Performance Improvement of Bulk Heterojunction Organic Photovoltaic Cell by Addition of a Hole Transport Material*

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A novel photovoltaic cell with an active layer of poly(phenyleneethynylene) (PPE)/C_{60}/N,N'-diphenyl-N,N'-di-(m-tolyl)-p-benzidine (TPD) is designed. In the active layer, PPE is the major component; C_{60} and TPD are the minor ones. Compared with a control BHJ device based on PPE/C_{60}, the short circuit current density J_{sc} is increased by 1 order of magnitude, and the whole device performance is increased greatly, however the open circuit voltage V_{oc} is largely decreased. The possible mechanism of the improved performance may be as follows: In the PPE/C_{60}/TPD device, PPE, C_{60}, and TPD serve as the energy harvesting material, the electron transport material, and the hole transport material, respectively. As the TPD and C_{60} are spatially separated by PPE, the charge recombination is effectively retarded.

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Organic photovoltaic cells have attracted a great deal of attention due to their low cost, easy fabrication, light weight, flexible, and etc.[1−4] In recent years, great improvement has been achieved in the device performance of the organic photovoltaic cells. Up to date, the solar-energy conversion efficiency η has achieved to 6%.[5,6] However, their device performance is rather low and still far from industrial applications compared to the traditional silicon based solar cells. Therefore, it is still an important issue to improve the device performance of the organic photovoltaic cell nowadays. During the past years, many kinds of approaches have been explored to improve the device performance. For example, selection of solar harvesting material, having a low band gap and broad absorption such as polythiophene, is one of the important approaches.[7] Careful control on the morphology of the active layer through annealing, solvent treatment, and other methods can also greatly improve the device performance.[8−10] Active layer structure design (bulk heterojunction (BHJ) structure[11]) and device structure design (tandem cell[5]) can improve the device performance revolutionarily. Ternary component system has been reported to improve the device performance, in which the additional component often helps to broaden the absorption spectrum of the active layer[12,13] or to increase the hole or electron transport mobility.[14−16] In this Letter, we propose a strategy to improve the solar-energy conversion efficiency of the organic photovoltaic cell. A ternary mixture of N,N'-diphenyl-N,N'-di-(m-tolyl)-p-benzidine (TPD), poly(phenyleneethynylene) (PPE), and C_{60} is used as the active layer of the photovoltaic cell, in which PPE is the major component, C_{60} and TPD are the minor ones. Compared to the PPE/C_{60} based device, the PPE/C_{60}/TPD based one has an increased short circuit current density J_{sc} and solar-energy conversion efficiency, except for a decreased open circuit voltage V_{oc}. This performance improvement may be attributed to the retarding of the charge recombination resulting from spatially separation of C_{60} and TPD, which serve as the electron and the hole transport pathway respectively.

PPE is a rigid-rod conjugated polymer composed of aromatic rings and alkyne functional groups and has been used as a donor material for photovoltaic application,[17] C_{60} is an electron transporting material, which is usually used as an acceptor material in photovoltaic application. TPD has been extensively used as a hole transport layer in the fabrication of organic light emitting diodes (OLEDs).[18]

In this study, four photovoltaic devices were prepared by spin coating the chloroform solution of different active layer materials: (Poly(2,5-bis(11-(9'-naphthylacetylate)-3,6,9-trioxaundecyl)-1,4-phenylene), $M_w = 10^4$ g/mol, synthesized in our lab, PPE, 10 mg/ml) (device 1), PPE(10 mg/ml)/TPD(5 mg/ml) (device

2), PPE(10 mg/ml)/C_{60}(0.5 mg/ml) (device 3), PPE(10 mg/ml)/C_{60}(0.5 mg/ml)/TPD(5 mg/ml) (device 4). The molecular structure of PPE, TPD, and C_{60} is shown in Fig. 1(a). The detailed preparation of the photovoltaic device can be found elsewhere.[17] The active layer was 4 mm^2 in area. Devices were all tested using an AM 1.5 G standard operating with an illumination intensity of 100 mW/cm^2. The four devices have a structure of ITO (about 17 Ω/sq)/PEDOT:PSS (30 nm)/active layer (100 nm)/LiF (1 nm)/Al (80 nm). The schematic representation of the device 4 is shown in Fig. 1(b). The calculation of the power conversion efficiency has been performed using the equation

$$\eta = FFI_{sc}V_{oc}/P_{in}, \qquad (1)$$

where V_{oc}, I_{sc}, FF, and P_{in} are the open circuit voltage, the short circuit current, the fill factor and the incident light power, respectively. The fill factor F is determined by

$$FF = (V_m I_m)/(V_{oc}I_{sc}), \qquad (2)$$

where V_m and I_m are the voltage and the current in the maximum power point of the I–V curve in the fourth quadrant.
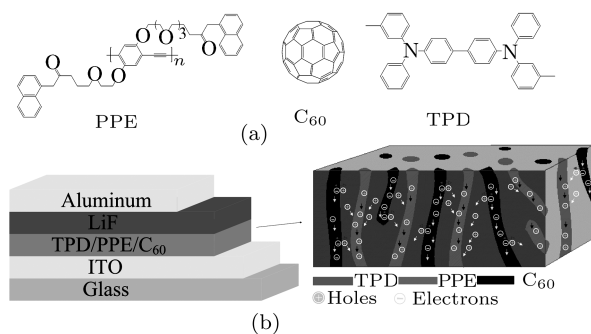

Fig. 1. (a) The molecular structure of PPE, C_{60} and TPD. (b) On the left, schematic representation of the photovoltaic device using PPE/C_{60}/TPD mixture as the active layer, which has a structure of ITO (about 17 Ω/sq)/PEDOT:PSS (30 nm)/PPE/C_{60}/TPD (100 nm)/LiF (1 nm)/Al (80 nm). On the right, the schematic representation of the active layer composed of PPE, C_{60} and TPD.

The logarithmic current density J versus the voltage V of the four devices under light as well as that of the PPE/C_{60}/TPD device in dark are plotted in Fig. 2. Under illumination, the device 1 gives an open circuit voltage V_{oc} of 0.4 V and a short circuit current density J_{sc} of 0.008 mA/cm^2. The device 1 is a single layered organic semi-conducting device based on pure PPE, whose V_{oc} value is governed by the work function difference between ITO (−4.7 eV) and Al (−4.3 eV) corresponding to the MIM model.[19] The device 2 has an active layer of PPE/TPD, which shows V_{oc} of 0.4 V

and J_{sc} of 0.02 mA cm^{-2}. J_{sc} greatly increases after adding TPD into PPE matrix, indicating that TPD facilitates the transport of charge carriers, especially the holes transport. The device 3 is a typical BHJ device based on PPE/C_{60}, in which PPE serves as the donor material and C_{60} severs as the acceptor material. V_{oc} is 1.4 V and the J_{sc} is 0.02 mA·cm^{-2}. In the traditional BHJ photovoltaic device, V_{oc} is governed by the difference between the HOMO energy of the donor and the lowest unoccupied molecular orbital (LUMO) energy of the acceptor[20] and can be influenced by some factors such as the feed ratio of the donor and the acceptor, processing conditions, and etc.[21,22] V_{oc} of the device 3 is 1.4 eV, which corresponds to the difference between the HOMO energy (−5.9 eV) of PPE and the LUMO (−4.5 eV) energy of C_{60}.[23] The LUMO (−3.5 eV) and HOMO energy (−5.9 eV) of the PPE were obtained from an electrochemical cyclic voltammetry (not shown in this study). The device 4 is a photovoltaic device based on a ternary mixture of PPE/C_{60}/TPD, which shows no current response in dark and gives V_{oc} of 0.7 V and J_{sc} of 0.38 mA/cm^2 under illumination. Interestingly, J_{sc} of the device 4 is much higher than the typical BHJ device (device 3), whereas V_{oc} is much smaller than that of the device 3. The solar energy conversion efficiency of the device 4 (0.05%) is the highest among the four devices in this study (0.0006% for device 1, 0.002% for device 2, and 0.01% for device 3), as listed in Table 1. Obviously, the great increase of J_{sc} can be attributed to the addition of the TPD.
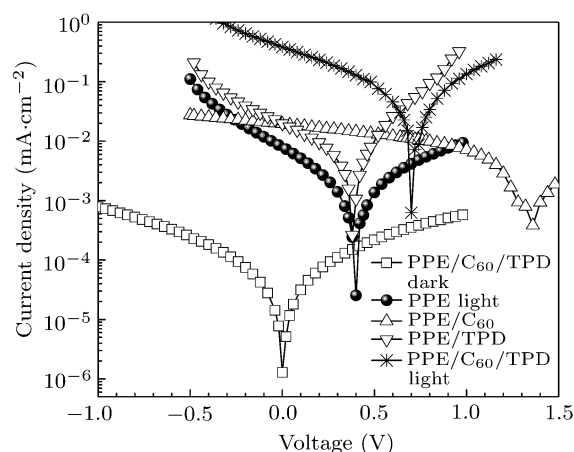

Fig. 2. Solar cell characteristics of the solar cell devices using active layer of PPE, PPE/TPD, PPE/C_{60}, PPE/C_{60}/TPD illuminated under air mass (AM) 1.5 global solar conditions with 100 mW/cm^2 and PPE/C_{60}/TPD in dark.

In the conventional BHJ device (e.g. device 3), PPE absorbs solar energy and produces excitons, which migrate to the PPE/C_{60} interface and dissociate into electrons and holes. The electrons then transport to the Al cathode through C_{60} phase and

the holes transport to the ITO anode through the PPE matrix. In this case, by entangling the two constituents, a region is formed whereby photons can be absorbed over a very long distance, and all excitons are within a diffusion length of a donor-acceptor interface where photo-induced charge transfer can occur. This approach results in a significant improvement in power conversion efficiency over that using a simple planar structure (e.g. device 1). However, the C_{60} phase and the PPE matrix are not spatially separated, and the recombination of the electrons and holes is still a key bottle neck limiting the power conversion efficiency.[6] By adding TPD into the PPE/C_{60} mixture, the cell performance especially J_{sc} greatly increases. TPD is a hole transport material which has higher HOMO level than PPE. Therefore, TPD may form the hole transport pathway in the ternary photovoltaic device (device 4), as shown in Fig. 1(b). PPE is a major content and forms a continuous matrix, C_{60} and TPD are separated by the PPE matrix and form interfaces with PPE. Under illumination, excitons are first produced in PPE phase, and then migrate to the interface of PPE/C_{60} and dissociate into electrons and holes. The electrons transport to the Al cathode through the C_{60} phase, and the holes transmit from the PPE to TPD phase at their interface because of the relatively higher HOMO level of TPD compared to PPE. Then the holes transport to the ITO anode through the TPD phase. Because C_{60} and the TPD phase are spatially separated by the PPE matrix, the recombination of the electrons and holes are effectively retarded. The schematic representation of the energy level of this process is also shown in Fig. 3.

Table 1. Device performance list of the devices 1 to 4 under air mass (AM) 1.5 global solar conditions with $100\,mW/cm^2$ illumination.

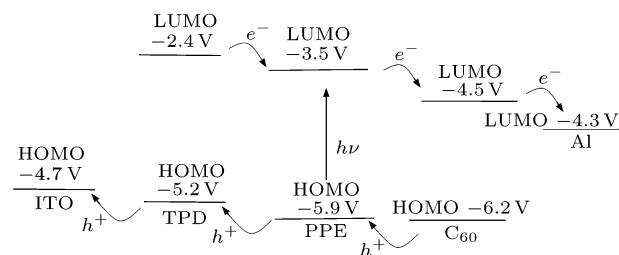| Device	Component	V_{oc} (V)	J_{sc} (mA/cm^2)	η (%)
1	PPE	0.4	0.008	0.0006
2	PPE/TPD	0.4	0.02	0.002
3	PPE/C60	1.4	0.02	0.01
4	PPE/C60/TPD	0.7	0.38	0.05

Fig. 3. Energy diagram of the ternary photovoltaic cell comprising of PPE, C_{60} and TPD.

There are three components in the device 4, therefore the origin of V_{oc} may be different from that in the BHJ device, different from the traditional BHJ photo-

voltaic device. V_{oc} of the device 4 is 0.7 V, which just corresponds to the difference between the HOMO level of TPD ($-5.2\,eV$)[24] and the LUMO level ($-4.5\,eV$) of C_{60}, not the difference of the HOMO level of PPE and the LUMO level of C_{60}. Therefore, V_{oc} of device 4 may be governed by the HOMO level of TPD and the LUMO level of C_{60}, which needs further experimental and theoretical investigations.

In summary, the energy conversion efficiency is greatly improved by use of a ternary component mixture of PPE/C_{60}/TPD. Compared with the PPE/C_{60} device, J_{sc} is increased by 1 order of magnitude, because the TPD and the C_{60} are spatially separated by PPE and the charge recombination is effectively retarded.

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