High performance organic solar cells based on ZnO: POT2T as an effective cathode interfacial layer

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Abstract. Interface engineering in organic solar cells (OSCs) plays an important role in improving electron extraction and suppressing carrier recombination. In this article, the improvement of device was achieved by doping POT2T into ZnO as a new electron transport layer (ETL). For PTB7-Th: PC71BM system, the device fabricated by using ZnO as ETL achieved a PCE of 9.03% with a JSC of 17.33 mA/cm², a VOC of 0.783V and a FF of 64.17%. After doping 5wt% POT2T in ZnO, the JSC increased to 18.01 mA/cm² and the FF increased slightly to 69.87%, as a result, the PCE increased to 9.84% with about 10% enhancement. The enhancement is attributed to the improved electron transport and conductivity, optimized ZnO surface morphology after adding POT2T, resulting in higher JSC and FF. Therefore, doping POT2T into ZnO as an ETL is a simple and effective method for obtaining high efficient OSCs.

1. Introduction
In the past few decades, organic solar cells (OSCs) have been widely studied because of their simple fabrication process, light weight, transparent, and large-area preparation, which is expected to become a clean and renewable energy source. [1-4] recently, the power conversion efficiency (PCE) over 16% had been achieved, both bulk-heterojunction (BHJ) and tandem devices. [12, 18] The enhancement of PCE is mainly due to synthesising new donor/acceptor materials, optimizing morphology of active layer, developing interface engineering, or improving device structure and device fabrication processes. [5-9, 16, 17] The main efficiency of devices is indeed dominated by the active layer, but on the other hand, the interface material between the active layer and the electrode is also important in determining device performance. Because they facilitate the efficient extraction of carriers from the active layer to electrodes, reduce charge recombination and exciton quenching. [2, 4] Therefore, it is necessary to deeply research on the transport layer in order to improve the performance of devices.

Inverted structure is a commonly device structure used in OSCs, the most important part of inverted structure is the electron transport layer (ETL). [1, 10] At present, many materials as ETL have been developed, of which, ZnO was become the most commonly used ETL because of its high transparency, matched energy levels and environmental stability. However, ZnO also has some disadvantages, including the slow charge transfer, surface defects leading to charge loss and relatively low conductivity, which leads increased barriers to charge collection by the electrodes. [3, 11, 19] The researchers solved these disadvantages by inserting a buffer layer between ZnO and the active layer or doping in ZnO. [6-8, 13-15] For the two solutions mentioned above, the latter preparation process is relatively simple.
In this study, we doped POT2T into ZnO as a new ETL. We proved that it is an effective strategy to improve device efficiency. In this study, we doped POT2T into ZnO as a new ETL and proved it is an effective strategy to improve device efficiency. We fabricated inverted devices by using poly (4,8-bis (5-(2-ethylhexyl) thiophen-2-yl)-benzo [1,2-b:4,5-b’] dithiophene-2,6-diyl-alt-(4-(2-ethylhexyl)-3-fluoro-thieno [3, 4-b] thiophene-) -2-carboxylate-2-6-diyl): [6, 6]-phenyl-C71-butyric acid methyl ester (PTB7-Th: PC71BM) as the active layer. The results show that PCE of the device doped with POT2T in ZnO is increased from 9.03% to 9.84%, compared to the device with ZnO as ETL. The improvement of performance is mainly due to the better JSC and FF. It can be seen by scanning electron microscopy (SEM) and atomic force microscopy (AFM) that after adding POT2T, the surface defects of ZnO are decreased, thereby reducing the charge loss. On the other hand, we also demonstrated that the addition of POT2T into ZnO increased the conductivity and allowed electrons to be efficiently transported from the active layer to the electrode.

2. Experimental Part

2.1. Fabrication of Organic Solar Cells

Organic Solar Cells were fabricated with traditional inverted structure, as shown in Figure 1a, and the molecular structure of the material involved in the experiment was shown in Figure 1b. ITO glass was cleaned in sonication of water, ethanol, acetone and ethanol, sequentially, and finally treated in UV/ozone for 30min. ETL was prepared by adding different concentration POT2T into ZnO precursor solution and then spin-casting onto the ITO glass. By dissolve PTB7-Th: PC71BM (weight ratios of 1:1.5) in CB solvent at PTB7-Th concentration is 10mg/ml. Then, this mixture solution with 3%DIO was spin-coated on the ETL to form active layers. The thickness of active layers is about 100 nm. Finally, the hole transport layer (HTL) of 10 nm MoO₃ and electrode of 150 nm Ag was sequentially deposited under vacuum (10⁻⁶ Torr).

![Figure 1. (a) Inverted structure of OSCs. (b) The molecular structure of the material involved in this study.](image)

2.2. Measurements of Organic Solar Cells

The J-V test was measured under AM 1.5G light by using a Keithley 2400 source-measure unit and a Newport Oriel Sol3A solar simulator. The thickness of devices as measured through an AMBIOS-XP2 step profilometer. Effect of ETL on the morphology of active layers were found by AFM and SEM. The external quantum efficiency (EQE) spectrum was carried out by using QEX10 Quantum Efficiency Measurement System (PV Measurements, Inc.).

3. Results and discussion

Under the same conditions, the HOMO/LUMO levels of the donor PTB7-Th and acceptor PC71BM were measured by cyclic voltammetry (CV). Figure 2a shows the energy levels of material that used in this study. The HOMO and LUMO of PTB7-Th are -5.2 eV and -3.6 eV respectively, and of PC71BM
are -6.0 eV and -4.0 eV respectively. Energy level matching between PTB7-Th and PC71BM facilitates electron and hole transport. We also calculated the HOMO offset and LUMO offset between the donor polymer and the acceptor based on the energy levels, the HOMO and LUMO offset is approximately 0.8 eV and 0.4 eV, respectively, which facilitated charge dissociation in organic solar cells. Therefore, we selected PTB7-Th, PC71BM as the active layer material, and used UV-visible spectrometer to characterize the optical properties of PTB7-Th, PC71BM. The UV-visible spectrum of the neat film is shown in Figure 2b. It can be seen from the absorption spectrum that the donor absorption is complementary to the acceptor absorption, which increased the absorption of incident light by the active layer in the visible region.

Figure 2. (a) Energy level diagram of the ETL, donor and acceptor. (b) Absorption spectra of neat films.

Figure 3a illustrates the J-V curves of devices based on different ETL and the relevant detailed performance parameters are summarized in Table 1. From Table 1, it can be found that devices without POT2T (i.e. for the reference OSC) exhibited the low PCE of 9.03%, a JSC of 17.33 mA/cm², a VOC of 0.783V and a FF of 64.17% was obtained. As expected, the performance of OSCs was significantly improved through incorporating POT2T into ZnO. When adding 2.5wt% POT2T, the JSC increased to 17.84 mA/cm² and the FF also increased to 67.85%, resulting in a PCE of 9.44%. With the doping of POT2T was further increased to 5wt%, the JSC and the FF still increased, up to 18.01 mA/cm² and 69.87%, respectively, a maximum PCE of 9.84% was obtained. We observed a significant improvement in JSC and FF after doping POT2T in ZnO, but the VOC did not change significantly. It is well known that the VOC are primarily determined by the interface buffer layer, electrodes, and the energy level offset between holes and electrons transport channels. In our experiments, the interface buffer layer is an only variable, but VOC not changed significantly. That indicated doping a small amount of POT2T has little effect on the energy level. To summary, by introducing POT2T into ZnO as ETL, efficient OSCs were achieved, resulting in improvement of the PCE compared with control OSCs.

Table 1. The relevant detailed performance parameters of OSCs

|     | VOC [V] | JSC [mA cm⁻²] | FF [%] | PCE [%] |
|-----|---------|---------------|--------|---------|
| Pure | 0.783   | 17.33         | 64.17  | 9.03    |
| 2.5wt% | 0.780   | 17.84         | 67.85  | 9.44    |
| 5wt%  | 0.783   | 18.01         | 69.87  | 9.84    |
| 10wt% | 0.786   | 16.48         | 69.88  | 9.06    |

In order to further verification, we measured the EQE spectrum. The EQE curves was shown in Figure 3b. We calculated the current value by EQE spectral integration, which is within 5% error compare with the current value we had tested. Compared to the control device, we can see that the EQE curves of the device is significantly increased by incorporating POT2T into ZnO. When adding 5wt% POT2T, the EQE spectrum shows a very high value in the range of 450 to 860 nm, exceeding 80%.
higher EQE value for the PTB7-Th: PC71BM-based device doped with 5wt% POT2T in ZnO coincides with its measured higher JSC under 1 sun illumination.

![Figure 3](image3.png)

To illustrate the effect of doped POT2T on exciton dissociation and charge collection, we measured the photocurrent density (Jph) plotted versus effective voltage (Veff) for OSCs with and without POT2T in Figure 4b. Jph is equal to JL-JD, where JL is the photocurrent density and JD is the dark current density. Veff is equal to V0-VA, where V0 is the corresponding voltage when Jph is equal to 0, VA is the actual applied voltage. The exciton dissociation efficiency can be evaluated by Jph/Jsat, where Jph is the value under short circuit conditions. Charge collection efficiency can also be assessed by Jph/Jsat, where Jph is the value at maximum power output. Via calculations, the exciton dissociation efficiencies of the devices with 0%, 1wt%, 5wt%, 25wt% POT2T are 94.1%, 94.6%, 95.6% and 95.5% respectively, and the charge collection efficiencies are 75.5%, 75.5%, 77.7% and 80.4% respectively. These results show that doping POT2T in ZnO as ETL could simultaneously improve exciton dissociation efficiency and charge collection efficiency. That means the recombination loss can be reduced, which is beneficial to obtain higher JSC and FF values.

We fabricated devices of ITO/ETL/AL structure to illustrate the effect of doping POT2T into ZnO on conductivity, as shown in Figure 4a. The slope of the J-V characteristic curve represents the conductivity of the devices. Obviously can be seen, when ZnO is used as ETL, the slope value of devices is lower. After doping POT2T, the slope is significantly increased, which means higher conductivity is obtained. Doping 5wt% POT2T, the conductivity is the largest. Based on the above results, it can be concluded that the doping of an appropriate concentration POT2T allows ETL to obtain higher electron mobility, thereby increasing JSC.

![Figure 4](image4.png)
In order to obtain more insight into the effect of the device doped POT2T on the charge recombination process, the J-V curves at various light illumination intensity were measured. The dependence of JSC and VOC on light intensity is depicted in Figure 5a and b, respectively. We can evaluate the situation of charge recombination from the slope of relationship curve between JSC and Plight. If the slope is close to 1, it means that the bimolecular recombination is weak. For OSCs with 0%, 2.5wt%, 5wt%, 10wt% POT2T, the slope of the JSC and Plight characteristics (on a double logarithmic scale) were 0.96, 0.97, 0.97 and 0.97, respectively. These results suggested that doping POT2T can partially inhibit bimolecular recombination, which is consistent with the increased JSC of the devices with POT2T. If the slope of the VOC and Plight characteristics (The abscissa scale is the natural logarithm) is close to kT/q, then bimolecular recombination dominates. When the slope is close to 2kT/q, indicated trap-induced charge recombination is the primary process of the devices. From Figure 5b, the slopes of devices without and with 2.5wt%, 5wt%, 10wt% POT2T were calculated to be 1.466kT/q, 1.315kT/q, 1.241kT/q and 1.184kT/q, respectively. Compared to the slope of control device, the reduced slope of devices when adding POT2T in ZnO as an ETL indicates trap-induced charge recombination was suppressed.

Figure 5. Light intensity dependence of (a) VOC and (b) JSC of devices without or with different doping concentration POT2T.

Figure 6. AFM images of ZnO doped with (a) 0wt% POT2T and (b) 5wt% POT2T, the image size is 5×5 um; SEM images of ZnO doped with (c) 0wt% POT2T and (d) 5wt% POT2T.
The surface free energy of ETL has great influence on the formation of active layer. By measuring the contact angle of two different solvents, the surface free energy of ZnO was calculated to be 33.18 mN/m. When 5wt% POT2T was added in ZnO, the surface free energy increased to 40.21 mN/m, which is closer to the value of organic active layers. The results suggested that the active layer solvents would form better contact on ZnO: POT2T than ZnO layers. Furthermore, AFM tests were used to study the effect of POT2T on ETL morphology. Figure 6 (a) and (b) show the height images of ZnO and ZnO: POT2T based films. The morphology can be seen from these images. The film containing POT2T formed a more uniform network structure than that of ZnO film. Good surface morphology guarantees ETL coverage and benefits interface contact. The result is agreed well with film surface free energy. The roughness of ZnO film is 1.41 nm, which is slightly lower than that of the film doped with 5wt% POT2T (1.66 nm). The higher film surface roughness is beneficial to active layer adhesion. Similarly, the SEM measurements also presented same results with AFM. These results indicate that adding proper concentration of POT2T could improve the morphology of ZnO film, which is conducive to promote charge transport and achieve high JSC and FF in OSCs.

4. Conclusion
In summary, POT2T was introduced into ZnO to form a new ETL. Based PTB7-Th: PC71BM OSCs, the advantages of doping POT2T in ZnO layer were studied. The experimental results show that after doping with POT2T, the conductivity of ETL is improved, and the defects of ZnO surface are reduced, which is beneficial to obtain higher electron mobility and charge extraction. When doped with 5wt% POT2T in ZnO as ETL, a PCE of the device increases to 9.84%, which is a significant improvement compare with ZnO as ETL (PCE=9.03%). We believe that doping an appropriate amount of POT2T in ZnO can be used as an effective ETL to fabricate efficient and low-cost OSCs.

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References
[1] J. Cheng, H. Zhang, Y. Zhao, J. Mao, C. Li, S. Zhang, K.S. Wong, J. Hou, W.C.H. Choy, Self-Assembled Quasi-3D Nanocomposite: A Novel p-Type Hole Transport Layer for High Performance Inverted Organic Solar Cells, Adv. Funct. Mater. (2018), 1706403.
[2] S.B. Dkhil, D. Duché, M. Gaceur, A.K. Thakur, F.B. Aboura, L. Escoubas, J.-J. Simon, A. Guerrero, J. Bisquert, G. Garcia-Belmonte, Q. Bao, M. Fahlman, C. Videlot-Ackermann, O. Margeat, J. Ackermann, Interplay of Optical, Morphological, and Electronic Effects of ZnO Optical Spacers in Highly Efficient Polymer Solar Cells, Adv. Energy Mater. 4 (2014), 1400805.
[3] R.T. Ginting, C.C. Yap, M. Yahaya, M. Mat Salleh, Improvement of inverted type organic solar cells performance by incorporating Mg dopant into hydrothermally grown ZnO nanorod arrays, J. Alloys Compd. 585 (2014), 696-702.
[4] J. Huang, J.H. Carpenter, C.Z. Li, J.S. Yu, H. Ade, A.K. Jen, Highly Efficient Organic Solar Cells with Improved Vertical Donor-Acceptor Compositional Gradient Via an Inverted Off-Center Spinning Method, Adv. Mater. 28 (2016), 967-974.
[5] J. Huang, C.-Z. Li, C.-C. Chueh, S.-Q. Liu, J.-S. Yu, A.K.Y. Jen, 10.4% Power Conversion Efficiency of ITO-Free Organic Photovoltaics Through Enhanced Light Trapping Configuration, Adv. Energy Mater. 5 (2015), 1500406.
[6] Z.N. Kayani, E. Abbas, Z. Saddique, S. Riaz, S. Naseem, Photocatalytic, antibacterial, optical and
magnetic properties of Fe-doped ZnO nano-particles prepared by sol-gel, Mater. Sci. Semicond. Process. 88 (2018), 109-119.

[7] J.K. Lee, W.L. Ma, C.J. Brabec, J. Yuen, J.S. Moon, J.Y. Kim, K. Lee, G.C. Bazan, A.J. Heeger, Processing Additives for Improved Efficiency from Bulk Heterojunction Solar Cells, J. Am. Chem. Soc. 130 (2008), 3619-3623.

[8] J. Li, J. Liu, J. Zhang, J. Ma, Y. Hu, G. Xie, J. Zhang, G. Tu, Efficient non-fullerene organic solar cells based on thickness-insensitive conjugated small molecule cathode interface, Sol. Energy 191 (2019), 219-226.

[9] H.-C. Liao, C.-C. Ho, C.-Y. Chang, M.-H. Jao, S.B. Darling, W.-F. Su, Additives for morphology control in high-efficiency organic solar cells, Mater. Today 16 (2013), 326-336.

[10] S.H. Liao, H.J. Jhoo, Y.S. Cheng, S.A. Chen, Fullerene derivative-doped zinc oxide nanofilm as the cathode of inverted polymer solar cells with low-bandgap polymer (PTB7-Th) for high performance, Adv. Mater. 25 (2013), 4766-4771.

[11] M. Kwon, E.A. Katz, T. Tromholt, F.C. Krebs, Electrical and Photo-Induced Degradation of ZnO Layers in Organic Photovoltaics, Adv. Energy Mater. 1 (2011), 836-843.

[12] L. Meng, Y. Zhang, X. Wan, C. Li, X. Zhang, Y. Wang, X. Ke, Z. Xiao, L. Ding, R. Xia, H.-L. Yip, Y. Cao, Y. Chen, Organic and solution-processed tandem solar cells with 17.3% efficiency, Science 361 (2018), 1094.

[13] S.R. Tirumalareddygari, P.R. Guddeti, K.T. Ramakrishna Reddy, A critical study of the optical and electrical properties of transparent and conductive Mo-doped ZnO films by adjustment of Mo concentration, Appl. Surf. Sci. 458 (2018), 333-343.

[14] M.B. Upama, N.K. Elumalai, M.A. Mahmud, M. Wright, D. Wang, C. Xu, A. Uddin, Effect of annealing dependent blend morphology and dielectric properties on the performance and stability of non-fullerene organic solar cells, Sol. Energy Mater. Sol. Cells 176 (2018), 109-118.

[15] G. Wang, X. Zhang, W. Jiang, L. Wang, A Study on the Structure and the Photoelectrical Properties of the Al-Doped ZnO Thin Films by Atomic Layer Deposition in Low Temperatures, J. Nanosci. Nanotechnol. 18 (2018), 8333-8336.

[16] Y. Wang, B. Wu, Z. Wu, Z. Lan, Y. Li, M. Zhang, F. Zhu, Origin of Efficient Inverted Nonfullerene Organic Solar Cells: Enhancement of Charge Extraction and Suppression of Bimolecular Recombination Enabled by Augmented Internal Electric Field, J. Phys. Chem. Lett. 8 (2017), 5264-5271.

[17] H. Yao, L. Ye, J. Hou, B. Jang, G. Han, Y. Cui, G.M. Su, C. Wang, B. Gao, R. Yu, H. Zhang, Y. Yi, H.Y. Woo, H. Ade, J. Hou, Achieving Highly Efficient Nonfullerene Organic Solar Cells with Improved Intermolecular Interaction and Open-Circuit Voltage, Adv. Mater. 29 (2017).

[18] R. Yu, H. Yao, Y. Cui, L. Hong, C. He, J. Hou, Improved Charge Transport and Reduced Nonradiative Energy Loss Enable Over 16% Efficiency in Ternary Polymer Solar Cells, Adv. Mater. 31 (2019), 1902302.

[19] Y.F. Zhu, D.H. Fan, Y.W. Dong, G.H. Zhou, Morphology-controllable ZnO nanostructures: Ethanol-assisted synthesis, growth mechanism and solar cell applications, Superlattices Microstruct. 74 (2014), 261-272.