Stabilising interconnecting layers for all-perovskite tandem photovoltaics

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Summary

Robust interconnecting layers are critical for all-perovskite tandems but are typically limited by acidic poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) and interdiffusive gold, compromising stability. Here, we substitute PEDOT:PSS with a conjugated polyelectrolyte-modified bithiophene-triphenylamine small molecule as the hole transport layer for tin–lead perovskite subcells, ensuring superior hole extraction and interfacial robustness. The gold recombination junction is replaced with 5-nm-thick sputter-coated indium-doped zinc oxide to eliminate metal diffusion and minimize parasitic absorption. This design yields certified efficiencies of 29.80% and 30.19% for double-junction tandems employing methylammonium (MA)-free and MA-containing narrow-bandgap subcells, respectively. Furthermore, 1.0-cm2 devices and 11.3-cm2 mini-modules show efficiencies up to 28.7% and 25.0%. Encouragingly, encapsulated tandems maintain 90% of their initial efficiency after over 770, 530, and 220 hours of maximum power point tracking under illumination at 45, 65, and 85 °C, respectively. This work presents a viable route beyond PEDOT:PSS for narrow-bandgap perovskites toward reliable all-perovskite tandem photovoltaics.

Keywords: photovoltaics, perovskite, tandem, interconnecting layers, stability, hole transport materials

Introduction

All-perovskite monolithic tandem solar cells—whose architectures enable photo-generated charge carriers to flow seamlessly through the interconnecting layers—offer a unique combination of high efficiency potential, broad adaptability, and low embodied energy and carbon footprint1–5. Thanks to the great efforts from academia and industry in the field6–12, all-perovskite tandems have achieved PCEs exceeding 30% in their double-junction devices, greatly outperforming their single-junction counterparts. Their stability advancement, especially when cells age under elevated temperatures and light, however, lags far behind the rapid efficiency progress6,7. Given the seamlessly stacked architecture of these devices, the relatively less explored interconnecting layers play a critical role in determining overall stability, complementing the widely studied perovskite active materials5,13,14.

The ideal interconnecting layers should combine high optical transparency and appropriate electrical conductivity—ensuring maximum light utilisation and efficient charge carrier recombination between subcells15—with sufficient robustness to secure interlayer stability for well-performing devices. In state-of-the-art all-perovskite tandems, the interconnecting layers linking the rear absorber typically consist of electron transport layer (ETL, C60)/atomic layer deposited (ALD) SnO_x/ultrathin Au (nominally ~1 nm)/hole transport layer (HTL, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS))5 (Table S1). In this interconnecting layer, however, PEDOT:PSS suffers from evident parasitic absorption, while its acidic and hygroscopic nature triggers harmful chemical reactions under operational conditions, leading to severe perovskite material loss and eventual device failure—for instance, through iodine generation and Sn(II) oxidation at the buried interface of Sn–Pb perovskite subcells16,17. Moreover, the presence of nanovoids and poor interfacial contacts at the buried interface accelerates the degradation18–22. On the other hand, Au nanoparticles in interconnecting layers introduce pronounced parasitic absorption through localised surface plasmon resonance excitation, although centred in the visible region of the spectrum, this does reduce the near-infrared light available to the bottom subcell for generating photocurrent in the tandem cells23,24. Further, it has been reported that Au may migrate from the interconnecting layers into the perovskite absorber at temperatures of about 65 °C, introducing an additional source of device instability5,10,25. Thus, advancing the interconnecting layer designs is crucial for achieving high operational stability in efficient all-perovskite tandems.

Here, we design an amphiphilic conjugated polyelectrolyte-modified bithiophene-triphenylamine small-molecule to substitute commonly employed PEDOT:PSS as HTL in NBG mixed Sn–Pb perovskite cells (Figure 1A). We demonstrate that the new HTL enables the growth of high-quality perovskite films and also minimises interfacial energy level mismatch and optical losses for optimal carrier dynamics and maximum quasi-Fermi level splitting. As a result, the methylammonium (MA)-free and MA-containing Sn–Pb perovskite single-junction cells show PCEs of up to 24.0% and 24.2%, respectively, with substantially enhanced stability. Prior to a tandem cell fabrication, we further develop a 5-nm-thick IZO layer with high transparency and adequate vertical conductivity to function as a recombination junction, thereby eliminating the need for diffusive and absorptive metals. The assembled interconnecting layers enable a successful fabrication of high-efficiency, up to 30.5%, double-junction tandems with an elongated operational stability even under the combined stressors of elevated temperature and simulated sunlight. Encouraged by this, we further evaluate the universality of these interconnecting layers using a triple-junction architecture, with the device showing PCE values of up to 27.1%.

Results

TPA-PFN HTL for NBG Sn–Pb PSCs

To circumvent the limitations of PEDOT:PSS, we design two dopant-free hole transport materials based on a tetrasubstituted bithiophene core functionalized with diphenylamine/triphenylamine units, denoted as BT-DPA and BT-TPA, respectively. The bithiphene core provides conformational tunability, introducing moderate steric hindrance while retaining sufficient planarity to balance solubility, energy level alignment, and optical absorption. Its sulfur-rich structure is expected to enhance interfacial interactions with Sn–Pb perovskites, enabling defect passivation. The triphenylamine and diphenylamine units ensure high hole mobility. This molecular design, synthesised in a simple one-step coupling reaction from off-the-shelf commercially raw materials (Figure 1B, S1-S7 and Note S1), aims to synergistically optimise energy level matching, charge transport, and interfacial stability.

Density functional theory (DFT) calculations and experimental measurements confirm that both BT-DPA and BT-TPA exhibit favourable energy-level alignment with Cs0.2FA0.8Pb0.5Sn0.5I3 perovskite (Figure S8-S11). Notably, BT-TPA possesses a larger work function value and a deeper highest occupied molecular orbital (HOMO) level compared to PEDOT:PSS, which effectively reduces the energy level offset at the p-side interface. Evaluation of intrinsic charge transport properties through hole reorganisation energy (λhs) calculation reveals a smaller value for BT-TPA (0.256 eV) relative to BT-DPA (0.280 eV) (Table S2). Based on space-charge-limited-current (SCLC) measurements, we also estimate the hole mobility of 5.91 × 10–4 cm2 V–1 s–1 for BT-TPA films, exceeding those of BT-DPA (4.48 × 10–4 cm2 V–1 s–1) and PEDOT:PSS (4.07 × 10–4 cm2 V–1 s–1) films (Figure S12). Based on comprehensive analyses—including electrical measurements, thermogravimetric analysis, UV–vis transmittance spectra (Figure S12-S15, Table S3), and energy level evaluations above—we reckon BT-TPA as a highly promising HTL for NBG Sn–Pb PSCs owing to its high mobility, enhanced thermal stability, reduced parasitic absorption, and suitable energy levels, prevailing conventional PEDOT:PSS.

Besides the superior intrinsic properties, a good hole transport material should also provide good compatibility with the consequent perovskite processing, where a suitable wetability is primarily key. We thus conduct the contact angle measurements (Figure S16-S17). We observe that the BT-TPA films show a contact angle of 57.0°, which is much larger than that of PEDOT:PSS films at 22.5°. The inferior wetability leads to incomplete coverage of Sn–Pb perovskite films coated on BT-TPA-based films. To this end, we introduce amphiphilic conjugated polyelectrolyte, poly(9,9-bis(3′-(N,N-dimethyl)-N-ethylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))di-bromide (PFN-Br)26,27, atop the BT-TPA layer, denoted as TPA-PFN (Figure 1C and 1D). For TPA-PFN films, we first observe that the wetability and coverage of the perovskites deposited atop are comparable with PEDOT:PSS, while substantially better than BT-TPA films. Considering the double-layer nature, we further perform the ultraviolet photoelectron spectroscopy (UPS) and Kelvin probe force microscopy (KPFM) measurements of the TPA-PFN HTL. We observe a slightly increased work function for the TPA-PFN films, compared to the neat BT-TPA films, presumably attributed to the surface dipole formation28,29. The calculated HOMO level of the TPA-PFN films is –5.30 eV, which lies close to the valence band maximum (VBM) of the Sn–Pb perovskite films, –5.34 eV (Figure 1E and S18-S20). These results suggest that the TPA-PFN films should serve as a suitable substrate for fabricating high-quality Sn–Pb perovskite films and their p-i-n solar cells.

We further evaluate the morphological and structural properties of Sn–Pb perovskites deposited on different HTLs using scanning electron microscopy (SEM) and X-ray diffraction (XRD) measurements (Figure S21-S22). Compared to PEDOT:PSS, perovskite films grown on the TPA-PFN layer exhibit uniform morphology and larger apparent grain sizes, as well as enhanced crystallinity. Furthermore, azimuthal integration of the (100) diffraction halos from the grazing incidence wide-angle X-ray scattering (GIWAXS) patterns reveals high intensity values at angles close to 90° for the perovskite films deposited on TPA-PFN films, suggesting a promoted out-of-plane perovskite film growth (Figure S23).

To evaluate the photoexcited charge-carrier dynamics, we perform steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) measurements on Sn–Pb perovskite films deposited on different HTL substrates (Figure 1F, 1G and S24). We observe a successive increase in the PL intensity for the perovskite films deposited on the PEDOT:PSS-, BT-TPA-, and TPA-PFN-based substrates. Looking at the PL dynamics of the TRPL results, we identify a fast initial decay and an extended tail for all the samples. We thus interpret the TRPL decay curves with the differential lifetime (τdiff) to decouple the potential interface charge carrier extraction and recombination at low laser fluences, following the method developed30,31. We observe asymptotically reached high lifetimes of over 450 and 350 ns for perovskite films on TPA-PFN and BT-TPA, respectively—substantially longer than the about 250 ns on PEDOT:PSS—indicating suppressed nonradiative recombination losses. The early-time sharp rise at a rising time of about 50 ns for TPA-PFN samples is two times shorter than ~100 ns of the BT-TPA- and PEDOT:PSS-based counterparts, suggesting a facilitated charge transfer. These are presumably a global contribution from both the TPA-PFN HTL and the as-grown perovskite films—including a surface dipole-enabled energy level matching, enhanced perovskite crystal quality, and released residual tensile stress, as well as suppressed defect density at the buried interface (Figure S25-S28 and Note S2).

Thanks to the enhanced buried interface, we fabricate single-junction Sn–Pb PSCs with an architecture of ITO/HTLs/Cs0.2FA0.8Pb0.5Sn0.5I3/passivation layer/C60/bathocuproine (BCP)/Ag to evaluate the device performance. Although MA-containing Sn–Pb perovskites are widely used in state-of-the-art PSCs (Table S1), MA-free perovskites are increasingly regarded as an essential factor for better device stability14,32–34, thus the MA-free composition, Cs0.2FA0.8Pb0.5Sn0.5I3, is used. The passivation layer is a mixture of ethylenediammonium diiodide (EDAI2)18 and 1,4-butanediamine (BDA)12,35, details given in the experimental section. Devices based on TPA-PFN show higher PCEs than those with PEDOT:PSS, yielding from improved metrics, i.e., open-circuit voltage (VOC), current density (JSC), and fill factor (FF) (Figure 1H, S29, and Table S4). Notably, PFN-Br exhibits more favorable interfacial compatibility with BT-TPA compared to inorganic nanoparticle wetting agents such as Al2O3 (Figure S30 and Note S3). The champion TPA-PFN device exhibits a PCE of 24.0%, with a VOC of 0.90 V, a JSC of 32.82 mA cm–2, and an FF of 81.46% under reverse scan (Figure 1I), representing one of the highest reported values for such devices (Figure 1J). The increase in integrated JSC from 31.58 mA cm–2 (PEDOT:PSS) to 32.26 mA cm–2 (TPA-PFN) (Figure 1K) is mostly attributed to improved external quantum efficiency (EQE) at wavelengths after 650 nm, corobarating the high transmittance of TPA-PFN, Figure 1D.

The improved VOC is primarily attributed to suppressed non-radiative recombination, as evidenced by a fivefold increase in electroluminescence EQE (EQEEL) compared to PEDOT:PSS, at injection current near device JSC. This is further supported by the detailed VOC loss analysis36 (Figure S31). Furthermore, TPA-PFN devices also show longer photovoltage decay lifetimes and shorter photocurrent decay lifetimes, indicating suppressed non-radiative recombination and improved charge extraction. These are also reflected on the reduced device ideality factor and enhanced built-in potential (Vbi) (Figure S32).

In addition, the TPA-PFN HTL shows good compatibility with other perovskite compositions, including MA-containing Sn–Pb perovskite (Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3, 1.25 eV) and neat Pb perovskite (Cs0.05FA0.95PbI3, 1.53 eV), both of which are key absorbers for high-efficiency single- and multi-junction devices11,37. In particular, the champion Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 device shows a PCE of up to 24.2% with a VOC of 0.89 V, a JSC of 32.98 mA cm–2, and an FF of 82.31% (Figure S33). Additionally, the TPA-PFN-based Cs0.05FA0.95PbI3 devices give high PCEs of up to 26.3% with a VOC of 1.18 V (Figure S34). These results verify the excellent compatibility and quality of TPA-PFN films as HTLs for p-i-n PSCs.

Buried interface stability of NBG PSCs

In addition to PV performance, we anticipate that our TPA-PFN-based HTL could enhance the buried interface stability of NBG Sn–Pb PSCs by eliminating interfacial degradation induced by PEDOT:PSS17,21. To this end, we prepare peeled perovskite films for SEM and laser confocal fluorescence lifetime imaging microscopy (FLIM) characterisations to examine the morphology and uniformity of the bottom surface in both fresh and aged samples deposited on different HTL substrates. Consistent with previous reports19,20, the fresh perovskite films deposited on the PEDOT:PSS exhibit numerous nanovoids around grain boundaries at the exposed bottom surface (Figure 2A), which results in markedly inhomogeneous PL lifetime distribution across the probed region (Figure 2B). By contrast, perovskite films grown on TPA-PFN show a dense, void-free bottom surface (Figure S35 and Note S4), with a more uniform PL lifetime distribution and enhanced PL lifetimes. After light-thermal ageing at 85 °C under 1-sun illumination for 15 days, the PEDOT:PSS-based perovskite films show severe degradation, manifested by enlarged voids and microcrack formation around grain boundaries. Correspondingly, the PL lifetime mapping becomes increasingly indistinct, with signal intensities in dominant regions dropping to the noise floor. In contrast, although a slight reduction in PL lifetime is also observed for TPA-PFN-based films under the same ageing conditions (Figure S36), their surface morphology remained relatively stable, suggesting a more robust buried interface. We further quantify the quasi-Fermi level splitting (QFLS) via PL quantum yield (PLQY) measurements for the fresh and aged samples (Figure 2C). Owing to improved interface, the average PLQY of fresh TPA-PFN samples reaches 5.43%, over 4 times of that of PEDOT:PSS samples (1.28%), with the calculated QFLS of 0.91 and 0.87 eV, respectively (Figure S37). After ageing, this difference becomes even more pronounced, where the PLQY of TPA-PFN is 1.69%, whereas that of PEDOT:PSS decreases largely to 0.06%, giving QFLS values of 0.88 and 0.79 eV, respectively. These results confirm the superior structural and optoelectronic stability of the TPA-PFN/Sn–Pb perovskite interface against light and thermal stressing.

To gain further insight into the enhanced interface stability regarding the material loss, we subject perovskite films to toluene solvent for an ageing test and conduct the UV-vis absorption measurements after. This method allows tracing the soluble degradation products, which are mainly I2 and SnI416,17 (Figure 2D and S38). We observe that the toluene solution containing the PEDOT:PSS-based samples turns pink after 5 days of ageing, along with pronounced absorption features of SnI4 and I2, suggesting a material loss. In contrast, the solution with the TPA-PFN sample remains colourless, with substantially fewer identifiable features for I2 and SnI4. We further conduct X-ray photoelectron spectroscopy (XPS) measurements on peeled film surfaces to analyse the chemical variations before and after ageing (Figure 2E, 2F and S39). The results suggest a substantial increase in the Sn4+/Sn2+ and I0/I ratios for the PEDOT:PSS-based samples after 15 days of ageing (by about 60% for Sn4+ and 18% for I0). In contrast, the TPA-PFN-based films exhibit minimal Sn4+ and I0 signals in the fresh state and only a slight increase after ageing (by 8.3% for Sn4+ and 2.9% for I0). These results suggest superior stability of the TPA-PFN/perovskite samples, with largely reduced material loss compared to PEDOT:PSS counterparts.

The degradation at the HTL/Sn–Pb perovskite interface is typically accompanied by increased density of I– (VI) and Sn2+ (VSn) vacancies, which lowers the energy barrier for ion migration38,39. To understand this, we derive the ion migration activation energy (Ea) via temperature-dependent conductivity measurements (Figure S40). The fresh PEDOT:PSS and TPA-PFN samples show nearly identical Ea values of 0.56 eV and 0.58 eV, respectively. After 15 days of light-thermal ageing, however, the Ea of the PEDOT:PSS samples decreases dramatically to 0.34 eV, while that of TPA-PFN samples changes only slightly to 0.50 eV. Moreover, the presence of nanovoids and structurally defective amorphous regions at the buried interface typically compromises interfacial adhesion between the perovskite and the underlying substrate40,41. We evaluate the mechanical durability of the HTL/perovskite interface using tensile strength measurements on aged samples with a configuration of glass/ITO/HTLs/perovskite/epoxy/glass42. The fresh TPA-PFN sample exhibited a slightly higher fracture energy (256.6 kJ m–3) than the PEDOT:PSS sample (243.2 kJ m–3). After 15 days of light-thermal aging at 85 °C under 1-sun illumination, however, the difference became more pronounced with TPA-PFN retaining 208.1 kJ m–3 compared to 97.8 kJ m–3 for PEDOT:PSS. (Figure 2G and S41). These results suggest that the TPA-PFN/perovskite interface maintains a better structural integrity and interfacial contact under different stressors.

From a device aspect, we subject unencapsulated devices to thermal ageing at 85 °C in a N2 atmosphere under dark conditions, following the ISOS-D2 protocol43 (Figure 2H). The TPA-PFN devices retain 83% of the initial PCE after 900 hours, while PEDOT:PSS-based devices degrade to 54% of the initial PCE after 500 hours. Additionally, the encapsulated TPA-PFN devices maintain 90% of the initial PCE after 1000 hours operating under 1-sun illumination at 45 °C in air, better than the PEDOT:PSS devices at only 69% (Figure 2I). These results verify that TPA-PFN is a suitable HTL material for achieving stable and efficient MA-free and MA-containing NBG cells as well as neat Pb PSCs (Figure S42 and Table S5).

Substitution of ultrathin Au with TCO as the recombination junction

Encouraged by the successful application of the TPA-PFN in single-junction NBG PSCs, we integrate the NBG subcells with wide-bandgap (WBG) perovskite (Cs0.2FA0.8PbI1.8Br1.2) subcells (Figure S43) to fabricate the monolithic all-perovskite double-junction devices. With an ultrathin Au (nominally ~1 nm) recombination junction in the interconnecting layer, TPA-PFN-based tandem devices show an average PCE of 28.9%, outperforming the PEDOT:PSS counterparts (27.3%) of the device batch (Table S6). The champion TPA-PFN device gives a reverse-scan PCE up to 29.6% with a VOC of 2.19 V, a JSC of 16.18 mA cm–2, and an FF of 83.34%, with negligible hysteresis (Figure S44).

We further perform accelerated thermal ageing tests to evaluate the reliability of the tandem devices (Figure S45 and S46). Cells aged in the dark at 85 °C show improved thermal stability in TPA-PFN-based tandems compared with PEDOT:PSS-based devices, though still markedly lower than that of single-junction Sn–Pb PSCs. Operational stability tests under ISOS-L-2I protocols43 show that after 320 hours at 65 °C and 270 hours at 85 °C, the TPA-PFN tandems retain 82.8% and 69.8% of their initial PCEs, respectively. The performance loss is primarily attributed to the decrease in VOC and FF. Previous reports suggested that Au migration from the interconnecting layers into the perovskite absorber could accelerate the degradation at elevated temperatures10,25. To examine this, we perform XPS and time-of-flight secondary-ion mass spectrometry (ToF-SIMS) tests on fresh and aged ITO/ALD-SnOx/1 nm-Au/HTLs/Sn–Pb perovskite samples. As shown in Figure 3A-C, we observe signals assigned to the Au 4f core levels on the peeled surfaces of aged perovskite films deposited on PEDOT:PSS and TPA-PFN films, while no S signals are determined. In addition, we conduct the ToF-SIMS tests for ITO/ALD-SnOx/1 nm-Au/TPA-PFN/ Sn–Pb perovskite samples (Figure 3D and S47). The sputtering time-dependent fragment collection suggests an early and more diffused emergence of Au at the buried interface region of samples upon ageing. These observations indicate that Au atoms could still migrate through both the PEDOT:PSS and TPA-PFN layers and reach the perovskite bottom region despite the ultrathin Au being fully covered by the HTLs.

The above results encourage us to seek alternative recombination junction material to replace Au for tandem devices. Transparent conductive oxides (TCOs), such as ITO and IZO, possess suitable electrical conductivity and excellent optical transmittance across the visible and near-infrared region, making them ideal candidates as recombination junction material to construct interconnecting layers for multi-junction cells (Figure 3E)15,44,45. We deposit 5 nm- or 10 nm-thin ITO and IZO layers via sputtering and evaluate their optical and electrical properties. The 5-nm-thick TCOs effectively minimise parasitic absorption in the interconnecting layers, where the IZO show high surface potential uniformity, satisfactory surface coverage, and desirable sheet resistance (Figure 3F, S48 and S49), which are beneficial for mitigating the detrimental impact of local shunts on overall device performance46. Critically, the suppression of undesirable metal diffusion helps preserve the electrical integrity of the interconnecting layers (Figure 3G, S50, and Note S5), which should contribute to slowing down the device degradation.

Performance of all-perovskite tandems

We further apply the optimised interconnecting layers to construct all-perovskite tandem devices (Figure 4A) and notice that incorporating a 5-nm-thick IZO layer together with TPA-PFN HTL enables the cells with high performance, average PCE of 29.3% (Figure S51 and Table S7). The champion tandem cell gives a PCE of up to 30.2% under reverse J–V scan, with a VOC of 2.21 V, a JSC of 16.43 mA cm–2 and an FF of 83.36%, as well as a steady-state PCE of 29.8% (Figure 4B and S52). We estimate the subcell current density by integrating the EQE spectra of the subcells using stardarded AM1.5G spectrum, giving a value of 16.2 mA cm–2 for the WBG cells on both types of stacks, while 15.4 and 16.1 mA cm–2 for NBG subcells on Au/PEDOT:PSS and IZO/TPA-PFN stacks, respectively, for the latter with a better current matching (Figure S52). As expected, this enhancement in photocurrent response of the NBG subcell is mainly in the 700–900 nm range, thanks to the transmittance gain of the IZO/TPA-PFN-based interconnecting layers. We also send our double-junction devices based on Cs0.2FA0.8Pb0.5Sn0.5I3 NBG subcells to an accredited independent laboratory for callibration, granting a certified PCE of 29.80% (VOC of 2.182 V and FF of 82.87%), and maximum power point efficiency of 29.00% upon 5 min monitoring (Figure S53). We also fabricate double-junction devices based on Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 NBG subcells (Figure S54), obtaining a champion PCE of 30.5% (certified at 30.19%, Figure S55) under reverse scan (Figure 4C). To the best of our knowledge, these values rank among the highest efficiencies reported for all-perovskite double-junction devices (Table S1).

To evaluate the scalability of the designed interconnecting layers and the double-junction cells, we fabricate 1-cm2 tandem cells and mini-modules with an aperture area of 11.3 cm2 (Figure 4D and S56). The champion 1-cm2 devices show a PCE of 28.7% (reverse scan, with a VOC of 2.20 V, a JSC of 16.04 mA cm–2 and an FF of 81.62%, steady-state efficiency of 28.4% upon 240 s tracking). The mini-modules comprising 5 subcells give a PCE of 25.0%, with a VOC of 10.66 V, a JSC of 2.95 mA cm–2, an FF of 79.5%, and a steady-state PCE of 24.4% after a 240 s operation (Figure 4E). We also extend the application of the developed interconnecting layers to triple-junction cells using bandgaps of 1.27, 1.61, and 1.97 eV to demonstrate their versatility11 (Figure S57-S59 and Table S8). Schematic illustration and cross-section SEM image of the triple-junction devices are shown in Figure 4A. Regarding the determination of the bandgap combination and thicknesses of the top and middle cells, we referred to the design guidelines established in previously reported state-of-the-art triple-junction devices11,54. The champion triple-junction devices based on Cs0.2FA0.8Sn0.5Pb0.5I3 and Cs0.1FA0.6MA0.3Sn0.5Pb0.5I3 NBG subcells exhibit PCEs of 26.6% and 27.1%, respectively (Figure 4B and 4C).

We then examine the stability of double-junction cells under elevated temperatures. The optimised interconnecting layers-based devices maintain over 90% and 75% of their initial PCEs after 850 hours of ageing under 65 and 85 °C, respectively, in the dark, following the ISOS-D2 protocol43 (Figure S60). Additionally, the encapsulated tandem devices maintain 90% of the initial PCE after 770 hours operating under simulated 1-sun illumination at 45 °C in air (Figure 4F). Moreover, we also evaluate the operational stability of the encapsulated tandem devices under continuous simulated 1-sun illumination at elevated temperatures, following the ISOS-L2 protocol43. Encouragingly, the encapsulated devices retain about 90% of the initial PCEs after over 530 and 220 hours of operation at 65 and 85 °C, respectively. To the best of our knowledge, these efficiency and operational stability results in monolithic double-junction all-perovskite cells represent the state-of-the-art performance in the field (Figure 4G). These results highlight the critical role of the designed interconnecting layers in enhancing the durability of tandem devices at elevated temperatures and also provide fundamental insights that address key challenges in the field.

Discussion

We have developed an efficient and stable interconnecting layers structure that significantly enhances the thermal and operational stability of monolithic two-terminal all-perovskite tandem solar cells. The designed TPA-PFN HTL exhibits enhanced hole transport capability, favourable energy level alignment and processing compatibility, effectively minimizes interfacial energy loss. Furthermore, replacing PEDOT:PSS with TPA-PFN successfully avoids acid-induced interfacial degradation. The use of ultra-thin TCOs as recombination junctions minimizes optical losses while maintaining the electrical transport properties of interconnecting layers under operational stress, thereby contributing to enhanced device performance. Our findings demonstrate a viable strategy for simultaneously improving the efficiency and high-temperature durability of perovskite-based tandem photovoltaics, providing fundamental insights that address key challenges in this field.

Methods

Materials

N, N-dimethylformamide (DMF, 99.9%), dimethyl sulfoxide (DMSO, 99.9%), chlorobenzene (CB, 98%), isopropanol (IPA, 99.9%), ethanol (99.8%), toluene (99.9%), ethyl acetate (EA, 99.8%), tin (II) fluoride (SnF2, 99%), tin (II) iodide (SnI2, beads, 99.99%, trace metals basis) and poly(9,9-bis(3′-(N,N-dimethyl)-N-ethylammoinium-propyl-2,7-fluorene)-alt-2,7-(9,9-dioctylfluorene))dibromide (PFN–Br, 99%) were obtained from Sigma-Aldrich. Caesium iodide (CsI, >99.0%), guanidine thiocyanate (GuaSCN, >99.0%), methylammonium chloride (MACl, >98.0%), piperazinium iodide (PI, >98.0%) and bathocuproine (BCP, >99.0%) were purchased from TCI chemicals. Formamidinium iodide (FAI), lead bromide (PbBr2), lead iodide (PbI2), methylammonium iodide (MAI) were obtained from Advanced Election Technology Co., Ltd. Potassium thiocyanate (KSCN, >99.0%), potassium iodide (KI, >99.0%), 1,4-butanediamine (BDA, >99.0%) were obtained from Shanghai Aladdin Biochemical Tech Co., Ltd. Phenylalanine hydrochloride (PhA, 99.0%) and (4-(7H-dibenzo[c,g]carbazol-7-yl)butyl)phosphonic acid (4PADCB, 99.0%) was bought from Suzhou Liwei Tech Co., Ltd. 1,3-propanediamine dihydriodide (PDAI2, 99.99%), fullerene (C60, 99%), PEDOT:PSS aqueous solution (Al-4083) and ethane-1,2-diammonium iodide (EDAI2) were obtained from Xi’an Yuri Solar Co., Ltd. Tetrakis(dimethylamino) tin (IV) (99.9999%) for atomic layer deposited (ALD) SnOx was bought from Nanjing Ai Mou Yuan Scientific Equipment Co., Ltd. Indium tin oxide (ITO) and indium zinc oxide (IZO) targets were purchased from Enam Optoelectronic Material Co., Ltd. Unless otherwise noted, materials purchased from commercial suppliers were used without further purification.

Preparation of perovskite films

1.25 eV-bandgap mixed tin–lead perovskites. The Cs0.1FA0.6MA0.3Pb0.5Sn0.5I347 perovskite precursor solution was prepared by mixing CsI (49.4 mg, 0.19 mmol), FAI (90.6 mg, 0.57 mmol), FAI (196.1 mg, 1.14 mmol), PbI2 (438.0 mg, 0.95 mmol), SnI2 (353.9 mg, 0.95 mmol), SnF2 (14.9 mg, 0.095 mmol), PhA11 (11.5 mg, 0.057 mmol) and GuaSCN48 (4.5 mg, 0.038 mmol) in a solvent mixture of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 1.9 M. The precursor solutions were stirred at room temperature overnight and filtered through a 0.22 μm PTFE filter before use. To spin coat the films, 80 μL of the precursor solution was applied to the substrate. A two-step spin coating program was used. The first step was 1000 rpm for 10 s with an acceleration of 200 rpm s–1, and the second was 4000 rpm for 40 s with a ramp-up of 1000 rpm s–1. Then 400 μL of CB was quickly dripped onto the surface of the spinning substrate over an interval of 1 s during the second spin coating step, 20 seconds before the end of the procedure. The substrate was then immediately annealed on a 100 °C hot plate for 10 min. For the passivation layer, 1.0 mg EDAI218,49 and 0.1 mg BDA were added to 1 mL IPA and toluene mixed solvent at a volume ratio of 1:112,18. The mixed solvent solution was stirred for 2 h and then filtered through a 0.22 μm PTFE filter before spin coating. 100 μL BDA-EDAI2 solution was spin-coated on the perovskite film at 4000 rpm for 20 s with an acceleration of 1333 rpm s–1 then the film was annealed at 100 °C for 5 min.

1.27 eV-bandgap mixed tin–lead perovskites. The perovskite film was prepared in a N2-filled glove box (H2O, O2 < 0.1 ppm). The Cs0.2FA0.8Sn0.5Pb0.5I3 perovskite precursor solution was prepared by mixing CsI (98.7 mg, 0.38 mmol), FAI (261.4 mg, 1.52 mmol), SnI2 (353.9 mg, 0.95 mmol), PbI2 (438.0 mg, 0.95 mmol), SnF2 (14.9 mg, 0.095 mmol), PhA11 (11.5 mg, 0.057 mmol) and GuaSCN48 (4.5 mg, 0.038 mmol) in a solvent mixture of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 1.9 M. The perovskite films preparation procedure was the same as with the 1.25 eV perovskite.

1.53 eV-bandgap neat lead perovskites. The 1.5 M Cs0.05FA0.95PbI3 perovskite precursor solution was prepared by dissolving CsI (19.5 mg, 0.075 mmol), FAI (245.1 mg, 1.425 mmol), PbI2 (705.3 mg, 1.53 mmol) and MACl (5.06 mg, 0.075 mmol) in a mixed solvent of DMF:DMSO = 5:1 (volume ratio). The perovskite film was prepared by spin-coating the perovskite precursor solution at 4000 rpm for 50 s. CB as an anti-solvent was injected into the centre of the rotating substrate at 20 s before the end of the spin program. The perovskite films were annealed at 100 °C for 30 min. The PI50–52 solution (0.4 mg mL−1 in IPA) was spin-coated on top of the perovskite layer at 3000 rpm for 30 s and annealed at 100 °C for 5 min.

1.77 eV-bandgap neat lead perovskites. The Cs0.2FA0.8Pb(I0.6Br0.4)3 perovskite precursor solution was prepared by mixing CsI (62.3 mg, 0.24 mmol), FAI (165.1 mg, 0.96 mmol), PbI2 (221.3 mg, 0.48 mmol), PbBr2 (264.2 mg, 0.72 mmol), and KI (4.0 mg, 0.024 mmol) in a solvent mixture of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 1.2 M. The precursor solutions were stirred at room temperature overnight and filtered through a 0.22 μm PTFE filter before use. To spin coat the films, 80 μL of precursor solution was applied to the substrate. The spin coating process was set at 5000 rpm for 60 s with an acceleration of 1000 rpm s−1. Then 350 μL of EA was quickly dripped onto the surface of the spinning substrate over an interval of 1 s during the second spin coating step, 30 s before the end of the procedure. The substrate was then immediately annealed on a 100 °C hot plate for 10 min. For post-treatment, 120 µL PDAI253 (1.5 mg mL−1 in IPA) solution was spin-coated onto perovskite films. The spin coating process was set at 4000 rpm for 20 s with an acceleration of 1333 rpm s−1. Following spin coating, the films were immediately annealed at 100 °C for 5 min.

1.61 eV-bandgap neat lead perovskites. The Cs0.2FA0.8Pb(I0.85Br0.15)3 perovskite precursor solution was prepared by mixing CsI (77.9 mg, 0.3 mmol), FAI (206.4 mg, 1.2 mmol), PbI2 (484.1 mg, 1.05 mmol), PbBr2 (165.2 mg, 0.45 mmol), and KI (5.5 mg, 0.03 mmol) in a solvent mixture of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 1.5 M. The perovskite films preparation procedure was the same as with the 1.77 eV perovskite.

1.97 eV-bandgap neat lead perovskites. The Cs0.15FA0.85Pb(I0.33Br0.67)3 perovskite precursor solution was prepared by mixing CsI (31.2 mg, 0.12 mmol), FAI (116.9 mg, 0.68 mmol), and PbBr2 (293.6 mg, 0.8 mmol) in a solvent mixture of 0.25 mL DMSO and 0.75 mL DMF to reach a concentration of 0.8 M. Additional 0.5 mol% PDAI2 (1.3 mg, 0.004 mmol), PbCl2 (1.1 mg, 0.004 mmol), and MACl (0.3 mg, 0.004 mmol) were added to the precursor as additives for better film quality according to previous report54. The perovskite films preparation procedure was the same as that with the 1.77 eV perovskite.

Device fabrication

Single-junction perovskite solar cells. Glass/ITO substrates were thoroughly cleaned by sequential ultrasonication for 15 min in a detergent solution, distilled water, and alcohol. Then, the substrates were dried with N2 flow and cleaned by UV-ozone for 30 min before use. For the 1.25 and 1.27 eV Sn–Pb PSCs, the diluted PEDOT:PSS solution with IPA at a volume ratio of 1:2 was spin-coated on ITO substrates at 3000 rpm for 30 s and annealed on a hotplate at 150 °C for 15 min in ambient air. After that, the samples were immediately transferred into a N2-filled glovebox to deposit the rest of the layers. For the other HTLs, the BT-DPA or BT-TPA solution (5 mg mL–1 in CB) was spin-coated in a N2-filled glovebox at 3000 rpm for 30 s and annealed at a 100 °C hotplate for 10 min. The PFN-Br solution (0.5 mg mL–1 in DMF) was spin-coated onto the BT-DPA or BT-TPA layer at 3000 rpm for 30 s without annealing. The perovskite layer was then prepared following the above-mentioned procedure. Finally, 20 nm C60, 5 nm BCP, and 120 nm Ag were sequentially thermally evaporated under a high vacuum (< 5×10–4 Pa).

For the 1.53 eV PSCs, the 4PADCB55 solution (0.5 mg mL–1 in ethanol) was spin-coated on ITO substrates at 3000 rpm for 30 s and annealed at 100 °C for 10 min. The perovskite layer was then prepared following the above-mentioned procedure. The PCBM solution (20 mg mL–1 in CB) was spin-coated onto perovskite films at 3000 rpm for 30 s and annealed on a hotplate at 70 °C for 10 min. The BCP layer was prepared by spin-coting the BCP saturated solution in IPA on the PCBM films at 5000 rpm for 30 s, and then annealing at 70 °C for 5 min. Finally, the 120 nm Ag was deposited.

For the 1.61 eV, 1.77 eV, and 1.97 eV PSCs, all the preparation process was conducted in a N2-filled glovebox. The 4PADCB, perovskite, C60, BCP, and Ag layer was then prepared following the above-mentioned procedure.

Double-junction all-perovskite tandem solar cells. The 1.77 eV- and 1.27 eV-bandgap perovskite subcells were fabricated as previously described. For the interconnecting layer, after deposition of 20 nm C60, 30 nm ALD-SnOx was then deposited on top at 100 °C and followed by thermally evaporating ~1 nm of Au. The PEDOT:PSS or TPA-PFN layer was then prepared following the above-mentioned procedure. To minimise the parasitic absorption of the interconnecting layer, a thin (5 or 10 nm) transparent oxide (ITO or IZO) layer is sputtered through a shadow mask to replace the gold clusters. Pure argon was used as a process gas. The sputtering power was fixed at 50 W. The working pressure was kept at 4 × 10–3 to 2 × 10–3 torr. The Cr/Cu (2.5 nm/120 nm) electrodes in the devices used for thermal stability tests were thermally evaporated with a controlled evaporation rate of 0.1 Å s–1 and 0.1–0.5 Å s–1, respectively. The fabrication process for the tandem modules followed our previously reported procedures21.

Triple-junction all-perovskite tandem solar cells. The 1.97 eV-, 1.61 eV- and 1.27 eV-bandgap perovskite absorbers were prepared as previously described. Between 1.97 eV- and 1.61 eV-bandgap perovskite subcells, after deposition of 20 nm C60, 30 nm ALD-SnOx was then deposited on top, followed by depositing 5 nm IZO. Subsequently, the NiOx nanoparticle ink with a concentration of 10 mg mL–1 in a mixed solution of deionised water and IPA (3:1, vol/vol) was spin-coated on substrates at 4000 rpm for 30 s, annealed on a hotplate at 100 °C for 15 min in ambient air and then transferred into a N2-filled glovebox. The 4PADCB solutions were spin-coated on NiOx at 3000 rpm for 30 s, and annealed at 100 °C for 10 min. Between 1.61 eV- and 1.27 eV-bandgap perovskite subcells, after deposition of 20 nm C60 and 30 nm ALD-SnOx, 5 nm IZO was then deposited on top and followed by spin coating TPA-PFN. Finally, the tandem device with an architecture of glass/ITO/4PADCB/1.97 eV perovskite/C60/ALD-SnOx/IZO/NiOx/4PADCB/1.61 eV perovskite/C60/ALD-SnOx/IZO/TPA-PFN/1.27 eV perovskite/C60/BCP/Ag was successfully fabricated.

Films characterisation

The 1H NMR spectra were recorded on a Bruker AscendTM 600 MHz spectrometer. MALDI-TOF HRMS was performed on a Bruker Autoflex instrument. TGA analysis was performed using TGA8000 (PerkinElmer Co., USA) under dry air conditions with a heating rate of 10 °C min–1. Differential scanning calorimetry (DSC) was recorded on a PerkinElmer 13 Diamond DSC instrument under a nitrogen atmosphere. The XPS was measured with a monochromatic Al Kα X-ray source (1486.6 eV) operating at 100 W (Thermo ESCALAB 250XI). SEM images were taken with a Nova NanoSEM 450 scanning electron microscope at 10 kV operating voltage. XRD spectra were measured on an X-ray diffractometer (PANalytical B.V. Co.) with Cu Kα radiation. The GIWAXS measurements were performed at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility. The wavelength of X-rays was 1.24 Å (10 keV), and diffraction patterns were collected by using a two-dimensional Mar225 detector with different incidence angles and 30 s exposure times. The GIXRD patterns were acquired by using a Rigaku Smartlab with Cu Kα radiation in the 2θ range of 30.6 to 32.6°. PL measurements were conducted with laser excitation at 532 nm, and the area of interest was fixed on the micro-spectral measurement system (ProSp-Micro40-VIS), together with a spectrograph (Ocean Insight, USA). TRPL measurements were conducted by a HORIBA DeltaFlex spectrometer. The repetition rate is 100 kHz and the spot size is 100 µm. The laser fluence is 15.8 nJ cm–2 and the power density is 0.0016 W cm–2. Absorption spectra were measured using a Lambda 950 UV-vis spectrophotometer (PerkinElmer Co., USA). The KPFM was performed in the tapping mode by AFM under ambient conditions (SPM9700, Shimadzu Co., Ltd., Japan). Each set of samples was arranged in proximity on a common substrate and was measured using the same tip and scanning parameters. The UPS spectra were measured on an AXIS-ULTRA DLD-600W Ultra spectrometer (Kratos Co., Japan). A He discharge lamp (hv = 21.22 eV), emitting ultraviolet energy at 21.22 eV, was used for excitation. The photoluminescence quantum yield (PLQY) of the corresponding film was measured on QuantaMaster 8000 (HORIBA, Canada) with an 808 nm laser to photoexcite the samples placed in an integrating sphere. The laser intensity was adjusted to 1 sun equivalent intensity using a PSC to obtain a current density at 0 V equal to its JSC.

Devices characterisation

The J■V curves of the devices were measured using a Keithley 2400 source measurement unit and a solar simulator (Oriel, model 9119) with an AM1.5G spectrum. The light intensity was calibrated using a certified WPVS standard silicon reference cell (Enlitech) at 100 mW cm–2. The active area of devices was determined by the black masks of 0.0484, 0.0498, 1.04 and 11.3 cm2. Device measurements were conducted at a scan speed of 100 mV s–1. The steady-state power output was achieved by monitoring the stabilised current density output under MPP bias voltage (extracted from the reverse scan J-V curves). EQE spectra were performed in ambient air using a QE system (Enlitech Co., Ltd.). For double-junction tandem devices, the EQE spectra were obtained in ambient air without bias voltage and the bias illumination from LEDs with emission peaks of 850 and 460 nm, which were respectively used for the WBG and NBG subcells. The Transient photovoltage (TPV), transient photocurrent (TPC), and Mott-Schottky plots were obtained by a Zennium electrochemistry workstation (Zahner, Germany). The light intensity-dependent VOC was measured under different light intensities, and the plots were shown on a logarithmic scale. External electroluminescence quantum efficiency (EQEEL) was measured on ELCT-3010 (Enlitech Co., Ltd.).

Stability tests

For the 85 °C light soaking test of the films in Figure 2d, the film was immersed in a transparent vial containing toluene. The vial was then sealed with sealing film and placed on an 85 °C hotplate inside a N2 glovebox for continuous light exposure. It is worth noting that the vial was oriented horizontally during the test to ensure the film was fully exposed to light.

For device encapsulation, the devices were first fabricated on 4.5 cm × 4.5 cm glass/ITO substrates. Electrical connections were extended by attaching tin-plated copper ribbon strips to the metal electrodes. The edges of the sealing glass were sealed with butyl tape approximately 0.5 cm in width, followed by vacuum lamination at 100 °C for 10 min using an industrial laminator. All encapsulation procedures were completed in an N2-filled glovebox.

The J–V characterisation were periodically measured to assess the dark thermal stability of the unencapsulated devices on a hotplate at 65 or 85 °C in a N2 glovebox. The operational stability tests were carried out under AM1.5G solar simulator illumination source with an intensity of 100 mW cm–2 using a maximum power point tracking system (Wuhan Jiuyao Optoelectronic Technology Co., Ltd.) in ambient conditions. For tracking the maximum power output at 45, 65, or 85 °C, devices encapsulated with a cover glass and butyl rubber edge seal were placed on a temperature-controlled hotplate, their temperature being concurrently verified by a Hikmicro thermal camera (Figure S45).

Computational details

All optimisation and single-point energy calculations in this work were carried out by using density functional theory (DFT) as performed by Gaussian 0956. The structures of BT-DPA, BT-TPA, PFN-Br, and the molecule in neutral and charged forms were optimised using the B3LYP functional57 and 6-31+G(d,p)58–60 basis set for describing intramolecular interactions.

The recombination energy is one of the most important factors affecting the rate of charge transfer and can be divided into internal recombination energy, related to intramolecular vibrations and external recombination energy related to the surrounding medium. For organic solids and weakly polar media, the contribution of the external recombination energy is very small (usually less than 0.01 eV), so the external recombination energy is generally neglected. Here, only the internal recombination energy is considered. Based on the optimised geometries, the reorganisation energy is determined by four energies (the Nelson four-point method)61,62, as

where the is the energy of the neutral molecule in the cation symmetry, and the E* is the energy of the cationic molecule in the neutral symmetry; the and E are the optimised energies of the cationic and neutral molecules.

When the intermolecular transfer integrals are much smaller than the charge reorganisation energy and the rates of charge transfer between neighbouring molecules, the charge-transport properties can be described by the Marcus-Hush equation63,64:

where λ is the reorganisation energy for holes or electrons, V is the transfer integral, T is the temperature (298.15 K for our calculations), kb is the Boltzmann constant, and h is the reduced Planck constant. The transfer integral V actually characterises the strength of electronic coupling between the two adjacent molecules, and the holes (electrons) transfer integral of organic materials is equal to half the HOMO energy and LUMO energy.

Mechanical strength measurements

Stress-displacement curve measurements were performed on an electronic universal testing machine (LGD-500) by using the double-cantilever beam delamination technique65. The samples adopted a device structure of glass/ITO/HTL/perovskite/UV epoxy/glass with a substrate size of 1.3 × 1.5 cm2. Perovskite films were prepared on PEDOT:PSS- or TPA-PFN-coated ITO/glass as described above. Then, UV epoxy was coated on a 1 × 1 cm2 glass substrate and adhered to the centre of the perovskite films, followed by UV solidification for 1 minute. The samples were mounted on a tensile test fixture and stretched at an operating rate of 0.5 mm min–1 to delaminate the interface. To calculate the specific fracture energy (W), the equation, , is used, where σ is the measured stress and ε is the measured strain.

Resource availability

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Wei Chen (wnlochenwei@hust.edu.cn).

Materials availability

BT-DPA and BT-TPA generated in this study will be made available on reasonable request, but we may require payment and/or a completed materials transfer agreement if there is potential for commercial application.

Data and code availability.

This study did not generate or analyze datasets or code.

All data needed to evaluate the conclusions in the study are presented in the paper or supplemental information

All data are available from the corresponding authors upon reasonable requests.

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Author contributions

Conceptualization, G.L., Z.L. and W.C; methodology, J.W., Y.L., H.Z., S.H. and F.R; investigation, J.W., Y.L., H.Z., S.H., Wentao L., J.Z., S.Z., F.R., S.L., T.M., R.C., Y.C., Z.T., Wenguang L., X.X., Q.Z., Y.W., H.M., X.L., G.M., A.K.; writing – original draft, J.W., H.Z. and S.H.; writing – review & editing, A.K., G.L., H.J.S, Z.L. and W.C; funding acquisition, Q.Z., A.K., G.L., H.J.S, Z.L. and W.C; resources, Z.L. and W.C; supervision, G.L., H.J.S, Z.L. and W.C.

Declaration of interests

H.J.S. is the co-founder and CSO of Oxford PV Ltd. W.C. is the founder and Chief Scientific Officer of Wuhan Jiuyao Optoelectronic Technology Co., Ltd.

Supplemental information

Document S1. Figures S1–S60, Tables S1–S8, and supplemental references.

Figure titles and legends

Figure 1. Characterisations of HTLs and Sn–Pb PSCs. (A) Illustration of single-junction Sn–Pb PSCs and the interconnection between BT-TPA, PFN-Br, and Sn–Pb perovskite layer. (B) Molecular structures of BT-TPA and PFN-Br. (C) Calculated electrostatic potential (ESP) maps of BT-TPA and PFN-Br. (D) UV–vis transmittance spectra of PEDOT:PSS-, BT-TPA-, and TPA-PFN-coated ITO/glass substrates. Inset shows photographs of PEDOT:PSS water dispersion and BT-TPA chlorobenzene

solution in glass vials. (E) Energy level diagram of the studied HTLs and $Cs_{0.2}FA_{0.8}Sn_{0.5}Pb_{0.5}I_3$ perovskite films. (F) Steady-state PL spectra of the peeled perovskite films deposited on PEDOT:PSS, BT-TPA, and TPA-PFN substrates. (G) TRPL of the perovskite films prepared on PEDOT:PSS, BT-TPA, and TPA-PFN substrates (excitation from the glass side). (H) Distributions of VOC and PCE values derived from 24 devices fabricated with different HTLs. (I) J–V curves of champion PEDOT:PSS, BT-TPA, and TPA-PFN devices under reverse (RS) and forward (FS) scans. (J) Summary of PCE and VOC of representative Sn–Pb NBG PSCs fabricated based on PEDOT:PSS and other HTLs. (K) EQE spectra of the champion devices fabricated with PEDOT:PSS, BT-TPA, and TPA-PFN.

Figure 2. Stability of Sn–Pb PSCs. (A) Top-view SEM of peeled 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 15 days. Scale bar: 1 μm. (B) FLIM images of corresponding perovskite films. Scale bar: 10 μm. (C) PLQY values of corresponding fresh and aged perovskite films. (D) UV-vis absorbance spectra of toluene solutions with perovskite films after light-thermal ageing at 85 °C under 1-sun illumination for 5 days. Inset shows pictures of the solutions in glass vials. (E) XPS spectra of Sn 3d core levels performed on the peeled surface of the PEDOT:PSS--based films. (F) XPS spectra of Sn 3d core levels performed on the peeled surface of the TPA-PFN--based films. (G) Fracture energy of the HTL/perovskite interfaces before and after 15 days of aging at 85 °C under 1-sun illumination. (H) Performance evolution of unencapsulated devices aged at 85 °C under dark conditions in the N_2 glovebox. The initial average efficiencies are 21.7% and 23.3% for PEDOT:PSS and TPA-PFN devices, respectively. (I) Continuous MPPT for the encapsulated devices under simulated AM1.5G illumination in air at 45 °C (of the cells) and 50% RH (of the room).

Figure 3. Design of interconnecting layers for all-perovskite tandems. (A) Schematic illustration of exposing the buried interface of NBG perovskite films prepared on PEDOT:PSS or TPA-PFN-coated ITO/SnO_x (30 nm)/Au (1 nm) substrates after light-thermal ageing for 15 days. (B) XPS spectra of S 2p core levels for the peeled surface of the corresponding perovskite films. (C) XPS spectra of Au 4f core levels for the peeled surface of the corresponding perovskite films. (D) ToF-SIMS results of the TPA-PFN-based films before and after light-thermal ageing. (E) Schematic diagram of four types of interconnecting layers (ICLs) in tandems.(F) UV-vis transmittance spectra of Au and IZO RJs. (G) I–V curves of ITO/SnO_x/TPA-PFN/Au, fresh and aged ITO/SnO_x/Au (1 nm)/TPA-PFN/Au, as well as fresh and aged ITO/SnO_x/IZO (5 nm)/TPA-PFN/Au samples.

Figure 4. Performance of all-perovskite tandems. (A) Schematics and cross-sectional SEM images of all-perovskite double-junction (2J) and triple-junction (3J) devices. (B) J–V curves of champion double-junction and triple-junction devices based on $Cs_{0.2}FA_{0.8}Sn_{0.5}Pb_{0.5}I_3$ NBG subcells. (C) J–V curves of champion double-junction and triple-junction devices based on $Cs_{0.1}FA_{0.6}MA_{0.3}Sn_{0.5}Pb_{0.5}I_3$ NBG subcells. (D) J–V curves of champion 1-cm^2 double-junction devices. Inset shows a photograph of a 1-cm^2 cell. (E) J–V curves of champion double-junction mini-modules. Inset shows a photograph of a tandem mini-module with an aperture area of 11.3 cm^2. (F) Under simulated AM1.5G illumination and 50% RH (of the room), the encapsulated tandems maintained 84%, 90%, and 82% of their initial PCEs after about 1070 h (at 45 °C), 530 h (at 65 °C), and 340 h (at 85 °C) of MPPT, respectively. T90 represents the time it took for the device efficiency to drop to 90% of its initial value. (G) Summary of operational stability and certified efficiency for double-junction devices under simulated AM1.5G illumination. For the data points without stating the temperature, the cells are aged at a temperature of no higher than 45 °C.

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