Conductive Water/Alcohol-Soluble Neutral Fullerene Derivative as an Interfacial Layer for Inverted Polymer Solar Cells with High Efficiency

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ABSTRACT: Dipole induced vacuum level shift has been demonstrated to be responsible for the enhanced efficiency in polymer solar cells (PSCs). The modified energy level alignment could reduce the energy barrier and facilitate charge transport, thereby increasing the efficiency of PSCs. Herein, we report a new mechanism toward enhanced efficiency by using a nondipolar water/alcohol-soluble neutral fullerene derivative to reengineer the surface of the zinc oxide (ZnO) electron extraction layer (EEL) in inverted PSCs. Because of the neutral property (ion-free) of the fullerene derivatives, no dipole moment was introduced at the EEL/active layer interface. A negligible change in open-circuit voltage was observed from inverted PSCs with the neutral fullerene derivative layer. The neutral fullerene derivative layer greatly increased the surface electronic conductivity of the ZnO EEL, suppressed surface charge recombination, and increased the short-circuit current density and fill factor. An overall power conversion efficiency increase of more than 30% from inverted PSCs was obtained. These results demonstrate that the surface electronic conductivity of the EEL plays an important role in high performance inverted PSCs.

KEYWORDS: inverted polymer solar cells, electron extraction layer, neutral, surface electronic conductivity, power conversion efficiency

INTRODUCTION

Polymer solar cells (PSCs), based on the bulk heterojunction (BHJ) composite of conjugated polymers blended with fullerene derivatives, have been attracting great attention in both academic and industrial sectors for the promising future as one of the renewable energy sources.1 BHJ PSCs are characterized by their light weight, high flexibility, and low cost in large-scale commercialization.2,3 In order to enhance the power conversion efficiency (PCE) of PSCs, conjugated polyelectrolytes and/or ionic C60 derivatives have been used as an interfacial layer to modify the band alignment between the BHJ active layer and the electrodes.4−6 The dipole formed by the counterions from either conjugated polyelectrolytes or ionic C60 derivatives has been demonstrated to contribute to the minimization of the energy barrier for electron extraction from the BHJ active layer toward the cathode. This resulted in enhanced PCE of PSCs incorporated with either conjugated polyelectrolytes or ionic C60 derivatives.7−10 The studies by ultraviolet photoemission spectroscopy and/or Kelvin probe microscopy indicated that enlarged, open-circuit voltage (Voc) was attributed to the presence of a dipole moment, which effectively shifts the vacuum level on the surface of the metal electrode, thus reducing the effective work function of the metal electrode.11,12 Recently, Heeger’s group reported the enhanced efficiency of PSCs by using the polar solvent methanol (MeOH) to treat the surface of the BHJ active layer. The report further revealed that the enhanced device performance was attributed to the increased surface charge density, which originated from an enlarged built-in voltage across PSCs.13 However, the origins of the enhanced, short-circuit current (Jsc) and fill factor (FF) are still not clear and are difficult to be

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attributed simply to a modified energy level alignment by the dipole moment.\textsuperscript{13,14}

Recently, our group demonstrated that reengineering the surface of the zinc oxide (ZnO) electron extraction layer (EEL) from the inverted PSCs with conjugated polyelectrolytes gave a ca. 38% enhancement in PCEs. It was determined that the surface electronic conductivity of the ZnO EEL plays an important role in enhanced $J_{SC}$ and FF.\textsuperscript{15} In order to further study the origins of both enhanced $J_{SC}$ and FF, herein, we report a study of using a conductive novel water/alcohol-soluble neutral fullerene derivative (PC$_{60}$BM-G2; see the Experimental Section) as an interfacial layer for the inverted PSCs. We found that over 30% enhancement in PCEs was observed from the inverted PSCs with the PC$_{60}$BM-G2 layer compared to those without the PC$_{60}$BM-G2 layer.

\section*{EXPERIMENTAL SECTION}

**Synthesis and Characterization of PC$_{60}$BM-G2.** [6,6]-Phenyldicyanovinyl C$_{61}$-butyric acid (135 mg, 150 μmol), compound 2 (Scheme 1) (238 mg, 165 μmol), and hydroxybenzotriazole (HOBt, 22 mg, 165 μmol) were added into a round-bottom flask (50 mL) equipped with a magnetic stir bar, and then freshly dried 3- dichlorobenzene (o-DCB, 10 mL) was input into the above flask to dissolve all of the solids. The flask was capped by a rubber septum and cooled to 0 °C. After that, N,N'-disopropylcarbodiimide (DIPC, 62 mg, 495 μmol) was added. The mixture was warmed to 25 °C and stirred for 24 h. The white precipitate was then filtered, and the filtrate was washed with water and brine, dried over Na$_2$SO$_4$, and evaporated in vacuo. The residue was purified by flash column chromatography on silica gel with toluene/EtOAc (v/v = 4/1) as the eluent to afford (75%) the product (Scheme 1), as a brown powder: 260 mg. Purification (75%) the product (Scheme 1) by flash chromatography with a 20% ethyl acetate in hexane mixture to afford (95%) the product as a brown powder: 89 mg.

**Absorption Spectrum of PC$_{60}$BM-G2.** The absorption spectrum of PC$_{60}$BM-G2 thin film was measured by a HP 8453 UV−vis spectrophotometer.

**Cyclic Voltammetry Measurement.** The electrochemical cyclic voltammetry (CV) was operated with a three-electrode system (Pt disk as working electrode, Pt wire as counter electrode, and Ag/AgCl as reference electrode). The electrolyte is 0.1 mol L$^{-1}$ tetrabutylammoniumhexafluorophosphate (Bu$_4$NPF$_6$) in MeCN. Ferrocene/ferrocenium (Fc/Fc$^+$) was used for calibration.

**AFM Measurement.** AFM images were taken on a Nano-Scan N53A system (Digital Instrument) to investigate the surface topology of ZnO, PC$_{60}$BM-G2/ZnO, and PBDT-DTBT:PC$_{71}$BM BHJ composites on pristine ZnO and on PC$_{60}$BM-G2/ZnO precoated ITO substrates. Peak force tunneling AFM (PFTUNA) was used to investigate the surface electronic conductivity of ZnO and PC$_{60}$BM-G2/ZnO thin layers. An AFM tip coated with 20 nm Pt/Ir on both the front and back sides was put into contact with the surfaces of ZnO and PC$_{60}$BM-G2/ZnO thin films. The PFTUNA module was used to measure TUNA current with bias voltage applied to ZnO and PC$_{60}$BM-G2/ZnO thin films.

**Device Fabrication and Characterization.** Two inverted PSCs, one with a structure of ITO/ZnO/PBDT-DTBT:PC$_{71}$BM/MoO$_3$/Ag and the other with a structure of ITO/ZnO/PC$_{60}$BM-G2/PBDT-DTBT:PC$_{71}$BM/MoO$_3$/Ag, and a normal PSC with a structure of ITO/PEDOT:PSS/PBDT-DTBT:PC$_{71}$BM/AI were fabricated. A ZnO thin film with a thickness of ~40 nm was made by spin-coating the precursor solution on the ITO-glass substrate with 3000 rpm for 10 s, followed by annealing at 200 °C for 1 h. The ZnO thin film was ultrasonicated in isopropanol and then stored in the oven overnight for further device fabrication. For the inverted PSCs with a device structure of ITO/ZnO/PC$_{60}$BM-G2/PBDT-DTBT:PC$_{71}$BM/MoO$_3$/Ag, a thickness ~ 5 nm (measured by tapping mode AFM) of PC$_{60}$BM-G2 was spin-coated on top of the ZnO thin film from 0.3 mg/mL methanol solution with 3000 rpm for 20 s. The PBDT-DTBT: PC$_{71}$BM (1:2 by weight) thin film with a thickness of 70 nm was spin-coated on top of either the ZnO thin film or the PC$_{60}$BM-G2/ZnO thin film from o-dichlorobenzene solution. Next, MoO$_3$ with a thickness of 10 nm was thermally evaporated on top of the PBDT-DTBT:PC$_{71}$BM BHJ composite layer, as the hole extraction layer. Then, a silver top was thermally evaporated through a shadow mask with an area of 0.045 cm$^2$ as the top electrode. For the normal device, precleaned ITO substrates were put in UV-ozone for 40 min. Then, ~30 nm PEDOT:PSS was spin-cast from aqueous solution. The active layer was fabricated the same as that in the inverted device fabrication. Finally, a 100 nm aluminum electrode was thermally deposited through the same shadow mask. The devices were characterized by using a Newport Air Mass 1.5 Global (AM 1.5G) full spectrum solar simulator with an irradiation of 100 mW m$^{-2}$ calibrated by standard silicon solar cells. The current density−voltage (J−V) characteristics were measured using a Keithley 2400 source meter. The polymer material PBDT-DTBT was provided by Dr. Jianhui Hou and Yongfang Li from the Institute of Chemistry, Chinese Academy of Science. The PC$_{60}$BM was bought from Solenne BV, The Netherlands, and used without further purification. MoO$_3$ 99.5% was bought from Alfa Aesar. The o-dichlorobenzene (99%) and methanol (99.8%) were purchased from Sigma-Aldrich and were used without further purification. The PEDOT:PSS (Clevios HTL Solar) was purchased from Heraeus and used as received.

**RESULTS AND DISCUSSION**

Scheme 1 presents the synthetic route for PC$_{60}$BM-G2, which was synthesized in two steps. Promoted by N,N'-disopropylcarbodiimide (DIPC) and hydroxybenzotriazole (HOBt), the reaction between [6,6]-phenyl-C$_{61}$-butyric acid (1) and a reported amine dendron\textsuperscript{16,17} (2) afforded 3, which was further
deprotected in a mixture of trifluoroacetic acid and methylene chloride to release the carboxylic acid groups. After deprotection, the existence of nine carboxylic acid groups in PC60BM-G2 instilled good solubility in highly polar solvents such as alcohol, MeOH, and dimethyl sulfoxide (DMSO). The details for the synthesis and characterization of PC60BM-G2 are provided in the Supporting Information.

The UV–visible absorption spectrum of PC60BM-G2 thin film is shown in Figure 1. The PC60BM-G2 thin film shows a strong absorption ranging from 200 to 350 nm with a negligible absorption from 400 to 900 nm. This feature indicates that a thin film of PC60BM-G2 can act as an interfacial layer on top of the ZnO EEL,18 which allows visible light to pass into the BHJ active layer. Both the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) energy levels of PC60BM-G2 were estimated based on the electrochemical data observed from cyclic voltammetry (CV) measurement.19 From the oxidation and reduction peaks (Figure S5, Supporting Information), the LUMO and HOMO energy levels of PC60BM-G2 are estimated to be −3.72 and −5.76 eV, respectively. These values are similar to those from [6,6]-phenyl-C71-butyric acid (PC71BM),20 indicating that there is matched band alignment between PC60BM-G2 and PC71BM and there is a negligible energy barrier for separated electrons being extracted from the BHJ composite by the thin layer of PC60BM-G2 to the respective electrode (Scheme 2).21 Therefore, the Voc of the inverted PSCs incorporating the PC60BM-G2 interfacial layer is expected to be the same as those without the PC60BM-G2 interfacial layer.6,10

The inverted devices were fabricated to investigate the photovoltaic properties of PSCs with and without the PC60BM-G2 interfacial layer. A conventional device with a structure of ITO/PEDOT:PSS/BHJ composite/Al was also fabricated for comparison studies. Here, ITO is indium tin oxide and PEDOT:PSS is poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate), respectively. The active layer consists of poly[4-(4-(2-ethylhexyl)-5-(8-((2-ethylhexyl)oxy)-4-((2-ethyloctyl)oxy)benzo[1,2-b:4,5-b’]dithiophen-2-yl)-alt-7-(4-(2-ethylhexyl)thiophen-2-yl)] (PBDT-DTBT)22 and PC71BM. The device structures of the inverted PSCs, band alignments among the materials used for construction of the inverted PSCs, and molecular structures.
of PBDT-DTBT and PC_{60}BM are shown in Scheme 2. Figure 2 shows J−V characteristics of the conventional PSCs and the inverted PSCs with and without the PC_{60}BM-G2 interfacial layer in the dark and under illumination of white light with the light intensity of 100 mW/cm\(^2\). It is found that the dark current densities under reverse bias from the inverted PSCs with and without the PC_{60}BM-G2 indicates that there is no dipole moment induced by the thin layer of PC_{60}BM-G2, but an enhancement in \(J_{SC}\) of the conventional PSCs is due to interfacial reengineering of the EEL and BHJ composite.\(^{6−8,15}\) In order to further verify it, the role of the thin film of PC_{60}BM-G2 used as a cathode interfacial buffer layer in the conventional PSCs was also investigated. The details of device fabrication and characterization of the conventional PSCs with a structure of ITO/MoO\(_3\)/BHJ composite/PC_{60}BM-G2/Al are provided in the Supporting Information. The performance parameters of the conventional PSCs are summarized in Table S1 (Supporting Information). It was found that there is no enlarged \(V_{OC}\) observed from the conventional PSCs incorporated with PC_{60}BM-G2, but there was more than a 20% enhancement of PCE, in particular in \(J_{SC}\) of the conventional PSCs is due to interfacial reengineering of the BHJ composite.

In PC_{60}BM-G2, the N atom exists in amide, not in the amine group. The N atom in PC_{60}BM-G2 cannot be ionized in either methanol or water solvent. Therefore, no dipole moment is introduced on either the surface of the ZnO EEL or the BHJ active layer after depositing PC_{60}BM-G2 on top of the ZnO EEL and BHJ composite.\(^{15}\) In both conventional and inverted PSCs incorporated with PC_{60}BM-G2, no dipole moment that originated from PC_{60}BM-G2 was involved in the enhanced PCE. To understand the underlying physics of the enhanced PCE of the inverted PSCs, both series resistance (\(R_S\)) and sheet resistance (\(R_{SH}\)) are estimated from J−V curves. The estimated \(R_S\) and \(R_{SH}\) are summarized in Table 1. With incorporation of PC_{60}BM-G2 on the ZnO EEL, the \(R_S\) decreased from 12.2 to 7.5 Ω cm\(^2\). The \(R_{SH}\) in the inverted PSCs with the PC_{60}BM-G2 interfacial layer is 907 Ω cm\(^2\), which is larger than that without

Table 1. Summary of Device Performance

<table>
<thead>
<tr>
<th>device structure(^a)</th>
<th>(V_{OC}) (V)</th>
<th>(J_{SC}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
<th>(R_S) (Ω cm(^2))</th>
<th>(R_{SH}) (Ω cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/ZnO/BHJ composite/MoO(_3)/Ag</td>
<td>0.74(0.74)(^b)</td>
<td>11.1(11.7)</td>
<td>58.1(60.2)</td>
<td>4.77(4.90)</td>
<td>12.2</td>
<td>805</td>
</tr>
<tr>
<td>ITO/ZnO/PC_{60}BM-G2/BHJ composite/MoO(_3)/Ag</td>
<td>0.73(0.73)</td>
<td>14.0(15.1)</td>
<td>62.8(64.0)</td>
<td>6.42(6.71)</td>
<td>7.5</td>
<td>907</td>
</tr>
<tr>
<td>ITO/PEDOT:PSS/BHJ composite/Al</td>
<td>0.78</td>
<td>11.3</td>
<td>62.4</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^b\)Data in ( ) represent the best device performance parameters.
the PC$_{60}$BM-G2 interfacial layer, 805 $\Omega$ cm$^2$. Generally, enhanced device performance can be expected with larger $R_{SH}$ and smaller $R_S$.$^{29,30}$ Therefore, the inverted PSCs with the PC$_{60}$BM-G2 interfacial layer possesses high PCE.

In order to further study the underlying device performance, atomic force microscopy (AFM) was carried out to investigate the thin film morphology of the PBDT-DTBT:PC$_{71}$BM BHJ composite on top of pristine ZnO and PC$_{60}$BM-G2/ZnO. Figure 3a shows the phase image of the BHJ composite on pristine ZnO. The domain size of PC$_{71}$BM aggregation is 34 $\pm$ 3 nm, and the domain size of PBDT-DTBT is 15 $\pm$ 6 nm. Figure 3b shows the phase image of the BHJ composite on PC$_{60}$BM-G2/ZnO. The domain size of PC$_{71}$BM aggregation is 32 $\pm$ 5 nm, and the domain size of PBDT-DTBT is 13 $\pm$ 8 nm. The BHJ composite spin-coated either on ZnO or on PC$_{60}$BM-G2/ZnO exhibits appropriate phase separation and domain size for charge separation.$^2$ The domain size of each component in the BHJ composite has little variation when the BHJ composite is spin-coated on ZnO or on PC$_{60}$BM-G2/ZnO layers. These results indicate that charge dissociation and charge transport in the BHJ composite could be similar in the devices with and without the PC$_{60}$BM-G2 interfacial layer. Therefore, with the same light absorption and charge dissociation in both devices, the enhanced PCE by the thin layer of PC$_{60}$BM-G2 solely resulted from the PC$_{60}$BM-G2/ZnO EEL.

The AFM height images of the PC$_{60}$BM-G2/ZnO and pristine ZnO EEL are shown in Figure 3c.d. The root-mean-square roughness (RMS) of PC$_{60}$BM-G2/ZnO is 1.605 nm, which is higher than that of the pristine ZnO thin film (1.320 nm). The rougher surface could provide a larger surface area and, hence, larger interfacial adhesion between the PC$_{60}$BM-G2/ZnO EEL and the BHJ active layer.$^{31,32}$ Moreover, high interfacial interactions between the PC$_{60}$BM-G2/ZnO EEL and the BHJ active layer would facilitate the transportation of the separated electrons to the respective electrode.$^{32}$ As a result, high $J_{SC}$ is observed from the inverted PSCs with the PC$_{60}$BM-G2/ZnO EEL.

The electronic conductivities of the pristine ZnO EEL and the thin films of PC$_{60}$BM-G2/ZnO EEL were further conducted on a Bruker Dimension Icon system with a Peak Force Tapping Tunneling AFM (PFTUNA) module.$^{15}$ Figure 4 shows the PFTUNA images of the ZnO EEL and PC$_{60}$BM-G2/ZnO EEL. The peak current observed from pristine ZnO is 2.5 pA within a 2 $\mu$m zoom, but the peak current appears only in the small domain size, not in the whole film (Figure 4a). However, under the same conditions, obvious changes were observed from the peak current image of PC$_{60}$BM-G2/ZnO. The peak current is 2.5 pA, but the domain size of the peak current is significantly increased when compared to those of the pristine ZnO thin films (Figure 4b). These results indicate that the surface electronic conductivities of the PC$_{60}$BM-G2/ZnO EEL...
the inverted PSCs. Because of the neutral property of the PC_{60}BM-G2, no dipole moment was introduced at the interface between the PC_{60}BM-G2/ZnO EEL and the BHJ composite, but an increased surface electronic conductivity of the PC_{60}BM-G2/ZnO EEL resulted in suppressed surface charge carrier recombination. Therefore, the same $V_{OC}$ and dramatically increased $F_{SC}$ and FF, and the consequently enhanced efficiency, were observed from the inverted PSCs with the PC_{60}BM-G2 interfacial layer. These results demonstrate that the surface electronic conductivity of the EEL plays an important role in the high performance of inverted PSCs.

# CONCLUSIONS

In conclusion, a novel conductive water/alcohol-soluble neutral fullerene derivative, PC_{60}BM-G2, was developed and used to reengineer the surface of the ZnO electron extraction layer in the inverted PSCs. Because of the neutral property of the PC_{60}BM-G2, no dipole moment was introduced at the interface between the PC_{60}BM-G2/ZnO EEL and the BHJ composite, but an increased surface electronic conductivity of the PC_{60}BM-G2/ZnO EEL resulted in suppressed surface charge carrier recombination. Therefore, the same $V_{OC}$ and dramatically increased $F_{SC}$ and FF, and the consequently enhanced efficiency, were observed from the inverted PSCs with the PC_{60}BM-G2 interfacial layer. These results demonstrate that the surface electronic conductivity of the EEL plays an important role in the high performance of inverted PSCs.

### REFERENCES


