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Sunseong Ok [a] & Youngson Choe [a]
[a] Department of Chemical Engineering , Pusan National University , Busan , 609-735 , South Korea

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Performance of PCDTBT:PC_{70}BM Organic Photovoltaic Cells Fabricated Using Dipolar and Common Dopants as Processing Additives

SUNSEONG OK AND YOUNGSON CHOE*

Department of Chemical Engineering, Pusan National University, Busan 609-735, South Korea

Polymer solar cells (PSCs) having donor-acceptor bulk heterojunction (BHJ) is one of the convenient solution for meeting the world's current energy demands. Herein, we report the fabrication and characterization of bulk heterojunction solar cells using the blend of PCDTBT and PC_{70}BM in 1,2-dichlorobenzene (o-DCB) with the device structure of ITO/PEDOT:PSS/PCDTBT:PC_{70}BM/BCP/Al. The effect of dipolar dopants such as dimethylsulfoxide (DMSO) and dimethylformamide (DMF) and common dopants such as 1,8-diiodooctane (DIO) and 1,8-octanedithiol (OT) as processing additive solvents on the performance of PCDTBT:PC_{70}BM based BHJ solar cells were studied and compared with the device without additive in terms of current density, open-circuit voltage and power conversion efficiency (PCE). The addition of additives significantly leads to the aggregation of PCDTBT molecule, thereby controlling the morphology of PCDTBT:PC_{70}BM films enhancing an efficient exciton dissociation and charge transport. Among the additives used the device containing DMSO showed the best performance with a PCE of 7.3%.

Keywords Morphology; PCDTBT; photoluminescence; polymer solar cell; processing additives

Introduction

Owing to the sustained increase in oil prices and the large consumption of electricity, solar energy is one of the prominent renewable energy sources to circumvent today's energy demand. Polymer solar cells based on bulk heterojunction (BHJ) structures with electron donating conjugated polymer and electron accepting fullerene derivatives is a promising technology to tackle these energy issues [1–9]. Polymer solar cells have great advantages such as solution processed fabrication, simple thin film architecture, and low material consumption. Moreover, these polymer materials are abundant and inexpensive compared to inorganic solar cell material, reducing the production cost. Recently, polymer solar cells with BHJ structures have achieved the power conversion efficiency of 8% and over [10–12].

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*Address correspondence to Youngson Choe, Department of Chemical Engineering, Pusan National University, Busan 609-735, South Korea. Tel.: (+82)51-510-2396; Fax: (+82)51-512-8634. E-mail: choe@pusan.ac.kr

Improving the efficiency of polymer BHJ solar cells is still a challenging issue, which the researchers are now trying to address through several approaches including new active material, varying the donor-acceptor ratio, solvents and processing additives. Poly[N-9′′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) is one of the new generation electron donor polymer material for efficient solar devices. This is because PCDTBT have a deep highest occupied molecular orbital (HOMO) level that can increase the open-circuit voltage (V_{oc}) of the devices [13–15]. Recently, PCDTBT:$PC_{60}BM$ based BHJ solar cells have reported a PCE of 4.35% through the optimization of active layer ratio and film thickness [15]. The addition of $PC_{70}BM$ as electron acceptor material to the PCDTBT spin cast from 1,2-dichlorobenzene (o-DCB) exhibited very promising performances with a PCE of 6% [16]. The addition of additives into active layer spin coated from organic solvent have recently shown to improve the performance of BHJ solar cells and found that the solvent additives have a crucial role to control the morphology of active layer [17–19].

Herein, we report the effect of two dipolar solvents - dimethyl sulfoxide (DMSO), dimethyl formamide (DMF) and two common solvents - 1,8-diiodooctane (DIO) and 1,8-alkanedithiol (OT) as processing additives on the performance of PCDTBT:$PC_{70}BM$ based solar cells with the device structure of ITO/PEDOT:PSS/PCDTBT:$PC_{70}BM$/BCP/Al. The addition of additives to the o-DCB solution of PCDTBT:$PC_{70}BM$ controlled the nanoscale morphology of BHJ films and hence enhanced the photovoltaic parameters such as short circuit current density (J_{sc}), open circuit voltage (V_{oc}) and power conversion efficiency (PCE) of the devices from 5.6 to 7.3%

Experimental

Poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) was purchased from HC-Starck and solvents used were obtained from Aldrich. Prior to the deposition of PEDOT:PSS, the ITO glass substrates were thoroughly washed in a mixture of acetone, ethanol and isopropyl alcohol in 1:1:1 v/v for 30 min using ultrasonic cleaner and then dried in air oven at 100°C for 20 min. After cleaning the ITO substrate, a thin film of PEDOT:PSS as a buffer layer was spin coated on the surface of ITO and baked at 140°C for 10 min in vacuum. The role of PEDOT: PSS is to smoothen the ITO surface as well as it serve as a hole injection layer material. Before spin coating the buffer layer, PEDOT:PSS solution was filtered using 0.45 μm Millipore Polytetrafluoroethylene (PTFE) syringe filter. The active layer of PCDTBT:$PC_{70}BM$ (1:4) from o-DCB solution with four different additives was spin-coated on top of the PEDOT:PSS layer and dried in vacuum for 1 h. Finally, a thin film of Al cathode was deposited on the top of BCP (6 nm) both by thermal evaporation method using a shadow mask under high vacuum.

The photovoltaic parameters of the resulting device, ITO/PEDOT:PSS/ PCDTBT:$PC_{70}BM$ /BCP/Al were measured in air using a KEITHLEY 2400 multi-source meter and a solar simulator (XES 301S, SAN-EL Electronics). The Xenon lamp (100 mW/cm^2) was used as a light source. The illumination intensity has been measured by a silicon photo-diode calibrated for an AM 1.5 spectrum. Absorption spectra of the thin films were carried out using 8453 UV-visible Agilent spectrophotometer. Photoluminescence (PL) emission spectra were recorded with F-7000 FL spectrocphotometer. The surface morphology of the films was measured using Atomic Force Microscopy (AFM, L – Trace II).

Results and Discussion

The UV-vis absorption spectra of the PCDTBT:PC_{70}BM films spin coated from pure o-DCB solution and those with optimized amount of additives such as DMSO (10%), DMF (10%), OT (3%), and DIO (3%) are shown in Fig. 1. The absorption spectrum of the PCDTBT:PC_{70}BM film spin coated from o-DCB solution shows two broad peaks around 384 and 556 nm respectively. The absorption bands between 360 and 440 nm of PCDTBT:PC_{70}BM films containing various additives is blue shifted compared to that of the pristine PCDTBT:PC_{70}BM film. However, higher intensity of absorption is obtained for the film spin coated from DMSO than the films containing DMF, OT, DIO and pristine PCDTBT:PC_{70}BM films, indicating the difference in degrees of dispersion of PC_{70}BM in PCDTBT [20]. Moreover, the broad absorption spectra of the PCDTBT:PC_{70}BM in different additives between 540 and 670 nm is red shifted compared to the pristine device and the intensity of absorption is increased substantially by the addition of additives, indicating the decrease in the solubility of PCDTBT. The selective insolubility of PCDTBT means that the decreasing interaction between polymer and solvent while the interaction between polymers chains are enhanced which in turn causes the close packing of polymer molecules and their aggregation in both solution and thin films [19, 21].

The photoluminescence (PL) emission spectra of PCDTBT:PC_{70}BM in o-DCB solution and those with various additives at room temperature are shown in Fig. 2. As shown in Fig. 2, the PCDTBT in o-DCB solution shows two emission maxima at 662 and 727 nm respectively. It is noted that a blue shift in emission maximum is observed for the solution containing both DMF and DMSO compared to the pristine PCDTBT:PC_{70}BM in o-DCB, however the difference in emission maximum is only 5 nm. The blue shift in emission maximum is due to the negative solvatochromic effect of the solvent that causes the stabilization of molecule in the ground state by solvation than the molecule in the excited state while positive solvatochromism (red shift) is observed for the solution containing OT

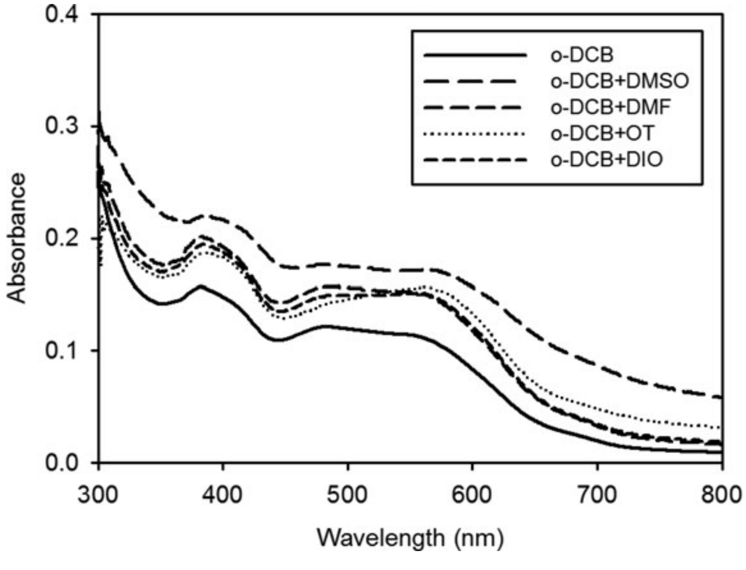

Figure 1. UV-vis absorption spectra of PCDTBT:PC_{70}BM films spin coated from pure o-DCB solution (solid) and those with optimized amount of additives such as DMSO (long dash), DMF (medium dash), OT (dotted), and DIO (short dash).

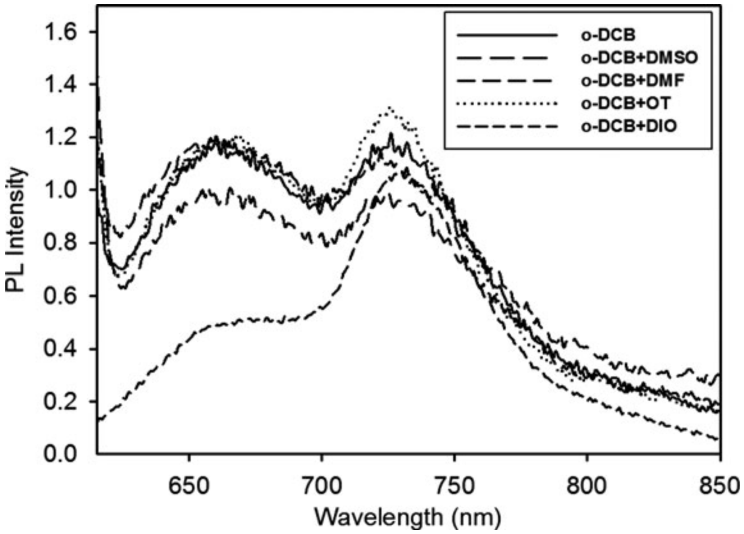

Figure 2. The photoluminescence (PL) emission spectra of PCDTBT:PC$_{70}$BM from pure o-DCB solution (solid) and those with optimized amount of additives such as DMSO (long dash), DMF (medium dash), OT (dotted), and DIO (short dash).

and DIO. Furthermore, the PL spectra of PCDTBT:PC$_{70}$BM with DMSO exhibits a reduced PL intensity than that containing the other additives. This quenching in PL intensity is due to the closer approach of fullerene to the polymer that may result in the efficient exciton dissociation and charge transfer [22].

The current density-voltage (*J*-*V*) curves of PCDTBT:PC$_{70}$BM devices spin coated from o-DCB solution and those incorporating different additives are shown in Fig. 3. The

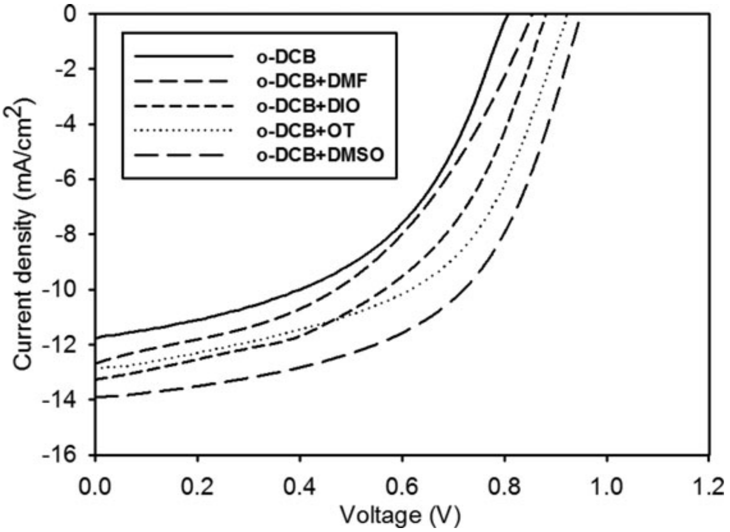

Figure 3. The current density-voltage (*J*-*V*) curves of PCDTBT:PC$_{70}$BM devices spin coated from o-DCB solution and those incorporating different additives.

Table 1. Photovoltaic parameters of PCDTBT:PC$_{70}$BM BHJ solar cells prepared from o-DCB solution and those containing various additives

Additive	V$_{oc}$ (V)	J_{sc} (mA/cm^2)	FF	PCE (%)
None	0.80	11.85	0.60	5.68
DMF	0.84	12.75	0.55	5.89
DIO	0.86	13.20	0.63	7.15
OT	0.88	12.78	0.58	6.52
DMSO	0.91	13.89	0.60	7.32

devices spin coated from o-DCB solution results in a maximum current density (J_{sc}) of 11.85 mA/cm^2 only. The short current density of devices was increased from 11.85 to 13.89 mA/cm^2 by the addition of additives to the o-DCB solution of PCDTBT:PC$_{70}$BM. The photovoltaic cells fabricated from o-DCB solution of PCDTBT:PC$_{70}$BM incorporating DMSO exhibited the highest current density compared to the devices containing other additives. Furthermore, the highest V$_{oc}$ (0.91 V) was obtained for the device containing DMSO additive. The increase in V$_{oc}$ may be due to the better wetting by the metal electrode or the structural change at the PEDOT:PSS/active layer interface [21]. As a result, a highly efficient device with a PCE of 7.32% was obtained for the PCDTBT:PC$_{70}$BM BHJ photovoltaic cells incorporating DMSO than the device without any solvent additives where the pristine device exhibited a PCE of only 5.68%. The photovoltaic parameters of all devices prepared from o-DCB solution of PCDTBT:PC$_{70}$BM and those containing various additives such as DMSO, DIO, OT and DMF are summarized in Table 1.

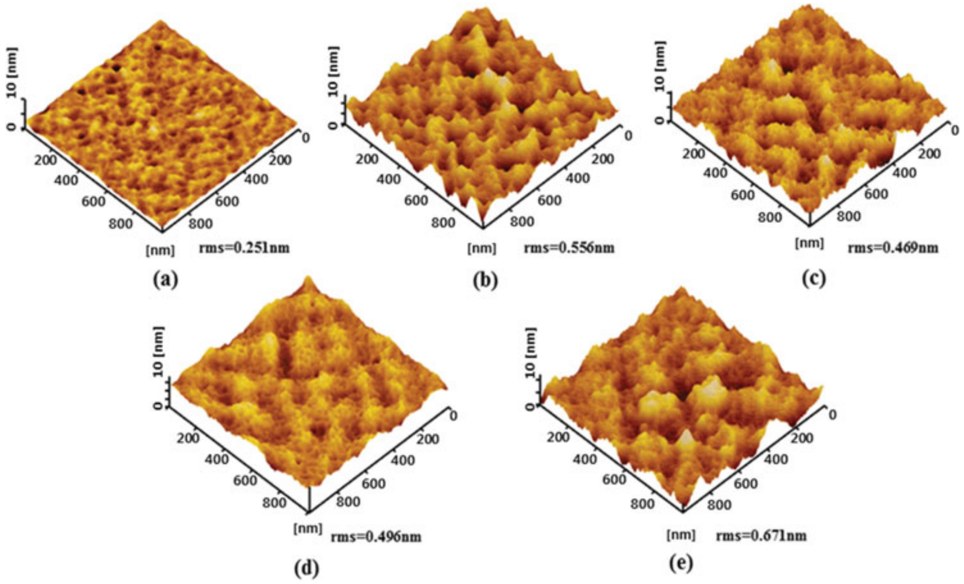

Figure 4. AFM images of PCDTBT:PC$_{70}$BM films spin coated on the top of PEDOT:PSS from pure o-DCB solution (a) and those containing various additives: DMF (b), DIO (c), OT (d) and DMSO (e).

The surface morphology of the PCDBT:PC_{70}BM films spin coated on the top of PEDOT:PSS from pure o-DCB solution and those containing various additives were measured by atomic force microscopy (AFM). Figure 4 shows the AFM images of PCDTBT:PC_{70}BM films spin coated from pure o-DCB solution and has a very smooth surface with root-mean-square (RMS) roughness of 0.25 nm only. The morphology of the films processed with various additives showed more elongated domains of PCDTBT molecules compared to the device without additives. As a result, the RMS roughness was increased from 0.25 to 0.67 nm by the addition of additive. The AFM image of the BHJ films showed perfect morphology by the controlled aggregation of PCDTBT for the films processed from DMSO that leads to the closer packing of the PCDTBT molecules in thin solid films, resulting in the efficient dissociation of exciton and makes superior pathways for carrier transport.

Conclusion

We have demonstrated the effect of dipolar and common solvent additives in o-DCB solution of the PCDTBT:PC_{70}BM films for the fabrication of BHJ solar cells. The addition of solvent additives to the PCDTBT:PC_{70}BM resulted in the aggregation and close packing of PCDTBT molecules, leading to a controlled surface morphology producing an efficient exciton dissociation and charge transport. Using this approach, we have improved the PCE of PCDTBT:PC_{70}BM solar from 5.6 to 7.3% and among the additives used DMSO showed the best performance.

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