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High efficiency of solution-processed inverted organic solar cells enabled by an aluminum oxide conjunction structure†

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The lack of solution-processed hole transport layers (HTLs) has become an obstacle not only to developing all-solution-processed inverted organic solar cells (OSCs) but also to enabling their full potential for high-throughput fabrication. One of the major problems is the distinct difference in surface-free energy between most HTLs and the organic bulk heterojunction (BHJ) active layer, which causes inherent wetting behavior problems and poor film quality. Here, we unveil the interesting features of the aluminum oxide (Al_2O_3) nanocrystal-based conjunction structure in improving the interfacial properties between a solution-processed HTL (namely PIDT-F:POM) and the organic active layer. Our results showed that the structure of Al_2O_3 /HTL can generally be applied to different active layers in inverted OSCs, providing high power conversion efficiency (PCE) and stability. By additional solution-processing of the Al_2O_3 conjunction structure on the hydrophobic active layer, the wettability of the hydrophilic HTL on the modified BHJ surface is significantly improved, as evidenced by the reduced water contact angles. Remarkably, the new structure of BHJ/ Al_2O_3 /PIDT-F:POM offers superior electrical properties, explained by the excellent hole extraction capability and reduced interfacial recombination. Consequently, Al_2O_3 /PIDT-F:POM yields high PCEs, reaching 18.4% in inverted OSCs. Notably, their PCE and stability are even better than those of the control cells made from widely adopted evaporated molybdenum trioxide (MoO_3). The work demonstrates the new concept of establishing efficient solution-processed HTLs and alternative pathways for promoting inverted OSCs for practical applications.

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Broader context

The extreme lack of solution-processed hole transport layers (HTLs) for active layer modification has become an obstacle to the development of inverted organic solar cells (OSCs) and the realization of their full potential of high-throughput fabrication. The biggest challenge is the different surface free energies between the hydrophobic active layer and hydrophilic carrier transport layers. This disparity leads to poor interfacial properties between the active layer and the HTL, resulting in poor device performance and stability. In this work, we propose and demonstrate an aluminum oxide (Al_2O_3) conjunction structure to enhance not only the wettability of the organic active layer to the HTL but also the dielectric constant and built-in electric field of OSCs, thereby improving the open-circuit voltage (V_{oc}). By using PM6:D18:L8-BO as the active layer, the Al_2O_3 /PIDT-F:POM-modified OSC achieves a decent PCE of 18.4%. Notably, our results show that the 'general' approach of Al_2O_3 conjunction structure can be adapted to other solution-processed HTL materials. Consequently, the work contributes not only to expanding the design of solution-processed HTLs in BHJ inverted OSCs but also to advancing the full potential of all-solution-processed inverted OSCs for the carbon neutrality commitment.

Introduction

Bulk heterojunction (BHJ) organic solar cells (OSCs) are promising candidates for next-generation solar energy conversion technology due to their potential low cost, lightweight, mechanical flexibility, and high-throughput solution processing.^{1–5} Over the past few decades, rapid progress has been made to improve the performance of OSCs with power conversion efficiency (PCE) of over 18%

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and 19% for the state-of-the-art inverted and conventional OSCs, respectively.^{6–14} OSCs are usually complex multilayered structures with charge transport layers (CTLs) between the electrodes and active layers to facilitate selective charge extraction, overcome potential energy barriers, and enhance carrier mobility.^{15–18} However, compared to the active layer, the development of CTLs, especially, the hole transport layer (HTL), is severely lagging. Although many solution-processed HTL materials have been developed recently, they are typically used for the bottom electrode modification in conventional OSCs. Particularly, they are rarely available for active layer modification in inverted devices due to their distinct differences in surface-free energies (causing interfacial contact issues between hydrophilic HTLs and hydrophobic organic active layers). To date, evaporated molybdenum oxide (MoO_3) remains the most widely used HTL for inverted OSCs. Overall, it is highly desirable to develop solution-based HTLs to promote all-solution-processed efficient inverted OSCs.

The solution processability (*i.e.*, film-forming property/wettability/uniformity) of HTLs is crucial to the performance of inverted OSCs. Especially, the low surface energy of the active layer can strongly affect the wettability of hydrophilic HTL materials.^{19–21} As a matter of fact, the wetting challenge of aqueous poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) on hydrophobic BHJ surfaces has been demonstrated in many studies.^{22–24} Indeed, a lot of prior efforts have been devoted to solving this issue. For instance, surfactants and other additives have been added to the aqueous HTL solution to improve its wetting properties on the organic surface, whereas, the residual surfactants typically degrade the stability and efficiency of the OSCs.^{25–27} Another common strategy is to increase the surface energy of the active layer through, for example, plasma or UV-ozone treatments.^{28–31} However, these techniques are not ideal for organic active layers as they are likely to cause serious damage. Apart from these, different kinds of buffer layers can be integrated into the active layer to enhance the printing and coating properties of HTLs.^{32–34} Furthermore, the surface tension, boiling points, and drying time of the solvents can also be optimized to improve the interfacial wettability.^{35–37} To further solve the de-wetting issue of the aqueous PEDOT:PSS on the active layer, an alcohol-dispersed formulation (PEDOT:F) has been reported by Zhou's group, where perfluorinated sulfonic acid was employed as a counterion to replace the traditional PSS counterion, achieving OSCs with a very good PCE of 17.02%.³⁸ Nevertheless, up till now, there are still very limited solution-processed HTLs available for efficient inverted OSCs.

Herein, we report an efficient inverted OSC composed of a solution-processed composite HTL (namely, PIDT-F:POM) together with an aluminum oxide (Al_2O_3) conjunction structure, which provides desired wetting properties over the hydrophobic organic active layer. Our results show that hydrophilic HTL materials can spread and wet well on the Al_2O_3 -modified BHJ surface. Hence, the surface wettability and film coverage of HTL are improved. On the one hand, better interfacial contact contributes to lower series resistance and reduced interfacial recombination, contributing to elevated short-circuit current

density (J_{sc}) and the fill factor (FF), and on the other hand, the proposed Al_2O_3 conjunction structure is beneficial to enhancing the dielectric constant and the built-in electric field of OSCs, resulting in a higher open-circuit voltage (V_{oc}). As a result, when using Al_2O_3 /PIDT-F:POM as HTL, champion PCEs of 17.2% and 18.4% are achieved in OSCs composed of PM6:BTP-eC9 and PM6:D18:L8-BO, respectively, which are superior to those of the MoO_3 cell. In addition, the Al_2O_3 /PIDT-F:POM-modified device can maintain 80% of its initial efficiency after 1000 h of storage in the dark while that of MoO_3 -based OSCs decreases to 64% of its original value under the same condition. The work contributes to not only expanding schemes in the design of solution-based HTLs for highly efficient and stable inverted OSCs but also promoting the development of full-solution-processed OSCs towards carbon neutrality.

Results and discussion

In this work, a composite of the conjugated polyelectrolyte (CPE) PIDT-F and the inorganic molecular cluster (POM) $\text{H}_6\text{P}_2\text{Mo}_3\text{W}_{15}\text{O}_{62}$ are utilized as HTL. The chemical structures of PIDT-F and POM are provided in Fig. 1a. Both PIDT-F and POM are readily soluble in water and methanol. For spin casting the PIDT-F:POM film, the solution was prepared by dissolving a mixture of PIDT-F and POM in methanol (Fig. 1b). The UV-vis absorption spectra of the PIDT-F and PIDT-F:POM solid films are presented in Fig. 1c. By utilizing POM as a doping agent, a significantly intensified absorption band in the long-wavelength region is observed in the PIDT-F:POM spectrum, indicating an enhanced p-doping effect of PIDT-F due to the addition of POM. This observation is consistent with prior findings that POM has a strong oxidizing ability to enhance the doping effect of CPE.³⁹ To verify the above inference, electron spin resonance (ESR) measurements were carried out to probe the free radical species in the solid samples. As shown in Fig. 1d, a remarkably enhanced ESR signal can be observed in PIDT-F:POM, indicating an intensified doping effect as well as improved hole-transporting capability. The result confirms that the strong oxidizing property of POM can facilitate the electron transfer from PIDT-F to POM, which is consistent with that of UV-vis absorption. Ultraviolet photoelectron spectroscopy (UPS) was performed to evaluate the work function (WF) and the energy level structures of PIDT-F and PIDT-F:POM. As shown in Fig. 1e, WF values of PIDT-F and PIDT-F:POM are found to be 4.79 and 5.20 eV, respectively. In addition, the highest occupied molecular orbital (HOMO) levels are calculated to be -5.23 and -5.24 eV concerning the vacuum level for PIDT-F and PIDT-F:POM, respectively. It is worth noting that PIDT-F:POM exhibits a much smaller HOMO to the Fermi level offset than PIDT-F, implying a deeper p-doping effect of PIDT-F:POM. (Fig. S1, ESI†) Since the electrical conductivity of conjugated polymers is strongly influenced by the doping level, the bulk conductivity of the pristine CPE and the composite was measured by the two-point probe method. The conductivities of PIDT-F, PIDT-F:POM, and PEDOT:PSS are

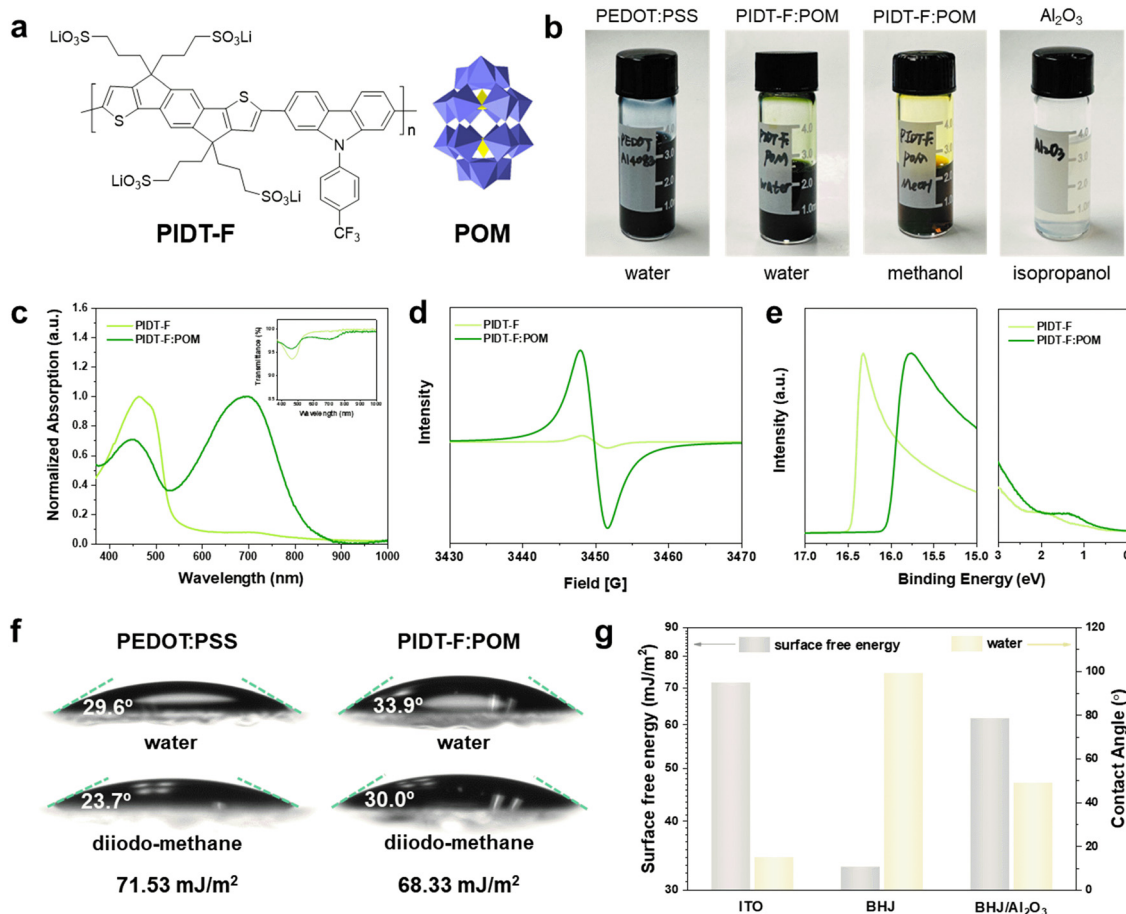


Fig. 1 (a) The chemical structure of PIDT-F and POM. (b) The pictures of solutions of different functional layers. (c) Normalized UV-vis absorption spectra and transmittance of PIDT-F and PIDT-F:POM solid films. (d) ESR spectra of PIDT-F and PIDT-F:POM in solid. (e) UPS spectra of PIDT-F and PIDT-F:POM films. (f) Contact angles of water and diiodo-methane on PIDT-F and PIDT-F:POM films. (g) Contact angles of water and diiodo-methane on different substrates and their corresponding surface free energies.

estimated to be 1.33×10^{-3} , 3.70×10^{-3} and $2.55 \times 10^{-3} \text{ S m}^{-1}$, respectively (Fig. S2, ESI†). Therefore, PIDT-F:POM has sufficiently high WF and conductivity to enable efficient hole extraction and transportation as HTL in OSCs, which could be attributed to the significantly enhanced p-doping effect of PIDT-F:POM.

The surface free energy (γ_s) and wetting properties of the HTLs are then investigated. As shown in Fig. 1f and g, the contact angles (CAs) of water and diiodo-methane on the PIDT-F:POM surface are 33.9° and 30.0° , respectively. Accordingly, the γ_s of PIDT-F:POM is calculated to be 68.33 mJ m^{-2} by the Wu model,⁴⁰ which is similar to that of PEDOT:PSS (71.53 mJ m^{-2}). Due to the hydrophilic nature of UV-ozone-treated indium tin oxide (ITO), as presented in Fig. S3 (ESI†), the HTLs with high γ_s have good coating properties and interfacial contact on the ITO surface. Subsequently, the surface morphology of PIDT-F:POM was studied by atomic force microscopy (AFM). As presented in Fig. S4 (ESI†), the root-mean-square roughness (R_q) value of ITO is reduced from 2.55 nm to 1.51 nm after modification by PIDT-F:POM. The uniform interfacial contact of PIDT-F:POM is favorable to depressing the

interfacial defects and pinholes of ITO. Consequently, the conventional device based on PIDT-F:POM exhibits a high PCE of 17.6% when using PM6:BTP-cC9 as the active layer, and the corresponding photovoltaic parameters are summarized in Table S1 (ESI†). The above results demonstrate that PIDT-F:POM can be used as an efficient HTL to modify ITO in conventional OSCs.

Obviously, there would be a mismatch of γ_s between BHJ and HTL, which may cause serious wetting problems in inverted OSCs. To solve this problem, we incorporate an Al_2O_3 conjunction structure between the active layer and HTL, as depicted in Fig. 2a. Accordingly, the contact angles of water dramatically decrease from 99.3° to 49.0° after modifying BHJ with an Al_2O_3 conjunction structure, and the γ is calculated to be 33.05 and 61.51 mJ m^{-2} , respectively. The smaller contact angle coupled to the elevated surface free energy should contribute to better wettability of the active layer towards the hydrophilic HTLs. To demonstrate the better surface coverage of HTL on the Al_2O_3 -modified active layer, X-ray photoelectron spectroscopy (XPS) was performed, and chlorine (Cl) was the characterizing element of BHJ. Consequently, compared with BHJ/PIDT-

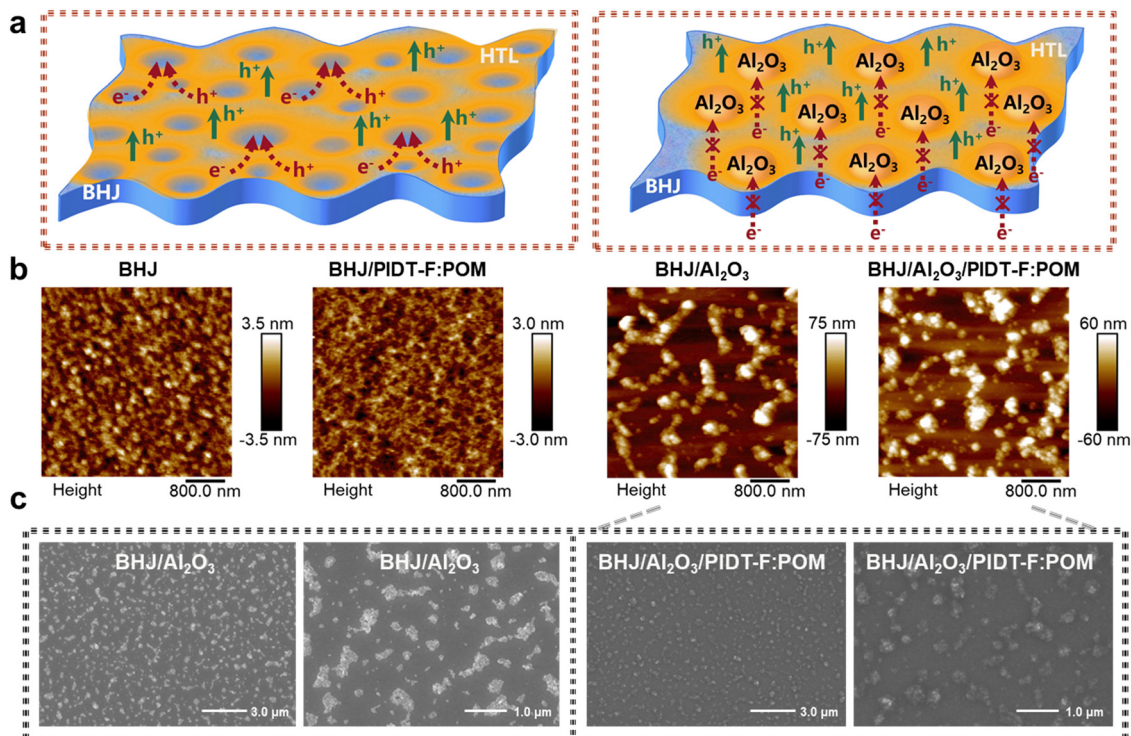


Fig. 2 (a) The schematic diagram of the BHJ/PIDT-F:POM contact and BHJ/Al₂O₃/PIDT-F:POM contact. (b) AFM height image of BHJ, BHJ/PIDT-F:POM, BHJ/Al₂O₃ and BHJ/Al₂O₃/PIDT-F:POM. (c) SEM image of BHJ/Al₂O₃ and BHJ/Al₂O₃/PIDT-F:POM.

F:POM, the integral area and atomic concentration of Cl 2p can be further reduced in BHJ/Al₂O₃/PIDT-F:POM, indicating a better surface coverage of HTL after using an Al₂O₃ conjunction structure (Fig. S5, ESI†). To verify the effect of Al₂O₃ conjunction structure on the active layer, AFM was conducted to study the surface topography. As shown in Fig. 2b, the morphology of BHJ/PIDT-F:POM is quite similar to that of the bare active layer, implying an incomplete surface coverage of HTL on the hydrophobic active layer, which is consistent with the XPS results mentioned above. While the AFM and scanning electron microscopy (SEM) images present a noticeably better coverage of BHJ/Al₂O₃/PIDT-F:POM compared to that of BHJ/Al₂O₃, suggesting a preferable surface coverage, see Fig. 2c. The better surface coverage of BHJ/Al₂O₃/PIDT-F:POM is favorable to depressing the interfacial defects, so as to improve the hole collection in the inverted OSCs.

To confirm the above findings, we fabricated OSCs with the device configuration of ITO/ZnO/BHJ/Al₂O₃/HTL/Ag, and the cells without Al₂O₃ conjunction structures were also fabricated for comparison. The details of the device fabrication are provided in the Experimental section. Here, the blend consisting of PM6 and BTP-eC9 was used as the active layer. Fig. 3a presents the current density *versus* voltage (*J*-*V*) characteristics of the OSCs with and without the Al₂O₃ conjunction structure under the illumination of AM 1.5 G, 100 mW cm⁻². The relevant photovoltaic parameters are listed in Table S2 (ESI†). The device with pristine PIDT-F:POM exhibits a moderate PCE of 15.9% (V_{OC} = 0.815 V, J_{SC} = 26.6 mA cm⁻², FF = 0.733), while the OSC modified by Al₂O₃/PIDT-F:POM exhibits a considerably

higher PCE of 17.2%, along with a high V_{OC} of 0.849 V, a J_{SC} of 27.0 mA cm⁻² and a FF of 0.752. Notably, the V_{OC} of the Al₂O₃/PIDT-F:POM cell is even higher than that of the MoO₃ control cell, denoting that Al₂O₃/PIDT-F:POM does not cause an additional charge extraction barrier compared to MoO₃. The above outcome confirms that the Al₂O₃ conjunction structure plays an important role in enhancing the wettability and interfacial contact between BHJ and HTL in inverted OSCs. Fig. 3b shows that the external quantum efficiency (EQE) curves and the integrated current densities match well with the J_{SC} values measured from *J*-*V* characterization.

To reveal the superior hole collection capabilities of Al₂O₃/PIDT-F:POM in the inverted OSCs, we studied the electrical properties of the devices. The built-in voltage (V_{bi}) of the devices is estimated by the Mott-Schottky analysis. As presented in Fig. 3c, the V_{bi} of the Al₂O₃/PIDT-F:POM-based OSC is 0.68 V, which is higher than that of the PIDT-F:POM device (0.65 V). The larger V_{bi} indicates that an ideal internal electric field can be achieved in the device, which is responsible for the high V_{OC} .⁴¹ As shown in Fig. 3d, the impedance analysis was carried out, and the dielectric constants were slightly increased by integrating an Al₂O₃ conjunction structure. The space-charge-limited current (SCLC) analysis was adopted to assess the trap density, as exhibited in Fig. S6 (ESI†). The trap density N_{trap} was calculated using the following equation: $N_{trap} = \frac{2\epsilon_0\epsilon_r V_{FTL}}{eL^2}$, where V_{FTL} is the trap-filled limit voltage, L is the thickness of the film, ϵ_0 is the vacuum permittivity, ϵ_r is the relative dielectric constant, and e is the elementary charge.⁴² The trap

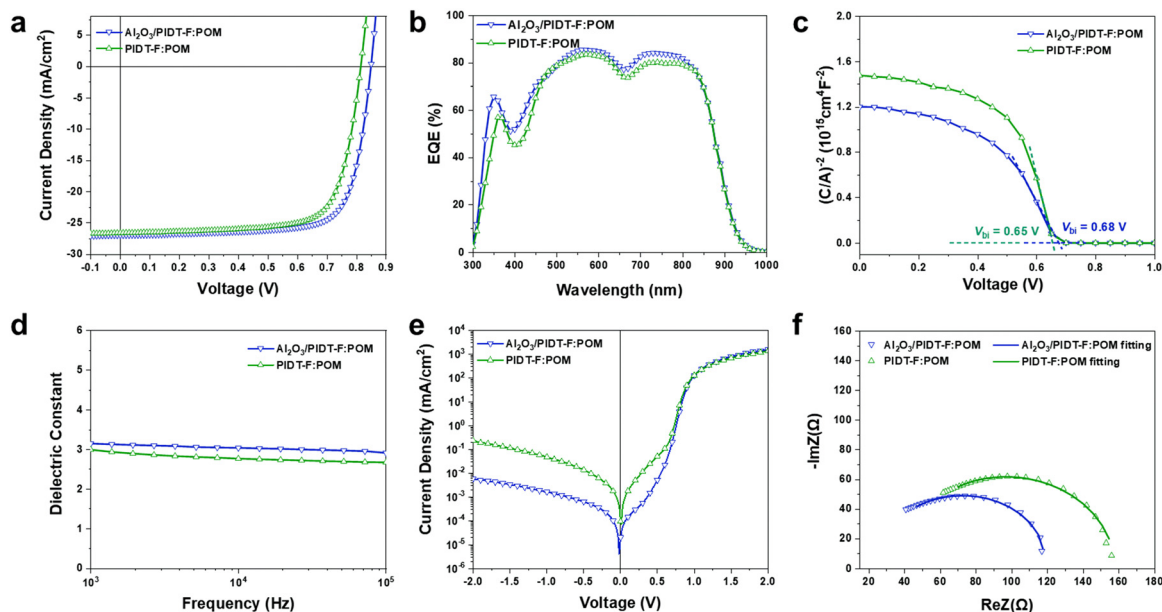


Fig. 3 (a) J - V characteristics of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices under the illumination of AM 1.5 G, 100 mW cm^{-2} . (b) EQE curves of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices. (c) Mott-Schottky analysis of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices. (d) The dielectric constant of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices calculated from the impedance spectrum. (e) J - V characteristics of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices in the dark. (f) Nyquist plots of the impedance spectra of PIDT-F:POM and Al_2O_3 /PIDT-F:POM based devices.

density of OSCs effectively decreased from $8.61 \times 10^{15} \text{ cm}^{-3}$ to $4.97 \times 10^{15} \text{ cm}^{-3}$ using an Al_2O_3 conjunction structure. The lower trap density is beneficial for suppressing the charge recombination, to surpass the energy loss at the anode interface.

Regarding the charge recombination behavior, we measured the relationship between V_{OC} and light intensity (P_{light}), in which the slopes of V_{OC} versus P_{light} for the cells with and without Al_2O_3 are 1.19 and $1.23 k_{\text{B}}T/q$, respectively, suggesting a suppressed trap-assisted recombination after modifying with the Al_2O_3 conjunction structure (Fig. S7, ESI†).⁴³ Moreover, light-dependent J_{SC} is shown in Fig. S8 (ESI†), and the slope of the $J_{\text{SC}}-P_{\text{light}}$ plot for the Al_2O_3 /PIDT-F:POM-based device is very close to unity ($\alpha = 0.98$), indicating a weak bimolecular recombination in the inverted device.⁴⁴ In addition, the dark J - V characteristics indicate that the Al_2O_3 -treated device exhibits an excellent diode rectification and small reverse leakage current, contributing to high J_{SC} and FF of the device⁴⁵ (Fig. 3e). The electrochemical impedance spectroscopy (EIS) was performed to assess the series resistances (R_{series}) of OSCs. Nyquist plots of the Al_2O_3 /PIDT-F:POM-modified devices are shown in Fig. 3f. The data were fitted using the equivalent-circuit model according to the literature,⁴⁶ which yielded satisfactory agreement with the measurements. The R_{series} values in the equivalent-circuit model were determined to be 1.90 and $4.39 \Omega \text{ cm}^2$ for the devices with and without Al_2O_3 conjunction structure, respectively. The above results demonstrate that the charge recombination at the BHJ/HTL interface is greatly suppressed by incorporating an Al_2O_3 conjunction structure, contributing to the high FF and PCE of the device.

Importantly, the approach of introducing the Al_2O_3 conjunction structure directly to the solution-processed HTL materials

can generally serve to realize inverted OSCs. To demonstrate the versatility of Al_2O_3 as the anode buffer layer, studies were performed by utilizing different solution-processed HTLs, including PEDOT:PSS, POM, PCP-2F-Li, Me-2PACz, and NiO_x . As depicted in Fig. S9 and Table S3 (ESI†), the device performance showed obvious enhancement with the proposed Al_2O_3 conjunction structure. Moreover, to assess the versatility of Al_2O_3 /PIDT-F:POM as an HTL, various active layers, such as PM6:IT-4F, PTO2:IT-4F, PM6:Y6, and PM6:D18:L8-BO were employed for inverted OSCs. The molecular structures of all the active layer materials are provided in Fig. S10 (ESI†). Photovoltaic parameters for these OSCs are summarized in Table S4 (ESI†). Each Al_2O_3 /PIDT-F:POM-modified OSC outperforms MoO_3 , as shown in Fig. 4a. Consequently, Al_2O_3 /HTL can serve as a general structure in different active layers for high-performance inverted OSCs better than the widely adopted evaporated MoO_3 HTL. Specifically, by using PM6:D18:L8-BO as the active layer, the Al_2O_3 /PIDT-F:POM-modified OSC achieved a decent PCE of 18.4%, together with a V_{OC} of 0.89 V, a J_{SC} of 27.0 mA cm^{-2} , and a FF of 0.76. To the best of our knowledge, this is the highest efficiency for the inverted OSCs using a solution-processed HTL, see Fig. 4b.

The intrinsic stability of the inverted OSCs modified with Al_2O_3 /PIDT-F:POM and MoO_3 was investigated. The encapsulated devices were stored in the glovebox at room temperature. As shown in Fig. 4c and Fig. S11 (ESI†), the OSC modified with Al_2O_3 /PIDT-F:POM maintained 80% of its initial PCE value after storage for 1000 h. In contrast, the efficiency of the MoO_3 device decreases to 64% of its original value during the same storage time. In addition, the operational stability of the OSCs was investigated by monitoring the efficiency of the encapsulated

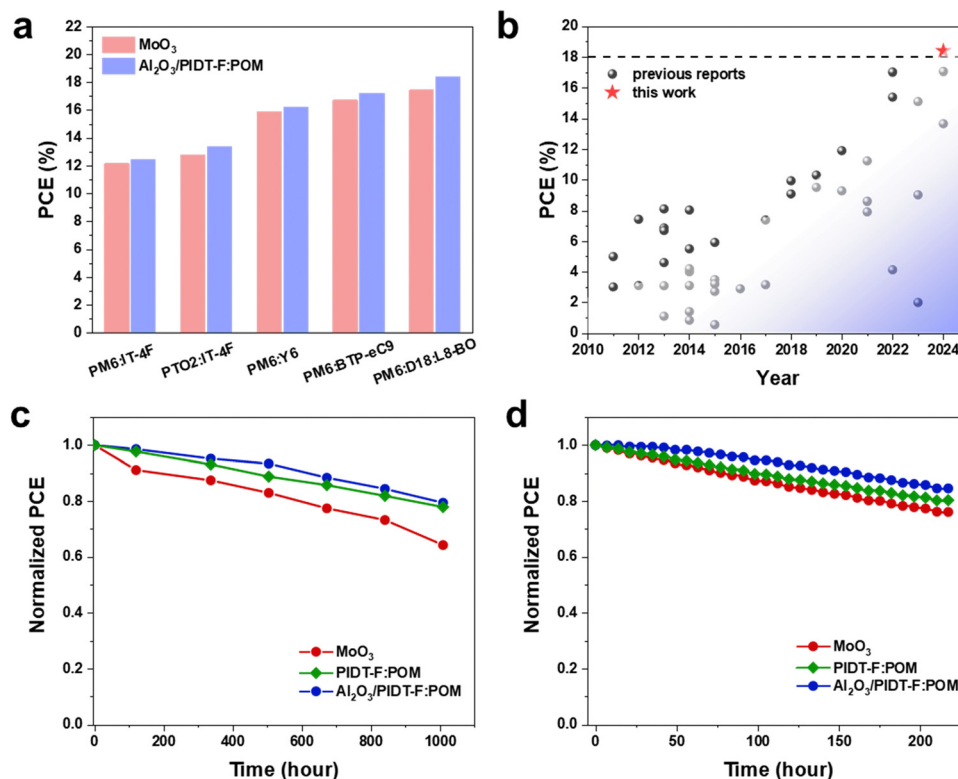


Fig. 4 (a) PCE of MoO₃ and Al₂O₃/PIDT-F:POM based devices based on different active layers. (b) Results of PCEs of the inverted OSCs with solution-processed HTL from previous studies (2011–2023) and in this work. (the references are provided in Table S5, ESI†) (c) Normalized PCE values as a function of storage time for MoO₃ and Al₂O₃/PIDT-F:POM based devices with encapsulation. (d) Normalized PCE values as a function of exposure time under illumination for MoO₃ and Al₂O₃/PIDT-F:POM based devices with encapsulation.

cells in the ambient air (60–80% humidity, 45–55 °C) under continuous illumination. As shown in Fig. 4d, the OSCs based on Al₂O₃/PIDT-F:POM and MoO₃ could reserve 86% and 77% (which is similar to previous studies^{47,48}) of their efficiencies, respectively, after 200 hours of illumination. It is worth mentioning that the storage and operational stability of PIDT-F:POM devices are improved by introducing the Al₂O₃ conjunction structure. As we discussed previously, the Al₂O₃ conjunction structure improves the hydrophilicity of the BHJ surface to enhance the interfacial interaction between BHJ and HTL. Accordingly, the stronger adhesion between BHJ and HTL contributes to better stability of the inverted OSCs. Consequently, the general structure of Al₂O₃/HTL can be used in inverted OSCs with high PCE and stability better than that of the widely adopted evaporated MoO₃ HTL.

Conclusions

In conclusion, we realized highly efficient inverted OSCs based on a solution-processed composite HTL with an Al₂O₃ conjunction structure. Our results show that the new general structure of Al₂O₃/HTL can serve in different active layers for inverted OSCs with high PCE and stability better than those of the widely adopted evaporated MoO₃ HTL. By inserting an ultrathin Al₂O₃ conjunction structure between hydrophobic BHJ and hydrophilic HTL, the wetting and coating properties were

greatly enhanced, resulting in the good surface coverage of PIDT-F:POM on the Al₂O₃-treated active layer. We find that such favorable contact can not only facilitate hole extraction and transportation at the interface but also depress the interfacial recombination, contributing to a lower voltage loss. Ultimately, the PM6:BTP-eC9 OSC modified by Al₂O₃/PIDT-F:POM exhibits a considerably higher PCE of 17.2%, while the control OSC without Al₂O₃ conjunction structure only exhibits an inferior PCE of 15.9%. Encouragingly, by using PM6:D18:L8-BO as the active layer, the Al₂O₃/PIDT-F:POM-modified device showed an outstanding efficiency of 18.4%, representing the highest PCE for the inverted OSCs with solution-processed HTLs. Consequently, the findings contribute to the expanding scheme in the effective approach to solving the severe interfacial problems caused by the mismatched surface energy between the design of solution-processed HTLs in and BHJ inverted OSCs as well as advancing the full potential for all-solution-processed inverted OSCs to carbon neutrality commitment.

Experimental

Materials

PM6, BTP-eC9 and other active layer materials were purchased from Solarmer Materials Inc. Al₂O₃ dispersion (30 nm, 20 wt% iso-propanol) was purchased from Aladdin. The other materials and solvents were commercially available. POM was prepared

as described in the literature before.⁴⁹ PIDT-F was synthesized as described in the literature before.⁵⁰

Instruments and measurements

The *J*-*V* characteristics of the devices were recorded using a Keithley 2400 source meter, and the measurement was carried out under AM 1.5 G illumination based on a solar simulator (SS-F5-3A, Enli Technology Co., Ltd). The intensity of the AM 1.5 G spectra was calibrated by a certified standard silicon solar cell. EQE spectra were measured using a solar cell spectral response measurement system QE-R3011 (Enli Technology Co., Ltd). The electron spin resonance spectra were recorded in the dark using a Bruker E500 at room temperature. UV-vis absorption spectra were obtained with a Shimadzu UV-visible spectrophotometer (UV-2600). Ultraviolet photoelectron spectroscopy (UPS) was performed using a Thermo Scientific ESCALab 250Xi with a He-discharged lamp (21.22 eV). The *C*-*V* characteristics of the Mott-Schottky analysis were measured by applying a low AC perturbation signal with a fixed frequency and sweeping the DC bias by the CHI650E electrochemical workstation. The morphology and microstructures were analyzed using SEM (Hitachi S-4800), and AFM (NT-MDT NTEGRA).

Fabrication of conventional OSCs

The device configuration was ITO/HTL/PM6:BTP-eC9/PFN-Br/Ag. The ITO substrates were cleaned with detergent, water, acetone and ethanol in an ultrasonic bath. After 30 min of ultraviolet-ozone treatment, PEDOT:PSS was spin-coated at 3000 rpm for 30 s on the ITO substrate, followed by thermal annealing for 15 min at 150 °C. PIDT-F and POM (weight ratio of 1 : 3) were dissolved in water. After being deposited, the films were annealed at 150 °C for 15 min. Subsequently, the active layer of the PM6:BTP-eC9 blend was spin-coated on the HTL from a solution with a polymer concentration of 8 mg mL⁻¹ and a PM6:BTP-eC9 ratio of 1 : 1.2 in chloroform/1,8-diiodoctane (0.5 vol%) mixed solvent at 3500 rpm for 30 s. The active layer was annealed at 100 °C for 10 min. Then, PFN-Br (dissolved in methanol with a concentration of 0.5 mg mL⁻¹) was spin-coated on the active layer. The devices were completed after the deposition of 100 nm Ag as a cathode. The 1 cm² devices were produced the same way as the spin-coated devices except that PIDT-F:POM was blade-coated on the ITO substrate.

Fabrication of inverted OSCs

The device configuration was ITO/ZnO/PM6:BTP-eC9/Al₂O₃/PIDT-F:POM/Ag. The ITO substrates were cleaned with detergent, water, acetone and ethanol in an ultrasonic bath. For sol-gel ZnO, the precursor was prepared by dissolving 0.1 g zinc acetate dihydrate and 28 μL ethanolamine in 1 mL methoxyethanol and aged for 24 h at room temperature. After 20 min of ultraviolet-ozone treatment, the precursor was spin-coated at 3000 rpm for 30 s on the ITO substrate, followed by thermal annealing for 50 min at 200 °C. Subsequently, the active layer of the PM6:BTP-eC9 blend was spin-coated on the ZnO from a solution with a polymer concentration of 7.5 mg mL⁻¹ and a PM6:BTP-eC9 ratio of 1 : 1.2 in chloroform/

1,8-diiodoctane (0.5 vol%) mixed solvent at 3000 rpm for 40 s. The active layer was annealed at 100 °C for 10 min. PM6:IT-4F (1 : 1) in a 20 mg mL⁻¹ chlorobenzene/1,8-diiodoctane (0.5 vol%) solution was spin-coated at 2000 rpm for 60 s, followed by annealing at 100 °C for 10 min. PTO2:IT-4F (1 : 1) in a 22 mg mL⁻¹ chlorobenzene/1,8-diiodoctane (0.5 vol%) solution was spin-coated at 1200 rpm for 60 s, followed by annealing at 100 °C for 10 min. PM6:Y6 (1 : 1.2) in a 16 mg mL⁻¹ chloroform/chloronaphthalene (0.5 vol%) solution was spin-coated at 2500 rpm for 40 s, followed by annealing at 100 °C for 10 min. PM6:D18:L8-BO (1 : 0.2 : 1.2) in a 15 mg mL⁻¹ chloroform/1,8-diiodoctane (0.25 vol%) solution was spin-coated at 3000 rpm for 40 s, followed by annealing at 85 °C for 5 min. Then Al₂O₃ dispersion (dissolved in isopropanol at a concentration of 0.4 mg mL⁻¹) was spin-coated on the active layer, followed by spin-coating the PIDT-F:POM (weight ratio of 1 : 3, dissolved in methanol). The details for optimization are summarized in Table S6 (ESI[†]). For other HTLs, PEDOT:PSS AI 4083 and NiO_x⁵¹ were spin-coated at 3000 rpm for 30 s in the atmosphere with annealing, while POM,⁵² PCP-2F-Li⁵³ and Me-2PACz⁵⁴ were spin-coated at 3000 rpm for 30 s in the glovebox without annealing. For the control device, 7 nm MoO₃ was thermally deposited on the active layer. The devices were completed after vacuum deposition of 100 nm of Ag as the anode.

Author contributions

Y. Y. and W. C. conceived this project and designed the experiments. W. C. supervised the project. Y. Y. fabricated and characterized the photovoltaic cells. M. C. and Z. J. helped with device characterizations. R. Z., X. H., H. L. and B. Z. offered suggestions about device optimization and characterizations. Y. Y. and W. C. drafted the manuscript. All authors participated in the discussions for manuscript preparation.

Data availability

The data supporting this article have been included as part of the ESI.[†]

Conflicts of interest

There are no conflicts to declare.

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