

High-Performance Inverted Organic Solar Cells via the Incorporation of Thickness-Insensitive and Low-Temperature-Annealed Nonconjugated Polymers as Electron Transport Materials

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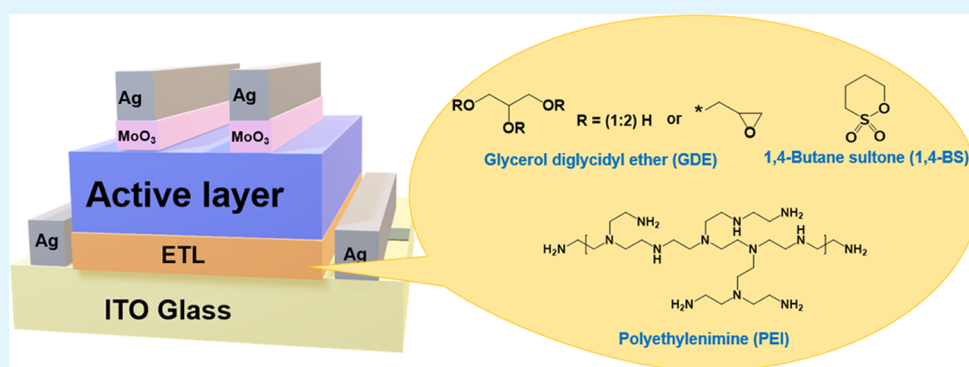
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ABSTRACT: Developing new electron transport layers has been an effective way to fabricate high-performance bulk-heterojunction organic solar cells (OSCs). Resolving the longstanding problems associated with commonly used zinc oxide (ZnO), such as electron traps and light-induced device deterioration, however, is still a great challenge. In this study, glycerol diglycidyl ether (GDE) and 1,4-butanedisulfone (BS) are blended with polyethylenimine (PEI) to produce cross-linkable PEI-based materials, PEI-GDE and PEI-GDE-BS, which can function as alternative electron transport layers to replace conventional ZnO cathode-modifying layers in inverted OSCs. PEI-GDE and PEI-GDE-BS are amenable to low-temperature annealing processes to produce cross-linked films. The inverted device structure of ITO/ETL/PM6:BTP-BO-4F:PC₇₁BM/MoO₃/Ag was used to evaluate the effects of incorporating PEI-GDE and PEI-GDE-BS as electron transport materials. Compared with ZnO-based devices, the PEI-GDE- and PEI-GDE-BS-based devices exhibit significant improvements in photovoltaic performances due to smoother surface roughness, higher charge collection and exciton dissociation efficiencies, higher electron mobilities, and stronger π - π interactions. In particular, a PEI-GDE-BS-based device shows an outstanding power conversion efficiency (PCE) of 17.55% with a V_{OC} of 0.83 V, a J_{SC} of 27.88 mA/cm², and an FF of 75.96%, which offers great possibilities in the applications of flexible solar cells.

KEYWORDS: BHJ OSCs, electron transport layer, inverted device structure, non-fullerene acceptors

INTRODUCTION

Organic solar cells (OSCs) demonstrate unique advantages in comparison with inorganic solar cells, such as light weight, low cost, and mechanical flexibility.^{1–6} To date, various strategies have been carried out to promote power conversion efficiencies (PCEs) of bulk-heterojunction (BHJ) OSCs above 19%,⁷ such as designing new active and interfacial materials, modifying device structures, and optimizing device processing parameters.^{8–14} Among various strategies, different electron transport layers (ETLs) have been introduced between indium tin oxide (ITO) electrodes and photoactive layers to improve device performances, especially for inverted OSCs.^{9,15} Moreover, for commercial applications, reducing electron traps is another key issue that needs to be addressed. ETL plays an important role in enhancing charge transfer to

cathodes. Zinc oxide (ZnO) is a commonly used ETL material because of its easy synthesis, high visible light transparency, and excellent electron mobility.^{16–19} ZnO, however, also has some drawbacks, such as surface vacancies and defects that could lead to charge loss. In addition, ZnO nanoparticle aggregation makes the ETL layers so rough that the aggregation sites become recombination centers.^{20–22} Fur-

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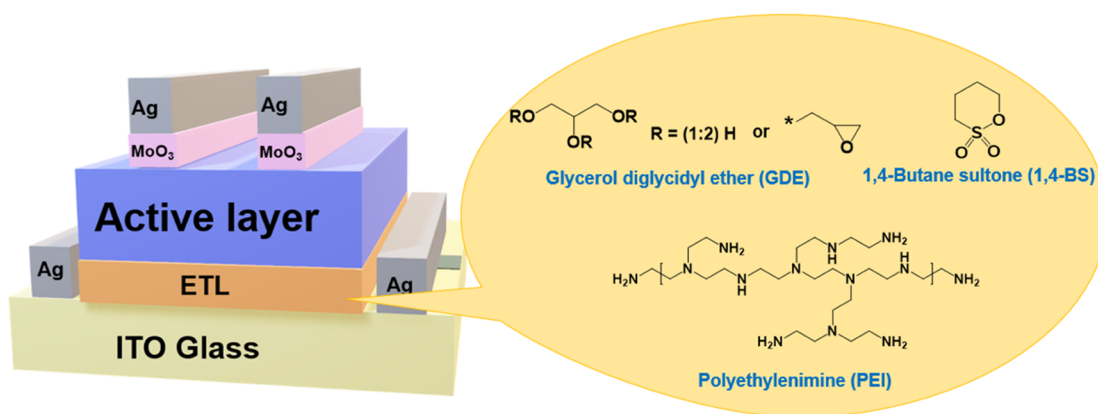


Figure 1. Schematic illustration of the inverted device architecture with chemical structures of the matrix materials of the electron transport layer.

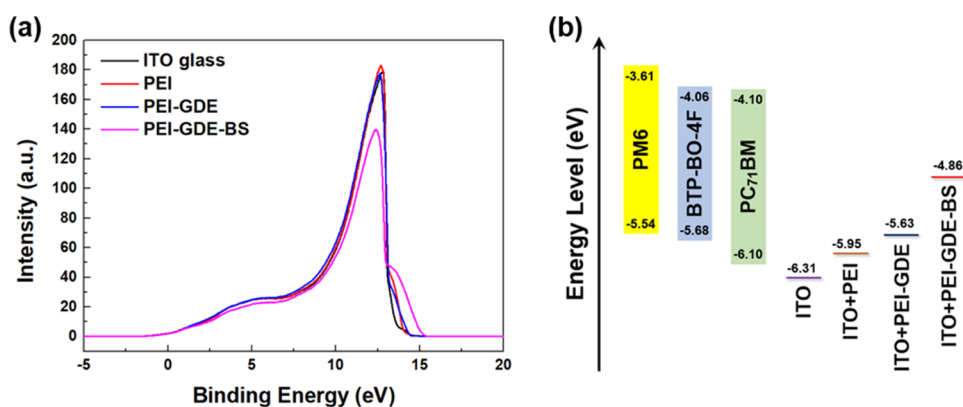


Figure 2. (a) UPS spectra of the ITO and ITO/ETLs. (b) Energy levels of the donor, acceptors, ITO, and ITO/ETLs.

thermore, the relatively high work function (WF) of metal oxide causes an energy barrier to transfer charge from active layers to electrodes, resulting in the reduced performances of the OSCs. Besides, ZnO is inherently brittle and tends to crack at high strains, which is detrimental to mechanical stability.^{23,24} To solve these problems, many strategies have been developed.^{25–35}

Recently, polyethylenimine (PEI) and polyethylenimine ethoxylated (PEIE) have been used as electron transport layers to resolve the problems of using ZnO layers.^{13,24,35–45} Bulliard et al. proposed an effective method based on amine groups to improve the performances of OSCs by controlling the surface energy.⁴³ Zhou et al. reported a method to coat the conductor surface with an ultrathin (1 to 10 nm) layer of polymers containing simple aliphatic amine groups (PEI/PEIE) to reduce the WF of conductors.³⁵ When the PEI/PEIE-based ETLs were applied to non-fullerene acceptors (NFAs), however, the PEI/PEIE-based devices performed worse than the ZnO-based devices. An “S” shape was observed in the current density–voltage (J – V) characteristics of the devices with PEI/PEIE-based ETLs due to the charge accumulation on the electrodes.^{44,45} For PEI/PEIE, electron lone pairs are responsible for destroying NFAs. Therefore, deactivating the lone electron pairs of the amine groups can effectively inhibit undesirable reactions between PEI/PEIE and NFAs. Xiong et al. proposed a strategy to protonate amine groups in PEIE to passivate the reactivity between the PEIE interfacial layer and the non-fullerene active layer.³⁹ The degree of protonation of PEIE can be adjusted by treating the polymer with different polar solvents, such as isopropanol,

ethanol, methanol, and water. Carbon dioxide (CO_2) and acetic and phosphoric acids were added into the aqueous PEIE solution to further increase its degree of protonation. On the other hand, chelation of amine groups with metal ions can also reduce the reactivity of lone electron pairs. Qin et al. suggested an approach to achieve chelation of PEI with Zn^{2+} by adding zinc acetate dihydrate to PEI solutions.⁴² Moreover, Prasetyo et al. introduced ethylenedithiol (EDT) between the PEIE layer and the active layer to reduce the reactivity between amine-rich groups and electron acceptors in ITIC-M.⁴¹ Zhang et al. used two other molecules 1,8-dibromooctane (DBO) and 1,8-dichlorooctane (DCO) quaternized PEIE to develop ETLs for OSCs.⁴⁰ These studies suggest that modifying PEI with other molecules is an effective strategy to inhibit the reactivity between the amine groups of ETLs and NFAs.

In this contribution, we investigated the effects of three ETLs, PEI, PEI-GDE, and PEI-GDE-BS, using PEI reacted with glycol diglycidyl ether (GDE) and 1,4-butanedisulfone (1,4-BS). These ETLs are used to replace the conventional electron transporting material, ZnO, which are also capable of reducing the WF of ITO for favorable electron transfer. The PEI-GDE-BS-based devices demonstrate the optimal device performances compared with those of ZnO-based devices due to higher exciton dissociation and charge collection efficiencies as well as the smoother surface roughness, stronger π – π interaction, and higher electron mobilities. The PCE of PEI-GDE-BS-based device with PM6:BTP-BO-4F:PC₇₁BM is 17.55% ($V_{\text{OC}} = 0.83$ V, $J_{\text{SC}} = 27.88$ mA/cm², and FF = 75.96%), while that of ZnO-based devices is 14.99% ($V_{\text{OC}} = 0.82$ V, $J_{\text{SC}} = 25.68$ mA/cm², and FF = 71.28%). The effective

and thickness-insensitive ETLs can be used in producing high-performance OSCs and potentially applicable for commercial roll-to-roll processing.

RESULTS AND DISCUSSION

The device structure and the materials for the three ETLs (PEI, PEI-GDE, and PEI-GDE-BS) are presented in Figure 1. PM6:BTP-BO-4F:PC₇₁BM is used to prepare the high-performance OSCs with inverted structures. The synthetic procedures for the three ETLs are provided in the Experimental Section. The three ETLs are soluble in highly polar solvents, such as water and butanol.

Figure S1 shows the ultraviolet–visible (UV–vis) absorption spectra of the three ETL solutions (PEI, PEI-GDE, and PEI-GDE-BS). The three polymers display their absorption in the range of 200–250 nm. It can be seen that the UV–vis absorption spectra of the three solutions have almost no absorption in the device measurement range (300–800 nm); thus, the ETLs have little effect on BHJ absorption. Ultraviolet photoelectron spectroscopy (UPS) is used to estimate the WF of ITO and ETL-modified ITO (Figure 2a), and the calculated WF values of ITO, ITO with PEI, ITO with PEI-GDE, and ITO with PEI-GDE-BS are 6.31, 5.95, 5.63, and 4.86 eV, respectively, as summarized in Table 1. Compared with ITO

glass are more in line with the energy levels of the acceptors, allowing more efficient charge transfer.

To investigate the surface morphology of the aforementioned ETLs, atomic force microscopy (AFM) in tapping mode is also used. Figure 3 shows the AFM height images of ETL films and ETL with active layer (AL) blends. Compared with the AFM image of ZnO, the PEI-GDE and PEI-GDE-BS images exhibit smooth morphologies with lower root-mean-square roughness (R_q) values; the R_q values of ZnO, PEI-GDE, and PEI-GDE-BS films are 8.25, 1.73, and 1.59 nm, respectively. Similar trends are also observed for ETL with AL blends. Compared with the AFM image of ZnO with AL, the PEI-GDE with AL and PEI-GDE-BS with AL images exhibit smooth morphologies with lower root-mean-square roughness (R_q) values; the R_q values of ZnO with AL, PEI-GDE with AL, and PEI-GDE-BS with AL films are 3.54, 1.41, and 1.28 nm, respectively. The results demonstrate that the surface roughnesses of the active layers are effectively reduced using PEI-based polymeric ETLs. In this way, when the active layers are coated on the ETL layers, the smoother roughness indicates that the compatibility between the organic materials is better than that between the organic and inorganic materials (ZnO), enhancing the performances of the devices.

To study the effects of the three ETLs (PEI, PEI-GDE, and PEI-GDE-BS) on the photovoltaic performances, BHJ OSC devices are prepared using inverted structures of ITO/ZnO or ETL/PM6:BTP-BO-4F:PC₇₁BM/MoO₃/Ag. Estimated by AFM, the thicknesses of the ETLs are measured to be ~5 nm. Figure 4a displays the current density–voltage (J – V) plots of the optimized OSC devices under the condition of AM 1.5G illumination (100 mW/cm²), and Table 2 summarizes the optimized photovoltaic device performances. Average PCE for each type is calculated from over 10 devices. The ZnO-based device with PM6:BTP-BO-4F:PC₇₁BM shows a PCE of 14.99% (V_{OC} = 0.82 V, J_{SC} = 25.68 mA/cm², and FF = 71.28%). Meanwhile, PEI-GDE- and PEI-GDE-BS-based devices exhibit enhanced photovoltaic performances. On the whole, the PEI-GDE-BS-based device achieves the best

Table 1. WF Values (ϕ) of ITO and ITO/ETLs

	ITO	ITO with PEI	ITO with PEI-GDE	ITO with PEI-GDE-BS
ϕ (eV)	6.31	5.95	5.63	4.86

devices, the WF of ITO/ETL is lower due to the polarity of the terminal groups on the ETLs. Inferred from the WF values, the energy levels of the three materials can be obtained, as listed in Figure 2b. When the energy levels between the acceptors and the ETLs are closer, the electron transfer is smoother. By reducing the WF values, the energy levels of the coated ITO

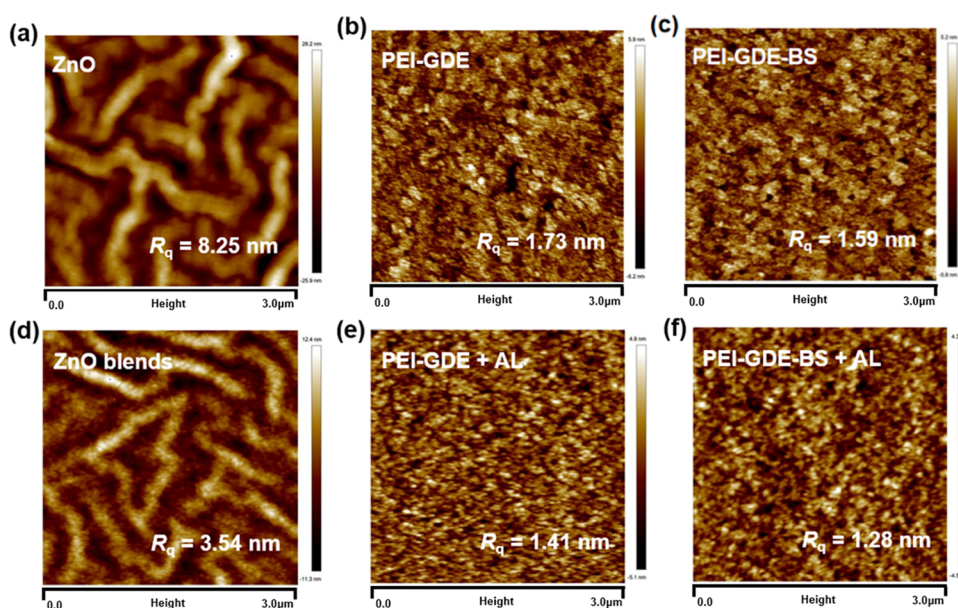


Figure 3. AFM height images of (a–c) ZnO, PEI-GDE, and PEI-GDE-BS films and (d–f) ZnO with the active layer (AL), PEI-GDE with AL, and PEI-GDE-BS with AL.

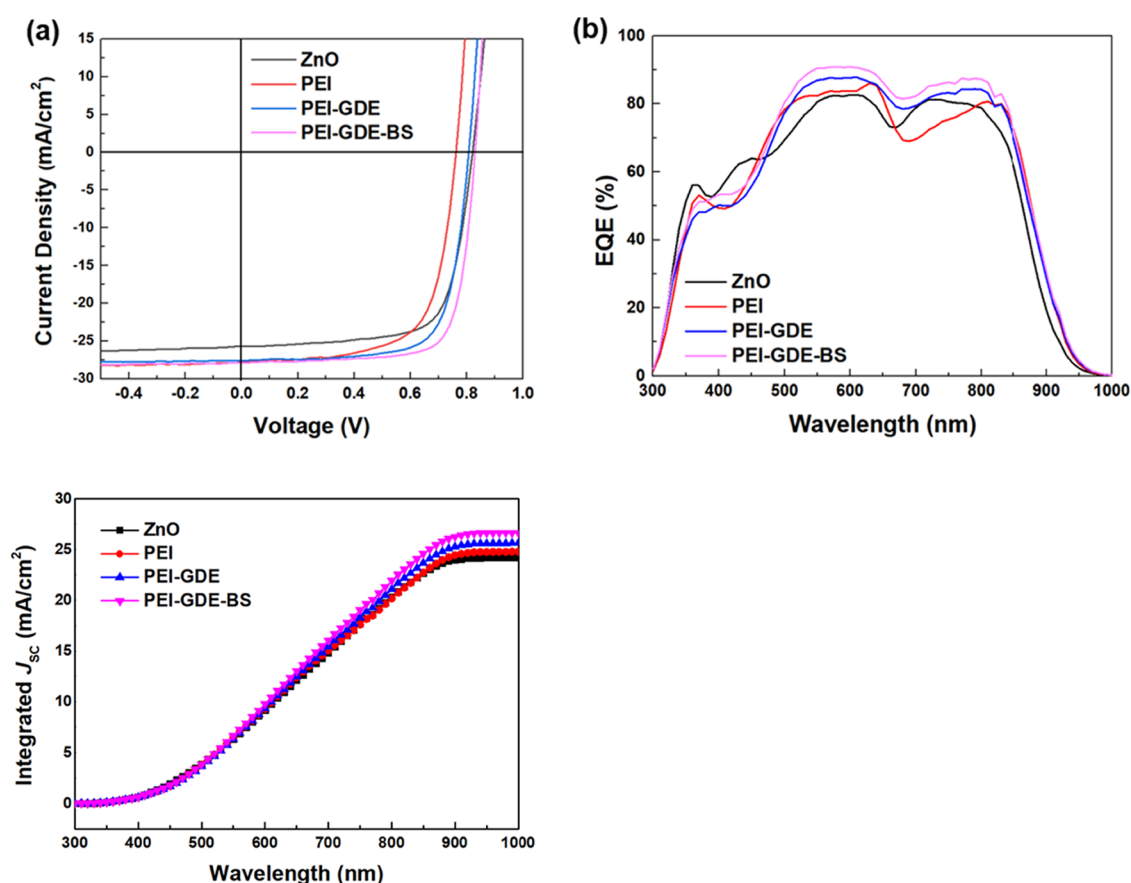


Figure 4. (a) J - V curves, (b) IPCE spectra, and (c) integrated J_{sc} values of PM6:BTP-BO-4F:PC₇₁BM blends with different ETLs.

Table 2. Optimized Device Performances of PM6:BTP-BO-4F:PC₇₁BM Blends with Different ETLs for Inverted BHJ OSCs under the Condition of AM 1.5G Illumination (100 mW/cm²)^a

BHJ film	ETL	V_{OC} (V)	J_{sc} (mA/cm ²)	$J_{cal.}$ (mA/cm ²)	FF (%)	PCE (%)	PCE _{avg.} (%)
PM6:BTP-BO-4F:PC ₇₁ BM	ZnO	0.82	25.68	24.19	71.28	14.99	14.99 ± 0.10
	PEI	0.79	27.34	24.77	65.69	14.27	14.24 ± 0.09
	PEI-GDE	0.81	27.59	25.61	72.88	16.21	16.15 ± 0.22
	PEI-GDE-BS	0.83	27.88	26.65	75.96	17.55	17.56 ± 0.10

^aAverage PCE for each type is calculated from over 10 devices.

Table 3. Device Performances of PM6:BTP-BO-4F:PC₇₁BM Blends Using PEI-GDE-BS with Different Spin-Coating Rates as the ETL for Inverted BHJ OSCs under the Condition of AM 1.5G Illumination (100 mW/cm²)

ETL	ETL spin-coating condition	V_{OC} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	R_s (ohm cm ²)	R_{sh} (ohm cm ²)
PEI-GDE-BS	2000 rpm/30 s	0.82	28.03	75.86	17.33	4.10	3491.6
	3000 rpm/30 s	0.82	28.28	75.78	17.45	4.06	5008.2
	4000 rpm/30 s	0.81	28.00	75.98	17.23	3.75	1850.1
	5000 rpm/30 s	0.80	28.21	76.14	17.26	3.26	1168.4
	6000 rpm/30 s	0.81	28.37	75.53	17.36	3.85	1122.2
	7000 rpm/30 s	0.81	28.04	75.86	17.23	3.77	898.1
	8000 rpm/30 s	0.81	28.10	75.81	17.27	3.80	505.4

photovoltaic performance; the PCE of the optimal device is 17.55% (V_{OC} = 0.83 V, J_{sc} = 27.88 mA/cm², and FF = 75.96%). The enhancement in PCE of the PEI-GDE-BS devices is mainly due to the improvement in J_{sc} and FF, caused by better Ohmic contacts between the active layer and the electrodes.

The results of the photovoltaic performances are consistent with the predictions of the AFM results. The lower roughnesses indicate that the top surfaces of the ETLs (PEI-

GDE and PEI-GDE-BS) are more homogeneous than the ZnO layer, thus reducing recombination losses. The lower roughnesses also contribute to better contact with the active layer, which facilitates effective electron extraction from the corresponding device and thus improves device performance. Figure 4b,c shows the external quantum efficiency (EQE) spectra and the integrated J_{sc} plots of the optimized devices with PM6:BTP-BO-4F:PC₇₁BM blends. Besides, Table 2 summarizes the J_{sc} values calculated from the EQE data.

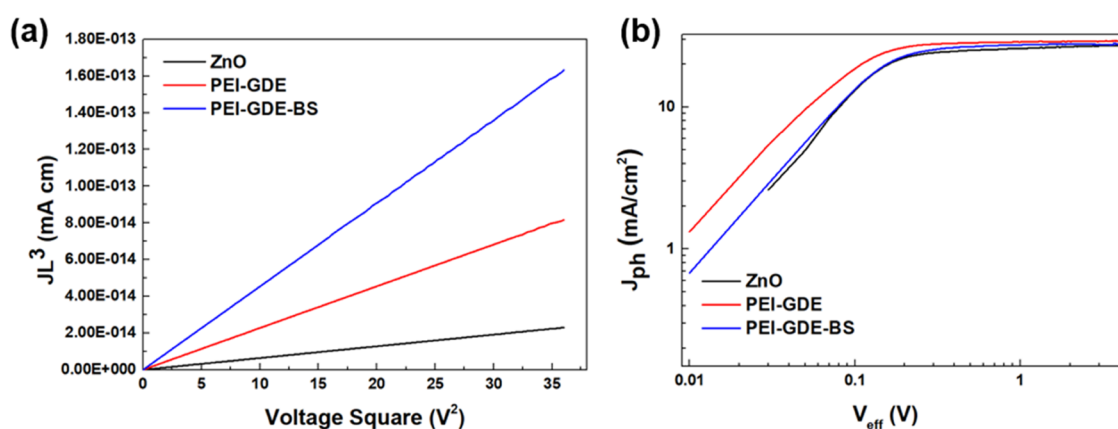


Figure 5. (a) Space-charge-limited current (SCLC) diagram and (b) J_{ph} – V_{eff} curves of PM6:BTP-BO-4F:PC₇₁BM blends with different ETLs.

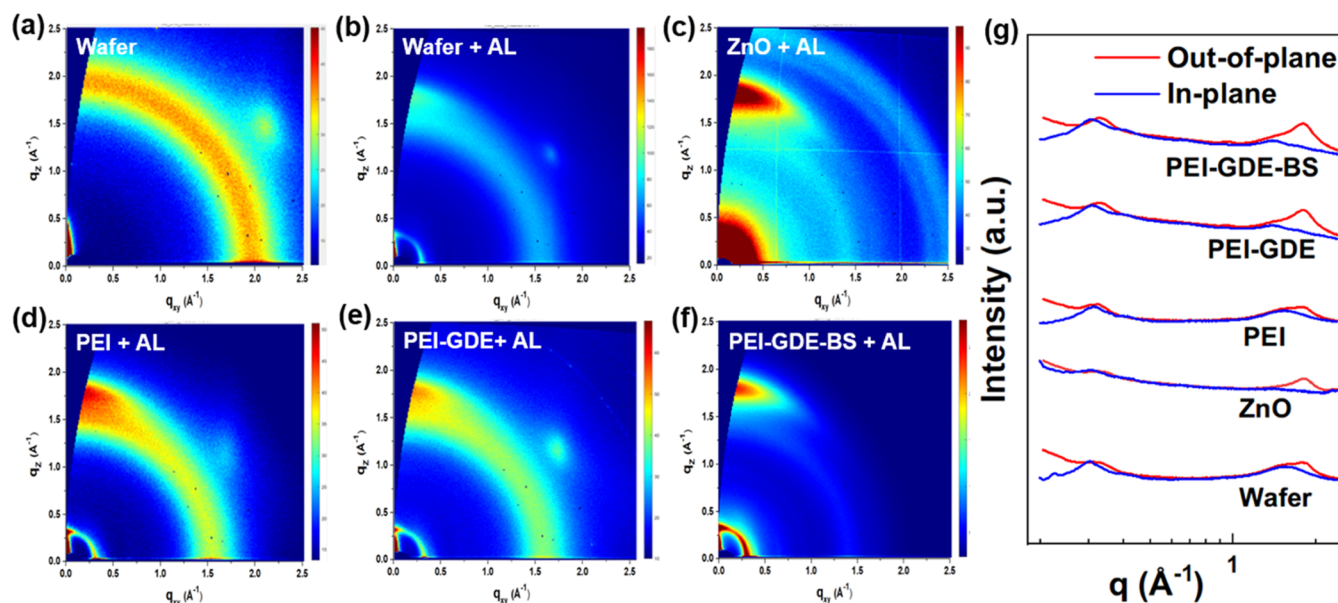


Figure 6. 2D GIWAXS patterns of (a) wafer and active layer films coated on (b) wafer-only, (c) ZnO, (d) PEI, (e) PEI-GDE, and (f) PEI-GDE-BS layers. (g) 1D GIWAXS profiles for out-of-plane (OOP) and in-plane (IP) directions of active layer films coated on wafer-only, ZnO, PEI, PEI-GDE, and PEI-GDE-BS layers.

Compared with the results of the ZnO-based devices, the EQE values of the PEI-GDE- and PEI-GDE-BS-based devices with PM6:BTP-BO-4F:PC₇₁BM photoactive blends are higher in the range of 500–1000 nm. The increased EQE values also contribute to the J_{SC} improvements of the PEI-GDE- and PEI-GDE-BS-based devices. Moreover, devices based on PEI-GDE-BS with different thicknesses are prepared by changing the spin-coating rates. As summarized in Table 3, similar photovoltaic device performances are observed, demonstrating the thickness insensitivity of the ETL layers.

To further examine the charge transfer characteristics of PM6:BTP-BO-4F:PC₇₁BM blends with different ETLs, space-charge-limited current (SCLC) measurements are conducted, as shown in Figure 5a. Based on the electron-only device structure of ITO/ETL/active layer/Ag, the electron mobilities (μ_e) of ZnO-, PEI-GDE-, and PEI-GDE-BS-based devices with PM6:BTP-BO-4F:PC₇₁BM blends are calculated to be 1.83×10^{-4} , 6.52×10^{-4} , and $1.30 \times 10^{-3} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. Electron transfer becomes more efficient because the good contact with the active layer reduces the energy barrier of charge carrier extraction. Using PEI-GDE and PEI-GDE-BS as

ETLs, the devices with PM6:BTP-BO-4F:PC₇₁BM exhibit higher electron mobilities, which is also consistent with the higher FF and is similar to the trend of increased J_{SC} in the ITO/ETL/active layer/MoO₃/Ag devices.

Figure 5b reveals the J_{ph} – V_{eff} curves of the ZnO-, PEI-GDE-, and PEI-GDE-BS-based devices with PM6:BTP-BO-4F:PC₇₁BM blends. The exciton dissociation values of the ZnO-, PEI-GDE-, and PEI-GDE-BS-based devices are estimated to be 95.98, 99.08, and 98.69%, respectively. In addition, the charge collection values of the ZnO-, PEI-GDE-, and PEI-GDE-BS-based devices are estimated to be 85.95, 86.93, and 91.74%, respectively. The data demonstrate that using PEI-GDE and PEI-GDE-BS as ETLs can improve the exciton dissociation and charge collection efficiencies of the devices, significantly enhancing the J_{SC} and FF. To understand the carrier recombination mechanism in the diode, we measure the V_{OC} values of the devices at different light intensities based on ZnO, PEI-GDE, and PEI-GDE-BS, as shown in Figure S2. The results show that the ideal factor (n) of the PEI-GDE-BS-based device is much smaller than the n value of the ZnO-based device. Good film morphology and low defect density

make the FF value of the PEI-GDE-BS-based device as high as 75.96%.

To achieve more in-depth understanding in the role of the PEI-based ETLs, grazing-incidence wide-angle X-ray scattering (GIWAXS) experiments are conducted, as displayed in Figure 6. The one-dimensional (1D) profiles for out-of-plane (OOP) and in-plane (IP) directions are also obtained to investigate the intermolecular π - π interactions and horizontal lamella interactions, as shown in Figure 6g. In the out-of-plane direction, the π - π stacking signals for the PEI-GDE- and PEI-GDE-BS-based devices are stronger than those for the ZnO-based devices, indicating that the PEI-based ETLs can improve the face-on alignments than ZnO.

CONCLUSIONS

In conclusion, we apply three ETLs using polyethylenimine (PEI), glycol diglycidyl ether (GDE), and 1,4-butanediol (1,4-BS) for BHJ OSCs. The devices are prepared with PM6:BTP-BO-4F:PC₇₁BM with inverted structures. The photovoltaic properties and BHJ arrangements of the PEI-GDE- and PEI-GDE-BS-based devices are compared with the ZnO devices. The PEI-GDE-BS-based devices demonstrate the optimal device performances compared with those of ZnO-based devices caused by lower WF_s, smoother surface roughness, higher charge collection and exciton dissociation efficiencies, higher electron mobilities, and stronger π - π interactions. In terms of device performances, the PEI-GDE-BS-based device exhibits the highest PCE of 17.55% in comparison with the ZnO-based device, which shows a PCE of 14.99%. The promising and thickness-insensitive ETLs with the advantages of low-temperature processing have great potentials for the industrial production of OSCs in the future.

EXPERIMENTAL SECTION

Materials and Instruments. The polymer donor (PM6) was bought from Ossila Ltd., and NFAs (BTP-BO-4F and PC₇₁BM) were provided by Ways Technical Co. Polyethylenimine (PEI) with the M_w = 25,000 g/mol and 1,4-butanediol (1,4-BS) were bought from Sigma-Aldrich. Diglycidyl ether (GDE) was bought from Combi-Blocks. The organic solvents, including *o*-xylene, chlorobenzene, and 1,8-diiodooctane (DIO) were obtained from Merck. The UPS spectra were recorded using an ESCALAB Xi⁺ from Thermo Fisher Scientific. The AFM film morphology images were measured using a Veeco MultiMode in tapping mode. The two-dimensional (2D) GIWAXS measurements were conducted at the TPS25A beamline in the National Synchrotron Radiation Research Center (NSRRC). The absorption spectra were measured using an HP8453 UV-vis spectrophotometer.

Preparation of PEI-Based ETL Solutions. *PEI ETL Solution.* PEI (1 g) was dissolved in 37 mL of 1-butanol and stirred at 80 °C for 12 h. The solution was then diluted to 0.05 wt % with deionized water.

PEI-GDE ETL Solution. PEI (1 g) and GDE (0.25 g) were dissolved in 37 mL of 1-butanol and stirred at 80 °C for 12 h. A few drops of phosphoric acid were added to the reaction mixture, and the reaction mixture was then diluted to 0.05 wt % (with respect to the weight of reagents added) with deionized water. The final pH was 7.5.

PEI-GDE-BS ETL Solution. PEI (1 g), GDE (0.25 g), and 1,4-BS (0.25 g) were dissolved in 37 mL of 1-butanol and stirred at 80 °C for 12 h. A few drops of phosphoric acid were added, and the reaction mixture was then diluted to 0.05 wt % with deionized water. The final pH was 7.5.

Fabrication of Inverted OPV Devices. BHJ OSCs were prepared using inverted device structures of ITO/ETL/PM6:BTP-BO-4F:PC₇₁BM/MoO₃/Ag. Detergent water, deionized water, acetone, and 2-propanol in an ultrasonic water bath were used subsequently (15 min for each step) to clean the indium tin oxide

(ITO) glass substrates. Afterward, the cleaned substrates were dried by N₂ gas and shone with UV-ozone for 25 min. Ethanolamine (0.28 mL) and zinc acetate dihydrate (1 g) were dissolved in 2-methoxyethanol (10 mL) and stirred for 3 h to prepare the ZnO precursor solution. The ZnO precursor solution was deposited on the cleaned ITO glass substrates by spin-coating at 4000 rpm for 30 s and then thermal annealing at 180 °C for 25 min. The PEI, PEI-GDE, and PEI-GDE-BS solutions were deposited on the cleaned ITO glass substrates by spin-coating at 3000 rpm for 30 s and then thermal annealing at 120 °C for 5 min. The PM6:BTP-BO-4F:PC₇₁BM (1:1.2:0.4) blends were fully dissolved in *o*-xylene at a total weight concentration of 20.8 mg mL⁻¹, and 1,8-diiodooctane (DIO) at a 0.5% volume concentration was used as the solvent additive. The BHJ active layer solution (PM6:BTP-BO-4F:PC₇₁BM) was spin-coated on top of the ETL layers at 1600 rpm for 30 s and thermally annealed at 100 °C/10 min. Finally, MoO₃ (7 nm) and Ag (100 nm) were sequentially deposited on top of the BHJ active layer by thermal evaporation at 3.7×10^{-7} mbar through a shadow mask. The photoactive area of each BHJ unit was 0.04 cm².

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsami.2c18946>.

UV-vis spectra and light intensity curves of ETLs (PDF)

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Notes

The authors declare no competing financial interest.

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