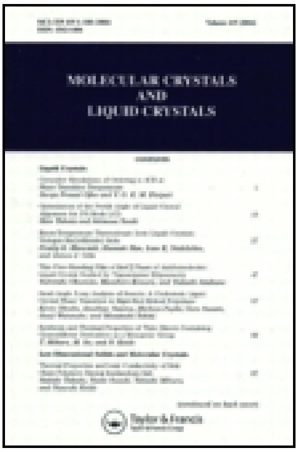

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High Open-Circuit Voltage of Organic Bulk Heterojunction Solar Cells Base on Poly(3-hexylthiophene): Fullerene Derivatives

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High Open-Circuit Voltage of Organic Bulk Heterojunction Solar Cells Base on Poly(3-hexylthiophene): Fullerene Derivatives

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*Here, we report the fabrication of high efficiency poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C61-butyric acid methyl ester (PCBM) and [6,6]-diphenyl-C_{62}-*bis*(butyric acid methyl ester) (bis-PCBM) blended photovoltaic cells. Bulk heterojunction photovoltaic cells with an ITO/G-PH/P3HT:PCBM (or bis-PCBM)/TiO_x/Al configuration were fabricated, and the device using P3HT:bis-PCBM (1:0.7) showed the best performance compared with those using P3HT:PCBM (1:0.7). A maximum power conversion efficiency (PCE) of 4.50% ($V_{oc} = 0.64$ V, FF = 0.62) was achieved with P3HT:bis-PCBM (1:0.7).*

Keywords Bis-pcbm; [6,6]-Diphenyl-C_{62}-bis(butyric acid methyl ester); open-circuit voltage; organic bulk heterojunction solar cells

Introduction

Organic bulk heterojunction (BHJ) solar cells offer solar energy harvesting characterized by low cost, ease of processing, physical flexibility, and large area coverage [1–2]. Recently, several research groups have reported that organic BHJ solar cells based on a composite film using poly(3-hexylthiophene) (P3HT) as an electron donor and [6,6]-phenyl-C_{61}-butyric acid ester (PCBM) as an electron acceptors show a power conversion efficiency (PCE) near 5–6% [3–4]. In order to enhanced PCE of organic BHJ solar cells, one approach will be to controlling of the lowest unoccupied molecular orbital (LUMO) of electron acceptor materials. When analyzing the energy levels of the organic BHJ solar cells system, due to the high exciton binding energy in donor materials, light absorption does not lead directly to free charge carriers, but an exciton is created. By mixing in an electron acceptor material, it becomes energetically favorable for electron to transfer to the LUMO of acceptor, thus breaking up the exciton [5]. For electron transfer from donor to acceptor to arise, the LUMO of the donor needs to be 0.3 eV to 0.5 eV higher than the LUMO

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of the acceptor [6]. There are two ways to ensure efficient electron transfer from donor to acceptor, either on the donor or on the acceptor side. One approach is design and synthesis of low-band gap polymers, which improved overlap of the polymer absorption spectrum with the standard solar spectrum under AM 1.5 global. Another method is development of new electron acceptor materials with high-lying LUMO, which increase of open-circuit voltage (V_{oc}) without affecting the absorption of the solar cell.

In the present article, we investigated PCBM and bis-PCBM as an electron acceptors for the fabrication of organic BHJ solar cells using P3HT as an electron donor and their characterization of photovoltaic properties of organic BHJ solar cells.

Experimental

Characterization

UV-visible absorption spectra were recorded on a V-570 UV-vis-near IR spectrophotometer model (JASCO). After both PCBM and bis-PCBM films for absorption measurements were spin-coated on quartz glass, films dried in air for 30 min without any heat treatment. The AFM images were acquired with a Digital Instrument Nanoscope^{TM} 3D ADC5, Mutimode (Veeco Instruments Inc., CA) in tapping mode. Samples for AFM image measurement were fabricated by first spin-coating G-PH buffer layer on top of ITO-coated glass substrates and then drying at room temperature under air. The active layer was spin-coated on top of the G-PH. The samples structure for AFM imaging of surface morphology were ITO/G-PH/P3HT:PCBM and ITO/G-PH/P3HT:bis-PCBM.

Fabrication and Testing of Organic BHJ Solar Cells

The organic BHJ solar cells were fabricated with ITO (indium tin oxide)/G-PH (adding glycerol to PEDOT:PSS)/P3HT:PCBM (or bis-PCBM)/TiO_x/Al. Figure 1 shows organic BHJ solar cell configuration. The patterned ITO-covered glass substrate was cleaned with detergent solution, distilled water, acetone, and isopropyl

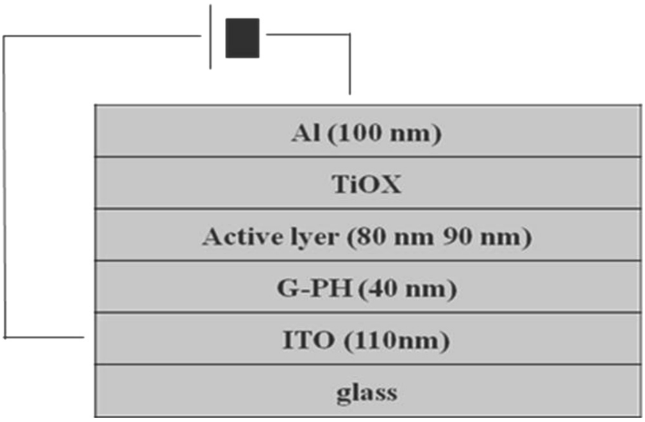


Figure 1. The device structure used for fabrication of the photovoltaic cells.

alcohol using an ultrasonication method and UV-ozone treatment. Subsequently, G-PH layer was spin-coated onto the cleaned ITO-covered glass substrate and the G-PH layer was dried on hotplate under air for 20 min at 150°C. The thickness of G-PH was around 40 nm. The P3HT, PCBM and/or bis-PCBM were dissolved in 1:1 weight ratio of *o*-dichlorobenzene and chloroform cosolvent system. Both P3HT:PCBM and P3HT:bis-PCBM were blended at 1:0.7 weight ratio and allowed to stir for 24 h. The active layer (80 nm) was spin-coated from the G-PH layer and dried at room temperature for 30–40 min. After drying the active layer, TiO_x was spin-coated on top of active layer and dried on hotplate under air for 10 min at 80°C. Organic BHJ solar cells were charged into the thermal evaporator for the deposition of the Al cathode. The Al cathode (100 nm) was deposited through a shadow mask on top of the active layer under a vacuum less then 5.0×10^{-6} torr, which yields a 4 mm^2 of active area per each pixel. Solar cell performances were studied by measuring photocurrent density-voltage (J-V) characteristics under light illumination. Measurement of the J-V characteristics of solar cells was carried out using a Solar Simulator (Orel 300 W simulator, models 81150) under a simulated solar light with ARC Lamp power supply (AM 1.5 G, 100 mW/cm^2) and a computer-controlled Keithley 236 source measure unit.

Results and Discussion

The [6,6]-diphenyl-C_{62}-*bis*(butyric acid methyl ester) (bis-PCBM), the adduct analogue of PCBM, is normally obtained as a by-product of the preparation of PCBM. PCBM and bis-PCBM show similar characteristic UV-visible absorption peaks as shown in Figure 2. The bis-PCBM exhibited more intense absorption peak than the PCBM. From the onset of absorption spectrum, the band-gaps of PCBM and bis-PCBM were calculated to be 1.80 eV and 1.75 eV.

We measured the HOMO and LUMO energy levels using cyclic voltammetry. The HOMO and LUMO energy levels of PCBM and bis-PCBM for the standard

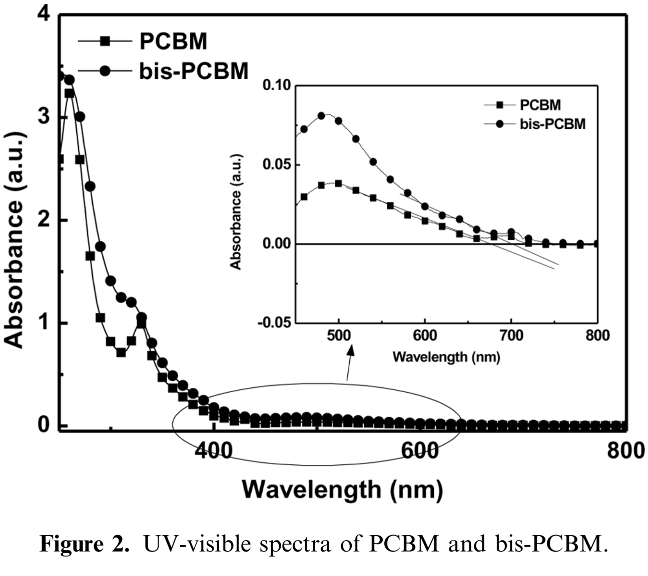


Figure 2. UV-visible spectra of PCBM and bis-PCBM.

ferrocene/ferrocenium (−4.8 eV) were −4.30 eV, −6.10 eV and −4.19 eV, −5.94 eV, respectively. The energy band diagram of ITO, PEDOT:PSS, P3HT, PCBM, bis-PCBM, TiO_x and Al is shown in Figure 3. In case of the P3HT:PCBM blended photovoltaic cell, due to the large offset between LUMO energy levels of the P3HT and PCBM, the electron transfer from the P3HT onto the PCBM takes place, and thus breaking up the excition. However, since the difference in LUMO levels of the P3HT and the PCBM is much larger than the exciton binding energy, the excess energy of the electron and the hole is dissipated quickly [7]. For an efficient electron transfer from the donor to the acceptor, the relative position of LUMO energy levels of the donor and acceptor is crucial. Due to the higher LUMO level of bis-PCBM than that of PCBM, the dissipation of electron and hole decreased and V_{oc} of the P3HT:bis-PCBM blended photovoltaic cell enhanced.

The organic BHJ solar cells were fabricated using the P3HT as an electron donor and fullerene derivatives (PCBM or bis-PCBM) as an electron acceptor. The BHJ solar cells, having device structure consisting of ITO (110 nm)/G-PH (40 nm)/ P3HT:fullerene derivatives (PCBM or bis-PCBM) (80 nm)/TiO_x/Al (100 nm) were optimized by the weight ratio of P3HT and fullerene derivatives (PCBM or bis-PCBM) (1:0.7) and the active layer thickness (80 nm). The conductivity and morphology of the buffer layer was improved by adding 6 wt% glycerol to the PEDOT:PSS (CLEVIOS PH) [8]. Furthermore, we inserted the TiO_x layer between the active layer and the Al cathode. LUMO energy level of the TiO_x near the Fermi level of Al and have the large band gap, which serves as electron transfer and hole blocking layer [9].

Figure 4 shows the current density-voltage characteristics (J-V) of the P3HT:PCBM and P3HT:bis-PCBM based on solar cells under illumination (AM 1.5) and these results are summarized in Table 1. Form the J-V curve, both the P3HT:PCBM and P3HT:bis-PCBM based on solar cells have nearly the same short-circuit current density (J_{sc}) and fill factor (FF) of 11.60 mA/cm^2 and 62%.

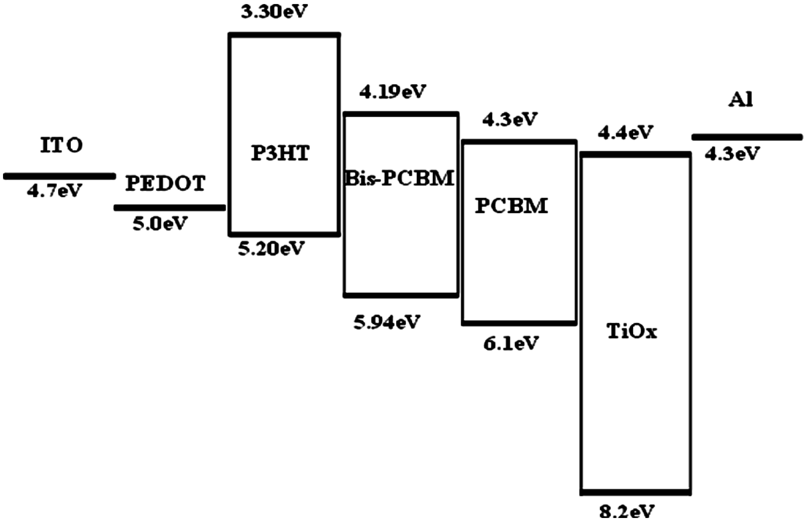


Figure 3. Energy band diagram of P3HT, PCBM, bis-PCBM and TiO_x.

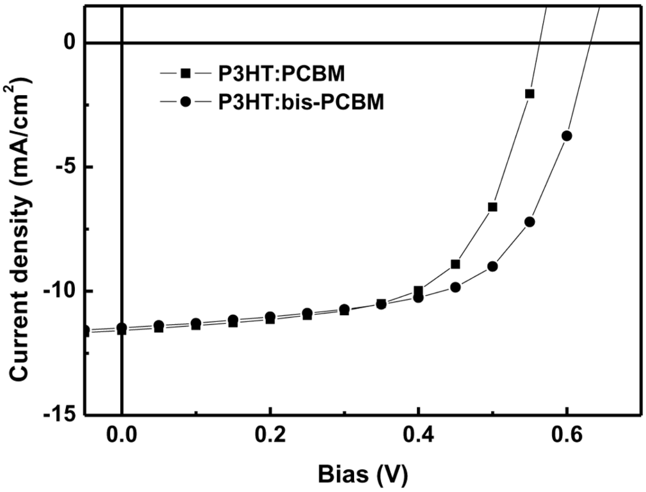


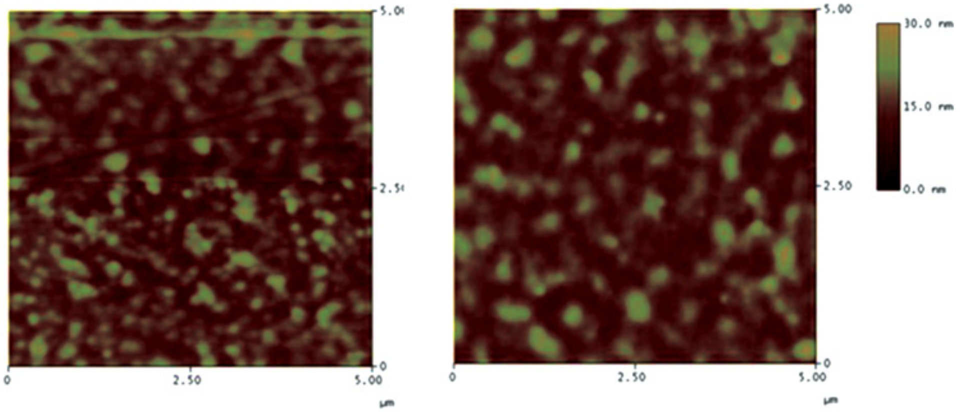
Figure 4. The current density-voltage (J-V) curves for the P3HT:PCBM and P3HT:bis-PCBM (AM 1.5 G condition with incident light power intensity of 100 mW/cm^2).

However, V_{oc} of the P3HT:bis-PCBM based on solar cell is 0.64 V, which value is higher than that of P3HT:PCBM based on solar cell (0.56 V). The increased V_{oc} leads to the enhanced the PCE of P3HT:bis-PCBM based on solar cell (4.50% compared to 4.01% for the P3HT:PCBM based on solar cell). This likely results from the fact that bis-PCBM was clearly the superior acceptor in combination with P3HT, due to bis-PCBM has a higher LUMO than PCBM [10].

AFM images of the active layers were investigated with 1:0.7 ratio of P3HT:PCBM and P3HT:bis-PCBM and the images are shown in Figure 5. Those images show that the similar surface is present in both P3HT:PCBM (a) and P3HT:bis-PCBM (b) blend samples. The analysis showed that the root-mean-square values for two samples are 3.08 nm and shows similar surface morphology. According to the BHJ solar cell, the V_{oc} is determined by the energy difference between the HOMO level of the donor and LUMO level of the acceptor, and it is also influenced by the quality of the film preparation condition. So we believe that although the morphologies are similar for the two samples, and may play a role in the V_{oc}.

Table 1. Photovoltaic performance of BHJ solar cells under AM 1.5 G illumination (100 mW/cm^2)

Active layer	Ratio (w/w)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
P3HT:PCBM	1:0.5	0.56	9.08	59.59	3.03
	1:0.7	0.56	11.58	61.84	4.01
	1:1	0.56	10.09	63.71	3.61
P3HT:bis-PCBM	1:0.5	0.64	9.51	61.61	3.75
	1:0.7	0.64	11.63	62.27	4.50
	1:1	0.64	10.35	64.92	4.30



(a) (b)

Figure 5. AFM micrographs of active layers produced from P3HT:PCBM (a) and P3HT:bis-PCBM (b). The RMS roughness over the 5 μm × 5 μm areas.

Conclusions

In conclusion, we studied the fullerene derivatives, bis-PCBM, with a higher LUMO level compared to that of PCBM, in order to reduce to energy loss in the electron transfer from the electron donor to electron acceptor material in BHJ solar cells. The V_{oc} values of P3HT:PCBM and P3HT:bis-PCBM blend cell are 0.56 V and 0.64 V, respectively while maintaining the J_{sc} and FF values of nearly 11.60 mA/cm^2 and 62% under AM 1.5 G illuminated conditions at an intensity of 100 mW/cm^2. As result, maximum PCE of 4.50% was reported for P3HT: bis-PCBM based on solar cell.

Acknowledgment

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