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Polymeric Photovoltaic Devices Based on Tricomponent System Composed of a Blend of Donor and PCBM Acceptor Material

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In this article, we report the fabrication of bulk heterojunction photovoltaic devices with combination of three materials. A blend of poly(3-hexylthiophene) (P3HT) and poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) has

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been used as donor polymer. A fullerene derivative, [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM) is used as an electron acceptor material. The donor blend ratio (50:50) is kept constant whereas the ratio of donor to acceptor is varied. The influence of the active layer thickness, and cathode metals on photovoltaic performance has been investigated. The results are compared with the performances of MEH-PPV:PCBM and P3HT:PCBM photovoltaic devices fabricated in similar conditions.

Keywords: MEH-PPV; PCBM; P3HT; photovoltaic devices; tricomponent

INTRODUCTION

Research on polymer photovoltaics has been attracted since most of them can be processed from solution, enabling the manufacture of large area, flexible, and lightweight devices compared to their inorganic counterparts. Low energy conversions of polymeric photovoltaic devices are due to limited absorption of light, poor excitons separation and low mobilities. However, the dissociation and charge separation problems can be overcome by blending the polymer with electron acceptor materials mainly the fullerene derivatives. This will enable to form a nanoscale interpenetrating networks within the photoactive layer called as bulk heterojunction. After introduction of bulk heterojunction concept, the polymer based photovoltaic research has attracted particular interest due to achievement of higher power conversion efficiencies (PCE) [1–3]. But, further increase of the PCE is required for practical applications. The need to improve the PCE requires the implementation of new materials, effective utilization of the existing materials, the exploration of new device architectures, etc.

Generally, the electric power extracted from a photovoltaic device depends on both the photocurrent and photovoltage of the diode under illumination of a given intensity. In order to increase the PCE of a photovoltaic device, the practicable approach is to increase the photocurrent as much as possible, since the photovoltage is limited by the built-in potential [4–6]. Different device geometries and interface morphologies are evaluated for the purposes of trapping more light, dissociating excitons more efficiently, transporting charges with fewer impediments and thus, extracting more photocurrent [2,3,7–9]. Till to date, a successful and the most promising polymer system in terms of efficiency and stability is based on the combination of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C₆₁-butyric acid methyl ester (PCBM). In this article, for the first time we introduced poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene) (MEH-PPV) as a third

component in P3HT:PCBM devices as another donor material in addition to P3HT. Because, MEH-PPV:PCBM is the other most promising polymer system developed so far in the literature other than P3HT:PCBM. The open-circuit voltage (V_{OC}) of the MEH-PPV based devices is higher than P3HT:PCBM device [10]. Hence, we expect that addition of MEH-PPV to P3HT:PCBM system may increase the V_{OC} of P3HT:PCBM system and may also improve the overall photovoltaic characteristics. To study the third component effect we designed a simple tricomponent system by keeping the donor (P3HT/MEH-PPV) blend ratio constant for preliminary studies on tricomponent systems. Donor to acceptor ratio, active layer thickness, and the cathode materials for tricomponent photovoltaic devices are optimized. Further, the photovoltaic performance of the tricomponent devices are compared with P3HT:PCBM and MEH-PPV:PCBM devices fabricated in the similar conditions.

EXPERIMENTAL

Materials

Poly(3-hexylthiophene), LiF and aluminum were purchased from Aldrich Co. All solvents used in this study were of HPLC grade and the other reagents were also purchased from Aldrich Co. Poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylenevinylene [11] and [6,6]-phenyl C_{61} -butyric acid methyl ester [12] were prepared according to the procedures published earlier.

Photovoltaic Device Fabrication

Glass substrate coated with ITO, whose conductivity was about 15 Ω /square (from Samsung Corning) served as anode electrode. ITO substrates were cleaned ultrasonically with detergent followed by distilled water, acetone, and 2-propanol sequentially. A 40 nm thick layers of PEDOT-PSS (Baytron P, AP Al 4083) was spin-coated on a cleaned ITO substrates after exposing the ITO surface to Ozone for 10 min. The PEDOT:PSS layer is baked on a hot plate at 120°C for 10 min. Active layer of polymer was spin coated from 1 wt% solution prepared in *o*-dichlorobenzene after filtering through 0.45 μ m PP syringe filters. The device structure was completed by depositing either Al (150 nm) or LiF (1 nm)/Al (200 nm) cathode as top electrode onto the polymer active layer under 2×10^{-6} torr vacuum in thermal evaporator. The overlap of the two electrodes defined the active area of the photovoltaic device and is 4 mm². The photovoltaic devices were

characterized under the illumination of simulated solar light with 100 mW/cm^2 (AM1.5) by Orel 300 W solar simulator. Electric data were recorded using a Keithley 236 source-measure unit. All other fabrication steps and characterization measurements were performed in an ambient environment without a protective atmosphere. Thickness of the thin films was measured using a KLA Tencor Alpha-step IQ surface profilometer with an accuracy of $\pm 1 \text{ nm}$.

RESULTS AND DISCUSSION

UV-visible absorption spectra of P3HT, MEH-PPV and a 50:50 blend of MEH-PPV with P3HT in film state are shown in Figure 1. The absorption maximum of MEH-PPV/P3HT is blue shifted about 20 nm compared to pure P3HT. This may be due to the dilution effect. The absorption spectrum of the blend is also broadened compared to P3HT and MEH-PPV spectra.

The interpenetrating network formed between donor/acceptor within a composite active layer of bulk heterojunction photovoltaic devices is an important factor to be considered. The challenge is to organize the donor and acceptor materials such that their interface area is maximized, while typical dimensions of phase separation are within the exciton diffusion range and continuous, preferably short, pathways for transport of charge carriers to the electrodes are ensured [13,14]. There are many parameters, but among them the composition of donor to acceptor, the solvent used to make blend solutions, cathode

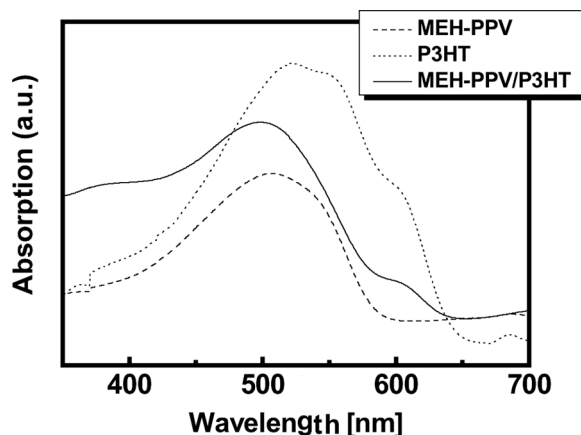


FIGURE 1 UV-visible spectra of P3HT, MEH-PPV and MEH-PPV/P3HT blends in film state.

materials, controlled phase separation, and crystallization are most significant [15].

In MDMO-PPV conjugated polymer, it has been observed that the charge carrier mobility of hole is more than three orders of magnitude lesser than the electron mobility in PCBM [16]. So, it is necessary to use the appropriate amount of electron acceptor to obtain balance between the mobilities of hole and electron in the photovoltaic devices. Photovoltaic devices were fabricated using a 50:50 blend of P3HT and MEH-PPV as donor and PCBM as acceptor materials. Donor (blend) to acceptor ratio was varied from 1:0.5, 1:1 and 1:4 at the fixed active layer thickness of 110 nm with Al cathode. The current density versus voltage (J-V) curves for these devices are presented in Figure 2. The device fabricated with 1:1 ratio of donor to acceptor showed higher PCE of 1.39% than the 1:4 (0.82%) and 1:0.5 (0.89%) ratio devices. The open-circuit voltage (V_{OC}), short-circuit current density (J_{SC}) and FF of 1:1 device are 0.66 V, 5.93 mA/cm² and 0.36, respectively.

Apart from the donor to acceptor ratio, thickness of the polymer active layer will also affect the efficiency of photovoltaic cell. If the active layer is thick, the absorption of light from the source is good, but at the same time the mobility of the charges will be restricted. Hence, it is important to optimize the thickness of the active layer. To do so, we have fabricated the devices with varying active layer thickness using 1:1 donor to acceptor ratio. J-V curves of the devices prepared with different active layer thickness are presented in

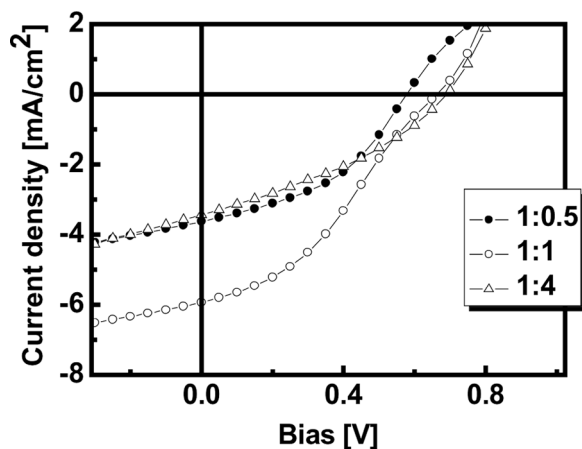


FIGURE 2 J-V curves of the devices fabricated with different donor to acceptor ratio with Al cathode.

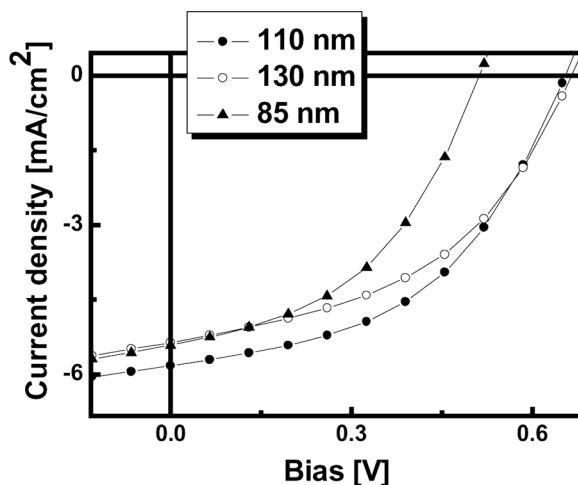


FIGURE 3 J-V curves of the devices fabricated with different active layer thickness with 1:1 donor to acceptor ratio.

Figure 3. The device prepared with 110 nm thick active layer has shown higher PCE of 1.39% than the other devices prepared with 85 and 130 nm thick layers. The lower V_{OC} value for the device prepared with 85 nm thick active layer may be due the pinholes and/or microcracks presents in the thin photoactive layer, which reduces the shunt resistance.

The other important parameter to be considered in the fabrication of photovoltaic devices is the cathode, because the contact between the metal used as cathode and the organic polymer layer will have effect on the final photovoltaic device performance. Here, we fabricated the devices with 1:1 ratio of donor to acceptor with Al and LiF/Al Al as top electrode and the J-V curves are presented in Figure 4. The V_{OC} of the two devices is similar where as varied FF and J_{SC} was observed. The higher PCE of 1.39% was observed with J_{SC} of 5.97 mA/cm^2 and FF of 0.36 for Al cathode devices compared to 1.06% of PCE for LiF/Al device.

The performance of the tricomponent (P3HT/MEH-PPV):PCBM device was compared with the performance of P3HT:PCBM and MEH-PPV:PCBM devices. P3HT:PCBM and MEH-PPV:PCBM devices were fabricated with 110 nm thick active layers and Al as cathode. The photovoltaic characteristics of all the three devices are given in Table 1. V_{OC} of the tricomponent system is improved when compared to P3HT:PCBM system and it is almost same as that of

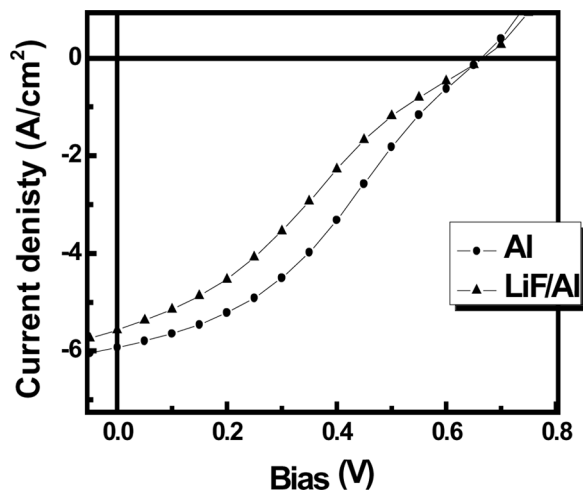


FIGURE 4 J-V curves of the devices fabricated using Al and LiF/Al cathodes with 1:1 donor to acceptor ratio.

MEH-PPV:PCBM device. Generally, V_{OC} of the device mainly depends on HOMO and LUMO energy levels of donor and acceptor materials. The combination of HOMO energy levels of MEH-PPV and P3HT donor blend polymers and LUMO level of acceptor PCBM may be responsible for the observed higher V_{OC} in tri component system device compared to P3HT:PCBM device. The J_{SC} was reduced after addition of MEH-PPV to P3HT:PCBM system. The addition of MEH-PPV in tricomponent system might have disrupted the arrangement of P3HT chains. When compared to MEH-PPV:PCBM system, the J_{SC} of the tricomponent device is higher. However, higher photovoltaic properties are reported for P3HT:PCBM [1–3,17] and MEH-PPV:PCBM [18,19] systems in literature compared to the data reported in Table 1. But, those values are obtained in different conditions such as thermal annealing of the devices, changing drying

TABLE 1 Comparison of Photovoltaic Properties of the Three Different Devices

Materials	V_{OC} (V)	J_{SC} (mA/cm ²)	FF (%)	PCE (%)
MEH-PPV:PCBM	0.664	2.25	0.29	0.44
(MEH-PPV/P3HT):PCBM	0.662	5.94	0.36	1.39
P3HT:PCBM	0.340	7.42	0.49	1.23

condition of solvent and use of different device geometries in case of P3HT:PCBM and use of different solvents and higher amount of PCBM in MEH-PPV:PCBM devices. In the present fabrication conditions, the PCE of tricomponent system designed in this work is higher compared to P3HT:PCBM and MEH-PPV:PCBM devices. The photovoltaic properties of the tricomponent system can further be improved by changing the conditions such as donor blend ratio, morphology of active layer using thermal treatment, different solvents etc.

CONCLUSIONS

The designed (P3HT/MEH-PPV):PCBM tricomponent system has shown improved performance than P3HT:PCBM and MEH-PPV:PCBM devices. As expected, the V_{OC} of the P3HT:PCBM system was improved by addition of MEH-PPV, but the J_{SC} was reduced. The device fabricated using 1:1 ratio of donor to acceptor with an active layer thickness of 110 nm using Al as cathode given the highest PCE of 1.39%.

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