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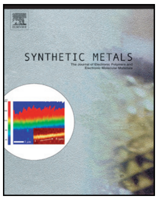

Enhanced performance of bulk heterojunction solar cells using double layers deposition of polymer:fullerene derivatives

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ABSTRACT

Poly[4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene-*co*-quinoxaline] (PBDTQx) copolymer; to be used as an electron donor in bulk heterojunction (BHJ) polymer solar cell; was synthesized from benzo [1,2-b:4,5-b′]dithiophene and quinoxaline via a Stille coupling reaction. BHJ polymer solar cells based on the ternary blend of PBDTQx; indene-C_{60} bisadduct (ICBA) and [6,6]-phenyl-C_{71}-butyric-acid-methyl-ester($PC_{71}BM$) were then fabricated and tested for the power conversion efficiency (PCE) values. From the IV curves; it was found that the open circuit voltage (V_{oc}) and current density (J_{sc}) of the solar cell increased with the addition of ICBA. This was related to the lowest unoccupied molecular orbital (LUMO) level of ICBA; which is suitable with those of $PC_{71}BM$ and PBDTQx. It was also found that PCE of the solar cell can be improved significantly by double layers coating of the active materials (PBDTQx:$PC_{71}BM$:ICBA). The above effect was ascribed to changes in morphology and crystallinity of the active layer.

1. Introduction

Polymer solar cells, particularly those based on bulk heterojunction (BHJ) structure, is known to be a kind of new generation solar cells, exhibiting some advantage properties such as low processing cost, light-weight and high flexibility [1–2]. This technology is considered interesting and promising in term of the progress in power conversion efficiency values [3–4]. At the present time, however, the polymer solar cell technology has yet to be further developed before its commercialization can be realized. These developments include the enhancement of its PCE, not to mention the improvements of cell's durability and its cost competitiveness. To achieve the above goals, it is worth reminding that properties and performance of the BHJ cell depend on many factors including material design and the parameters during the fabrication process which have to be controlled and optimized.

Generally, the BHJ solar cells can be prepared by blending an electron donor material with an electron acceptor material together before sandwiching them between two different electrodes [5–6]. In addition, the use of a donor-acceptor blend (so called an active layer) from more than two components is also interesting and worth exploring. In fact, work by Khlyabich et al. [7] and Yang et al. [8] demonstrated that by adding a secondary p-type donor polymer as the third component, light absorption of the active layer was extended to a wider spectrum region. Similarly, Khlyabich et al. [9] showed that an open circuit voltage (V_{oc}) and the PCE of photovoltaic devices were enhanced by blending two different electron acceptors in the ternary active layer. Recent work by Cheng et al. [10], using ternary blend polymer solar cells based on poly([10-b′]dithiophene-2,6-diyl]{3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b′]thiophenediyl}) (PTB7), indene-C60 bisadduct (ICBA) and $PC_{71}BM$, showed that LUMO energy levels of the three-components are matched and thus charge transfer across the donor/acceptors interface was improved. The common electron donor material used for BHJ polymer solar cell is poly (3-hexylthiophene) (P3HT). However, several attempts have been made to develop newer kind of lower band gap polymers, in order to enhance light harvesting [11]. One possible strategy is that by synthesizing copolymers with alternating electron rich and electron deficient units in the backbone [12]. With this copolymer

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structure, a better charge transfer from the donor to the acceptor phase can be expected due to an enhanced π–π stacking between copolymer chains [13–14]. In this regard, copolymer based on benzo[1,2-b:4,5-b′]dithiophene (BDT) is particularly interesting. The BDT repeating units have a planar and symmetric conjugated structure. Its occupied molecular orbital (HOMO) level is considerably high, contributing to a high V_{oc} of devices [15–20]. Consequently, BDT has a great potential to be used as building blocks for coupling with various electron withdrawing materials. On the other hand, quinoxaline (Qx) and its derivatives have been designed and used as an electron acceptor material. This was due to the strong electronegativity of the two nitrogen atoms and relatively high stability of the quinoid form [21–23].

Apart from the materials design and synthesis, the fabrication process also plays role. In a fabrication of BHJ solar cell, the active layer was normally applied onto the electrode by a spin coating technique. This technique is considerably simple, rapid and required inexpensive equipment. However, one of the drawbacks of this technique is that significant amount of the semi-conducting materials, which are generally expensive, can be loss during the fabrication. To solve this problem, an alternative coating technique called rapid convective deposition was used to deposit polymer and metal oxide from solution. Only 5–20 uL of the solution was used to cover one square inch thin film. This technique was originally used for monolayer deposition of colloidal silica on a flat substrate [24–26]. Effects of meniscus formation at a corner between substrate and deposition blade on film thickness and deposition morphology during the deposition was described elsewhere [27]. Besides, photovoltaic performance of a BHJ solar cell can be further enhanced by annealing the fabricated cell [28]. There are several types of annealing, including a thermal annealing [29] and a solvent annealing [30]. Both of which have something in common, i.e., by carrying out an annealing process, percentage crystallinity of the active layer can be induced. Particularly, in the case, of a solvent annealing, it was believed that the enhancement of percentage crystallinity was attributed to a slow growth of a crystalline polymer. Consequently, a better intermolecular charges transfer and the enhancement of polymer solar cell performance were resulted [31–32]. In our opinion, the above statement implies that any parameter and process capable of inducing more percentage crystallinity of polymer in the active layer should brought about a greater power conversion efficiency of the solar cell. In this regard, it was believed that if a solidification time of the active layer that was coated on top of an ITO substrate was increased or prolonged, the polymer chains would have more time to form a high crystalline phase and a greater power conversion efficiency of the solar cell can be expected. Therefore, in this study, rather than fabricating the photovoltaic device with an architecture containing a single layer of the active materials as usual, we hypothesized that an annealing effect might be induced if the materials were sequentially coated on top of the substrate by two steps. This architecture is so called a double layers coating herein. This is an aspect deserving a clarification. Considering the above logics, synthesis and photovoltaic performance of BHJ solar cells containing PBDTQx, fabricated by a novel convective deposition technique, is worth exploring. The aim of this work is to investigate the power conversion efficiency of the BHJ cell based on an active layer consisted of a ternary blend PBDTQx:PC71BM with and without adding an indene-C60 bis-adduct (ICBA). In addition, the effect of coating a double active layers of the ternary blend (PBDTQx:PC71BM:ICBA) on photovoltaic performance of the cell is also of our interest.

2. Experimental

2.1. Materials

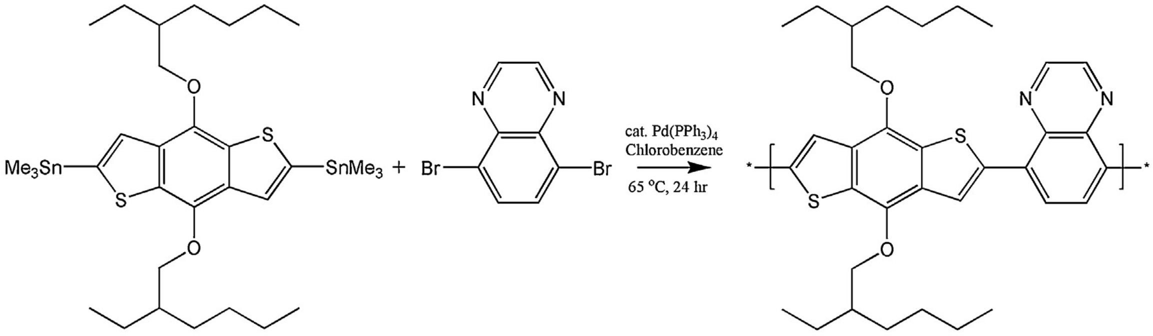
All of the reagents are purchased from Aldrich and used as received. 5,8-Dibromoquinoxaline was recrystallized from acetone.

2.2. Synthesis

The polymer was synthesized by Stille coupling [33–34]. The synthesis route of PBDTQx is shown in Scheme 1. Experimentally, 231.7 mg (0.3 mmol) of 2,6-bis(trimethyltin)-4,8-bis(2-ethylhexyloxy)benzo[1,2-*b*:4,5-*b*′]dithiophene and 88.2 mg (0.3 mmol) of 5,8-dibromoquinoxaline was weighted into the test tube and 15 mg of $Pd(PPh_3)_4$ were added. Then, 3 ml of chlorobenzene was added via a syringe. The tube was sealed and the polymerization was carried out at 65 °C for 24 h. under nitrogen protection. The raw materials was precipitated into 500 ml of methanol and collected by filtration. The precipitate was dissolved in 50 ml of chlorobenzene and filtered with celite to remove the Pd catalyst. The solution was concentrated and precipitated in 500 ml of methanol. The polymer was subjected to soxhlet extraction with methanol, hexane, and chloroform. The polymer was recovered from chloroform fraction and dried under vacuum for 24 h to get the final product yielding (60%) of a dark violet solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.05–8.07$ (m, 4H), 7.59–6.91 (m, 2H), 4.89–3.49 (m, 4H), 2.18–0.88 (m, 30H)

2.3. Characterizations and measurements

NMR spectra was recorded by a Bruker Furier at 300 MHz and was referred to tetramethylsilane. UV–vis absorption spectra were measured on a Agilent Cary 5000 UV–vis–NIR. The thermal property of PBDTQx is investigated by thermogravimetric analysis TGA. The (TGA) was recorded on a NETZSCH STA 409 PC over the temperature ranging from 30 to 600 °C under nitrogen gas atmosphere at a



Scheme 1. Synthetic route of PBDTQx.