-acceptor alignment between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO) of the LAs and LBs. However, such simple energy-level comparisons alone cannot reproduce the coordination trends in such complex systems, because the achievable orbital splitting (ΔE_{sp}), which reflects the strength of donor-acceptor coupling upon approach, is further modulated by steric accessibility, molecular size and approach geometry^{51,52}. These factors are particularly decisive in weak LA-LB interactions and suppress intermolecular coupling to prioritize defect coordination over solution-phase association (Fig. 1a).

It was hypothesized that undesired strong LA-LB interactions could be suppressed through an asymmetric steric-electronic gating

design. In this design, the σ -hole of the LA exhibits a highly directional electrostatic anisotropy, requiring a strict linear alignment with the LB's lone pair. However, the bulky steric pocket of the LB blocks this specific approach geometry. By contrast, surface ionic defects offer a wider manifold of accessible approach vectors, acting as relatively unhindered sites that do not impose such stringent directional constraints. This asymmetry ensures that LA-LB complexation is suppressed owing to steric penalties, while defect coordination remains spatially and energetically accessible. As a result, the LA and LB exhibit only weak and transient interactions in solution, readily dissociating when a more favourable binding partner becomes available. Upon adsorption, each passivator adopts a defect-anchored orientation that sterically and electronically shields the complementary partner, impeding LA-LB re-coordination and enabling sustained, selective passivation (Fig. 1b). On the basis of this design principle, we developed a sequential filtering framework to select and evaluate molecular candidates (Supplementary Fig. 3). The angular dependence of the LA-LB

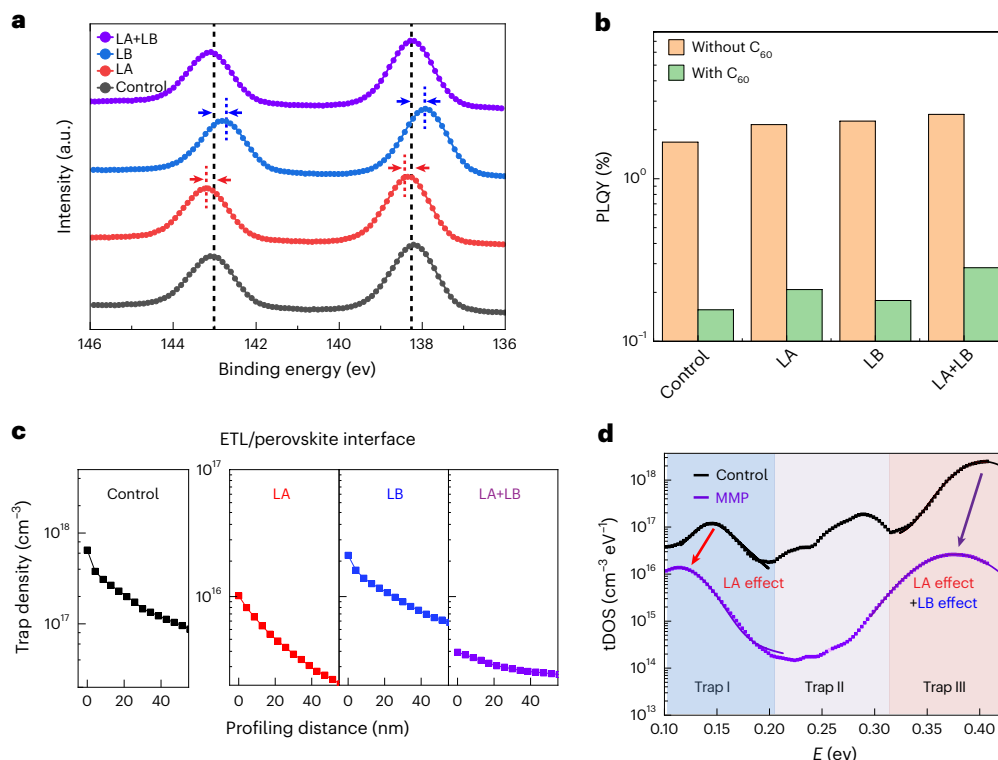


Fig. 3 | Electronic and photophysical properties enabled by MMP. a, XPS Pb 4f spectra of control, LA-, LB- and co-treated samples. **b,** PLQY of perovskite films for the passivation before and after C₆₀ deposition. **c,** Quantification of trap density reduction around the ETL/perovskite interface after treatment with LA,

LB and their combination using DLCP. **d,** Energy-resolved density of states from TAS, identifying changes in shallow (trap band I) and deep (trap band III) traps. Dashed curves represent the fitted line with the Lorentz fitting.

interaction energy, demonstrated by potential energy surface (PES) scans (Supplementary Fig. 4), provides direct quantitative validation of the steric gating principle, showing that the accessible low-energy angular range is confined to a narrow cone along the C–I axis, compared with a broader angular range for a compact base lacking steric bulk.

Guided by this concept, we examined how fluorination modulates the σ -hole potential and steric profile of halogenated aromatic LAs. Increasing the fluorination enhanced the positive electrostatic potential around the iodine site and lowered LA LUMO, thereby strengthening halogen-bond donor ability towards anionic defects (Supplementary Fig. 1). Density functional theory (DFT) calculations of binding energies with defects corroborate these trends, and IPFB exhibited the strongest interaction with defects, closely followed by IBTFMB (Fig. 1c,e). Consequently, devices treated with these halogenated aromatics exhibited improved device performance, consistent with the trends in the calculated binding energies (Supplementary Figs. 5 and 6). Meanwhile, the rigid aromatic scaffold and σ -hole-driven directionality introduced geometric constraints that hindered nucleophilic bases from accessing the electrophilic iodine site, suppressing tight adduct formation.

For LBs, we examined four phosphine donors whose substituents modulate both steric accessibility and donor strength. Phosphorus-based molecules with sp^3 -hybridized lone pairs effectively passivate uncoordinated Pb²⁺ defects^{31,33}, and their umbrella-like geometry provides intrinsic steric shielding against intermolecular association. DFT calculations indicate that TDEP and TPP possess higher HOMO levels (Supplementary Fig. 2) and stronger binding energies (Fig. 1d,e); however, device performance showed that steric accessibility, rather than intrinsic donor strength, governs efficacy (Supplementary Figs. 6 and 7). The bulky substituents of TDEP and TPP impede access to defect sites, limiting surface coverage. Conversely, the more compact TDMP and TMP readily accommodate surface sterics to achieve dense passivation while potentially retaining sufficient bulk to suppress LA–LB coupling.

To capture steric and size-dependent effects more accurately, we evaluated binding energies normalized by van der Waals surface area, providing a size-independent measure of intrinsic binding affinity that correlates well with device performance, particularly for sterically shielded LBs (Supplementary Fig. 8 and Supplementary Table 1). It also accentuates differences in molecular–molecular association, enabling the identifications of LA–LB pairs that may be prone to over-coordination. Using this framework, the combinations were mapped onto a steric–electronic landscape that separates a ‘balanced region’, where defect-selective binding is favoured, from a ‘high-interaction region’, where excessive LA–LB coupling dominates (Fig. 1f). For example, over-compact pairs such as IPFB + TMP, although individually strong passivators, lack sufficient steric separation and therefore tend to over-associate, reducing their defect-selective activity.

Dynamic molecular interaction and mechanistic origins

To evaluate whether the steric–electronic design principle manifests in actual material behaviour, device performance was measured across LA–LB combinations. IBTFMB-containing LA–LB pairs delivered the highest PCEs, and IBTFMB–TDMP and IBTFMB–TMP exhibited the best performance among all combinations. By contrast, pairs containing IB or IPFB, which strongly bind both defects and bases, exhibited much lower efficiencies (Fig. 2a).

To directly probe molecular interactions, ³¹P{¹H} nuclear magnetic resonance (NMR) spectroscopy was performed. The ³¹P{¹H} NMR spectrum of the IBTFMB–TDMP mixture exhibited a minimal shift within 0.01 ppm, indicating negligible electronic perturbation and no evidence for strong, persistent LA–LB adduct formation (Fig. 2b). By contrast, TDEP, TMP and TPP mixtures exhibited pronounced chemical shifts, evidence of stronger electronic redistribution and tighter binding (Supplementary Fig. 9). Furthermore, as a positive control for the adduct state, we performed a ‘forced-contact’ test using a high-concentration equimolar mixture. Under these conditions, the

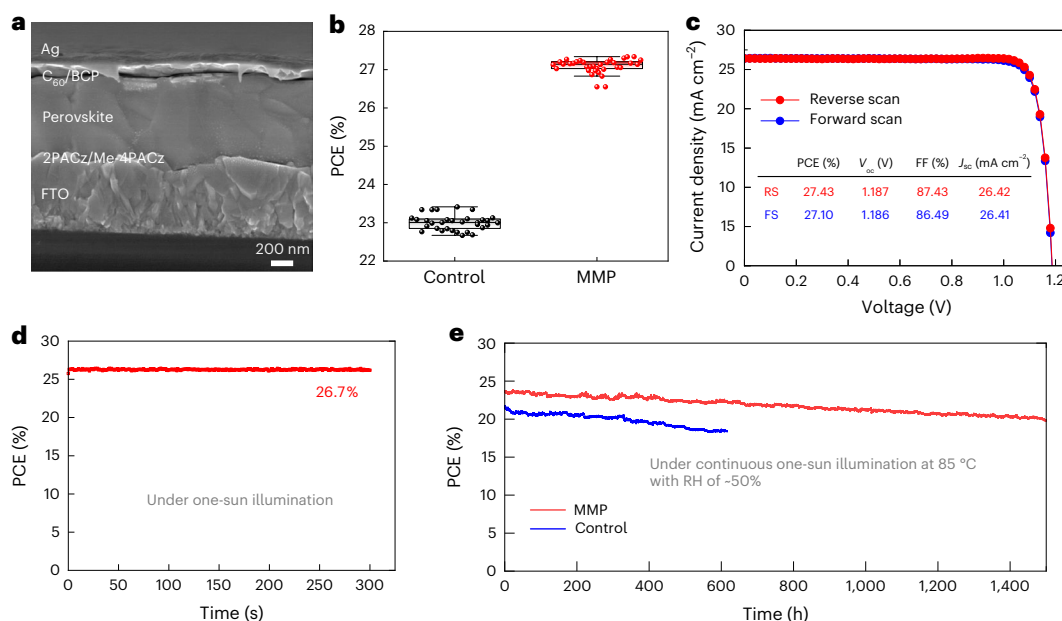


Fig. 4 | Device performance and operational stability. **a**, A cross-sectional SEM image of the inverted PSC architecture. **b**, PCE comparison of the control and MMP devices ($n = 30$ independent devices for each condition). Box plots: centre line, median; bounds, 25th/75th percentiles; whiskers, $1.5 \times \text{IQR}$; and

outliers are shown as points. **c**, Current density–voltage (J – V) characteristics of the highest-performing MMP-treated device. **d**, The stabilized power output of the MMP-treated device under maximum power point tracking. **e**, The stability of control and MMP-treated devices under one-sun illumination at 85 °C.

$^{31}\text{P}\{^1\text{H}\}$ NMR signal underwent an upfield shift from 122 ppm to a cluster of peaks between 50 and 70 ppm (Supplementary Fig. 10), diagnostic of the tight LA–LB adduct.

Variable temperature (VT) $^{31}\text{P}\{^1\text{H}\}$ NMR further clarified the interaction dynamics (Fig. 2c). The IBTFMB–TDMP mixture showed a gradual upfield shift in the phosphorus resonance from 122.28 to 120.83 ppm as temperature decreased, along with signal sharpening. This upfield shift indicates increased electronic shielding^{53,54}, consistent with weak and reversible LA–LB interactions in a fast exchange regime^{55,56}, where rapid interconversion between free and bound states produces a single averaged peak. By contrast, IBTFMB–TMP showed a downfield shift from –61.24 to –60.55 ppm, and the appearance of two distinct peaks at low temperature, reflecting stronger and more persistent binding in a slow-exchange regime⁵⁵. These results support that, while both bases reversibly interact with IBTFMB, TDMP maintains a dynamic and labile interaction conducive to defect coordination, whereas TMP forms a more strongly bound, less dissociative adduct, potentially limiting effective surface passivation.

Fourier-transform infrared (FTIR) spectroscopy corroborated this structural insight. In TDMP, adjacent nitrogen atoms delocalized the phosphorus lone pair through resonance or π -interactions⁵⁷ (Supplementary Fig. 11), slightly reducing Brønsted basicity, as shown in Supplementary Fig. 7, but promoting moderate steric hindrance and reversible interactions. Consequently, the C–I stretching vibration in IBTFMB–TMP red-shifted, consistent with strong halogen bonding⁵⁸, whereas IBTFMB–TDMP exhibited only minor shifts (Fig. 2d). Similarly, C–F stretching modes were perturbed in IBTFMB–TMP but remained largely unchanged for IBTFMB–TDMP (Supplementary Fig. 12). UV–visible spectra showed negligible changes for the TDMP–IBTFMB mixture (Supplementary Fig. 13), further providing the absence of strong ground-state complexation.

These spectroscopic results are consistent with IBTFMB–TDMP operating via a dynamic equilibrium that thermodynamically favours defect passivation over solution-phase complexation. This mechanism is consistent with control experiments showing negligible performance differences between sequential and simultaneous passivation, supporting the system's dynamic flexibility (Supplementary Fig. 14). DFT

calculations further validated this stability; upon the approach of a LA, the TDMP–defect complex demonstrated remarkable robustness, with a negligible reduction in binding energy (<0.1 eV) (Supplementary Fig. 15). Consequently, the complex preserved its energetically favourable binding state, indicating that TDMP maintained a stable and persistent coordination with the defect without being displaced by the nearby LA. This structural stability ensures effective and sustained cooperative dual-passivation.

To quantify this competitive binding relationship, an empirical efficiency index (η) was defined as the geometric mean of acid and base binding energies to their respective defects, normalized by their mutual

interaction energy: $\eta = \sqrt{\frac{|E_{\text{LA-Defect}^-}^{\text{binding}}| \times |E_{\text{LB-Defect}^+}^{\text{binding}}|}{|E_{\text{LA-LB}}^{\text{binding}}|}}$. A higher η indicates

greater chemical orthogonality—stronger binding to defects relative to mutual association. Among all tested pairs, IBTFMB–TDMP exhibited the largest η , consistent with its superior device performance and minimal spectroscopic perturbation (Fig. 2e and Supplementary Table 1). The complete design-space analysis underlying η , in which all LA–LB combinations are plotted according to their defect-binding and intermolecular interaction energies, is provided in Supplementary Fig. 16.

Finally, to complete the MMP, propane-1,3-diammonium iodide (PDAI₂), a field-effect passivator previously reported by our group³⁴, was incorporated sequentially after the LA–LB pair. PDAI₂ operates via a mechanistically distinct pathway from coordinate bonding, introducing a surface dipole field that repels minority carriers without perturbing the orthogonality of the LA–LB pair. This sequential addition further suppressed interfacial recombination without altering the independent defect selectivity of the LA–LB pair. The synergistic interplay between the three passivators was evaluated using a combinatorial spray-inking system that created a gradient, leading to the development of a three-passivator system to maximize device performance (Supplementary Fig. 17 and Supplementary Note 1).

Optoelectronic properties enabled by MMP

To assess how the MMP strategy influences interfacial energetics, we examined surface-level chemical interactions and electronic

structures using spectroscopic probes. X-ray photoelectron spectroscopy (XPS) manifested distinct binding energy shifts depending on the passivator type (Fig. 3a). TDMP-treated electron exhibited a Pb 4f downshift, consistent with increased local electron density from LB coordination with uncoordinated Pb²⁺ sites^{33,34}. By contrast, IBTFMB-treated films showed an upshift, reflecting electron withdrawal probably arising from halogen bonding with possible antisite I_{Pb} (ref. 59). Notably, co-treated TDMP–IBTFMB films displayed minimal net shifts, suggesting that each molecule retained its independent functionality without mutual interference or chemical neutralization. As a comparative reference, the forced adduct displays distinct N 1s peak splitting and a noticeable shift in the F 1s signal. Conversely, the target device films retain a sharp, single N peak with less F shifts relative to the control, indicating that adduct formation is suppressed (Supplementary Fig. 18). XPS measurements further indicate that the addition of PDAl₂ does not perturb the coordination equilibrium of the LA–LB pair, with an independent Pb 4f shift consistent with electrostatic surface interaction rather than direct defect coordination (Supplementary Fig. 19). In addition, X-ray diffraction (XRD) measurements were consistent with no detectable structural degradation following treatment (Supplementary Fig. 20). Ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe force microscopy (KPFM) provided further evidence of a reduced energy offset between the conduction band minimum and Fermi level (E_F), along with improved surface potential uniformity in MMP-treated films (Supplementary Figs. 21 and 22), correlating with enhanced *n*-type character and charge extraction across the interface. Scanning electron microscopy (SEM) images further indicate that the passivation treatments do not induce substantial morphological disruption, with structural integrity corroborated by XRD (Supplementary Fig. 23).

Photoluminescence quantum yield (PLQY) and time-resolved photoluminescence (TRPL) measurements demonstrated that both TDMP and IBTFMB individually suppress non-radiative recombination, and their combination produced an additive enhancement in PLQY (Fig. 3b and Supplementary Fig. 24). Even after deposition of the C₆₀ electron transport layer, the co-treated films maintained the highest PLQY, signifying persistent interfacial passivation. Time-resolved reflection measurements further corroborated suppressed recombination at the perovskite top surface (Supplementary Fig. 25 and Supplementary Note 2).

Mechanistic analysis of trap-state suppression via chemically orthogonal passivation

Electrical defect spectroscopy was used to analyse how LAs and LBs influence trap energetics (Fig. 3c,d). Drive-level capacitance profiling (DLCP) demonstrated that trap densities were concentrated near the charge-transport interfaces (hole transport layer or electron transport layer (ETL)/perovskite interface) (Supplementary Fig. 26), consistent with prior studies^{60,61}. After MMP treatment, the trap density at the ETL/perovskite interface decreased by approximately two orders of magnitude (10^{18} – 10^{16} cm⁻³ at 5 kHz) (Fig. 3c), consistent with the overall suppression of interfacial trap states^{60,62}. To isolate trap-related responses, the high-frequency (500 kHz) component was subtracted, minimizing contributions from free carrier transport (Supplementary Fig. 27).

Thermal admittance spectroscopy (TAS) further clarified the energetic distribution of traps (Fig. 3d and Supplementary Figs. 28–30). Distinct suppression patterns were observed for the two passivators. Films treated with the IBTFMB exhibited a broad reduction across the trap spectrum, particularly in regions consistent with halide-related shallow states and antisite-derived deeper states. By contrast, TDMP treatment more effectively suppressed deeper trap states (trap band III), in line with preferential passivation of undercoordinated Pb²⁺ or cation-interstitial-related defects⁶². Although both passivators reduced trap densities across multiple energy levels, their dominant regions of suppression differed systematically with chemical character. The

hypothesized defect origins for each observed trap feature, together with supporting experimental and computational evidence, are summarized in Supplementary Table 2.

The perovskite surface is generally considered iodine-poor, as supported by XPS stoichiometry showing a lower iodine-to-lead ratio⁶³. Consequently, LB passivation exerts a more dominant effect by coordinating to electron-deficient Pb centres and efficiently mitigating deep-level traps. LAs, in turn, also contribute to defect passivation by interacting with electron-rich sites such as iodine interstitials or antisite I_{Pb} defects, which can give rise to both shallow and deep states but are less favourably formed under iodine-poor conditions⁶³. Despite their lower abundance, these halide-related defects still allow the acid to complement the base in reducing the overall trap density. This cooperative contribution, where the LB plays the dominant role while the LA provides auxiliary stabilization, accounts for the broad and balanced suppression of trap states observed in the MMP-treated films.

Photovoltaic performance

Inverted PSCs with the device structure fluorine-doped tin oxide (FTO)/NiOx/[2-(9H-carbazol-9-yl)ethyl]phosphonic acid (2PACz)–[4-(3,6-dimethyl-9H-carbazol-9-yl)butyl]phosphonic acid (Me-4PACz)/perovskite/C₆₀/bathocuproine (BCP)/Ag were fabricated using the MMP strategy, as depicted in Fig. 4a. Using time-of-flight secondary ion mass spectrometry (ToF-SIMS), we demonstrated that both P (LB) and F (LA) signatures remain co-localized at the perovskite interface even after C₆₀ deposition, underscoring the robust post-processing stability (Supplementary Fig. 31). The PCEs of the control and MMP are shown in Fig. 4b, and the current density–voltage (*J*–*V*) characteristics of the champion MMP device are presented in Fig. 4c; the device achieved a PCE of 27.4%, a short-circuit current density (J_{sc}) of 26.4 mA cm⁻², an open-circuit voltage (V_{oc}) of 1.187 V and a fill factor (FF) of 87.43% with a steady-state PCE of 26.7% (Fig. 4d). The individual and combined contributions of PDAl₂ and the LA–LB pair to device performance are compared in Supplementary Fig. 32. Under the asymptotic protocol, the devices achieved certified quasi-steady state PCEs of 25.8% from the National Laboratory of the Rockies (Supplementary Fig. 33). The current responses are seen in the external quantum efficiency spectra (Supplementary Fig. 34). Operating stability was evaluated by maximum power point tracking under one-sun illumination in ambient air. Following the ISOS-L-3 protocol at 85 °C, MMP-treated devices retained 90% (T90) of their initial PCE (23.6%) after 1,030 h (Fig. 4e). In comparison, the control device reached T90 in only 423 h.

Discussion

This study establishes a modular passivation framework that enables spatial and functional separation of LA and LB molecules to address chemically diverse defects in halide perovskites. Pairing a halogenated aromatic acid with a bulky phosphine donor allows selective coordination towards oppositely charged surface sites while minimizing undesired complexation. Spectroscopic analyses are consistent with the two molecules remaining electronically independent, and defect spectroscopy revealed complementary suppression of shallow and deep traps: the base mitigates electron-deficient deep states, whereas the acid alleviates halide-related shallow ones.

This orthogonality arises from asymmetric steric–electronic design. The acid features a highly directional σ -hole, while the base employs a sterically bulky donor framework, enabling defect-specific binding without mutual deactivation. Unlike multifunctional single passivators that suffer from internal competition, this modular approach decouples reactivity and accessibility, yielding cooperative defect suppression, a PCE above 27% and stable operation beyond 1,000 h at 85 °C. Deliberate and systematic control over steric and electronic asymmetry thus reconciles selectivity and durability in complex semiconductor interfaces.

Online content

Any methods, additional references, Nature Portfolio reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at <https://doi.org/10.1038/s41557-026-02261-z>.

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Methods

Materials

FAI (99.9%) and MAI (99.9%) were purchased from GreatCell Solar Materials. CsI (99.999%), PbI_2 (99.99%), MACl (99.9%) and PbCl_2 (99.9%) were purchased from Sigma-Aldrich and stored in a nitrogen glovebox without further purification. 2PACz, Me-4PACz and PDAl_2 were purchased from Tokyo Chemical Industry. Halogenated aromatic LAs (iodobenzene (IB), 4-iodobenzotrifluoride (IBTF), 1-iodo-3,5-bis(trifluoromethyl)benzene (IBTFMB) and iodopentafluorobenzene (IPFB)) and phosphine-based LBs (tris(diethylamino)phosphine (TDEP), tris(1-pyrrolidinyl)phosphine (TPP), tris(dimethylamino)phosphine (TDMP) and trimethylphosphine (TMP)) were purchased from Sigma-Aldrich and handled under inert conditions in a glovebox. Patterned FTO glass substrates ($25 \times 25 \text{ mm}^2$), obtained from TFD, were used for all devices.

Precursor solutions

A 1.53 M perovskite precursor solution was prepared by dissolving CsI, FAI, MAI, PbI_2 , MACl and PbCl_2 with proper stoichiometry ratios ($\text{FA}_{0.85}\text{MA}_{0.1}\text{Cs}_{0.05}\text{PbI}_3$ with 5 mol% MAPbCl_3 addition) in a DMF:DMSO (4:1 v/v) solvent mixture. The precursor was stirred at 30 °C for 1 h and filtered using a 0.22- μm PTFE syringe filter before use. The NiOx solution was diluted in ethanol and filtered using a 0.45- μm PTFE syringe filter. For the surface passivation, LAs and LBs were investigated at various concentrations and ratios to optimize the device performance. The passivation solutions were freshly prepared by dissolving the compounds in a CB:IPA (1:1 v/v) solvent mixture. For the initial LA–LB combinatorial screening shown in Fig. 2a, all devices were fabricated at a fixed molar ratio of LA:LB 1:1 to identify performance trends and evaluate potential adduct formation. The optimal molar ratio within the IBTFMB–TDMP pair was subsequently determined by spray-based combinatorial screening (Supplementary Note 1 and Supplementary Fig. 17). Among the various conditions tested, the best performance was achieved with a molar ratio of approximately 3.5:1 (specifically 17.5 mM IBTFMB and 5 mM TDMP).

Solar cell fabrication

Inverted (p–i–n) devices with the architecture FTO/NiOx/2PACz–Me-4PACz/perovskite/ C_{60} /BCP/Ag were fabricated. Substrates were cleaned by sequential ultrasonication in detergent, deionized water, acetone and IPA, followed by UV–ozone treatment for 20 min. NiOx and SAM layers were deposited as reported previously. The perovskite layer was spin-coated and annealed at 100 °C for 10 min. Surface passivation was performed sequentially in two steps. First, the LA–LB passivation solution containing IBTFMB and TDMP (molar ratio 3.5:1; 17.5 mM IBTFMB and 5 mM TDMP in CB:IPA (1:1 v/v)) was spin-coated onto the annealed perovskite film and annealed at 100 °C for 10 min. The film was allowed to cool to room temperature before the subsequent PDAl_2 passivation step. PDAl_2 was dissolved in CB:IPA (1:1 v/v) and spin-coated onto the LA–LB-treated film, followed by annealing at 100 °C for 5 min. C_{60} , BCP and Ag were deposited by thermal evaporation.

Device testing measurement

J – V curves were recorded in a nitrogen environment at room temperature using a Keithley 2401 source meter. The light source is a Xe arc lamp from a Science Tech Al Light Line Class AAA solar. The illumination intensity was adjusted with a calibrated silicon reference cell (SCI-REF-Q). Measurements were conducted under nitrogen flow with a scan step of 20 mV and a delay time of 20 ms. A metal aperture mask (0.049 cm^2) defined the active area. The operational stability tests at elevated temperatures were conducted under continuous one-sun illumination at 85 °C without UV filtering, in ambient air with relative humidity of ~50%, following the ISOS-L-3 protocol. Temperature was monitored by an infrared thermometer. Devices were encapsulated

using a capping glass slide with ultraviolet adhesive (Lumtec LT-U001) as sealant. The active device area was 0.049 cm^2 , and stability was tracked by maximum power point tracking. T90 is defined from the initial PCE per ISOS-L-3 convention.

Statistics and reproducibility

No statistical method was used to predetermine sample size; sample sizes were chosen on the basis of common practice in the perovskite photovoltaics field. No data were excluded from the analyses. The experiments were not randomized. The Investigators were not blinded to allocation during experiments and outcome assessment. Photovoltaic statistics in Fig. 4b were derived from $n = 30$ independent devices per condition. Photovoltaic statistics in Fig. 2a and Supplementary Fig. 6 (LA–LB combinatorial screening at LA:LB 1:1) were derived from $n = 40$ independent devices per condition across 16 combinations. Box plots show the median (centre line), 25th/75th percentiles (box bounds) and whiskers extending to $1.5 \times$ the interquartile range, with data beyond the whiskers plotted as individual outliers.

Characterizations

Acid dissociation constant measurement. The pK_a values of LBs were determined by titrating 5 ml of a 0.1 M solution with 0.1 M HCl at 25 °C. The pH values were recorded using a calibrated pH meter (buffer standards at pH 4.00, 7.00 and 10.00). The pK_a was identified from the pH at the half-equivalence point, determined from the first derivative of the titration curve.

ToF-SIMS. Depth profiling was performed on an IONTOF M6 system using a 30-keV Bi^+ primary ion gun. A 500-eV O_2 ion gun was used for sputtering across an analysis area of $50 \times 50 \mu\text{m}^2$. Samples were measured as the full-stack device.

Photoluminescence and TRPL. PLQY was measured using an Edinburgh Instruments FS5 spectrofluorimeter. The system was equipped with a 1,200 grooves mm^{-1} diffraction grating and a Hamamatsu R928P photomultiplier tube. A 375-nm pulsed laser diode was used for TRPL, while PLQY measurements employed a Spectralon integrating sphere with 520-nm excitation at 1 mW cm^{-2} fluence.

Photoluminescence mapping. Photoluminescence mapping was performed using a HORIBA LabRAM HR Evolution confocal microscope equipped with a 633-nm laser operated at 0.1% power to minimize potential photodamage. The focal plane was aligned to the top surface of the perovskite film. A two-dimensional scan mode was employed to collect photoluminescence data over a 100×100 grid, corresponding to ~100 μm lateral spacing between adjacent data points. Photon counting was conducted for approximately 2 s per data point, balancing the tradeoff between the inherently low photon flux resulting from the use of low laser power and the need to scan a large number of spatial data points.

NMR. ^1H , ^{31}P and ^{19}F NMR spectra were obtained using a Bruker Avance III HD 500-MHz spectrometer equipped with a BBO Prodigy probe. VT ^{31}P NMR was carried out on a Bruker Avance III 600-MHz system from –40 °C to 40 °C with 5 °C increments.

KPFM. Surface potential maps were collected via KPFM on a Bruker Icon system equipped with PtIr5-coated conductive tips (PPP-EFM, nanosensors; spring constant: 2.8 N m^{-1} , resonance frequency: 75 kHz).

FTIR spectroscopy. FTIR spectra were collected using a transmission mode in a Thermo Scientific Nicolet iS50 spectrometer using a NaCl-window liquid cell. The C–I and C–F stretching regions were analysed to investigate acid–base interactions and halogen bonding strength.

UV-visible absorption spectroscopy. UV-visible spectra were measured using a Cary 5000 spectrophotometer over the 175–3,300 nm range with appropriate light sources and detectors.

Transient reflection spectroscopy. Femtosecond transient reflection measurements were performed in a HARPIA commercial instrument (Light Conversion) equipped with a Kymera 193i (Oxford Instruments) spectrometer and a broadband Si NMOS detector (Hamamatsu S3901+C7884). An amplified 260-fs pulse train, centred at 1,026 nm, with an average power of 20 W and a repetition rate of 50 kHz was generated from a Pharos Yb:KGW laser (Light Conversion). The pulse train was divided into three parts. An optical parametric amplifier (Orpheus, Light Conversion) was pumped with 17.5 W and generated a pulse train centred at 740 nm, this train served as the pump pulse and was further modulated at 40 Hz. For the probe pulse, 0.5 W of the initial 1,026-nm pulse train was routed to a motorized delay stage, providing 7 ns of delay, and a white light supercontinuum was generated by attenuating it with a variable neutral density filter and focusing it into a YAG crystal. The remaining 2 W was not used in the experiment. The pump and probe beams were then spatially and temporally overlapped onto the sample with a couple of parabolic mirrors. The sample was tilted at an 8° angle, and the reflected probe beam was directed to the detector. All experiments were performed at room temperature.

SEM. Surface images of passivated perovskite films and cross-sectional images of devices were obtained on a Hitachi S8030 at an accelerating voltage of 3 kV.

DLCP and TAS measurements. To characterize the impact of passivants on the defect properties of the devices, we employed DLCP and TAS, which allow investigation of the spatial distribution and energetic position of defect states, respectively, as shown in Fig. 3c,d. All capacitance-based measurements (DLCP and TAS) were performed using PAIOS, an all-in-one measurement platform for photovoltaic and LED devices.

For the TAS measurements, the frequency scanning range was 5 Hz to 10 MHz, and the amplitude of the a.c. bias was 20 mV. The DLCP measurements were conducted from a bias range of 0 V to 1.2 V, while the amplitude of the a.c. biases ranged from 20 to 200 mV in 20-mV increments. For each a.c. bias, an additional offset d.c. voltage was applied to keep the maximum and minimum bias constant. The measured capacitances at each d.c. bias were collected and then fitted with a polynomial function to obtain C_0 , the intercept component, and C_1 , the linear component. For the comparison of the trap densities, the trap densities measured at 5 kHz are representatively given. The trap density of states (tDOS) calculated via TAS is calculated by using equation $N_t = -\frac{1}{qkT} \frac{dC}{d\omega} \frac{V_{bi}}{W}$ and the energy range being profiled is calculated using $E_\omega = kT \ln\left(\frac{\omega_0}{\omega}\right)$, where W and V_{bi} are the depletion width and built-in potential, respectively, which were derived from the Mott–Schottky analysis of C–V measurements. For the energy range being profiled, q , k , T , ω and C are elementary charge, Boltzmann's constant, temperature, angular frequency and capacitance, respectively. The drive-level capacitance profiling formulas are given by $N = -\frac{C_0}{2q\epsilon A^2 C_1}$, which gives the density of states, and $x = \frac{E_A}{C_0}$, which gives the profiling distance. The defect-related trap densities and energies were obtained by further analysis of the TAS data, performed by extracting the trap density-of-states $N_t(E)$, reading each band's fitted peak energy as E_a , and integrating $N_t(E)$ over the band windows to get N_r . The values are listed in Supplementary Table 2.

To investigate the trap energy levels, we performed TAS (Supplementary Figs. 28–30) and recorded the peak in the derivative for use in constructing an Arrhenius plot to extract the attempt-to-escape frequency. To investigate the spatial orientation of the defects, we performed DLCP (Supplementary Figs. 26 and 27). We further investigated

the frequency dependence (Supplementary Fig. 28) to support the conclusion that lower-frequency measurements correspond to deep-level defects as opposed to free carriers.

XPS and UPS. XPS was conducted using a Thermo Scientific Nexsa G2 system (Al K α source, 400- μ m spot). UPS was performed with He I (21.22 eV) excitation and gold as reference. Samples included control, LA-treated, LB-treated and MMP-treated films.

XRD. XRD patterns were collected using a Rigaku SmartLab diffractometer using Cu K α radiation at 45 kV and 160 mA to evaluate crystal structures before and after passivation.

DFT calculations. First-principles binding energy and PES calculations based on DFT were performed using the Vienna Ab initio Simulation Package (VASP)⁶⁴. The generalized gradient approximation of Perdew–Burke–Ernzerhof exchange–correlation functional and the projector augmented wave pseudopotentials were used. The DFT-D3 method was used to implement the van der Waals corrections. The perovskite was modelled by three layers of 2×4 supercells with a vacuum space of 20 Å to separate the neighbouring surfaces in the z -direction (see examples in Supplementary Fig. 5). The atoms in the bottom layer were fixed, and the atoms on the other layers and the passivation molecules were allowed to relax. In the calculations of the energetic and electronic properties, 400 eV was used as the plane-wave energy cutoff, and 10^{-5} eV and 0.02 eV Å $^{-1}$ as the energy and force convergence criteria, respectively. The Brillouin zone was sampled with Γ -centred k -mesh at a density of $2\pi \times 0.02$ Å $^{-1}$. For the binding energy calculations, the major defects in the perovskites were considered, that is, I_{pb} antisites for LAs⁵⁹ and uncoordinated Pb $^{2+}$ for LBs^{33,34}, as shown in Supplementary Fig. 5a,b. The binding energies (E_b) of the passivation molecules with perovskite surface were calculated as $E_b = E_{mol+pvsk} - E_{pvsk} - E_{mol}$, where $E_{mol+pvsk}$, E_{pvsk} and E_{mol} are the total energies of the combined system, pure perovskite system and passivation molecule, respectively. For the PES, we scanned the system's potential energy as a function of various iodine–phosphorus distances and angles, comparing two systems: IBTFMB approaching TDMP and IBTFMB approaching TMP, with both TDMP and TMP adsorbed on the perovskite surface, as illustrated in Supplementary Fig. 4. The molecular orbitals and electrostatic potentials of the passivation molecules were calculated by using the ORCA package at the B3LYP/def2-TZVP level with DFT-D3 corrections⁶⁵.

Reporting summary

Further information on research design is available in the Nature Portfolio Reporting Summary linked to this article.

Data availability

The data supporting the findings of this study are available within the Article and its Supplementary Information. The underlying datasets obtained and analysed during the study are available via Zenodo at <https://doi.org/10.5281/zenodo.21960974> (ref. 66). Source data are provided with this paper.

Code availability

The VASP is a proprietary commercial software. Access to the source code and licensing information can be obtained via the Official VASP Portal. The ORCA package is freely available for academic use through FACCTs.

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Author contributions

D.S., S.K., L.D., C. Liu and C. Li contributed equally to this work. E.H.S. and B.C. supervised the project. D.S. and S.K. conceived the idea and designed the experiments. D.S. and S.K. conducted the chemical analysis and film characterizations. D.S., L.D. and C. Liu optimized the photovoltaic performance of solar cells. D.S., C.H., Y.Y. and S.A.R. measured stability performance. J.B. and J.L. developed and implemented the spray-optimization technique. H.W.K. and J.-Y.S. performed microscope experiments. D.S. and D.C. performed TRPL and ToF-SIMS. C. Li performed DFT calculations. D.S., U.H.K. and R.L.-A. performed the defect analysis. D.S. wrote the

first draft of the paper. All authors contributed to data analysis and manuscript preparation.

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Competing interests

E.H.S., B.C., D.S. and S.K. have filed an invention disclosure with Northwestern University (disclosure no. NU2025-284) related to the MMP strategy described in this work. The other authors declare no competing interests.

Additional information

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Solar Cells Reporting Summary

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} Experimental design

Please check the following details are reported in the manuscript, and provide a brief description or explanation where applicable.

1. Dimensions

Area of the tested solar cells	☒ Yes ☐ No	The aperture area for the solar cells was 0.049 cm² (Methods) + Explain why this information is not reported/not relevant. +
Method used to determine the device area	☒ Yes ☐ No	The aperture area of the solar cells was defined by an opaque metal mask with square + Explain why this information is not reported/not relevant. +

2. Current-voltage characterization

Current density-voltage (J-V) plots in both forward and backward direction	☒ Yes ☐ No	See Fig. 4b. + Explain why this information is not reported/not relevant. +
Voltage scan conditions	☒ Yes ☐ No	The scanning step was 20 mV with a delay time of 20 ms between -0.1V and 1.3V. + Explain why this information is not reported/not relevant. +
Test environment	☒ Yes ☐ No	Current density (J)-voltage (V) characteristics of the devices were characterized at + Explain why this information is not reported/not relevant. +
Protocol for preconditioning of the device before its characterization	☒ Yes ☐ No	No preconditioning of the device was applied before the measurement. + Explain why this information is not reported/not relevant. +
Stability of the J-V characteristic	☒ Yes ☐ No	See Fig. 4d + Explain why this information is not reported/not relevant. +

3. Hysteresis or any other unusual behaviour

Description of the unusual behaviour observed during the characterization	☒ Yes ☐ No	The devices showed negligible hysteresis behaviors. + Explain why this information is not reported/not relevant. +
Related experimental data	☒ Yes ☐ No	See Fig. 4b. + Explain why this information is not reported/not relevant. +

4. Efficiency

External quantum efficiency (EQE) or incident photons to current efficiency (IPCE)	☒ Yes ☐ No	Supplementary Fig. 34 + Explain why this information is not reported/not relevant. +
A comparison between the integrated response under the standard reference spectrum and the response measure under the simulator	☐ Yes ☒ No	State where this information can be found in the text. + Explain why this information is not reported/not relevant. +

For tandem solar cells, the bias illumination and bias voltage used for each subcell	☐ Yes ☒ No	Provide a description of the measurement conditions. + Explain why this information is not reported/not relevant. +
5. Calibration		
Light source and reference cell or sensor used for the characterization	☒ Yes ☐ No	Light source is a Xe arc lamp from a Science Tech Al Light Line Class AAA solar + Explain why this information is not reported/not relevant. +
Confirmation that the reference cell was calibrated and certified	☒ Yes ☐ No	The light intensity was calibrated by the reference solar cell (SCI-REF-Q) from + Explain why this information is not reported/not relevant. +
Calculation of spectral mismatch between the reference cell and the devices under test	☐ Yes ☐ No	We rely on certified efficiency results. + Explain why this information is not reported/not relevant. +
6. Mask/aperture		
Size of the mask/aperture used during testing	☒ Yes ☐ No	The aperture are of the solar cells was defined by an opaque metal mask with square + Explain why this information is not reported/not relevant. +
Variation of the measured short-circuit current density with the mask/aperture area	☐ Yes ☒ No	We didn't measure the solar cells with different size of apertures + Explain why this information is not reported/not relevant. +
7. Performance certification		
Identity of the independent certification laboratory that confirmed the photovoltaic performance	☒ Yes ☐ No	National Laboratory of the Rockies (NLR, previous NREL) + Explain why this information is not reported/not relevant. +
A copy of any certificate(s)	☒ Yes ☐ No	Supplementary Fig. 33 + Explain why this information is not reported/not relevant. +
8. Statistics		
Number of solar cells tested	☒ Yes ☐ No	For Fig 2a and Supplementary Fig, 6 devices for each condition (16 ombinations) we + Explain why this information is not reported/not relevant. +
Statistical analysis of the device performance	☒ Yes ☐ No	See Fig2a, Fig4b, and Supplementary Fig. 6, 14, and 17f. + Explain why this information is not reported/not relevant. +
9. Long-term stability analysis		
Type of analysis, bias conditions and environmental conditions	☒ Yes ☐ No	The maximum power point tracking (MPPT) measurement was conducted on the + Explain why this information is not reported/not relevant. +