Subtle side chain modification of triphenylamine-based polymer hole-transport layer materials produces efficient and stable inverted perovskite solar cells

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Abstract

Polymer hole-transport layers (HTLs) are critical components of inverted perovskite solar cells (IPVSs). Triphenylamine derivatives P3TA (poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine]) and Poly-TDP (poly[N,N'-bis(4-butylphenyl)-N,N'-bis(phenyl)benzidine]) have been widely adopted as hole-transport materials due to their perovskite passivation effects and suitable energy levels. However, the passivation mechanism (i.e., the functional group responsible for perovskite passivation) of triphenylamine derivative polymers remains unclear, hindering the development and application of this polymer type. Here, we develop a novel Poly-TDP derivative, S-Poly-TDP, by replacing the n-butyl functional group of Poly-TDP with an isobutyl group to explore the influence of alkyl groups on HTL performance and top-deposited perovskite properties. Compared with Poly-TDP, the increased CH3-terminal unit density and the decreased spatial distance between the –CH–CH3 and –CH2–CH3 units and the benzene ring in S-Poly-TDP not only enhanced the hole-transport ability but also improved the perovskite passivation effect, revealing for the first time the role of the alkyl groups in perovskite passivation. As a result, the S-Poly-TDP-based IPVSCs demonstrated high power-conversion efficiencies of 15.1% and 21.3% in
1 | INTRODUCTION

With the rapid development of perovskite solar cells (PVSCs), the recorded power-conversion-efficiency (PCE) of single-junction PVSCs has reached 25.7% within 10 years,[1–3] exhibiting great commercialization potential. According to the device structure, PVSCs can be broadly divided into inverted (p-i-n) and regular (n-i-p) structures.[4–6] For regular structure PVSCs, metal oxide materials (e.g., TiO₂, meso-TiO₂, ZnO, and SnO₂) are typically selected as the electron transport layer (ETL), and a high-temperature thermal annealing process at over 150°C is commonly required, limiting the application of regular PVSCs in flexible devices.[7,8] In contrast, inverted perovskite solar cells (IPVSCs) with polymer hole-transport layers (HTLs) (e.g., poly[bis(4-phenyl)-
(2,4,6-trimethylphenyl)amine] (PTAA), poly[N,N′-bis(4-butylyphenyl)-N,N′-bis(phenyl)benzidine] (Poly-TPD)) are prepared at a relatively low thermal annealing temperature (<120°C) and are more compatible with various device substrate compositions, making IPVSCs suitable for flexible devices and large-scale commercialization fabrication processes, such as doctor blading and roll-to-roll technologies.[9–12] However, limited by the charge transport material performance, IPVSCs suffer from more serious voltage loss issues than regular structure PVSCs, which hinders high-efficiency device development—the highest reported PCE for IPVSCs is still lower than 23%.[2,9,13,14] Therefore, high-performance HTL development is urgently needed for the advancement of IPVSC technology.

In an IPVSC, the HTL is sandwiched between the anode (indium tin oxide [ITO] or fluorine tin oxide [(FTO)]) and the perovskite layer, acting as the electron-blocking layer and hole-extracting layer and determining the charge carrier transport/recombination properties of the perovskite/HTL interface and the performance of the IPVSC.[14] As a metal oxide HTL, the material properties of NiOₓ are sensitive to the fabrication process and the precursor material properties; moreover, a high annealing temperature (>200°C) is commonly required, which raises the difficulty of synthesizing high-quality materials and limits the feasibility of commercialization.[15–17] Polymer HTLs were developed to address these limitations.

Wide-bandgap [MAPbI₂Br(SCN)₀.₁₂] and normal-bandgap [(FAPbI₃)₀.₉₂(MAPbBr₃)₀.₀₈] devices, respectively.

**KEYWORDS**
alkyl group, inverted perovskite solar cells (IPVSCs), perovskite passivation, polymer hole transport layers (HTLs), Poly-TPD, PTAA

Triphenylamine derivatives PTAA and Poly-TPD are the most widely adopted polymer HTMs in IPVSCs, due to their favorable energy levels, lower annealing temperatures, and intrinsic hydrophobicity.[18–21] Poly-TPD and PTAA also exhibit perovskite passivation effects[22,23]; however, the exact mechanism (i.e., the functional group responsible for passivation) is still unclear, which hinders the further development of these materials.

In addition to HTL perovskite passivation, passivation additives can be added directly into the perovskite film to achieve high-quality passivated perovskites.[24] For example, Zheng et al. reported the passivation effect of choline chloride in quaternary ammonium halides for inhibiting the defect states in the perovskite films.[25] Jiang et al. revealed the perovskite surface passivation effect of 2-phenylethylammonium iodide (PEAI) via the formation of PEA₂PbI₄, which boosted the device PCE to 23.32%.[26] Liu et al. demonstrated the passivation effect of benzylammonium (BA), 4-fluorobenzylammonium (FBA), 4-chlorobenzylammonium (CBA), and 4-bromobenzylammonium (BBA) on perovskites via the formation of halogenated low-dimensional perovskites.[27] Recently, by adopting unilateral alkylamine additives with different alkyl chain lengths (methylamine, n-butylamine, hexylamine, and octylamine), Feng et al.[28] revealed the passivation effect of alkyl chain length in amine perovskite precursor materials for inhibiting perovskite defect states.

In this study, we sought to determine whether the alkyl group in polymer HTLs acts as the perovskite passivator. We developed a new Poly-TPD derivative, S-Poly-TPD, by changing the butyl connecting group from n-Bu to isobutyl (iso-Bu). Systematic comparisons of the material properties of Poly-TPD and S-Poly-TPD and corresponding IPVSC performances were conducted to explore the effect of alkyl chains on perovskite passivation and HTL properties. We found that the iso-Bu units of S-Poly-TPD were beneficial for intermolecular stacking, improving hole mobility. More importantly, the perovskite passivation ability of S-Poly-TPD exceeded that of Poly-TPD, confirming the perovskite passivation effect of the alkyl chain in charge transport materials. Exploiting the advantages of S-Poly-TPD, we fabricated a MAPbI₂Br(SCN)₀.₁₂-based mixed-halide wide-bandgap...
IPVSC with a stabilized 15.1% PCE. The novel IPVSC maintained 98% of its initial PCE after 15 h of maximum power point (MPP) tracking. Moreover, to explore the performance of S-Poly-TPD, we prepared a (FAPbI$_3$)$_{0.92}$ (MAPbBr$_3$)$_{0.08}$-based normal-bandgap IPVSC, which achieved a new record PCE for Poly-TPD and Poly-TPD derivative-based IPVSC devices of 21.3%.

2 | RESULTS AND DISCUSSION

To facilitate comparison, the adopted Poly-TPD and S-Poly-TPD have similar molecular weights ($M_n$) of 40 kDa. As illustrated in Figure 1A,B, Poly-TPD and S-Poly-TPD have identical molecular structures except for the alkyl chain connection to the benzene. Compared with the straight alkyl chain group (–CH$_2$–CH$_2$–CH$_2$–CH$_3$) of Poly-TPD, the alkyl chain of S-Poly-TPD comprises two-branched –CH–CH$_3$ and –CH$_2$–CH$_3$ alkyl units. Density functional theory (DFT) calculations were previously conducted to investigate the molecular packing properties. An obvious angle can be observed between the adjacent monomers of Poly-TPD (Figure 1C), whereas the adjacent monomers of S-Poly-TPD are parallel to each other (Figure 1D), which is a favorable characteristic for carrier transport. To further investigate the packing condition and crystallinity properties of Poly-TPD and S-Poly-TPD, grazing-incidence wide-angle X-ray scattering (GIWAXS) patterns were obtained. As depicted in Figure 1E,F, both films exhibit an obvious lamellar signal located around $q_{xy} = 1.7$ (Å$^{-1}$), which represents the π–π stacking in the out-of-plane direction. In agreement with the DFT results, the GIWAXS signal of S-Poly-TPD is stronger, reflecting the higher crystallinity and more condensed intermolecular stacking than those of Poly-TPD.

Space charge-limited current (SCLC) measurements were conducted to quantify the hole mobility of the materials. Consistent with the above results, the hole mobility of S-Poly-TPD is $9.7 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$, more than four times higher than that of Poly-TPD ($2.1 \times 10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$) (Figure 1G). Furthermore, the film morphologies and contact potential differences (CPD) of Poly-TPD and S-Poly-TPD were assessed using Kelvin probe force microscopy (KPFM). Compared with the Poly-TPD film, the S-Poly-TPD film has a lower root-mean-square roughness ($R_s$) and more homogeneous

**FIGURE 1** Molecular structure of (A) Poly-TPD and (B) S-Poly-TPD. Density functional theory (DFT) calculation results of the stacking model of (C) Poly-TPD and (D) S-Poly-TPD. Grazing-incidence wide-angle X-ray scattering (GIWAXS) images of spin-coated (E) Poly-TPD and (F) S-Poly-TPD films. (G) The dark $J–V$ curves of Poly-TPD- and S-Poly-TPD-based hole-only devices. The inset is the adopted device structure. (H) Ultraviolet photoelectron spectroscopy (UPS) spectra of the hole-transport layers. The inset table shows the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).
potential distribution (Figure S1), which indicates improved charge transport at the perovskite/HTL interface, consistent with the DFT results.[21]

Ultraviolet (UV) photoelectron spectroscopy and UV-Vis absorption measurements were performed (Figure 1H; Figure S2) to investigate the energy levels of the HTLs. The Poly-TPD and S-Poly-TPD solutions have the same UV-Vis absorption cut-off edge of 415 nm; in the solid-state, their cut-off edges are located at 422 and 418 nm, respectively (Figure S2), a difference that can be attributed to their different molecular packing conditions.[34] As shown in Figure 1H, S-Poly-TPD has a slightly shallower highest occupied molecular orbital (HOMO) energy level (−5.14 eV) than Poly-TPD (−5.11 eV). Considering the superior carrier mobility and the favorable lowest unoccupied molecular orbital (LUMO) level (−2.14 eV) of S-Poly-TPD, the influence of this tiny HOMO level difference on the device performance can be ignored.[35,36]

To investigate the influence of the HTLs on the top-deposited perovskite properties, wide-bandgap perovskite films (MAPbl3Br(SCN)0.12) were prepared via a simple one-step solution process with the structures of ITO/ Poly-TPD/perovskite and ITO/S-Poly-TPD/perovskite. Scanning electron microscopy (SEM) measurements were conducted to examine the surface morphology of the films. The Poly-TPD-based perovskite film contains nonuniform perovskite grains with blurred boundaries (Figure 2A), whereas the S-Poly-TPD-based perovskite film is fully covered with well-defined regular perovskite grains (Figure 2B), illustrating the positive effect of S-Poly-TPD on the perovskite film GIWAXS and X-ray diffraction (XRD) (Figure 2C,D) measurements were conducted to investigate the influence of the HTMs on the crystallization properties of the deposited perovskite films. The diffraction signals located at \( q_{xy} = 1.1 \) (Å\(^{-1}\)) and \( q_{xy} = 2.2 \) (Å\(^{-1}\)) represent the (100) and (200) lattice planes of \( \alpha \)-phase MAPbl3Br(SCN)0.12 perovskite (Figure 2C,D), and the signal at \( q_{xy} = 0.9 \) (Å\(^{-1}\)) represents the PbI\(_2\) phase.[37,38] A highly concentrated Bragg spot indicates the preferential orientation of crystals, whereas a ring-like diffraction pattern indicates randomly oriented crystals.[39] Compared with the Poly-TPD-based MAPbl3Br(SCN)0.12 film, the S-Poly-TPD film has a more concentrated signal in the out-of-plane direction (Figure 2D), indicating that the (100) lattice planes of the 3D \( \alpha \)-phase MAPbl3Br(SCN)0.12 crystals are nearly parallel to the substrates. This characteristic is favorable for charge transport from the bulk perovskite to the HTL and ETL, thereby improving the device performance.[40]

As shown in Figure S3, the XRD patterns of both films exhibit the standard \( \alpha \) perovskite phase, with the high XRD intensity of the S-Poly-TPD-based perovskite film indicating an enhanced crystallinity. Combined with the GIWAXS results, we can deduce that S-Poly-TPD produces favorable crystallization properties in top-deposited perovskite films.

Time-resolved photoluminescence (TRPL) measurements were performed by exciting the perovskite films deposited on Poly-TPD and S-Poly-TPD to examine the influence of the HTLs on the electronic properties of the deposited perovskite films.[41] As depicted in Figure 2E, the S-Poly-TPD-based perovskite film exhibits a faster average photoluminescence PL quenching time (\( \tau_{av} \)) of 12.3 ns than the Poly-TPD-based film (26.7 ns), reflecting a more efficient hole-extraction process from the perovskite film to the HTL.[37,42]

X-ray photoelectron spectroscopy (XPS) was performed on the pristine perovskite film (ITO/perovskite) and the HTL-based perovskite films (ITO/perovskite/HTL) to investigate the effect of S-Poly-TPD on the film qualities. The full XPS spectra are shown in Figure S5, and Figure 2F shows the detailed Pb 4 f peaks of the XPS spectra. Compared with the pristine perovskite film, both HTL-based perovskite films have XPS spectra with lower binding energies, which indicates the passivation effect of the HTLs on the perovskite film.[3] The Pb peaks (=141.5 and 136.5 eV) that originate from the under-coordinated Pb\(^{2+}\) defects in the pristine perovskite film are absent in the HTL-based films, which confirms the passivation effect of the HTLs on the perovskite film.[43,44] Moreover, compared with the Poly-TPD-based perovskite film, the spectrum of the S-Poly-TPD-based perovskite film is blue-shifted; the corresponding 4f\(_{5/2}\) and 4f\(_{7/2}\) peaks shift from 138.5 to 138.4 eV and from 143.4 to 143.3 eV, respectively. This result indicates an enhanced interaction between S-Poly-TPD and perovskite[22] and reflects its stronger perovskite passivation effect than Poly-TPD.

The UV-Vis absorption properties of the perovskite films were examined. As illustrated in Figure S4A, the S-Poly-TPD-based perovskite film has a stronger absorption intensity than the Poly-TPD-based film, consistent with the enhanced crystallinity and modified film morphology.[45,46] KPFM tests showed that the \( R_s \) values of the perovskite films deposited on Poly-TPD and S-Poly-TPD are 38.6 and 37.4 nm (Figure 3A,B), respectively. Additionally, the perovskite film deposited on S-Poly-TPD has a more homogeneous surface potential distribution (Figure 3C,D), confirming the effect of S-Poly-TPD on the perovskite crystallization properties.

Fourier transform infrared (FTIR) spectroscopy was used to explore the interaction mechanism between the HTLs and perovskite. The FTIR results are shown in Figure 4A,B and the related characteristic vibration bands are summarized in Table 1. In general, the
presence of a strong electron-donating unit on molecules will increase the electron density, leading to a decreased FTIR spectrum wavenumber. The wavenumbers of the asymmetric stretching vibrations of C–H and bending vibrations of CH$_2$ in Poly-TPD are located at 2929.5 and 1451.5 cm$^{-1}$, respectively; the corresponding vibrations in S-Poly-TPD are lower at 2927.9 and 1446.6 cm$^{-1}$, respectively. The wavenumbers of the rocking vibrations of CH$_3$ are also lower in S-Poly-TPD (894.4 cm$^{-1}$) than in Poly-TPD (896.8 cm$^{-1}$). The decreased vibration wavenumbers of C–H, CH$_2$, and CH$_3$ reflect the increased electron-donating ability of S-Poly-TPD. The lower wavenumbers may be ascribed to two factors. First, compared with Poly-TPD, the S-Poly-TPD molecules have more CH$_3$-terminal units, which can serve as Lewis bases to provide a stronger trap-passivation capability, resulting in the blue-shifts of these signals. Second, a $\sigma$–$\pi$ ultra-conjugation effect exists between the alkyl chain units and the benzene rings; compared with Poly-TPD, the spatial distance between the branched alkyl chain unit (containing –CH$_3$ and –CH$_2$–CH$_3$) and the benzene ring in S-Poly-TPD is decreased, which is likely to promote a more uniform electron density and stronger electron-donating capabilities of the two terminal units.

**FIGURE 2** Scanning electron microscopy (SEM) images of MAPb$_4$Br(SCN)$_{0.12}$ perovskite films based on (A) Poly-TPD and (B) S-Poly-TPD. 2D GIWAXS patterns of MAPb$_4$Br(SCN)$_{0.12}$ perovskite film based on (C) Poly-TPD and (D) S-Poly-TPD hole-transport layers (HTLs). (E) The steady-state photoluminescence (PL) spectra of the perovskite films based on different HTLs. (F) The X-ray photoelectron spectroscopy (XPS) spectra of Pb signals in perovskite films.
FIGURE 3  Topography of MAPbI$_2$Br(SCN)$_{0.12}$ perovskite films deposited on (A) Poly-TPD and (B) S-Poly-TPD films, and (C, D) the corresponding contact potential distribution (CPD) tested by Kelvin probe force microscopy (KPFM). The inset images in (C, D) show the CPD values of yellow cut lines; scale bars are on the right.

FIGURE 4  Fourier transform infrared (FTIR) spectra of the pristine Poly-TPD and S-Poly-TPD films in the range of (A) 4000–1750 cm$^{-1}$ and (B) 1800–800 cm$^{-1}$. FTIR spectra of the pristine MAPbI$_2$Br(SCN)$_{0.12}$ film and the MAPbI$_2$Br(SCN)$_{0.12}$ films with Poly-TPD and S-Poly-TPD hole-transport layers in the range of (C) 4000–1750 cm$^{-1}$ and (D) 1800–800 cm$^{-1}$. The dotted line marks the position of the characteristic vibration signal.
FTIR measurements were then performed on the perovskite films to determine the passivation mechanism. Compared with the pristine perovskite film, both the HTL-based films have lower CH₃ bending and CH₃ rocking vibration wavenumbers (Figure 4C and Table S1), confirming the effect of the CH₃ group on perovskite passivation. Compared with the Poly-TPD-based perovskite film, the CH₃ bending and CH₃ rocking vibrations of the S-Poly-TPD-based perovskite film shift from 1385.3 to 1372.5 cm⁻¹ and from 912.6 to 909.2 cm⁻¹, respectively, demonstrating a stronger interaction between the CH₃ group in S-Poly-TPD and perovskite. Therefore, the additional CH₃-terminal units are likely to be responsible for the enhanced passivation ability of S-Poly-TPD. On the other hand, the HTL-based films have lower C=H stretching and CH₂ bending vibration wavenumbers than the pristine perovskite film, confirming the effect of C=H and CH₂ on perovskite passivation. The lower wavenumbers of the S-Poly-TPD-based film indicate that reducing the distance between the branched alkyl chain unit and the benzene ring promotes the perovskite passivation effect of the HTL. Moreover, the C=N stretching vibrations of S-Poly-TPD and Poly-TPD are at the same wavenumber, which excludes the influence of the alkyl chain on the C=N vibration (Figure 4B,D, ν₅). The passivation effect of the C=N unit itself on perovskite can also be excluded based on the identical C=N vibration wavenumbers of Poly-TPD and S-Poly-TPD deposited on perovskite (Figure 4D, ν₅). Because the only difference between Poly-TPD and S-Poly-TPD is the connecting alkyl group, we can reasonably deduce that the increased –CH₃ density and the decreased distance between the –CH₂CH₃ and –CH₂–CH₃ units and the benzene ring promote the enhanced perovskite passivation effect of S-Poly-TPD, and the perovskite passivation effects of PTAA and Poly-TPD are endowed by their alkyl groups. Combining this with the XPS (Figure 2F) results, it is deduced that the electron-donating capability of alkyl chains can promote the formation of high-quality Pb-free perovskite films through forming a stronger coordination bond with the Pb²⁺, which results in the lower binding energies of Pb 4f peaks. Such interaction also provides better surface trap passivation of the perovskite film. To the best of our knowledge, this is the first study to demonstrate the perovskite passivation effect of the alkyl units in charge transport materials.

Finally, MAPbI₃Br(SCN)₀.12-based wide-bandgap IPVSCs with device structures of ITO/Poly-TPD or S-Poly-TPD/perovskite/PCBM ([6,6]-phenyl C₆1 butyric acid methyl ester)/BCP (bathocuproine)/Ag were fabricated. Promoted by the high carrier mobility and perovskite passivation ability, the S-Poly-TPD-based IPVSCs have an improved Voc (open-circuit voltage) and fill factor (FF), with reduced hysteresis (Figure 5A) and high reproducibility compared with the Poly-TPD-based IPVSCs (Figure 5B). The best-performing S-Poly-TPD-based device achieved a high PCE of 15.1% and a short-circuit current density (Jsc) of 16.7 mA cm⁻², improved Voc of 1.17 V, and FF of 77.0%. In contrast, the optimized efficiency of the Poly-TPD-based device is limited to 14.1% (Jsc = 16.5 mA cm⁻², Voc = 1.12 V, FF = 75.7%). As shown in Figure 5B, compared with the Poly-TPD-based IPVSC, the S-Poly-TPD-based IPVSC has a higher external quantum efficiency (EQE) at short wavelengths (300–480 nm), which is consistent with the modified perovskite/HTL interface of the S-Poly-TPD-based device. The integrated Jsc matches well with the J–V curves. MPP tracking was used to test the device stability in an N₂ glovebox maintained at around 60°C under constant one-sun illumination (Figure 5C). The Poly-TPD-based IPVSC PCE decreased to 90% of the initial value after 11.0 h of illumination. In contrast, the S-Poly-TPD-based IPVSC retained 90% of the initial
PCE after 45.0 h because of the stability-enhancing effect of S-Poly-TPD on perovskite.

Electrochemical impedance spectroscopy (EIS) measurements were performed to study the interfacial charge transport dynamics in the corresponding devices. During the test, a $V_{oc}$ applied bias with a frequency range of 1 MHz to 10 Hz and a 10 mA AC amplitude illuminated under simulated 0.1 sunlight was applied. The resulting Nyquist curves were fitted according to a circuit model (Figure 5D), where $R_s$ describes the charge transport resistance. As the only difference between the devices is the HTL, the changes in the EIS should be attributable to the HTL properties. The $R_s$ of the S-Poly-TPD-based device was smaller (4.9 Ω) than that of the Poly-TPD-based device (14 Ω), which confirms the increased hole extraction capability of S-Poly-TPD.

To explore the compatibility of S-Poly-TPD with other perovskite systems, normal-bandgap (FAPbI$_3$)$_{0.92}$ (MAPbBr$_3$)$_{0.08}$ IPVSCs based were fabricated using the HTLs. As shown in Figure S7, compared with the Poly-TPD-based film, the S-Poly-TPD-based film has obviously enhanced crystallinity, confirming the feasibility of S-Poly-TPD application in different perovskite systems. The S-Poly-TPD-based (FAPbI$_3$)$_{0.92}$(MAPbBr$_3$)$_{0.08}$ perovskite film also shows enhanced UV-Vis absorption intensity over all wavelengths (Figure S4b). The surface morphologies of the perovskite films were evaluated by SEM (Figure S8). Consistent with the above results, the strong passivation effect of S-Poly-TPD also promotes the formation of a condensed (FAPbI$_3$)$_{0.92}$(MAPbBr$_3$)$_{0.08}$ film with the inhibited formation of PbI$_2$ particles. In contrast, the perovskite film deposited on Poly-TPD was covered with impurities—most likely the precipitated PbI$_2$ phase—that might compromise the device’s performance.

Next, we evaluated the photovoltaic properties of IPVSCs comprising (FAPbI$_3$)$_{0.92}$(MAPbBr$_3$)$_{0.08}$ films deposited on the HTLs. Consistent with the perovskite film properties, the S-Poly-TPD-based device exhibited a high PCE of 21.3% (Figure 6A,B), with $J_{sc}$, $V_{oc}$, and FF values of 24.4 mA cm$^{-2}$, 1.08 V, and 80.9%, respectively, and enhanced reproducibility (Figure 6C). A relatively low PCE of 19.0% was achieved for the Poly-TPD based device ($J_{sc} = 22.3$ mA cm$^{-2}$, $V_{oc} = 1.06$ V, FF = 80.3%).

**Figure 5** (A) $J$–$V$ characteristics, (B) external quantum efficiency (EQE) spectra, (C) maximum power point (MPP) tracking (conducted in an N$_2$ glove box at around 60°C and under one-sun constant illumination), and (D) electrochemical impedance spectroscopy (EIS) properties of MAPbI$_2$Br(SCN)$_{0.12}$-based inverted perovskite solar cells (IPVSCs) with Poly-TPD and S-Poly-TPD as the hole-transport layers.
The calculated $J_{sc}$ values of 21.23 and 23.21 mA cm$^{-2}$ from the EQE results (Figure 6B) matched well with the $J-V$ curves. More importantly, as illustrated in Figure 6D, the PCE of the S-Poly-TPD-based device is the highest reported PCE for IPVSCs with Poly-TPD and Poly-TPD derivative-based HTLs. Moreover, it is among the highest PCEs reported for polymer HTL-based 3D IPVSCs.\textsuperscript{[18,25,52–65]}

**3 | CONCLUSIONS**

In summary, we developed a novel S-Poly-TPD HTL for fabricating high-performance IPVSCs by replacing the $n$-Bu of Poly-TPD with an iso-Bu unit. The higher carrier mobility of S-Poly-TPD than Poly-TPD confirms the role of alkyl groups in modulating HTL mobility. Compared with Poly-TPD, the enhanced perovskite passivation effect of S-Poly-TPD reveals for the first time that this influence of the alkyl group in the HTLs improves perovskite passivation. As a result, the S-Poly-TPD-based IPVSCs demonstrated a record PCE of 15.1\% for MAPbI$_2$Br(SCN)$_{0.12}$-film based wide-bandgap IPVSCs with improved device stability. Meanwhile, S-Poly-TPD also exhibited good compatibility with normal-bandgap IPVSCs. A high PCE of 21.3\% with a $V_{oc}$ of 1.08 V was achieved for the (FAPbI$_3$)$_{0.92}$(MAPbBr$_3$)$_{0.08}$ film-based devices. Overall, we believe that this study not only introduces a new HTL but also provides a novel molecular design strategy for synthesizing high-performance charge transport materials for PVSCs.

**4 | EXPERIMENTAL SECTION/METHODS**

**4.1 | Material preparation**

For the carrier transport materials, Poly-TPD, S-Poly-TPD, and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) were purchased from Xi’an Polymer Light Technology Corp, PCBM was bought from Nano-c, and MoO$_3$ was obtained from Sigma-Aldrich. For the perovskite precursor materials, methylammonium iodide (MAI) and formamidinium iodide (FAI) were got from Greatcell Solar Materials Pty Ltd. For the lead sources, lead bromide (PbBr$_2$) and lead thiocyanate (Pb(SCN)$_2$) were provided by...
Acros Organics, and lead iodide (PbI₂) was produced by Tokyo Chemical Industry Co., Ltd. All the solvents used in this study, that is, anhydrous N, N-dimethylformamide (DMF), anhydrous dimethyl sulfoxide (DMSO), anhydrous ethanol, and anhydrous chlorobenzene (CB) were supported by Sigma-Aldrich.

4.2 Solution preparation

The wide-bandgap perovskite precursor solutions were prepared by dissolving the precursor materials in DMF: DMSO (4:1) mixed solvent with a concentration of 1 mmol/ml. MAPbI₂Br(SCN)₀.₁₂ solution was got by mixing all the precursor sources MAI, PbI₂, PbBr₂ and Pb(SCN)₂ together with the molar ratio of 1.06:0.5:0.5:0.06 (168.54:230.25:183.5:19.4 mg). The normal-bandgap perovskite solutions were prepared by dissolving 70 mg FAI, 4 mg MABr, and 10 mg MACl into 1 ml IPA, and 1.4 M PbI₂ into a mixed solution of DMSO and DMF with the volume ratio of 6:94. For the PCBM solution, 25 mg PCBM was dissolved into 1 ml CB directly.

4.3 Device fabrication

The ITO substrates were first cleaned with IPA (isopropanol) in an ultrasonic bath for 20 min, then change with IPA with deionized water and also ultrasonicated for 20 min. Repeat the clean process three times, after that move into an oven annealed at 70°C for 24 h. The precleaned ITO substrates were further cleaned by plasma for 5 min before the deposition of materials. First, Poly-TPD/S-Poly-TPD was firstly spin-coated on the ITO, under the ambient atmosphere, with the spin-coating speed of 2000 rpm for 30 s, then moved to a hotplate annealed at 110°C for 10 min. After annealing, Poly-TPD/S-Poly-TPD films were treated by plasma for 1 s. For the deposition of wide-bandgap perovskites, the detailed method can be found in Ref. [42,44]. For the fabrication of normal-bandgap perovskites, the PbI₂ layer was previously deposited on the HTLs with the spin-coating speed of 2000 rpm, then annealed for 1 min under 70°C. To convert the PbI₂ layer into (FAPbI₃)₀.₉₂ (MAPbBr₃)₀.₀₈, 50 µl of the mixed solution (MACI, FAI, and MABr in IPA) was deposited on the PbI₂ layer at 1500 rpm for 45 s, after that, the film was annealed at 150°C for 10 min. Then, the PCBM layer was spin-coated at 2000 rpm for 30 s, and annealed at 65°C for 2 min. Finally, BCP and Ag were sequentially thermally deposited in a high vacuum thermal evaporator under 4 × 10⁻⁶ torr.

4.4 Characterizations

The SEM results were got from by Philips XL30 FEG. The XRD data were got from the D2 Phaser instrument (Bruker) facility. The UV-Vis measurement was conducted by the SHIMADZU UV-3600 UV-VIS-NIR spectrophotometer. For the TRPL test, the perovskite samples were deposited on ITO substrates. The TRPL results were gotten from a time-correlated single-photon counting spectrometer (Edinburgh Instruments FLS 980) equipped with a 480 nm laser source. The average lifetimes (τav) are calculated by the equation below:

\[ \tau_{av} = A_1 \times \tau_1 + A_2 \times \tau_2, \]

where \( \tau_i \) refers to the time constant of exponential component, \( A_i \) denotes the fractional amplitude for each exponential. \(^{[66,67]}\) Both of the J–V characteristics and steady-state outputs were measured by a solar simulator (Enlitech, SS-F5, Taiwan). EQE measurements were performed using a commercialized quantum efficiency measurement system (QE-R, Enlitech) equipped with a Xenon lamp source and elliptical collector. EIS measurements were carried out with a Paios 4.0 measurement instrument (FLUXiM AG). The EIS spectra were carried out under the dark condition, at the applied bias of \( V_{oc} \) of the device with the 10 MHz–10 Hz frequency range and 10 mV oscillating amplitude. For the transient photovoltage (TPV) and transient photocurrent (TPC) measurements, the devices were serially connected using a digital oscilloscope (Tektronix TDS 3052 C) with the resistance adjusted to 50 Ω and 10 MΩ to track the extraction efficiency and the recombination rate of charge carriers, respectively. For stabilized PCE test, the IPVSCs were tested in an N₂ glove-box under constant 1 sun illumination. The XPS and ultraviolet photoelectron spectroscopy (UPS) results were harvested from ESCALAB 250Xi ThermoFisher. The KPFM was obtained from the Cypher AFM instrument.

For the space-charge-limit current (SCLC) analysis, the I–V curve can be divided into three distinct regions: an ohmic region with the order \( n = 1 \), an \( n = 2 \) child region, and an > 3 trap-filling limited (TFL) region. The voltage marking the transition from the ohmic region to TFL region (\( V_{TFL} \)), is adopted to calculate the trap density (\( n_T \)), according to the equation:

\[ V_{TFL} = e_n L^2/2\varepsilon_0, \]

where \( e \) represents the elementary charge, \( n_T \) stands for the trap density, \( L \) indicates the perovskite film thickness, \( \varepsilon \) means the perovskite film’s relative dielectric constant, and \( \varepsilon_0 \) is expressed as the vacuum permittivity.
4.5 | Simulations

All calculations were performed in the Gaussian09 program using Becke’s three-parameter exchange function combined with the Lee–Yang–Parr correlation functional (B3LYP) with Grimme’s DFT-D3BJ empirical dispersion correction, and the 6-31 G** basis set. The geometries of the molecules have been optimized and no imaginary frequencies for the harmonic frequency.

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CONFLICTS OF INTEREST

The authors declare no conflicts of interest.

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