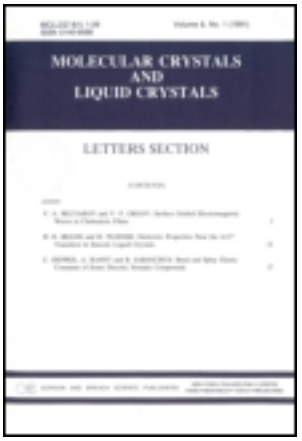

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

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Published online: 08 Jan 2014.

To cite this article: Sunseong Ok & Youngson Choe (2013) Effect of Processing Additives on PCDTBT:$PC_{60}BM$ Based Organic Photovoltaic Cells, Molecular Crystals and Liquid Crystals, 586:1, 95-103, DOI: 10.1080/15421406.2013.851537

To link to this article: http://dx.doi.org/10.1080/15421406.2013.851537

Mol. Cryst. Liq. Cryst., Vol. 586: pp. 95–103, 2013

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.851537

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Effect of Processing Additives on PCDTBT:$PC_{60}BM$ Based Organic Photovoltaic Cells

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We investigated the effect of processing additives on the morphology, charge transport and device performance of poly[N-9′′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) and [6,6]-phenyl C61 butyric acid methyl ester ($PC_{60}BM$) based bulk heterojunction (BHJ) photovoltaic cells. To carry out this investigation, dimethylsulfoxide (DMSO) and dimethylformamide (DMF) were separately added as processing additives in ortho dichlorobenzene (o-DCB) solution of PCDTBT. A progressive aggregation of PCDTBT in both solutions and films were resulted through the addition of both DMSO and DMF additives. The optimization of the additives resulted in fine tuning the morphology of PCDTBT/$PC_{60}BM$ based solar cells, leading to improved domain structure and hole mobility on the active layer, and significantly enhanced photovoltaic performance.

Keywords Additives; bulk heterojunction; morphology; organic photovoltaic cell; polycarbazole; processing

Introduction

During the past decade, polymer solar cells have received more attention as a promising technology due to their great advantages as solution processed thin film fabrication, low material consumption and low-cost roll-to-roll fabrication technology [1–4]. The introduction of donor-acceptor bilayer planar heterojunction to the organic photovoltaic cell (OPV) was first reported in 1979 [5–6]. The concept of bulk heterojunction (BHJ) in OPV was first put forward in 1992 in which the mixture of donor and acceptor materials were spin coated from solvent [7]. Thereafter, the bulk heterojunction (BHJ) photovoltaic cells containing the mixture of conjugated polymers and fullerene derivatives as the electron-donor and acceptor material have drawn increased attention and exhibited a high efficiency over 8% [8–9]. Recently, tremendous efforts have been performed to improve the power conversion efficiency (PCE) of the organic photovoltaic cells by inducing crystalline nanoscale domains in the active layer, thermal treatment [4], solvent selection [10], solvent mixture [11,12] and also by the addition of processing additives [13–16].

The addition of 1,8-octanedithiol as processing additives to poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopental[2,1-b;3,4-b′]-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]

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(PCPDTBT)/$PC_{71}BM$ in ortho-dichlorobenzene (o-DCB) improved the power conversion efficiency (PCE) of BHJ solar cells from 2.8% to 5.5% [15]. Recently, poly [N-9"-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT) have gained attraction as a promising candidate for next generation materials due to its deep highest occupied molecular orbital energy (HOMO) level to enhance the PCE as well as the open circuit voltage (V_{oc}) of BHJ polymer photovoltaic cells [17,18]. The PCE of 4.35% was reported for PCDTBT:$PC_{60}BM$ based BHJ solar cells through the optimization of active layer ratio and thickness [19]. PCDTBT exhibited very promising performances with a PCE of 4.6% when $PC_{70}BM$ was used as an electron-acceptor.

Herein, we report the use of two dipolar solvents such as dimethylsulfoxide (DMSO) and dimethyl formamide (DMF) as processing additives in o-DCB solution of PCDTBT in order to enhance the device performance of PCDTBT:$PC_{60}BM$ based BHJ solar cells. The addition of DMSO or DMF (3–15%) into the o-DCB solution of PCDTBT, resulting in the significant increase in short circuit current density (J_{sc}), and open circuit voltage (V_{oc}) of the devices with an active area of 1.0 cm^2. The PCE of the devices also increased from 5.5 to 6.5% upon the addition of processing additive to PCDTBT:$PC_{60}BM$ active layer.

Experimental

Materials

Poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS) as hole conducting layer material was purchased from (Baytron P from H. C. Starck GmbH). Poly[N-9″-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT, Mn = 389 Kg/mol, PDI (Polydispertsity index) = 2.05) and [6,6]-phenyl C61-butyic acid methyl ester (PCBM) as an electron donor and acceptor material respectively were purchased from Nano-C. Bathocuproine (BCP, formula: $C_{26}H_{20}N_2$, molecular weight: 360.46 g/mol, melting point: 277–285 °C) was purchased from Aldrich and used as hole/exciton blocking layer material. Aluminum (formula: Al, molecular weight: 26.98 g/mol, melting point: 660.30 °C, boiling point: 2467.00 °C) as cathode was purchased from CERAC, Inc.

Fabrication of Photovoltaic Cells

The pre-patterned ITO glass substrates were cleaned in a mixture of acetone, ethanol and isopropyl alcohol in 1:1:1 v/v for 30 min using ultrasonication and then dried at 100 °C for 20 min. Prior to the deposition of active layer, a thin film of PEDOT:PSS was spin coated on the pre-cleaned ITO substrate and baked on the hot plate at 140 °C for 10 min in air. The thickness of PEDOT:PSS film was controlled to be 40 nm. Before spin coating the buffer layer, PEDOT:PSS solution was filtered using a 0.45 μm Millipore polytetrafluoroethylene (PTFE) syringe filter. The active layer was then spin-coated from o-DCB solution of PCDTBT:$PC_{60}BM$ (1:4) to form a thickness of 80 nm and dried in vacuum for 1 h. Two different additives were separately added to the active layer in 3–15% to improve the performance of the devices. Thin film of BCP (6 nm) was evaporated thermally on the active layer and then Al cathode (100 nm) was thermally evaporated on the BCP using a shadow mask under high vacuum. The energy level diagram and the device structure of PCDTBT:$PC_{60}BM$ based photovoltaic cells are shown in Fig. 1.

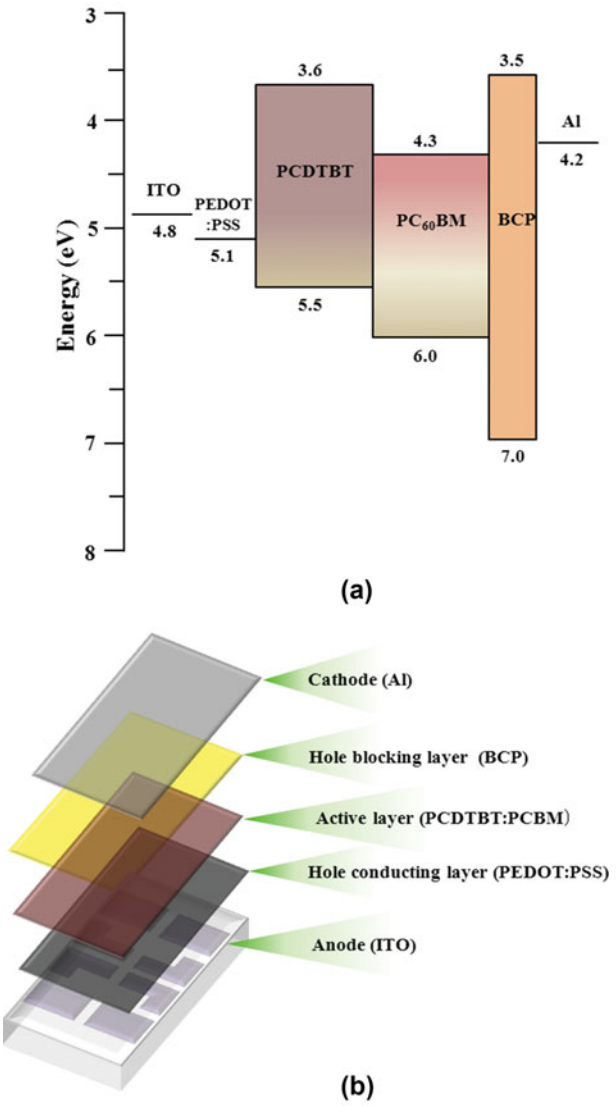


Figure 1. The energy level diagram (a) and the device structure (b) of PCDTBT:$PC_{60}BM$ based photovoltaic cell.

Measurements

The thickness of PEDOT:PSS thin film were controlled by the digitalized rpm system in spin coater (MS-A100, Mikasa Co. Ltd). The thickness of organic (BCP) and cathode (Al) materials were measured using a well calibrated quartz crystal thickness monitor (CRTM-600, ULVAC kiko Co. Ltd.) with thermal evaporator (VPC-260, ULVAC kiko Co. Ltd). The J-V characteristics and power conversion efficiencies of all the devices were measured in air using a multi-source meter (KEITHLEY 2400) 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 AM1.5 spectrum.

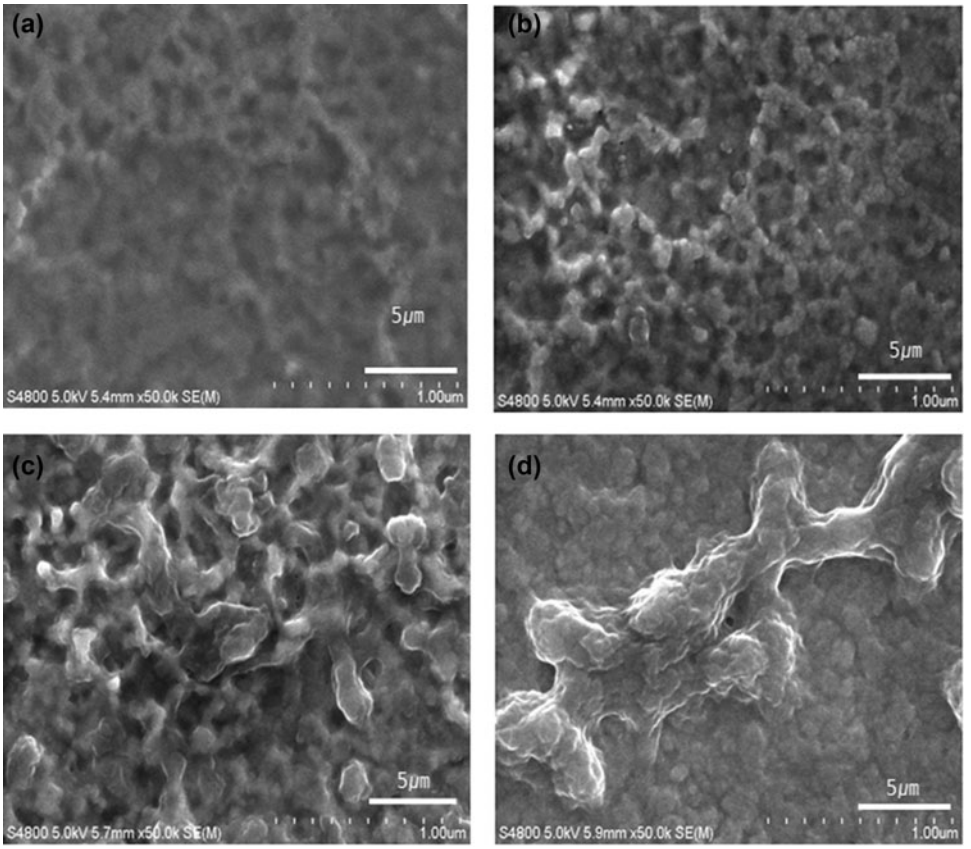


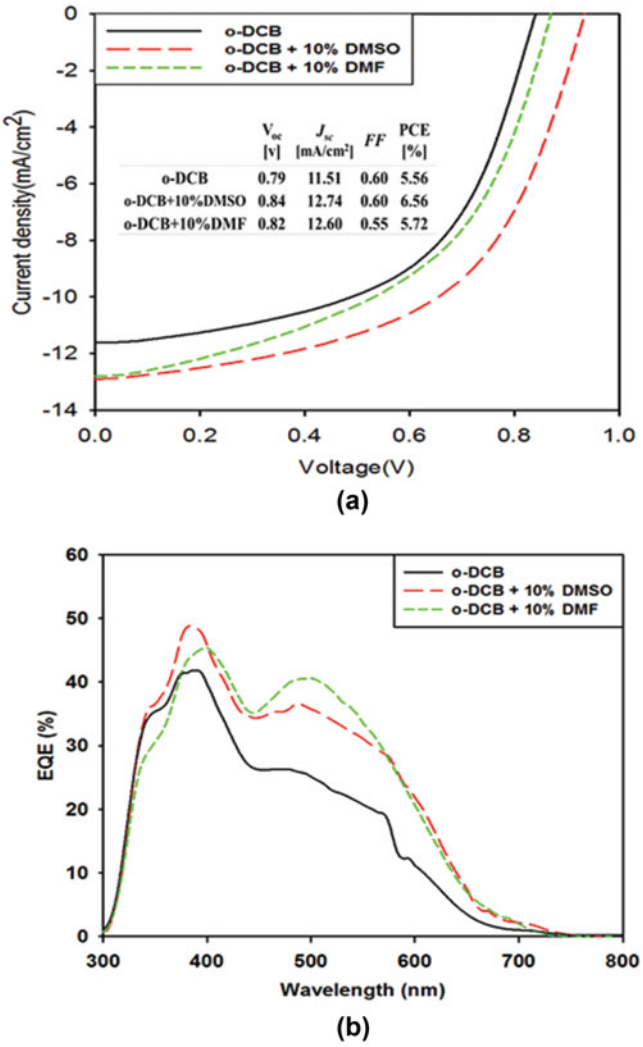
Figure 2. SEM images of PCDTBT films spin coated from (a) pure o-DCB solution, (b) o-DCB with 10% DMF, (c) o-DCB with 10% DMSO and (d) o-DCB with 15% of DMSO.

The external quantum efficiency (EQE) measurement was performed using a 150W Xenon arc lamp for probe source and calibrated with a reference Si photodiode (QE-C4).

Results and Discussion

The surface morphology of the PCDBT film spin coated from pure o-DCB solution and the films from mixed o-DCB and additives (DMSO and DMF) were investigated using scanning electron microscope (SEM) as shown in Fig. 2. Figure 2 shows that PCDTBT films spin coated from pure o-DCB solution possess a very smooth surface while the addition of DMSO and DMF to the o-DCB solution results in the aggregation of the PCDTBT molecules in films. However, the addition of DMSO (10%) to the o-DCB solution of active layer resulted in the aggregated networks of PCDTBT which were formed by evaporation of o-DCB and DMSO. The formation of 3D networks together with $PC_{60}BM$ creates a large area of PCDTBT:$PC_{60}BM$ interfaces for the high dissociation of excitons and hence facilitates the efficient transportation of charge carriers [12,20].

The devices, with and without dipolar additives with an active area of 1.0 cm^2, were fabricated and characterized. The photovoltaic parameters of PCDTBT:$PC_{60}BM$ BHJ photovoltaic cells fabricated from pure o-DCB, o-DCB with DMF and DMSO are summarized



	V_{oc} [v]	J_{sc} [mA/cm²]	*FF*	PCE [%]
o-DCB	0.79	11.51	0.60	5.56
o-DCB+10%DMSO	0.84	12.74	0.60	6.56
o-DCB+10%DMF	0.82	12.60	0.55	5.72

Figure 3. (a) J-V characteristics and (b) EQE spectra of PCDTBT:PC_{60}BM BHJ based photovoltaic cells fabricated from pure o-DCB, o-DCB with 10% of DMF and DMSO. The inset of (a) shows the summary of photovoltaic parameters.

in Fig. 3(a). The devices prepared from o-DCB solution of PCDTBT:PC_{60}BM with 10% of DMSO and DMF showed a significant increase in short circuit current density (J_{sc}), and open circuit voltage (V_{oc}) while the fill factor of the devices kept constant for DMSO (0.60) and decreased to 0.55 for the device containing DMF as shown in Fig. 3(a). The PCE of 6.5% was obtained from PCDTBT:PC_{60}BM (1:4 wt. ratio) based photovoltaic cells with DMSO additive.

The external quantum efficiency (EQE) of a photovoltaic cell is given by the ratio between the number of electrons produced in the outer circuit and that of photons incident on the device. The EQE spectra of PCDTBT:PC_{60}BM BHJ solar cells incorporated with

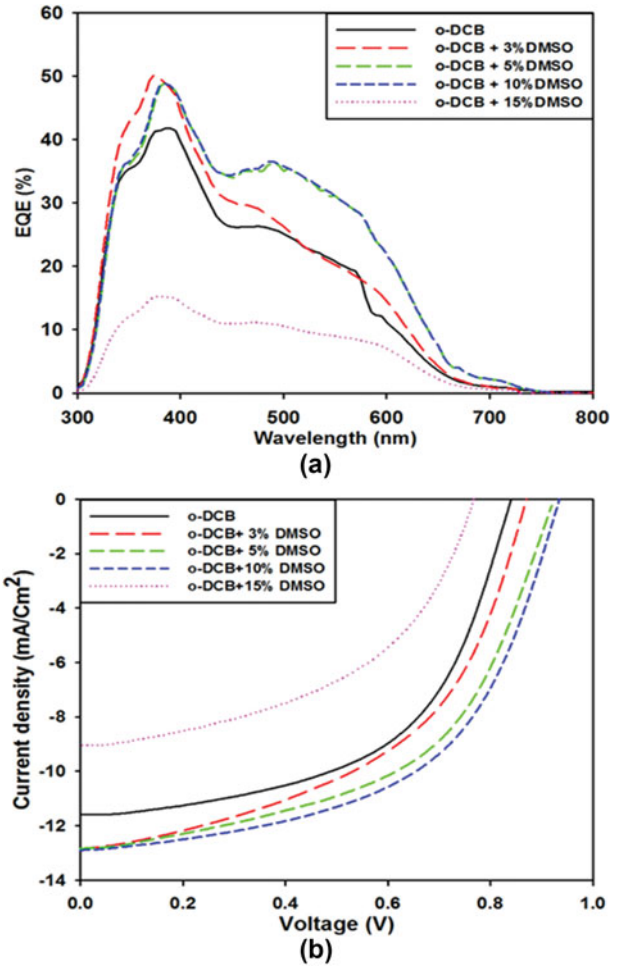


Figure 4. (a) EQE spectra and (b) J-V characteristics of PCDTBT:PC_{60}BM BHJ solar cells with different of volume % of DMSO.

different additives in the fabrication process are shown in Fig. 3(b). The highest monochromatic EQE values for devices prepared by DMSO and DMF are 49 and 45%, respectively, but that of the device prepared by pure o-DCB is less than 41%. The device prepared using DMSO as additive shows the best overall EQE but also has the slowest drying rate among two additives that result in the aggregation of PCDTBT molecules during the fabrication process.

In order to optimize the ratio of DMSO to PCDTBT:PC_{60}BM, BHJ photovoltaic cells were again fabricated and their effects on the device performance were studied. The EQE spectra of photovoltaic cells with different volume ratios of DMSO are shown in Fig. 4(a). Although the EQE curve obtained from the 0 and 15% of DMSO in o-DCB solution shows a poor photo-response, a comparatively higher EQE values are obtained from the device containing 3, 5 and 10% of DMSO in o-DCB solutions. This is in good agreement with the J-V characteristics obtained as shown in Fig. 4 (b).

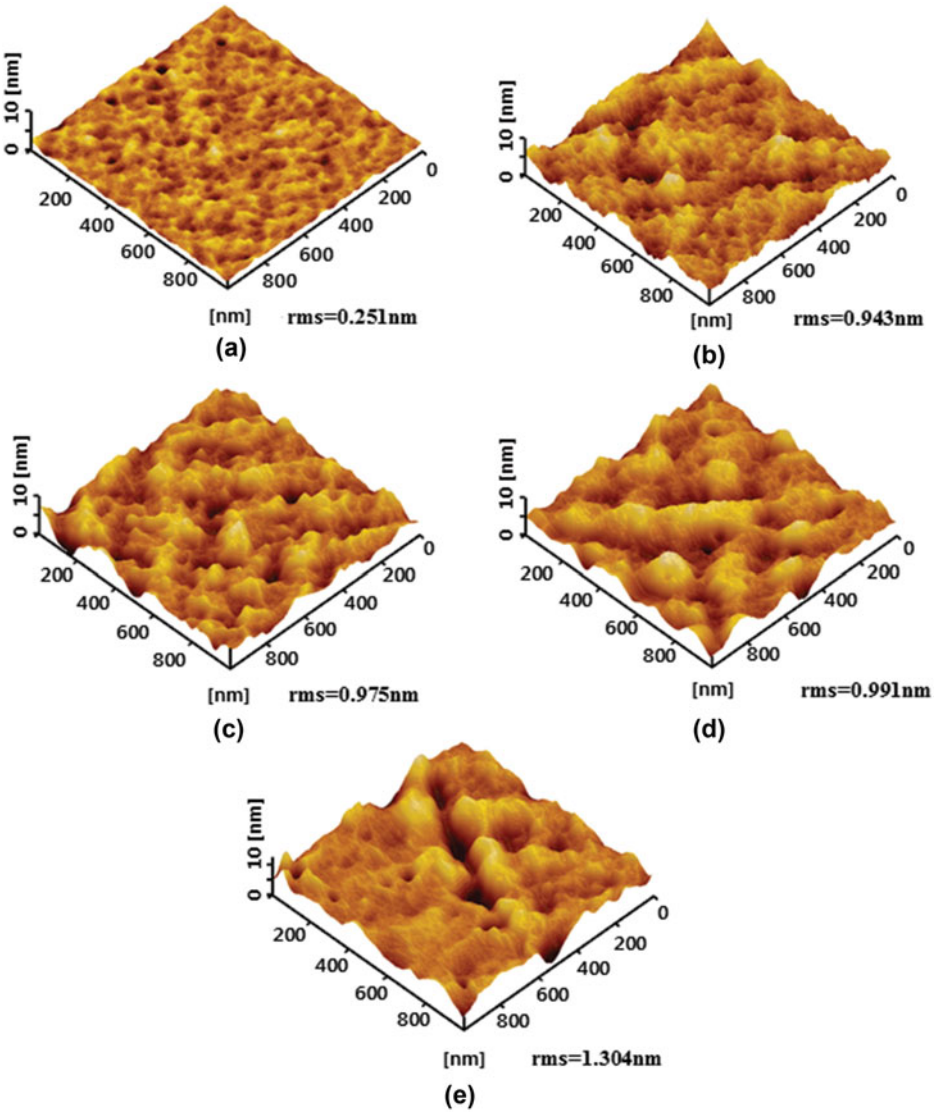


Figure 5. AFM images of PCDTBT:PC_{60}BM films prepared from (a) 0, (b) 3, (c) 5, (d)10 and (e) 15% of DMSO in o-DCB solutions.

The atomic force microscopy (AFM) images of PCDTBT:PC_{60}BM films prepared from 0, 3, 5, 10 and 15% of DMSO in o-DCB solutions are shown in Fig. 5. Figure 5 shows that the root-mean-square (rms) roughness of neat PCDTBT:PC_{60}BM films increases with increasing DMSO ratio from 0 to 15% which further results in more aggregation of PCDTBT molecules in thin solid films.

The photovoltaic parameters of photovoltaic cells with different volume% of DMSO are plotted versus V_{oc}, fill factor, J_{sc} and PCE as shown in Fig. 6. The short circuit current densities of devices increased from 11.51 to 12.74 mA/cm^2 by increasing DMSO to 10% and then diminished at 15%. The open circuit voltage also increased until 10% of DMSO

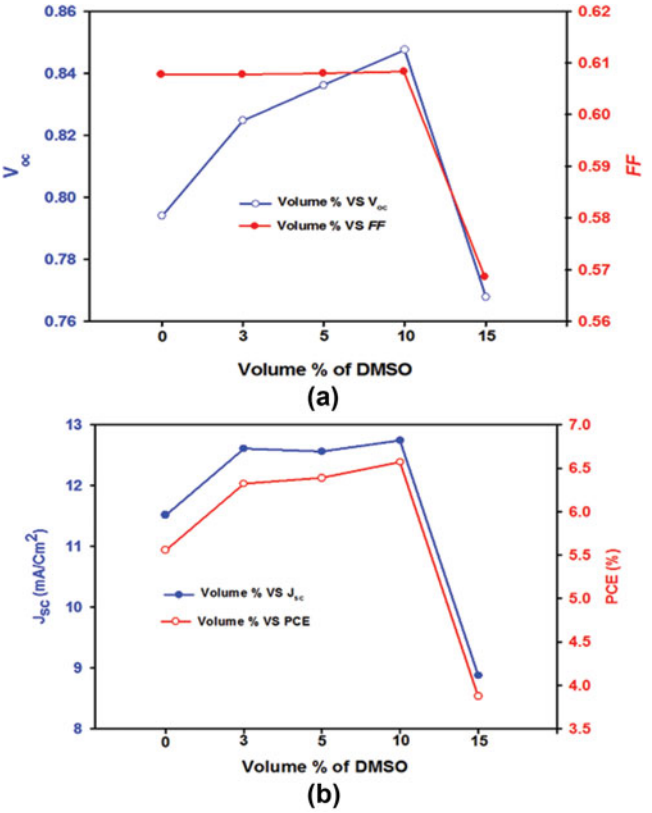


Figure 6. The photovoltaic parameters of photovoltaic cells with various volume % of DMSO.

but the fill factor remains same for all the devices. The SEM (Fig. 2(d)) and the AFM image (Fig. 5(e)) displayed a larger size of the aggregated PCDTBT clusters (domains) for the device prepared from 15% of DMSO, resulting in an increased rate of exciton recombination while the domain size of the film prepared from 0% of DMSO in o-DCB solution were found small which is inadequate for the efficient dissociation of excitons, charge separation and charge transportation [12]. The domain size of PCDTBT aggregation was optimized using 10% DMSO in o-DCB which results in the highest PCE of 6.56%, J_{sc} of 12.74 mA/cm^2, V_{oc} of 0.85 V, and fill factor of 0.60 as shown in Fig. 6.

The results show that the morphology of an active layer was controlled by the addition of dipolar additives and hence improved the electrical properties of the devices except fill factor. The enhanced device performance is due to the formation of polymer aggregation in the PCDTBT:PC_{60}BM BHJ film which were then uniformly packed and facilitates the efficient exciton dissociation. The room temperature UV-vis absorption spectrum of PCDTBT shows a broad peak at 557 nm for the film spin-coated from the o-DCB solution. The UV-vis spectra of the film containing DMSO and DMF (3–15%) were red shifted by 7 nm in o-DCB solution indicating that the addition of DMSO and DMF into the o-DCB solution of PCDTBT decreases the solubility of PCDTBT. The controlled addition of both DMSO and DMF induces the polymer chains to adopt a tight and contracted interaction which results in the aggregation of polymer molecules in both solutions and thin films [20].

Conclusions

In summary, the effect of dipolar solvents such as DMSO and DMF, as processing additives on the o-DCB solution of PCDTBT/PC60BM BHJ based photovoltaic cells were studied. The addition of dipolar additives to the PCDTBT induces crystalline nano scale domains in BHJ films, leading to efficient exciton dissociation, charge separation and transportation. Among the additives added, the device containing 10% of DMSO showed best performance through the fine tuning of thin film morphology. The resulting devices exhibited the highest power conversion efficiency of 6.56%.

Acknowledgments

This work was supported by the Basic Science Research Program through the National Research Foundation (NRF) of Korea funded by the Ministry of Education, Science and Technology (NRF-2013R1A1A4A03009795) and the Brain Korea (BK) 21 Plus project.

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