

Controlling the morphology of the active layer by using additives and its effect on bulk hetero-junction solar cell performance

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Abstract—Improvement of the surface roughness and power conversion efficiency (PCE) of bulk hetero-junction (BHJ) solar cells was made by the addition of organic additives for the cells based on a low energy-gap polymer, poly [2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta [2,1-b;3,4-b'] dithiophene)-alt-4,7(2,1,3-benzothiadiazole)] (PCPDTBT), as an electron donor and [6,6]-phenyl C61 butyric acid methyl ester (PC61BM) as the electron acceptor. The PCPDTBT : PC61BM active layers were prepared by spin-coating process from four different organic solvents: pure chlorobenzene, chlorobenzene with 2.5 vol% 1,2-ethanedithiol (EDT) additive, chlorobenzene with 2.5 vol% 1,8-octanedithiol (ODT) additive, and chlorobenzene with a combination of 2.5 vol% EDT and 2.5 vol% ODT additives. The smoothest surface of the active layer, which was observed by AFM, was obtained in the case of PCPDTBT : PC61BM prepared with a combination of EDT and ODT additives in chlorobenzene, and a maximum PCE of 3.5% was achieved.

Keywords: Organic Solar Cells, Bulk Hetero-junction, 1,2-Ethanedithiol, 1,8-Octanedithiol, Additives

INTRODUCTION

Over the past decades, organic photovoltaics (OPV) have attracted considerable attention [1-3]. They have several advantages over conventional inorganic solar cells, including low-cost, flexibility, small thickness, light-weight, and simple fabrication process [4]. Significant progress in bulk hetero-junction polymer solar cell technology has been achieved over the last decade. At present, single-junction organic solar cells have power conversion efficiency (PCE) more than 10% with the state-of-art devices [5]. High efficiency devices always rely on both material development and state-of-the-art device architecture [6]. The efficiency of OPVs can be improved through advances in device architecture and successive optimizations, including morphology control [7-12], interface modification [13-20], and optical modulation [21-24]. As a powerful approach, morphology control is commonly used to improve device performance.

A range of morphology control approaches are available for OPV devices. One of the most effective methods to control the morphology of BHJ films is the addition of a third non-reacting chemical compound, a processing additive, to the donor and acceptor solution [10]. The addition of a small volume of alkanedithiols to the solution used to prepare active layer films results in a significant increase in the power conversion efficiency of photovoltaic cells through alterations of the BHJ morphology [25]. This approach provides a way to control the morphology of BHJ active layers when thermal annealing is either undesirable or ineffective. The effect of adding additives was explained by the formation of an optimal nano-morphology in BHJ active layers because of the ability of alkanedithiols to selectively dissolve the fullerene component, whereas

the polymer is less soluble [26].

This paper reports the performance of PCPDTBT : PC61BM OPVs devices prepared in chlorobenzene (CB) solvent with different additives, such as 1,8-octanedithiol (ODT), 1,2-ethanedithiol (EDT), and a combination of EDT and ODT. The active layers were prepared by a wet process using spin-coating technique. Four mixture solvents of CB with different additives were used to prepare the BHJ active layer solutions, and the effects of the additives on the surface morphology of active layer, optoelectronic properties and performance of device were investigated.

EXPERIMENTAL DETAILS

PCPDTBT (M_w in the range 7000-20000), PC61BM (>99.9%), ODT, EDT, poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT : PSS) and CB were purchased from Aldrich. The active layers of OPV devices were prepared using PCPDTBT and PC61BM as the organic electron donor and electron acceptor material, respectively. Fig. 1 shows the molecular structure of PCPDTBT, PC61BM, ODT, and EDT.

Spin-coating technique was used to form the active layer of OPV

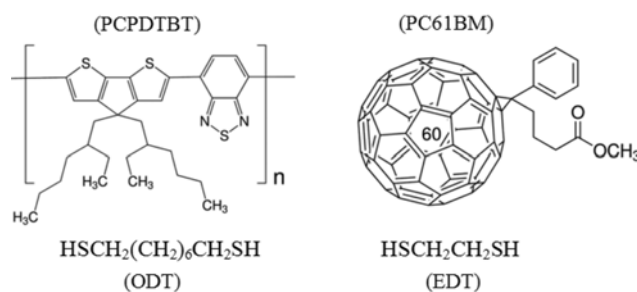


Fig. 1. Molecular structure of PCPDTBT, PC61BM, ODT, and EDT.

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devices. First, ITO-coated glass substrates were cleaned by ultrasonication in neutral detergent and washed with deionized water, isopropyl alcohol, ethanol, and acetone. A hole transport layer of PEDOT:PSS was deposited on top of the cleaned ITO-glass by spin coating at 4,000 rpm for 40 s. Water-soluble PEDOT:PSS inter-layer acts as a buffer layer to reduce the roughness of the ITO surface and protects the active layer from diffusion of indium coming from the ITO substrate. The PEDOT:PSS film was then annealed at 120 °C for 20 minutes in a glove box filled with nitrogen.

The following four mixture solvents of CB with additives were prepared: (1) 2 ml of pure chlorobenzene, (2) 2 ml of chlorobenzene with EDT 2.5 vol% (CB-EDT 2.5 vol%), (3) 2 ml of chlorobenzene with ODT 2.5 vol% (CB-ODT 2.5 vol%), and (4) 2 ml of chlorobenzene with EDT 2.5 vol% and ODT 2.5 vol% (CB-(ODT 2.5 vol%+EDT 2.5 vol%)). 30 mg PCPDTBT and 90 mg PC61BM (weight ratio 1:3) were dissolved in each organic solvent, stirred for 24 hr at 50 °C, and then filtered through a 45 μm Whatman filter. BHJ PCPDTBT:PC61BM active layers were deposited on top of the PEDOT:PSS layer at 1,200 rpm for 30 s. Thickness of active layer was approximately 90-100 nm, as determined by a profilometer (Dektak 150 surface profilometer). Aluminum electrode (~100 nm) was deposited by thermal evaporation with the base pressure of 1.0×10^{-6} mTorr through a shadow mask. The effective area of the resulting device was 9 mm^2 . Fig. 2 shows the schematic of energy band structure and cross-sectional view of a PCPDTBT:PC61BM OPV device.

Current density-voltage (J-V) characteristics of OPV devices were measured by using a Keithley 2400 source meter under simulated

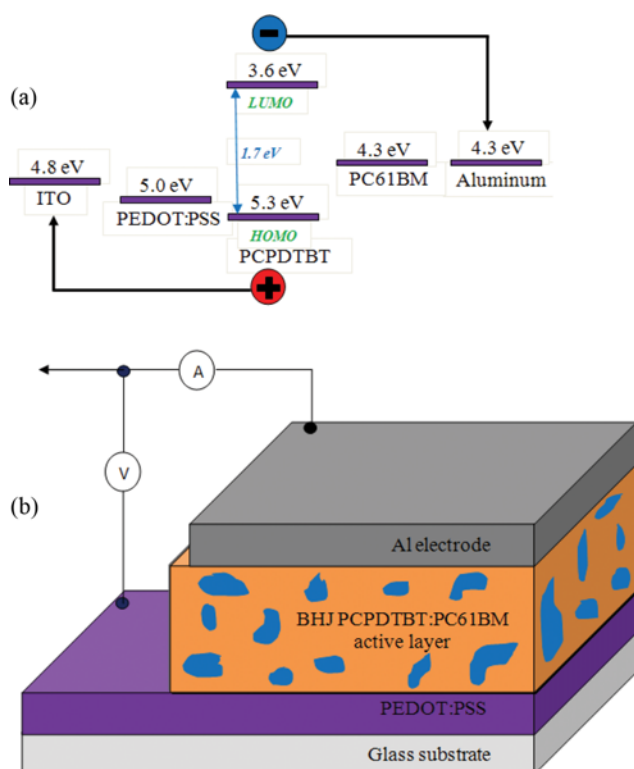


Fig. 2. Schematics of (a) energy band structure and (b) cross section view of BHJ PCPDTBT:PC61BM device.

AM1.5G radiation ($100 \text{ mW}/\text{cm}^2$). Surface morphology of active layers was measured by atomic force microscopy (AFM) in tapping mode (NanoScope[®] IIIa, Digital Instruments, Veeco Metrology Group). UV-vis spectra were recorded over 200-1,800 nm with a UV-vis spectrophotometer (Cary 5000, Varian). All measurements were at room temperature in air without encapsulation.

RESULTS AND DISCUSSION

1. Absorption Spectral Studies

Fig. 3 shows the absorption characteristics of four different PCPDTBT:PC61BM active layers measured by UV-vis. PCPDTBT:PC61BM films prepared from CB with organic additives were red-shifted approximately 40-50 nm of the absorption peak in the region 750-800 nm compared to the case of without additives. The results suggest that the films prepared with alkanedithiols (ODT, EDT, ODT and EDT) have PCPDTBT chains interact more strongly with PC61BM fullerene derivative, leading to increased crystallinity in the PCPDTBT phase compared to the film processed without additives [25].

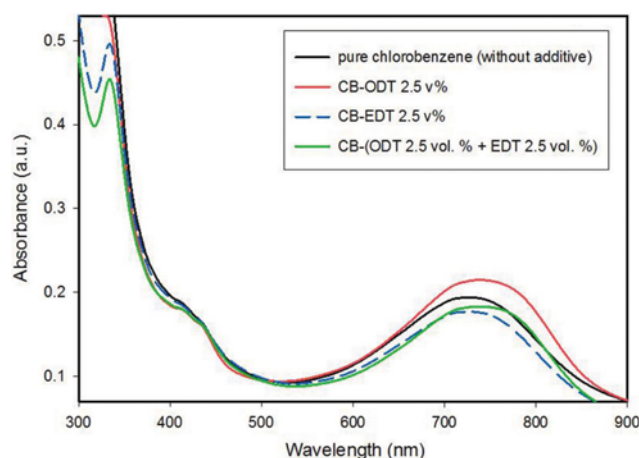


Fig. 3. UV/VIS spectra of four different PCPDTBT:PC61BM active layers prepared from different organic solvents.

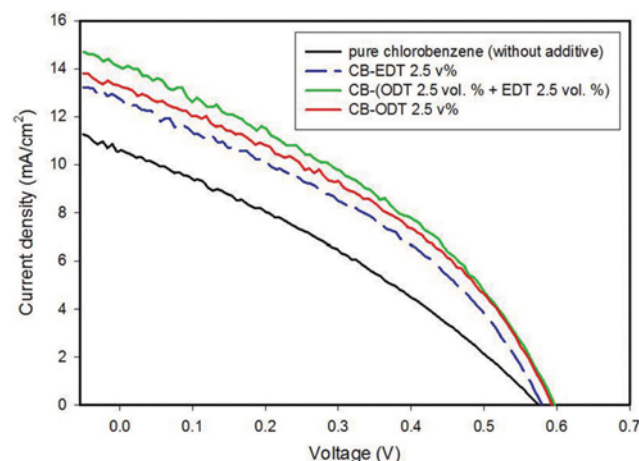


Fig. 4. J-V curves of the four different PCPDTBT:PC61BM OPV prepared from different organic solvents.

2. Current Density (J)-Voltage (V) Characteristics

Fig. 4 shows the J-V characteristics of OPV devices based on four different active layers of PCPDTBT:PC61BM. Table 1 summarizes the device parameters of four different OPV devices. The device prepared from pure chlorobenzene had a PCE of 1.9%, which

is lower than those of devices prepared from mixture solvents of chlorobenzene with additives. The devices prepared from the CB-EDT 2.5 vol%, CB-ODT 2.5 vol% and CB-(ODT 2.5 vol%+EDT 2.5 vol%) solvents have higher PCE of 2.7%, 3.0% and 3.5%, respectively. This dramatic improvement of the photovoltaic performance

Table 1. Photovoltaic parameters of the four different PCPDTBT:PC61BM OPVs prepared from different organic solvents

PCPDTBT:PCBM OPVs prepared from	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)
Pure chlorobenzene (CB)	0.58±0.01 (0.58)	10.4±0.1 (10.6)	32.1±0.4 (32.3)	1.9±0.2 (2.0)
CB-EDT 2.5 vol%	0.58±0.00 (0.58)	12.3±0.3 (12.7)	36.5±0.2 (36.8)	2.7±0.1 (2.7)
CB-ODT 2.5 vol%	0.59±0.01 (0.60)	13.1±0.2 (13.3)	37.4±0.1 (37.6)	2.9±0.1 (3.0)
CB-(ODT 2.5 vol%+EDT 2.5 vol%)	0.60±0.00 (0.60)	14.1±0.1 (14.1)	36.5±0.6 (37.2)	3.4±0.1 (3.5)

Four devices of the same batch were tested to obtain average values. Parentheses denote highest performance device

Table 2. Surface roughness parameters of the PCPDTBT thin films obtained from AFM analysis

Thin films PCPDTBT prepared from	Peak to valley (nm)	Root mean square roughness (nm)
Pure chlorobenzene (CB)	5.1±0.4 (5.4)	1.00±0.01 (1.01)
CB-EDT 2.5 vol%	3.7±0.2 (4.0)	0.89±0.01 (0.89)
CB-ODT 2.5 vol%	15.6±0.5 (16.0)	2.96±0.02 (2.97)
CB-(ODT 2.5 vol%+EDT 2.5 vol%)	14.2±0.6 (14.7)	3.25±0.01 (3.27)

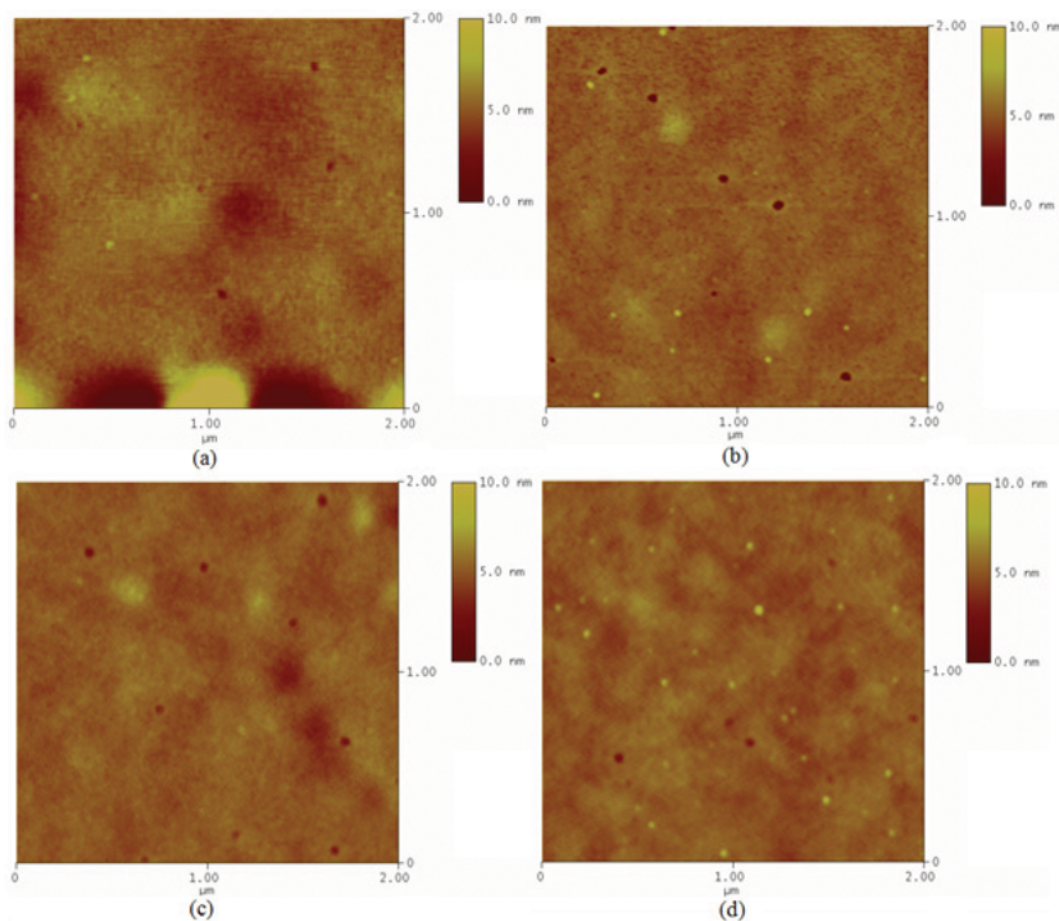


Fig. 5. AFM images of the PCPDTBT:PC61BM active layers prepared from: (a) Pure chlorobenzene, (b) CB-EDT 2.5 vol%, (c) CB-ODT 2.5 vol%, (d) CB-(ODT 2.5 vol%+EDT 2.5 vol%).

Table 3. Surface roughness parameters of PCPDTBT : PC61BM active layers obtained from AFM analysis

Thin films PCPDTBT : PC61BM prepared from	Peak to valley (nm)	Root mean square roughness (nm)
Pure chlorobenzene (CB)	7.8±0.3 (8.0)	1.56±0.01 (1.58)
CB-EDT 2.5 vol%	4.6±0.4 (4.8)	0.56±0.02 (0.57)
CB-ODT 2.5 vol%	3.6±0.2 (3.6)	0.42±0.03 (0.47)
CB-(ODT 2.5 vol%+EDT 2.5 vol%)	2.2±0.2 (2.4)	0.43±0.01 (0.44)

can be explained by the formation of an interpenetrating network with better morphology due to the addition of additives to the blend film [25-27]. On the other hand, devices prepared from CB-EDT 2.5 vol% solvent only showed a moderately improved PCE of 2.7% compared to the PCE of 3.0% of device prepared from CB-ODT 2.5 vol% solvent. This suggests that relatively lower boiling point of EDT (146 °C) than that of ODT (270 °C) might have resulted in the moderate formation of a nano-morphology of the active layer. The maximum PCE of 3.5% was obtained from the device prepared from CB-(ODT 2.5 vol%+EDT 2.5 vol%) mixture organic solvent. This indicates that the PCE of OPV devices can be improved by adding a small volume of EDT and ODT additives to the composite solution.

3. Atomic Force Microscopy Studies

The effects of additives on the solubility of polymer PCPDTBT in different solvents were investigated by AFM. The surface roughness parameters, such as peak-to-valley (PTV) and root-mean-square (RMS), of PCPDTBT films are summarized in Table 2. PCPDTBT films prepared from different solvents had PTV values spread over a broad range from 4 nm to 16 nm, indicating that PCPDTBT has different solubility in different organic solvents. RMS values were in the range 0.89 to 3.27 nm, suggesting that the surface roughness of PCPDTBT films was strongly affected by the additives.

Fig. 5 shows the effects of additives on the surface morphology of PCPDTBT : PC61BM active layer. Table 3 lists the surface roughness parameters of active layers prepared from different solvents. The active layer prepared from pure CB had highest PTV (8.0 nm) and RMS (1.58 nm) values. This can be explained by the fact that the molecules of PCPDTBT and PC61BM did not have enough sufficient reciprocal solubility during the film coating process, leading to the formation of rough surfaces. On the other hand, active layer prepared from CB-EDT 2.5 vol% or from CB-ODT 2.5 vol% solvent had lower RMS values, corresponding to the formation of small micro-grains on the surface, as shown in Fig. 5(b), (c), which could explain the better PCE (2.72% and 2.95%) (Table 1). The active layer prepared from CB-EDT 2.5 vol% solvent (Fig. 5(b)) has rougher surface than the active layer prepared from the CB-ODT 2.5 vol% solvent (Fig. 5(c)). This might explain why OPV devices prepared from CE-EDT2.5 vol% solvent only has moderate PCE of 2.7%, which is lower than that of the device prepared from CB-ODT 2.5 vol% solvent, but slightly higher than the OPV devices prepared from pure chlorobenzene. The best result was achieved in the case of the PCPDTB : PC61BM active layer prepared from CB-(ODT 2.5 vol%+EDT 2.5 vol%) mixture solvent (Fig. 5(d)). The addition of EDT might have resulted in the formation of the best surface morphology (RMS~0.441 nm) of the active layer, leading to an increase in the PCE of OPV devices up to 3.5%.

CONCLUSION

Effects of additives in bulk hetero-junction polymer solution on the surface morphology of active layer and corresponding performance of OPV devices were investigated in detail. Results showed that the efficiency and morphology of PCPDTBT : PC61BM OPVs could be enhanced by adding a small volume of additive. The addition of a small volume of EDT and ODT (alkanedithiol additives) helped improve reciprocal solubility between PCPDTBT and PC61BM. The OPV devices prepared from CB-(ODT 2.5 vol%+EDT 2.5 vol%) mixture solvent showed the best performance due possibly to the self-formation of interpenetrating network, leading to an increase in PCE of OPV device up to 3.5%.

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