

EFFICIENT POLYMER PHOTOVOLTAIC DEVICES BASED ON POLYMER D-A BLENDS*

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Abstract Recent work demonstrated that efficient solar-energy conversion could be achieved in polymer photovoltaic cells (PVCs) based on interpenetrating bi-continuous networks^[1, 2]. In this paper we present a comprehensive study on improving energy conversion efficiencies of PVCs based on composite films of MEHPPV and fullerene derivatives. Carrier collection efficiency of ca. 30% el/ph and energy conversion efficiency of 3.9% were achieved at 500 nm. At reverse bias of 15 V, the photosensitivity reached 0.8 A/W, corresponding to a quantum efficiency over 100% el/ph. These results suggest that high efficiency photoelectric conversion can be achieved in polymer devices with M-P-M structure. These devices are promising for practical applications such as plastic solar cells and plastic photodetectors.

Keywords Photovoltaic cell, Hetero-junction, Conjugated polymer, Fullerene

INTRODUCTION

Electroluminescent effects in semiconductor polymers have attracted broad attention and have been used for fabricating high efficiency emissive displays^[3]. The inverse process (electric current generation under light illumination) in organic semiconductors can also be very efficient^[4]. The photoresponse of a homo semiconductor polymer can be further enhanced by blending the homopolymer with another polymer or an organic molecule with different electronic structures^[5-7]. Charge separation and charge transfer (CT) occur for charges generated by photoexcitation: the photoinduced electrons energetically favor moving into the polymer phase with greater electron affinity (acceptor phase) while the photoinduced holes energetically favor moving into the polymer phase with smaller ionization potential (donor phase). The photoinduced CT separates electrons and holes and prevents them from early recombination. The polymer D/A blends (composites) provide a molecular approach to high efficiency solar cells and high sensitivity photodetectors. By controlling the morphology of the phase separation into an interpenetrating bi-continuous network of D and A phases, one can achieve high interfacial area within a 'bulk D/A heterojunction' material. Moreover, a bicontinuous network can provide the needed pathways for collecting the separated carriers at external electrodes; holes from the donor phase and electrons from the acceptor phase. Thus, thin film sandwich devices with a bicontinuous D/A composite as the active material can function as efficient photovoltaic cells and efficient photodetectors with high carrier collection efficiency^[8-10]. In addition to their excellent optoelectric performance, these polymer photosensors can be fabricated by simple coating or printing processes at room temperature. Such processes

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enable large size, low cost photovoltaic cells and photosensors to be deposited on flat-panel substrates, on flexible substrates or on curved substrates.

However, the energy conversion efficiency of polymer photovoltaic cells is lower compared to their inorganic counterparts. Aimed at improving the performance parameters of the polymer PVCs, in this paper we investigate the relationship of the performance parameters with the device structure and film morphology of the CT blend.

EXPERIMENTAL

Fullerene molecule C60 was purchased from Tianan Co. PCBM was synthesized according to Ref. [11]. MEHPPV (poly(2-methoxy-5-(2-ethylhexoxy)-1,4-phenylene vinylene)) was synthesized according to the procedure described in reference^[12]. C60 and PCBM were dissolved in chloroform to give a concentration of 0.3% *W/V*. MEHPPV was dissolved in THF/*p*-xylene mixture (2:8) solution.

Photovoltaic cells were fabricated using MEHPPV doped with C60 or PCBM in different ratios as the active layer. The thickness of the MEH-PPV:PCBM blend films was 100 nm, as determined by a surface profilometer (Tencor, ALFA-Step 500). Indium/tin oxide (ITO) was used as the anode and a 50 nm thick poly(ethylene dioxythiophene)/polystyrene sulphonic acid (Bayer Batron-P) layer was incorporated between ITO and MEH-PPV layer to reduce device leakage. Finally, 150 nm thick metal layers (Al or Ag) were thermally evaporated onto the top of photoactive polymer. The deposition rate and the thickness of the evaporation layers were monitored by a thickness/rate meter (Sycon). The deposition rate for aluminum was usually 1–2 nm/s. The crossing area between the cathode and the anode defined the sensing active area. Unless described specifically, a sensing area of 0.15 cm² was typically used in this paper. All the fabrication steps except spin-casting PEDT:PSS layer were carried out in a nitrogen glove box. Dark and photo *I-V* characteristics of the devices were measured with a Keithley 236 source-measure unit. Photocurrent was measured under illumination (10 mW/cm²) with a tungsten lamp. The photosensitivity was measured with a commercial photomodulation spectroscopic setup (MERLIN digital Lock-in, ORIEL) including a xenon lamp, an optical chopper, a monochromator and lock-in amplifier operated by PC computer. Calibrated Si photodiode was used as the standard in the determination of photosensitivity.

The energy conversion efficiency η_e , and fill-factor (*F.F.*) were calculated according to the following equations^[13].

$$\eta_e = F.F. \times I_{sc} \times V_{oc} / P_{in} \quad (1)$$

$$F.F. = I_m V_m / I_{sc} V_{oc} \quad (2)$$

where P_{in} is the incident radiation flux, I_{sc} and V_{oc} are the short-circuit current and open-circuit voltage, I_m and V_m are the current and voltage for maximum power output.

RESULTS AND DISCUSSIONS

The typical device structure used in this study was a sandwich structure with ITO/PEDT as the hole collecting electrode and Al as the electron collecting electrode: ITO/PEDT/MEHPPV+C60/Al. MEHPPV was used as the donor phase and C60 or PCBM as the acceptor phase. The typical thickness of an active layer was 100 nm. Table 1 summarizes the performance parameters of PVCs made with MEHPPV:C60 or MEHPPV:PCBM blends. A device with pure MEHPPV was also fabricated as a reference. The weight fraction of C60 or PCBM in the active materials was kept at 80% in this experiment. Figure 1 shows the typical *I-V* characteristics (both in the dark and under illumination with white light, 10 mW/cm²) of a BCBM+MEHPPV device. We note that at zero bias the ratio of photocurrent to dark current is more than 10³. As can be seen from Table 1, the open circuit voltage (V_{oc}) of ITO/PEDOT/MEHPPV/Al is 1.1 V which is similar to that reported in ITO/MEHPPV/Al devices^[4]. Similar V_{oc} was also achieved in ITO/PANI/MEHPPV/Al devices^[14]. The insensitivity of the V_{oc} to the work function of ITO (≈ 4.8 eV), PANI (≈ 5.0 eV) and PEDOT (≈ 5.2 eV) suggests that the HOMO of MEHPPV

is not higher than 4.8 eV plus polaron energy (0.15–0.2 eV) that ohmic contacts were achieved in all three cases.

Blending PCBM into MEHPPV results in a reduction of V_{oc} from 1.1 V to 0.8 V. Since the V_{oc} in MEHPPV/Al devices is determined by the p -polaron energy (≈ 4.8 eV) and the work function of the aluminum cathode^[1], the V_{oc} of 0.8 eV in MEHPPV:PCBM/Al devices implies that the V_{oc} in the DA blend devices is determined by the LUMO of PCBM. The value of $V_{oc} = 0.8$ V suggests a LUMO(PCBM) at ≈ 4.0 eV. Cyclovoltic spectroscopic measurement confirmed this result.

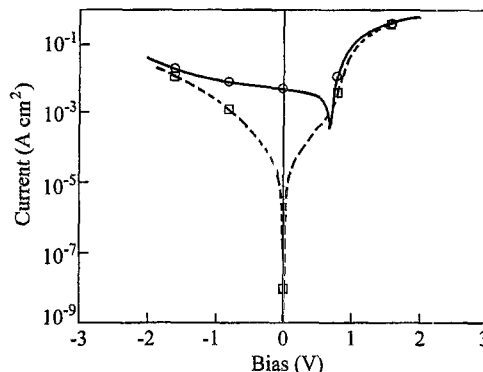


Fig. 1 I - V characteristics of device ITO/PEDT/PCBM+MEHPPV/Al

Table 1. Comparison of device characteristics ITO/PEDT/PCBM+MEHPPV/Al with different active materials (A:D = 4:1)

Active layer	Illumination under 10 mW/cm ²				Photosensitivity at 0 bias, 550 nm (A/watt)
	V_{oc} (V)	I_{sc} (mA/cm ²)	$F.F.$ (%)	η_e (%)	
MEHPPV	1.1	0.001	31.8	0.0034	0.0010
MEHPPV + C60	0.7	0.28	24.4	0.34	0.020
MEHPPV + PCBM	0.8	3.6	41.6	2.6	0.081

The short-circuit current (I_{sc}) increases from 0.003 mA/cm² for a pure MEHPPV device to 0.28 mA/cm², 3.6 mA/cm² for C60 + MEHPPV and PCBM + MEHPPV blend, respectively. Enhancement of I_{sc} in the device fabricated with the acceptor-doped MEHPPV blend clearly indicates that the photoinduced electrons and holes in the blend are effectively separated within the blend and collected by the electrode. One order of magnitude higher I_{sc} in PCBM-blended device than that in corresponding C60-blend device is consistent with the previous report^[2], suggesting that the side chain in PCBM molecules prevents the crystallization and molecular aggregation commonly seen in C60 film. The substituted C60 (PCBM) also improves the solubility that guarantees an effective blending at high molecular ratio of C60 and PCBM molecules. As can be seen from Table 1, the energy conversion efficiencies and photosensitivity are also increasing in the order of pure MEHPPV < C60:MEHPPV < PCBM:MEHPPV. In PCBM:MEHPPV devices, the energy conversion efficiency reaches 2.6% at 550 nm.

The effect of molecular ratio of PCBM to MEHPPV on the device performance was studied. Table 2 shows the performance of the devices that have three different weight ratios (PCBM:MEHPPV = 1:3, 1:1 and 4:1). The open circuit voltage does not change with PCBM/MEHPPV ratio, while I_{sc} , energy conversion efficiency and photosensitivity increase with increasing PCBM content. This is slightly different from the results observed in MEHPPV:CNPPV devices^[8]. We note that an increase in energy conversion efficiency along with the increase of PCBM ratio is the result of an increase in both collecting efficiency and photosensitivity. In the case of MEHPPV:CNPPV, the efficiency saturates at relatively low acceptor contents (for example CNPPV:MEHPPV < 10%)^[8]. This fact must be related with the morphology and the interface between donor and acceptor phases. We note that a further increase in PCBM fraction (larger than 4:1) leads to decreasing I_{sc} and efficiencies due to the deterioration of film quality. Figure 2 shows the spectral response of PCBM+MEHPPV at different

BCBM:MEHPPV ratio. Although the magnitude of photosensitivity increases drastically with the PCBM content, the spectral profile remains almost unchanged.

Table 2. Device characteristics as a function of D/A ratio

Weight fraction of PCBM in the blend	Illumination under 10 mW/cm ²				Photosensitivity at 0 bias, 550 nm (A/watt)
	<i>V</i> _{oc} (V)	<i>I</i> _{sc} (mA/cm ²)	<i>F.F.</i> (%)	<i>η</i> (%)	
25%	0.8	0.06	23.0	0.1	0.006
50%	0.8	0.5	24.6	0.8	0.060
80%	0.8	2.0	37.4	2.4	0.080

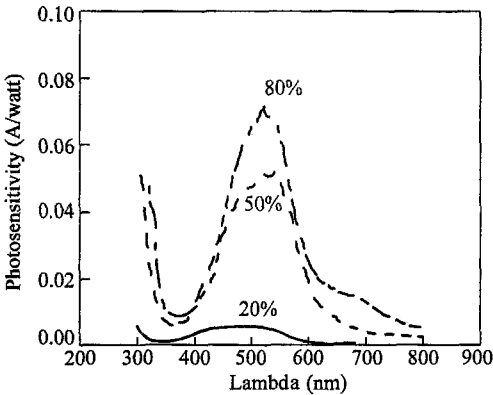


Fig. 2 Photosensitivity of devices with different PCBM weight fraction at 0 bias

We also investigated device performance as a function of thickness of the active layer. Table 3 shows the device characteristics with 5 different thicknesses. It is interesting to note that the filling factor increases monotonically with the thickness of the active layer except at a very high thickness of 200 nm. It would be expected to have a reverse dependence for polymer photodiodes due to low mobility and high trap concentration. The photosensitivity increases with thickness too. We have observed the remarkable reverse dependence for devices with undoped PPV type polymer^[15], where photosensitivity was increasing dramatically with decreasing device thickness until 20 nm. These facts again indicate the importance of microscopic phase separation in the D-A type blend system. Resulted from these two factors, the energy conversion efficiency was maximized at ca. 100 nm.

Table 3. Device characteristics as a function of polymer thickness

Thickness (nm)	Illumination under 10mW/cm ²				Photosensitivity at 0 bias, 550 nm (A/watt)
	<i>V</i> _{oc} (V)	<i>I</i> _{sc} (mA/cm ²)	<i>F.F.</i> (%)	<i>η</i> (%)	
40	0.4	1.8	30.6	0.58	0.054
60	0.6	2.4	39.7	1.52	0.070
100	0.7	3.2	42.4	2.34	0.080
160	0.8	3.1	45.6	2.18	0.068
200	0.8	1.9	38.8	1.62	0.050

It was reported by Sacriciftci *et al.*^[15] that inserting a thin LiF exciton-blocking layer between the Al cathode and the active layer can substantially improve energy conversion efficiency (due to improved fill-factor). When we inserted a thin layer barium (10 nm) layer between the MEHPPV and Al electrode, we observed a dramatic increase in device performance. Table 4 shows the characteristics of devices of ITO/PEDT/BCBM:MEHPPV/Ba/Al structure. A device with Al cathode only was fabricated for comparison. The data in Table 4 indicate that inserting a thin Ba metal layer between the active layer and aluminum improves the photosensitivity.

The filling factor, on the other hand, is not sensitive to the work function of the cathode. As we indicated previously in light-emitting devices, a thin layer of Ba and BaO gives practically identical device performance^[16]. This leads us to postulate that at not very low vacuum (ca. 1×10^{-6} torr) in the evaporating chamber, a thin layer of Ba must be partially oxidized to BaO (perhaps non-stoichiometric $Ba_{1+x}O_{1-x}$). Salaneck pointed out the occurrence of possible oxidation of Ca in a low-vacuum evaporating chamber^[17]. Thus, we tentatively assign the function of the thin Ba layer as the exciton-blocking layer.

Table 4. Device characteristics with or without a thin barium layer (PCBM:MEHPPV= 4:1, thickness of active layer = 80 nm, Ba thickness = 10 nm)

Active layer	Illumination under 10 mW/cm ²				Photosensitivity at 0 bias, 550 nm (A/watt)
	<i>V</i> _{oc} (V)	<i>I</i> _{sc} (mA/cm ²)	<i>F.F.</i> (%)	<i>η</i> (%)	
MEHPPV	1.0	0.007	24.5	0.0034	0.0004
PCBM+MEHPPV	0.8	3.0	42.5	3.60	0.106
PCBM+MEHPPV*	0.8	2.2	39.7	3.87	0.122
PCBM+MEHPPV**	0.8	2.0	37.4	2.4	0.08

* Active area of device = 3 cm²; ** Control device without Ba layer

As noted by Yu *et al.*^[1], the photosensitivity of MEHPPV:PCBM devices can be further improved under reverse bias. In Fig. 3 we show the evolution of spectral response of photosensitivity with the magnitude of the reverse bias. As can be seen from the figure, the photosensitivity reached 0.8 A/W at -15V for 550 nm. This value corresponds to the quantum yield 180% el/ph. Second carrier emission under high biasing field could account for this effect^[1]. Photoconductivity gain due to high field strength and geometric arrangement may also contribute to the > 100% quantum yield^[16]. No matter what the detailed mechanism is, the data in Fig. 3 demonstrate the discovery of a polymer photodetector having high quantum efficiency. These devices appear promising for use in practical applications.

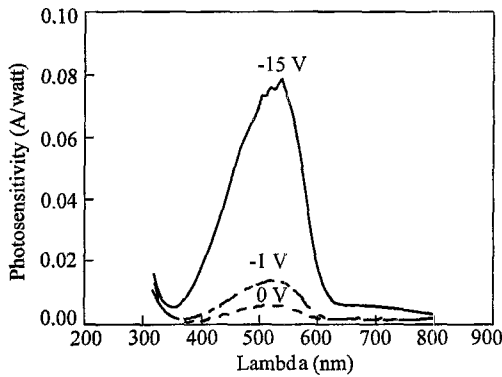


Fig. 3 Photosensitivity of ITO/PEDT/PCBM+MEHPPV (4:1)/Al devices at negative bias

In summary, we have fabricated and characterized in detail a device with PCBM-blended MEHPPV as an active materials. Highest energy conversion efficiency at single wavelength reaches 3.9% as the photovoltaic device. At negative bias the photosensitivity of the device reaches 0.8 A/W which is even higher than those of visible photodetectors made from inorganic semiconductor crystals.

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