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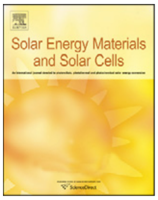

Effect of blend composition in BisEH-PFDTBT:$PC_{70}BM$ solar cells

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ABSTRACT

The photovoltaic properties of bulk-heterojunction solar cells with an active layer made of an alternating fluorene copolymer, poly{[2,7-(9,9-bis-(2-ethylhexyl)-fluorene)]-alt-[5,5-(4,7-di-2′-thienyl-2,1,3-benzothiadiazole)]}, and [6,6]-phenyl-C_{71}-butyric acid methylester are investigated by varying the blend composition and the incident light power intensity. An efficient donor–acceptor intermixing is reached with donor to acceptor weight ratios of at least 1:3, while at lower acceptor content charge trapping effects are evidenced by the light intensity dependent study. Reverse bias analysis demonstrates that a major limiting factor for the performance of the investigated solar cells is represented by the poor ability of the generation of free charge carriers, attributed to the low hole mobility in the polymer phase.

1. Introduction

Polymer solar cells are attracting increasing attention because of their compatibility with flexible substrates, easy and low-cost processability from solution, and roll-to-roll production process [1]. The most successful approach for the active layer of polymer solar cells is represented by the bi-continuous composite of an electron-acceptor (A) and an electron-donor (D) material, realized in the so-called bulk-heterojunction (BHJ) structure [2]. The strong effort in the past years in the development of new conjugated polymers as electron-donors [3], with improved electronic properties with respect to the past, has led to a steep increase of the performance of polymer solar cells, and power conversion efficiencies between 6% and 8% have been achieved [4] for BHJ cells based on a conjugated polymer and a soluble derivative of fullerene. The energy level engineering [5] is indeed a promising strategy to improve the performance of BHJ solar cells, through the design of “specialized” conjugated polymers for the photovoltaic application. One successful approach in the synthesis of new electron-donors is to push their highest occupied molecular orbital (HOMO) level towards lower energy [6], in order to maximize the difference between the lowest unoccupied molecular orbital (LUMO) energy level of the acceptor, usually a fullerene derivative, and the HOMO of the donor. Through this approach, solar cells exhibiting high open-circuit voltage (V_{oc}) can be obtained, as first demonstrated by Brabec et al. [7].

An effective strategy in the chemical synthesis of new conjugated polymers for photovoltaic application is based on the alternation of electron poor and electron rich monomer units in the polymer chain, to attain a low energy gap, and on the fine tuning of the electronic structure of the electron-rich units to lower the HOMO level. Alternating fluorene copolymers with electron deficient units (benzothiadiazole, benzopyrazine) and π-conjugated spacers are an example of this approach [8]. Poly{[2,7-(9,9-bis-(2-ethylhexyl)-fluorene)]-alt-[5,5-(4,7-di-2′-thienyl-2,1,3-benzothiadiazole)]} (BisEH-PFDTBT, Fig. 1) is an alternating fluorene copolymer with an optical energy gap of 1.9 eV and a deep HOMO level of -5.5 eV [9]. A V_{oc} of around 1 V has been reported for solar cells made with BisEH-PFDTBT blended with common soluble fullerene derivatives in a donor to acceptor (D:A) weight ratio of 1:3 [9,10]. However, a systematic characterization of devices based on this conjugated polymer has not been performed yet, so the factors limiting the cell performance have not been established. Herein, we present a detailed study of solar cells made with BisEH-PFDTBT as electron-donor and [6,6]-phenyl-C_{71}-butyric acid methylester ($PC_{70}BM$) as electron-acceptor. The effect of blend composition on the photovoltaic properties of BisEH-PFDTBT:$PC_{70}BM$ solar cells is described, as well as the dependence of photovoltaic parameters on light power intensity and a study of the generation ability of free carriers. From the

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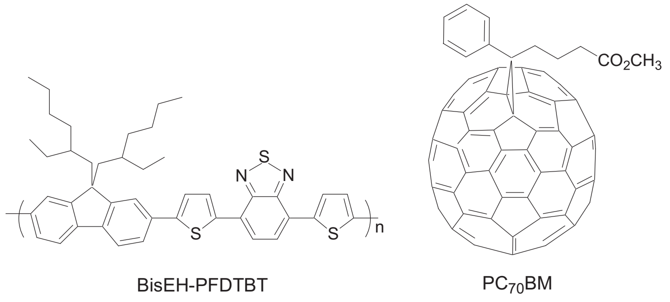

Fig. 1. Molecular structures of materials used in this study.

combination of such investigations the major factors limiting the performance of BisEH-PFDTBT:PC$_{70}$BM solar cells are indicated.

2. Experimental

BisEH-PFDTBT was prepared through Suzuki polymerization, slightly modified in the product purification step [11] (Mw=13600, PDI=2.5). Solar cells were fabricated on patterned ITO-coated glass substrates previously cleaned with detergent and water, then ultrasonicated in acetone and isopropyl alcohol for 15 min each. A PEDOT:PSS (Clevios P VP AI 4083) layer was spin-coated at 4000 rpm onto UV-ozone-treated ITO-coated substrates to a thickness of around 40 nm, then baked in an oven at 140 °C for 10 min. BisEH-PFDTBT was blended with PC$_{70}$BM (Aldrich) and dissolved in 1,2-dichlorobenzene (25 g L^{-1}). The solutions were stirred at 40 °C for four days. The blend solutions were spin-coated in air onto the ITO/PEDOT:PSS substrates. The thickness of the active layers, measured with a Tencor AlphaStep profilometer, ranged between 100 nm and 120 nm. Then the samples were transferred to an argon glove-box, where the device structure was completed with the thermal evaporation of the LiF (0.9 nm)/Al (80 nm) cathode at a base pressure of 3×10^{-6} mbar. The active device area, defined by the shadow mask used for the cathode deposition, was 8 mm^2. Some devices were post-production thermal annealed in glove-box at 110 °C for 10 min.

The device electrical characterization was carried out at room temperature in an argon glove-box. Solar cells were illuminated using a solar simulator (SUN 2000, Abet Technologies) and the light power intensity was calibrated using a certified silicon solar cell. For light-intensity dependent measurements, a set of quartz neutral filters was used to vary the incident light power. The current–voltage curves were taken with a Keithley 2400 source-measure unit.

3. Results and discussion

Solar cells with the structure ITO/PEDOT:PSS/BisEH-PFDTBT:PC$_{70}$BM/LiF/Al were prepared with the following donor to acceptor weight ratios: 1:1, 1:2, 1:3, and 1:4. The photovoltaic parameters were extracted from the current–density–voltage (*J*–*V*) curves under AM 1.5G illumination condition (100 mW cm^{-2}), at room temperature. Their dependence on blend composition is shown in Fig. 2 for devices with active layers of comparable thickness, ranging between 100 nm and 120 nm.

The open-circuit voltage is roughly independent on the blend composition, in the investigated range, and its value of around 1.0 V (Table 1) is well correlated to the difference between the LUMO level of PC$_{70}$BM (−4.3 eV, see, e.g., Ref. [4b]) and the HOMO level of BisEH-PFDTBT. Short-circuit current (J_{sc}) and fill factor (FF) have the same trend with the D:A ratio and show their maximum value for the highest amounts of the acceptor component. The increase of both fill factor and J_{sc} indicates that high D:A ratios are necessary in BisEH-PFDTBT:PC$_{70}$BM blends to achieve sufficient phase percolation and the formation of an appropriate donor–acceptor intermixing, required for efficient charge transport, as also confirmed by the evolution of the blend morphology. Indeed, the atomic force microscopy (AFM) phase images (see Supplementary data) showed that the 1:1 blend has a coarser morphology, that becomes finer by increasing the fullerene content, suggesting that the formation of percolating paths is favoured. The most significant variation in the blend morphology occurred by changing the D:A ratio from 1:1 to 1:2, and, accordingly, the maximum variation of the photovoltaic parameters was also observed (Table 1).

A more efficient charge transport is usually accomplished by a reduced series resistance (R_s) [12], as also observed for the

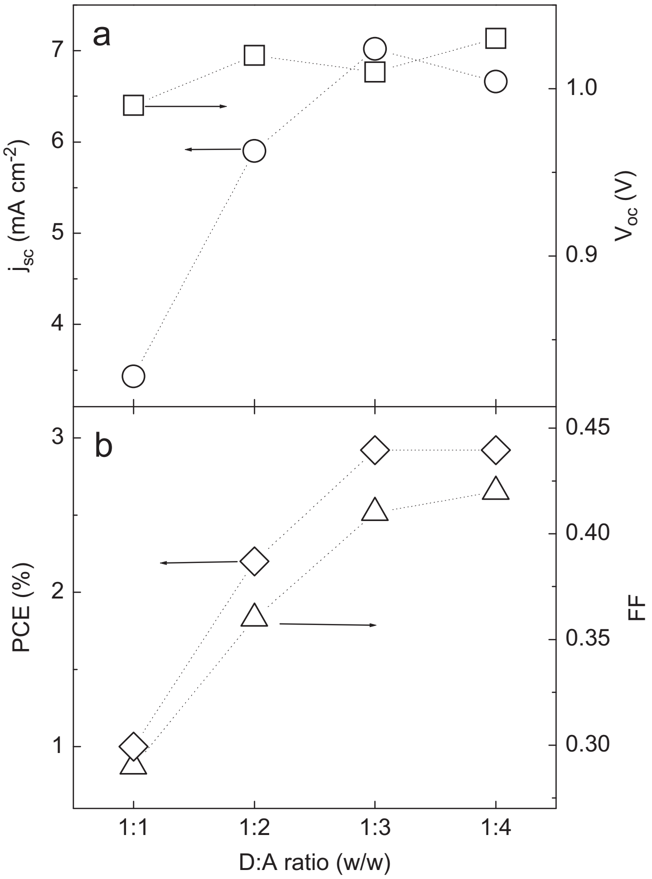

Fig. 2. (a) Short-circuit current (circles) and open-circuit voltage (squares), (b) power conversion efficiency (diamonds) and fill factor (triangles) of ITO/PEDOT:PSS/BisEH-PFDTBT:PC$_{70}$BM/LiF/Al solar cells, under AM 1.5G simulated solar irradiation (100 mW cm^{-2}), for different D:A weight ratios. The lines are shown to guide the eye.

Table 1
Summary of the parameters extracted from the *J*–*V* characteristics of ITO/PEDOT:PSS/BisEHPFDTBT:PC$_{70}$BM/LiF/Al solar cells.

Thickness (nm)	D:A ratio (w/w)	R_s (Ω cm^{-2})	Photovoltaic parameters (AM 1.5G, 100 mW cm^{-2})			
			J_{sc} (mA cm^{-2})	V_{oc} (V)	FF	PCE (%)
98	1:1	11.41	3.43	0.99	0.29	1.00
119	1:2	3.13	5.90	1.02	0.36	2.20
105	1:3	2.24	7.02	1.01	0.41	2.92
102	1:4	2.52	6.66	1.03	0.42	2.92