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Simple Structured Polyetheramines, as Electron Transporting Modified Layers for Efficient Organic Photovoltaics

Yao-Yu Tsai[1], Bing-Huang Jiang[1] and Chih-Ping Chen [1]*

[1] Department of Materials Engineering, Ming Chi University of Technology, 84 Gunjuan Road, Taishan, New Taipei City, 24301, Taiwan
Phone: +886-2-2908-9899#4439
E-mail: cpchen@mail.mcut.edu.tw

Abstract

In this study, we have successfully found that interfacial layers (IFLs) based on Jeffamines (industrial polyetheramine derivatives) can improve the performance of organic photovoltaics (OPVs).We used two different Jeffamines—D2000 and ED2003—(average molecular weight: 2000 g mol^{-1})having either a monoamine or diamine structure and various ratios of ethylene oxide (EO) and propylene oxide (PO) for their suitability as IF materials for OPV applications. The presence of the Jeffamine improved the electron transport and altered the work function of ZnO, thereby causing the ZnO layers to function more efficiently as electron-selective electrodes. The power conversion efficiencies (PCEs) of inverted devices having the layered configuration glass/indium tin oxide (ITO)/ZnO (with or without the Jeffaine)/PTB7:PC71BM /MoO3/Ag increased from 8.1 ± 0.11 to 8.6 ± 0.37% when containing the Jeffamine-D2000 under illumination with AM 1.5G solar light (1000 W m^{-2}), the result of a significantly increased fill factor (FF). The greatest OPV performance was that of the device incorporating Jeffamine-D2000—a PCE of 9.1% and a remarkable FF of 74.2%.

1. Introduction

Great efforts have been exerted in the development of roll-to-roll, cost-effective, low energy consumption OPVs as promising alternatives to traditional PVs for certain applications. Advances in device engineering and materials development have led to the power conversion efficiencies (PCEs) of bulk-heterojunction (BHJ) OPVs reaching 12%. Interfacial (IF) layers play a unique and important role in the enhanced performance of OPVs. Many IF materials have been tested successfully, including polyelectrolytes, self-assembled layers, organic, inorganic hybrid materials and non-conjugated organic materials [e.g., polyethylenimines(PEIs) and their ethoxylated derivatives (PEIEs)]. Several mechanisms have been proposed to explain how the IFs improve the performance of OPVs; for example, improving charge extraction to minimize series resistance, by suppressing carrier recombination, altering the work function (built-in dipole) to facilitating efficient energy level pinning for high-performance carriers extraction, smoothening the surface of ZnO, and changing the BHJ morphology of the active layers for efficient charge transfer and transportation (well-defined nanoscale phase segregation or a gradient distribution of the donor/acceptor morphology for enhanced carrier transport). The most studied cathode modifying layers, PEIs and PEIEs, form efficient interface dipoles on the cathode and, hence, change the work function (WF) of the electron transporting layer(ETL) or cathode, thereby improving carrier extraction.

2. Results and discussion

In this study, we assessed two Jeffamines [average molecular weight (MW): 2000 g mol^{-1}]—D2000 and ED2003, having monoamine or diamine structures and various ratios of propylene oxide (PO) and ethylene oxide (EO)—for their suitability for use as efficient cathode-modified layers for OPV applications (Fig. 1).

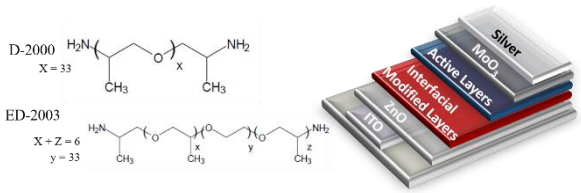

Figure 1. Schematic representation of the OPV device; chemical structures of the Jeffamines.

We fabricated OPV devices having an inverted architecture with a layer structure: glass/ ITO /ZnO (with or without a Jeffamine)/PTB7:$PC_{71}BM$/MoO_3 (3 nm)/Ag (100 nm). We denote the standard cell (without the IF) as the ZnO device, and the devices containing the various IFLs as the D2000 and ED2003 devices. Table 1 summarizes the average and best OPV performances of the devices. The average values and standard deviations in Table 1 were calculated from 10 cells. The standard ZnO device had a PCE of 8.1 ± 0.11% under AM 1.5G illumination (100 mW cm^{-2}), with a value of Jsc of 15.7 ± 0.33 mA cm^{-2}, a value of Voc of 0.72 ± 0.01 V, and an FF of 71.6 ± 2.28%. The PCEs of the devices embedding D2000, and ED2003, were 8.6 ± 0.37, and 8.0 ± 0.42, respectively. The highest PCE of 9.1% was observed with a value of Jsc of 16.8 mA cm^{-2}, a value of Voc of 0.73 V, and an FF of 74.2% (**Fig. 2a, Table 1**). Compared with the ZnO device,the PCE for the D2000 device had increased by 11%.

Table 1. J–V properties of the OPV devices.

Devices	J_{sc} (mA cm^{-2})	V_{oc}(V)	FF(%)	PCE (%)	Best PCE(%)	R_{sh} (Ω cm^2)	R_s (Ω cm^2)
ZnO	15.7±0.33	0.72±0.01	71.6±2.28	8.1±0.11	8.2	1086±314	2.0±0.2
D2000	15.9±0.89	0.73±0.01	74.6±0.99	8.6±0.37	9.1	2118±672	1.5±0.2
ED2003	15.4±0.06	0.73±0.01	71.4±3.00	8.0±0.42	8.3	1040±632	2.0±0.2

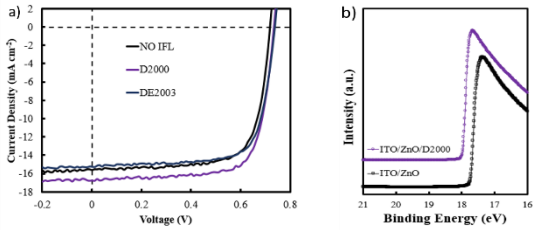

Figure 2. (a) I–V characteristics and (b) Photoemission cut-off and valence band regions, obtained using UPS, for ZnO with and without D2000.

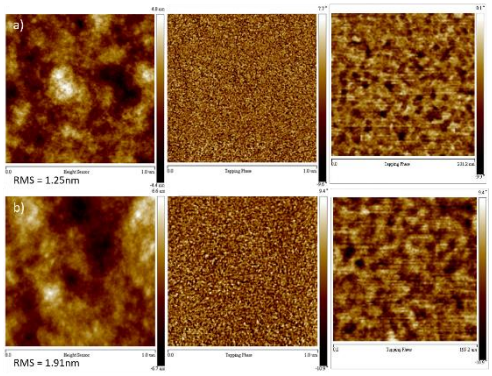

Figure 3. AFM topographic (1 μm × 1 μm), phase (1 μm × 1 μm), and enlarge phase images (200 nm × 200 nm) of a) ZnO- and b) D2000-derived blend films.

To understand why embedding D2000 significantly improved the FF and the value of Jsc value of the device, we employed ultra-violet photoelectron spectroscopy (UPS) to observe whether or not this IF changed the WF; the factors that affected the carrier mobility (transport in the BHJ; extraction at the interfaces) were presumably the differences in the morphologies of the active layers (observed through AFM) and the WFs. The incorporation of an IF layer having an amino functional group will typically build up an interfacial dipole that alters the WF of the electrode, thereby potentially facilitating efficient energy level pinning for high-performance carrier extraction. To determine whether incorporating the Jeffamine played a role in changing the WF, we used UPS to compare the WFs of ITO/ZnO and ITO/ZnO /D2000. Figure 2b presents the cutoff and valence band regions of the UPS spectra of the samples. After interlaying D2000, we observed a decrease in the WF of the ITO/ZnO substrate by 0.24 eV. By embedding an amine-based IF layer, the WF of ITO/ZnO would likely be reduced. The change in surface status would affect the energy level alignment at the interface between ITO/ZnO/D2000 and the active layer. The true WF of ITO/ZnO was −3.47 eV; it decreased by 0.24 V to −3.23 eV after embedding the D2000 interlayer. The AFM data revealed that the phase segregation morphology of the BHJ changed after embedding the IF layers.

Figs 3 presents AFM images of the BHJ films deposited on the various ZnO surfaces. These very small surface roughnesses suggested nanoscale phase segregated behavior. This structure is consistent with the excellent device performance, with average FFs of these devices being greater than 71% (Table 1). A closer look revealed differences in the phase images. The enlarged phase images (200 nm × 200 nm) in Fig. 3 feature two phase regions: dark regions representing fullerene-rich domains and bright domains representing PTB7-rich phases. The blend film cast on ZnO featured phase segregation of the PC71BM-rich phase (domain size: <15 nm) surrounded by a PTB7-rich phase (10–25 nm). The D2000-drived blend film exhibited a larger phase separation domain in which the PC71BM-rich domains having an irregular structure (domain sizes from several to tens of nanometers) were dispersed within 25–40-nm PTB7-rich area. Because the D2000-derived blend film formed larger polymer domains, with larger PCBM domains dispersed well in the polymer matrix, and the D/A domain sizes of the D2000 film were within the efficient exciton diffusion length, this well-defined morphology facilitated the transmission of electrons and holes within the PTB7 and PCBM regions to the corresponding electrodes. In contrast, the possibility of unwanted carrier recombination was higher for the ZnO blend, due to its smaller D/A domain size; hence, we observed lower values of Rsh and FF for the ZnO devices.

3. Conclusions

We have successfully showed that Jeffamines can be used as ETL modified layers for high-performance OPVs. The incorporation of these materials changed the surface energy, thereby affecting the wetting properties of the active layer solution and, hence, altering the morphologies of the blend films. The PCE of the de-vice embedding D2000 as the IF layer increased by 6.2% (from 8.1 ± 0.11 to 8.6 ± 0.37%) because of a significant increase in the FF. Because of the wide variety and low price of the Jeffamines, their judicious selection should result in the development of inexpensive cathode interlayers for large-area OPVs and other optoelectronic devices.

Acknowledgements

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