Supplementary Note S1: Synthesis process of BT-DPA and BT-TPA.

Synthesis process of BT-DPA. All reagents and chemicals were commercially purchased and are used without further purification unless otherwise stated. Solvents were purified by standard methods and dried if necessary. A mixture of [4-(4-Methoxyanilino)phenyl]methanol (940 mg, 4.1 mmol), 3,3',5,5'-Tetrabromo-2,2'-bithiophene (400 mg, 0.83 mmol), Pd2(dba)3 (152 mg, 0.166 mmol), XPhos (118 mg, 0.249 mmol), and sodium tert-butoxide (478 mg, 4.98 mmol) in toluene (20 mL) was heated to reflux for 12 h. After cooling down, methylene dichloride was used to extract 3 times, and the combined organic phases were dried with MgSO4, and the solvent was removed over a rotary evaporator. The remaining solids were subjected to column chromatography for purification to afford the BT-DPA product as a yellow solid (724.8 mg, 81.2%). 1H NMR (600 MHz, DMSO-d6): δ 6.94–6.89 (m, 8H), 6.85–6.82 (m, 8H), 6.80–6.77 (m, 8H), 6.70–6.66 (m, 8H), 5.72 (s, 2H), 3.71 (d, J = 4.1 Hz, 24H). 13C NMR (151 MHz, DMSO-d6): δ 155.65, 154.18, 150.03, 140.00, 139.77, 138.12, 124.67, 122.00, 115.86, 114.53, 114.13, 112.50, 55.91, 55.10, 18.45. HRMS-ESI (m/z): [M+H]+ Calcd. for (C64H59N4O8S2): 1075.37688, found 1075.37440.

Synthesis process of BT-TPA. A mixture of 3,3',5,5'-Tetrabromo-2,2'-bithiophene (241 mg, 0.5 mmol), (4-(Bis(4-methoxyphenyl)amino)phenyl)boronic acid (1048 mg, 3 mmol), Pd(PPh3)4 (60 mg, 0.05 mmol), and K2CO3 (1382 mg, 10 mmol) in tetrahydrofuran (20 mL) was heated to reflux for 12 h. After cooling down, methylene dichloride was used to extract 3 times, and the combined organic phases were dried with MgSO4, and the solvent was removed over a rotary evaporator. The crude product was purified by column chromatography (silica gel, hexyl hydride: CH2Cl2 = 1:4 as the eluent) to afford a light-yellow solid in 79.4% (547.7 mg) yield. 1H NMR (400 MHz, CDCl3): δ 7.39 (d, J = 8.8 Hz, 4H), 7.14 (s, 2H), 7.07 (d, J = 9.0 Hz, 8H), 6.98 (d, J = 8.9 Hz, 12H), 6.91 (d, J = 8.8 Hz, 4H), 6.84 (d, J = 9.0 Hz, 8H), 6.76 (d, J = 9.0 Hz, 12H), 3.80 (s, 12H), 3.76 (s, 12H). 13C NMR (101 MHz, CDCl3): δ 156.04, 155.62, 148.39, 147.27, 143.89, 141.15, 140.73, 128.94, 127.51, 126.18, 123.79, 120.90, 120.63, 114.81, 114.67, 55.56. HRMS-ESI (m/z): [M+H]+ Calcd. for (C88H75N4O8S2): 1379.50208, found 1379.50151.

Figure S1. Synthetic routes for BT-DPA and BT-TPA.

Figure S2. 1H NMR spectrum of BT-DPA in DMSO-d6.

Figure S3. 13C NMR spectrum of BT-DPA in DMSO-d6.

Figure S4. HR-Mass spectrum of BT-DPA.

Figure S5. 1H NMR spectrum of BT-TPA in CDCl3.

Figure S6. 13C NMR spectrum of BT-TPA in CDCl3.

Figure S7. HR-Mass spectrum of BT-TPA.

Figure S8. DFT calculations of BT-DPA and BT-TPA. (a) Top view of optimised ground-state molecular configurations. (b) Electrostatic potential (ESP) surface for two molecules.

Figure S9. DFT calculations of BT-DPA and BT-TPA. DFT calculated (a) LUMO and (b) HOMO energy levels of BT-DPA (left) and BT-TPA (right).

Figure S10. UV-vis absorption spectra of BT-DPA and BT-TPA solutions and corresponding films.

Figure S11. Energy level analysis for HTLs and perovskite. Secondary electron cut-off and valence band regions of the UPS spectra for (a) Sn–Pb perovskite (Cs0.2FA0.8Sn0.5Pb0.5I3), (b)

PEDOT:PSS, (c) BT-DPA, and (d) BT-TPA films deposited on ITO substrate. (e) Energy level diagram of the PEDOT:PSS, BT-DPA, BT-TPA, and Sn–Pb perovskite films.

Figure S12. Conductivity and SCLC measurements of HTLs. (a) I–V curves of devices with the structure of ITO/HTLs/Au for conductivity measurement. The conductivity of PEDOT:PSS, BT-DPA, and BT-TPA films can be estimated from the slope of the corresponding I–V curves. (b) SCLC measurements of PEDOT:PSS, BT-DPA, and BT-TPA films. The curves are collected with samples of ITO/NiOx/HTLs/MoO3/Ag. The thickness of the HTLs is around 18 nm.

Figure S13. AFM and conductive AFM images of PEDOT:PSS, BT-DPA, and BT-TPA films deposited on ITO substrate. Scale bar: 1 µm. The spatial mean currents for PEDOT:PSS, BT-DPA, and BT-TPA films are 154.2, 301.7, and 426.8 pA, respectively. The combination of higher hole mobility and enhanced conductivity facilitates efficient charge extraction in the device.

Figure S14. TGA analysis of PEDOT:PSS, BT-DPA, and BT-TPA materials (10 °C min–1, N2). BT-TPA exhibits good thermal stability with a decomposition temperature of 399 °C, which is considerably higher than that of PEDOT:PSS (285 °C) and BT-DPA (335 °C).

Figure S15. UV–vis transmittance spectra of PEDOT:PSS-, BT-DPA- and BT-TPA-coated ITO/glass substrates. Compared to PEDOT:PSS, both BT-DPA and BT-TPA materials exhibit a greater level of transparency, particularly in the region after 650 nm.

Figure S16. Contact angles of perovskite precursor solution on ITO/PEDOT:PSS, ITO/BT-TPA, and ITO/TPA-PFN substrates.

Figure S17. Photographs of Sn–Pb perovskite films deposited on different HTLs. We note that due to the poor wetting of perovskite solutions on BT-DPA and BT-TPA, it is difficult to obtain a fully covered perovskite film on BT-DPA and BT-TPA films. However, coating BT-TPA with a hydrophilic interlayer (PFN-Br) improves the wettability, enabling an easy preparation of perovskite films with full coverage.

Figure S18. DFT calculated LUMO and HOMO energy levels of PFN-Br.

Figure S19. UPS spectra for TPA-PFN. (a) Secondary electron cut-off and (b) valence band regions of the UPS spectra for TPA-PFN films deposited on the ITO substrate.

Figure S20. AFM images and KPFM mapping with CPD distributions for PEDOT:PSS, BT-TPA, and TPA-PFN films deposited on ITO substrate. Scale bar: 1 µm. The KPFM results further confirm the work function reduction of TPA-PFN on the ITO substrate observed in Figure 1e.

Figure S21. Morphological analysis of perovskite films. (a) Top-view SEM images, (b) AFM images, and (c) cross-sectional SEM images of the Sn–Pb perovskite films prepared on PEDOT:PSS-, BT-TPA-, or TPA-PFN-coated ITO/glass substrates. Scale bar: 1 µm. Insets in the SEM images show the grain size distribution of the prepared films. Nanovoids observed at the buried interface of films deposited on PEDOT:PSS substrates could match the morphological features revealed in the top-view SEM images of peeled films in Figure 2a. Additionally, the surface roughness of the perovskite film on TPA-PFN (31.6 nm) is also slightly smaller than that of PEDOT:PSS (34.8 nm).

Figure S22. Perovskite film properties. (a) XRD patterns and (b) UV-vis absorption spectra of the Sn–Pb perovskite films prepared on PEDOT:PSS-, BT-TPA-, or TPA-PFN-coated ITO/glass substrates. The full width at half maximum (FWHM) values of the (100) diffraction peak for the perovskite films deposited on PEDOT:PSS, BT-TTA, and TPA-PFN films are 0.133, 0.129, and 0.125, respectively. The narrowest peak width observed in the TPA-PFN-based perovskite film suggests a superior crystallinity. The optical bandgap of the corresponding perovskite films is derived from a calculation of Tauc plots in the inserted figure, 1.267 eV. The response after ~1000 nm may arise from an optical interference, and shall not be the absorption of the perovskite material.

Figure S23. Crystallinity analysis. GIWAXS patterns of the Sn–Pb perovskite films prepared on (a) PEDOT:PSS- or (b) TPA-PFN-coated ITO/glass substrates. (c-d) The azimuthal integration of the (100) crystal plane.

Figure S24. The differential lifetime τdiff of perovskite films prepared on PEDOT:PSS-, BT-TPA-, and TPA-PFN-based substrates. PL decay at early and longer decay times is dominated by the transfer of charge carriers from perovskite to HTL and interfacial recombination, respectively. We find that TPA-PFN is beneficial for carrier extraction and suppresses non-radiative recombination at the HTL/perovskite interface, as it shows faster decay at early times as well as longer carrier lifetimes at longer delay times.

Figure S25. Residual strain analysis. GIXRD patterns are obtained from the exposed buried interface of the (a) PEDOT:PSS and (b) TPA-PFN perovskite film at different tilt angles ranging from 5° to 45°, using an incidence angle of 0.3°. (c) The residual strain is estimated by linearly fitting the 2θ-sin2ψ plot for the PEDOT:PSS- and TPA-PFN-based perovskite films, with the tensile stress calculated at 9.63 and 2.21 MPa, respectively.

Supplementary Note S2: The interaction of PFN-Br with Sn–Pb perovskite

Previous reports suggested potential interactions between PFN-Br and the lattice of perovskite films1–3. To verify this in our work, we spin-coat PFN-Br solution (0.5 mg mL–1 in methanol) onto the surface of Sn–Pb perovskite films and conduct the XPS measurements. As shown in Figure S26, the Pb 4f and Sn 3d core levels shift to a lower binding energy direction upon the PFN-Br-treatment, indicating altered chemical environments and the interaction between the PFN-Br and perovskites. Moreover, Dinesh Kabra et al. demonstrated hydrogen bonding between FA■ cations and PFN-Br, which may facilitate perovskite layer formation and crystallisation during spin-coating. This hydrogen bonding likely persists in the final perovskite film and potentially contributes to enhanced device stability1. We propose that the PFN-Br application may passivate defects at the buried interface of Sn–Pb perovskite films, thereby suppressing non-radiative recombination while simultaneously enhancing hole extraction.

As shown in Figure S27, PL mapping measurements were performed on ITO/HTLs/perovskite samples (excited from the glass side). Compared to the BT-TPA samples, the TPA-PFN samples exhibited stronger and more uniform PL intensity, indicating that non-radiative recombination losses at the bottom interface of the Sn–Pb perovskite film were suppressed. Additionally, we fabricated hole-only devices and conducted space-charge-limited current (SCLC) measurements to estimate the defect density of the perovskite films. As shown in Figure S28, the defect density decreased from 1.01 × 1016 cm–3 for the BT-TPA device to 8.4 × 1015 cm–3 for the TPA-PFN-based device. This suggests that the introduced PFN-Br has a potential defect passivation ability, which contributes to further improving the film quality.

Figure S26. XPS results. XPS spectra of the (a) Br 3d, (b) Pb 4f, and (c) Sn 3d core levels for the Sn–Pb perovskite films with and without PFN-Br (dissolved in methanol) surface treatment.

Figure S27. PL mapping of perovskite films deposited on PEDOT:PSS, BT-TPA, and TPA-PFN substrates (excitation from the glass side). Scale bar: 50 µm.

Figure S28. SCLC results. (a-c) SCLC curves of hole-only devices based on PEDOT:PSS, BT-TPA, and TPA-PFN. (d) Calculated trap density values for the corresponding samples.

Figure S29. Distribution of photovoltaic parameters for devices based on different HTLs. Distributions of (a) VOC, (b) JSC, (c) FF, and (d) PCE values derived for 24 devices with different HTLs. The data includes values derived from both reverse J–V scans.

Supplementary Note S3: The role of PFN-Br in enhancing device performance

In recent years, the use of inorganic materials such as Al2O3 nanoparticles to improve the wettability of highly hydrophobic substrates (e.g., PTAA, Me-4PACz) has shown great potential. In the initial stage of our experiments, we attempted to enhance the wettability of the BT-TPA substrate using Al2O3 and our previously reported MSN-SH nanoparticles4, systematically comparing the effects of different wetting agents on device performance. As shown in Figure S30, PFN-Br-based devices exhibited superior photovoltaic parameters compared to those using Al2O3 or MSN-SH. This improvement arises because PFN-Br not only effectively enhances the wetting and spreading of the perovskite precursor on the hydrophobic substrate through its polar functional groups but, more importantly, forms an interfacial dipole layer that optimizes the energy level alignment, thereby promoting hole extraction and suppressing non-radiative recombination. It is this synergistic effect—combining improved wettability with favorable electronic modulation—that constitutes the primary rationale for selecting PFN-Br in this study.

Figure S30. Distribution of photovoltaic parameters for devices based on different treatment strategies. Distributions of (a) VOC, (b) JSC, (c) FF, and (d) PCE values derived for 10 devices based on BT-TPA, BT-TPA/Al2O3, BT-TPA/MSN-SH, and BT-TPA/PFN-Br substrates.

Figure S31. VOC loss analysis. (a) d(EQE)/dλ versus wavelength suggests an identical PV bandgap of ~1.27 eV for both Sn–Pb PSCs fabricated on different HTLs. (b) EQE of the Sn–Pb PSCs based on different HTLs. The emitted spectral photon flux is calculated when the device is in equilibrium with the black-body (BB) radiation of the environment at 300 K. The J0,rad is calculated to 8.8 × 10–16 mA cm–2. (c) Electroluminescence quantum efficiency versus current density for PEDOT:PSS- and TPA-PFN-based devices. (d) Detailed VOC loss analysis of PEDOT:PSS- and TPA-PFN-based devices.

Figure S32. Charge recombination properties of Sn–Pb PSCs with different HTLs. (a) TPC and (b) TPV decay curves of PEDOT:PSS- and TPA-PFN-based Sn–Pb PSCs. (c) Semilogarithmic plots of VOC as a function of illumination intensity for the devices based on PEDOT:PSS and TPA-PFN (K is Boltzmann's constant, T is 298 K, and q is the unit of electronic charge). (d) Mott-Schottky plots of the PEDOT:PSS- and TPA-PFN-based Sn–Pb PSCs. Vbi is determined from the X-axis intercept of the linear fit in the plot tail.

Figure S33. Performance of Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite films and devices on different substrates. (a) Top-view SEM images of the buried interface of Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite films deposited on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates. (b) Cross-section SEM images of all-perovskite tandem device with Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite subcells deposited on PEDOT:PSS or TPA-PFN substrate. (c) Steady-state PL spectra of the peeled perovskite films deposited on PEDOT:PSS, BT-TPA, and TPA-PFN substrates. (d) PLQY values of the perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates. (e) Distributions of the photovoltaic parameters for PEDOT:PSS and TPA-PFN devices based on 12 cells. (f) J–V curves of the champion TPA-PFN device under reverse and forward scans. (g) The EQE spectrum of the corresponding device. The d(EQE)/dλ versus wavelength suggests a PV bandgap of 1.25 eV.

Figure S34. Performance of Cs0.05FA0.95PbI3 perovskite films and devices on different substrates. (a) XRD patterns of the Cs0.05FA0.95PbI3 perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates. (b) Steady-state PL spectra of the peeled perovskite films deposited on

PEDOT:PSS and TPA-PFN substrates. (c) PLQY values of the Cs0.05FA0.95PbI3 perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates. (d) J–V curves of the champion TPA-PFN device under reverse and forward scans. (e) Steady-state power output of the corresponding device. (f) The EQE spectrum of the corresponding device. The d(EQE)/dλ versus wavelength suggests a PV bandgap of 1.53 eV.

Supplementary Note S4: Role of TPA-PFN in suppressing nanovoid formation at the buried interface of Sn–Pb perovskite films

In our previous study4, we observe that in Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite films, only those with the specific combination of the PEDOT:PSS substrate induced the formation of voids at the buried interface, regardless of thickness. A similar morphological characteristic is also observed for the Sn–Pb perovskite sub-absorber deposited on WBG subcell/PEDOT:PSS substrate during tandem cell fabrication. Notably, even when deposited on hydrophobic Me-4PACz substrate, no voids were observed at the buried interface of perovskite films. Based on these observations, we propose that the formation of nanovoids at the buried interface of Sn–Pb perovskite is not strongly correlated with substrate wettability. This also explains why the bottom surface of the film deposited on BT-TPA remains dense and void-free in Figure S35, despite BT-TPA substrate being more hydrophobic than PEDOT:PSS.

As shown in Figure S33, Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite films deposited on TPA-PFN substrates exhibit dense, void-free domains at the buried interface while maintaining favourable crystal morphology throughout tandem device fabrication. The void-suppressing effect of TPA-PFN is further validated in Cs0.2FA0.8Sn0.5Pb0.5I3 films (Figure 2A and S21), highlighting its critical role in fabricating high-quality Sn–Pb perovskite absorbers.

Figure S35. Top-view SEM images of peeled perovskite films prepared on PEDOT:PSS-, BT-TPA- or TPA-PFN-coated ITO/glass substrates. Sale bar: 1μm.

Figure S36. PL lifetime distribution is obtained from FLIM images of perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates before and after ageing at 85 °C and 1 sun illumination for 15 days.

Figure S37. QFLS values calculated with the PLQY values of perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated glass substrates before and after ageing at 85 °C and 1 sun illumination for 15 days.

Figure S38. UV-vis absorption spectra of I2 and SnI4 dissolved in toluene.

Figure S39. XPS analysis. XPS spectra of the I 3d5/2 core levels for the peeled surface of perovskite films prepared on (a) PEDOT:PSS- or (b) TPA-PFN-coated glass substrates before and after light-thermal ageing.

Figure S40. Calculation of ionic migration barriers. Temperature-dependent dark conductivity results of perovskite films prepared on (a, c) PEDOT:PSS or (b, d) TPA-PFN-coated glass substrates before and after light-thermal ageing. The activation energy for ion migration can be calculated from the Nernst-Einstein relation of σT = σ0exp (–Ea/kBT) (σ0 is a constant and kB is Boltzmann's constant, σ and T are conductivity and temperature, respectively, and Ea is the activation energy for ion migration). Ea can be derived from the slope of the ln(σT) versus the 1/T plot.

Figure S41. Fracture energy of the BT-TPA/perovskite interface before and after 15 days of aging at 85 °C under 1-sun illumination. Comparison with the results from PEDOT:PSS and TPA-PFN samples confirms the role of PFN-Br in enhancing interfacial adhesion. This improved mechanical stability contributes to maintaining the morphological integrity of the films under thermal or operational stress, preventing the formation of defect sites that accelerate device degradation.

Figure S42. Stability of films and devices. PL mapping (50 μm × 50 μm) of peeled (a) Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 and (b) Cs0.05FA0.95PbI3 perovskite films prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass substrates before and after light-thermal ageing at 85°C and 1 sun illumination for 5 days. Shelf-stability of unencapsulated cells with PEDOT:PSS and TPA-PFN for (c) Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 PSCs and (d) Cs0.05FA0.95PbI3 PSCs at 85 °C in N2. The error bars represent the standard deviation. The data includes values derived from both reverse J–V scans of 3 devices for each condition.

Figure S43. Photovoltaic performance of WBG PSCs. (a) Distributions of VOC, JSC, FF, and PCE values derived for 1.77 eV WBG single-junction PSCs. The data includes values derived from reverse J–V scans. (b) J–V curves and (c) EQE spectra of champion devices of 1.77 eV WBG PSCs.

Figure S44. Photovoltaic performance of tandem devices. (a-d) Statistical distribution of the PV parameters for PEDOT:PSS and TPA-PFN tandem devices based on 16 devices. The data includes values derived from reverse J–V scans. J–V curves of champion (e) PEDOT:PSS and (f) TPA-PFN tandem device under reverse and forward scans.

Figure S45. Experimental setup for operational stability testing. (a) Photograph of the experimental setup used for operational stability testing of tandem devices at 85 °C. The devices are encapsulated using butyl rubber edge glass lamination technology. During the testing process, the encapsulated devices were placed directly on the surface of a precision temperature-controlled platform, with a constant-temperature environment maintained through a high-precision temperature control system. Real-time monitoring data from the temperature controller indicated that both the set temperature of the heating plate and the actual surface operating temperature remained stable at 85 °C. (b) Hikmicro thermal camera was used to verify that the device temperature during 85 °C operation.

Figure S46. Stability of tandem devices. (a) Performance evolution of unencapsulated tandem devices aged at 65 and 85 °C under dark conditions in the N2 glovebox. The error bars represent the standard deviation. The data includes values derived from both reverse J–V scans of 3 devices for each condition. (b) Continuous MPPT for the encapsulated tandem devices under simulated AM1.5G illumination at 65 °C and 85 °C. (c) J–V curves of TPA-PFN tandem device before and after 586 h thermal ageing under 85 °C. (d) J–V curves of TPA-PFN tandem device before and after 271 h MPPT operation at 85 °C.

Figure S47. ToF-SIMS results. ToF-SIMS results of the ITO/ALD-SnOx/1 nm-Au/TPA-PFN/perovskite samples (a) before and (b) after 15 days of aging at 85 °C under 1-sun illumination.

Figure S48. Properties of recombination junction. (a) UV-vis transmittance spectra of Au and ITO recombination junction. (b) The sheet resistance of IZO and ITO samples at 5 and 10 nm.

Figure S49. AFM images and KPFM mapping with CPD distributions for TCOs with 5 and 10 nm deposited on WBG subcell/ALD-SnOx substrates. Scale bar: 2 μm. When the thickness of the TCO layer was reduced from 10 nm to 5 nm, the samples still exhibited uniform electrical characteristics. No potential fluctuations caused by pinholes or discontinuous coverage were observed. This indicates that under these optimized processing conditions, the 5-nm-thick TCO layer achieved good surface coverage on the WBG subcell/ALD-SnOx surface.

Supplementary Note S5: The degradation analysis of interconnecting layers

First, we prepare ITO/SnOx/1 nm-Au/TPA-PFN/Au and ITO/SnOx/5nm-IZO/TPA-PFN/Au samples for J–V measurements to compare the electrical properties of different interconnecting layers (Figure S50). To evaluate the stability of interconnecting layers under elevated temperatures, we also prepare ITO/SnOx/1 nm-Au/TPA-PFN/perovskite and ITO/SnOx/5 nm-IZO/TPA-PFN/perovskite samples and age them at 85 °C and 1 sun illumination for 10 days. Subsequently, the perovskite layers of both samples are washed off using DMF, followed by the evaporation of Au electrodes for J–V measurements. Notably, no residual perovskite crystals are observed on the surface of the ITO/SnOx/1 nm-Au/TPA-PFN sample after DMF washing, thereby avoiding any impact on the J–V results of the aged samples.

As shown in Figure 3G, the conductivity of the ITO/SnOx/1 nm-Au/TPA-PFN/Au sample decreases significantly after ageing. This is attributed to the migration of Au nanoparticles into the perovskite layer, which causes irreversible degradation of the electrical transport properties of the interconnecting layers. In contrast, the ITO/SnOx/5 nm-IZO/TPA-PFN/Au sample remains nearly unchanged. This demonstrates that the designed interconnecting layers exhibit superior thermal stability, which will mitigate the performance degradation of tandem devices under elevated temperature conditions.

Figure S50. Interface stability and aging behavior of SnOx/Au or IZO/TPA-PFN stacks. (a) I–V measurements of fresh ITO/SnOx/1 nm-Au or 5 nm-IZO/TPA-PFN/Au samples. (b) Schematic diagram of the preparation process and I–V measurements of aged ITO/SnOx/1 nm-Au or 5 nm-IZO/TPA-PFN/Au samples. (c) Photographs of ITO/SnOx/1 nm-Au/TPA-PFN/perovskite samples before and after DMF washing. (d) Surface SEM image of aged ITO/SnOx/Au/TPA-PFN samples.

Figure S51. Statistical analysis of photovoltaic parameters for tandem devices based on different recombination junctions. Statistical distribution of (a) VOC, (b) JSC, (c) FF, and (d) PCE values derived for tandem devices with different interconnecting layers based on 16 devices. The data includes values derived from reverse J–V scans.

Figure S52. Photovoltaic performance of tandem devices. (a) Steady-state power output of the champion tandem device measured by fixing the voltage at 1.93 V under AM1.5G illumination. (b) The EQE spectra of double-junction devices with different interconnecting layers.

Figure S53. Certified performance of tandem device with an aperture area of 0.0498 cm2 provided by the Shanghai Institute of Microsystem and Information Technology (SIMIT). The certified PCE is 29.84% from the scanned J–V curve, and a certified steady-state efficiency of 29.00% at a maximum power point of 1.849 V.

Figure S54. Distributions of VOC, JSC, FF, and PCE values derived for 32 all-perovskite double-junction devices based on MA-containing Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite subcells. The data includes values derived from reverse J–V scans.

Figure S55. Certified performance of tandem device based on Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 perovskite subcells with an aperture area of 0.0484 cm2 provided by the National Photovoltaic Product Quality Supervision & Inspection Center. The certified PCE is 30.19% from the scanned J–V curve.

Figure S56. Photovoltaic performance of large-area tandem devices. Statistical distribution of the PCE for (a) 1.04 cm2 tandem devices and (b) tandem minimodules with an aperture area of 11.3 cm2. Steady-state power output of the champion (c) 1.04 cm2 tandem device and (d) tandem mini-module was measured under AM1.5G illumination with voltages fixed at 1.89 V and 8.67 V, respectively.

Figure S57. Photovoltaic performance of 1.61 and 1.97 eV PSCs. Distributions of (a) VOC, (b) JSC, (c) FF, and (d) PCE values derived for 20 1.61 and 1.97 eV single-junction PSCs. The data includes values derived from reverse J–V scans. (e) J–V curves and (f) EQE spectra of champion single-junction devices based on 1.61 eV and 1.97 eV perovskites. d(EQE)/dλ versus wavelength curves are shown in dashed lines.

Figure S58. Photovoltaic performance of triple-junction device. (a) Distributions of VOC, JSC, FF, and PCE values derived for 24 all-perovskite triple-junction devices based on Cs0.2FA0.8Sn0.5Pb0.5I3 NBG subcells. The data includes values derived from reverse J–V scans. (b) Steady-state power output of the champion triple-junction device measured by fixing the voltage at 2.82 V under AM1.5G illumination. (c) EQE spectra of the triple-junction devices.

Figure S59. Distributions of VOC, JSC, FF, and PCE values derived for 12 triple-junction devices based on Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 NBG subcells. The data includes values derived from reverse J–V scans.

Figure S60. Performance evolution of unencapsulated double-junction devices aged at 65 and 85 °C under dark conditions in a N2 glovebox. The data includes values derived from both reverse J–V scans of 3 devices for each condition.

Table S1. Summary of the high-efficiency (≥29%) monolithic all-perovskite double-junction devices.

Table S2. The hole reorganisation energy (λh) of BT-DPA and BT-TPA, obtained from the DFT method.

Table S3. Photophysical, electrochemical and charge transport properties of PEDOT:PSS, BT-DPA, and BT-TPA.

Table S4. Summary of PV parameters for PEDOT:PSS, BT-TPA, and TPA-PFN-based Sn–Pb PSCs. Average performance parameters of 24 devices for each type are presented.

Table S5. Summary of elevated temperature (65 °C) stability for Sn–Pb PSCs.

Table S6. Summary of PV parameters for PEDOT:PSS- and TPA-PFN-based double-junction devices with the Au (~1 nm) recombination layer. Average performance parameters of 16 devices for each type are presented.

Table S7. Summary of PV parameters for double-junction devices with different interconnecting layers. Average performance parameters of 16 devices for each type are presented.

Table S8. Summary of PV parameters of champion 1.61, 1.97 eV PSCs, and triple-junction devices.

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