Effects of Organic Solvents for Composite Active Layer of PCDTBT/PC$_{71}$BM on Characteristics of Organic Solar Cell Devices

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1. Introduction

The 2007 Nobel Prize for peace was awarded to Al Gore and intergovernmental panel on climate change (IPCC). The IPCC has created an ever-broader informed consensus about the connection between human activities and global warming. Furthermore, the IPCC predicted climate change would significantly impact every aspect of human life in this generation [1]. On replying to the issue, in the 34th G8 Toyako summit, it has been agreed to cut carbon emissions by at least 50 percent by 2050 [2]. To realize that goal, development of new energy sources is inevitable. As for new energy, several candidates have been suggested: wind power; solar energy; biomass energy; geothermal energy. Usage of solar energy would be one of the most promising technologies, because the solar energy has the greatest potential to meet world’s growing electricity needs compared to other renewable energy sources. Production of solar cells has grown drastically with annual growth rate of over 40% in recent years, and the output in 2007 has reached over 3.5 GW, which corresponds to 3.5 nuclear power plants of 100 M kW output [3].

From the beginning of organic solar cell (OSC) having power conversion efficiency (PCE) of ~1% [4], various research works have been devoted to enhance the performance [5–7], which is still lower than the marginal threshold of 10% and quite inferior to those of the Si based counterparts. Nevertheless, OSC attracts more and more attention due to advantages such as light weight, flexibility, and easy and low-cost fabrication process [8–10]. Researchers have adopted many ways to achieve high power conversion efficiency (PCE) in OSCs and to cover a large area at low cost [11]. Among the various polymers used, conjugated small-band-gap polymer-based active layers yielded high PCE of 5–9% [12–15]. However, PCEs greater than 10% are needed for commercial viability [16]. Power conversion efficiency (PCE) of OSC device could be possibly enhanced by several
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factors: (1) increase of light absorption area; (2) improvement of charge carrier transport; (3) higher efficiency of exciton generation [17]. To improve performance of OSC devices, bulk heterojunction (BHJ) structure with blended active layer of electron accepter and electron donor has been studied, where interface area between active bilayer could be drastically enlarged and thereby charge separation efficiency could be improved [18–20]. Organic polymer of poly [N-9′-heptadeca-nyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzo-thiadiazole)] (PCDTBT) with deeper highest occupied molecular (HOMO) level and shallow band gap has been focused as a promising material for electron donor layer in BHJ structure [21]. Increase of light absorption area and open circuit voltage \( V_{OC} \) could be achieved by using the PCDTBT as an electron donor material [21]. The extended red absorption of such materials can lead to improved performance via the harvesting of a greater fraction of the sun’s radiation. Solar cells based on PCDTBT:PC\(_{71}\)BM blend show high PCE of 5.6% [22]. Park et al. reported a PCE of 6.1% for a solar cell with a titanium suboxide as an optical spacer between the PCDTBT:PC\(_{71}\)BM active layer and the cathode [13]. The addition of two dipolar solvents of dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF) to the 1,2-dichlorobenzene solution of PCDTBT led to an improved PCE of 6–7.1% [23]. Wang et al. reported a PCE of 71% for devices prepared by spin-coating 1,2-dichlorobenzene:chlorobenzene solution of PCDTBT:PC\(_{50}\)BM (3:1) with silver nanoparticles used in the active layer [24]. As for an electron accepter material, a fulleren material of [6,6]-phenyl-C\(_{71}\)-butyric acid methyl ester (PC\(_{71}\)BM) has been proposed due to superior electron transporting property [25].

In the present work, varieties of organic solar cell devices were fabricated using currently most representative conjugated polymers of PCDTBT and fullerene of PC\(_{71}\)BM. Precursor mixture solutions of the PCDTBT and PC\(_{71}\)BM were prepared with various compositions in three different organic solvents: (1) 1wt% of chloroform; (2) 2wt% of chlorobenzene; (3) 3wt% of o-dichlorobenzene. The precursor mixture solutions were then used for spin-coating process to fabricate BHJ structure based OSC devices. Critical surface parameters of the resulting organic active layers were extracted from surface morphology by using atomic force microscopy (AFM). Standard performance parameters were then investigated for the OSC devices having different blend ratio of PCDTBT and PC\(_{71}\)BM. Effects of the organic solvents on the characteristic of the resulting OSC devices were discussed to suggest an appropriate organic solvent to achieve better performance parameter.

2. Experimental Procedure

2.1. Preparation of Precursor Solutions for Organic Polymer Active Layers. To prepare a bulk heterojunction of organic polymer active layers for organic solar cell device, electron donor layer was prepared with PCDTBT having relatively deeper HOMO level of 5.45 eV. In case of electron acceptor, representative fulleren material of PC\(_{71}\)BM with better electron transport property was used. It has been reported that morphology of the active layer could play an important role in the performance of the resulting OSC device, which could be influenced by organic solvent and blend ratio for active layers [26–28]. To clarify the influence of the organic solvent on the characteristic and/or the OSC device performance, three different organic solvents were utilized to prepare precursor solution mixtures for blended active layer preparation: (1) chloroform of 1wt%; (2) chlorobenzene of 2wt%; (3) o-dichlorobenzene of 3wt%. Different precursor solution mixtures of PCDTBT and PC\(_{71}\)BM with various blend ratios were prepared using the organic solvents: (1) PCDTBT:PC\(_{71}\)BM (1:3–1:6) dissolved in 1wt% of chloroform; (2) PCDTBT:PC\(_{71}\)BM (1:3–1:6) dissolved in 2wt% of chlorobenzene; (3) PCDTBT:PC\(_{71}\)BM (1:3–1:6) dissolved in 3wt% of o-dichlorobenzene.

2.2. Organic Thin Film Solar Cell Device Fabrication. ITO coated glass (Asahi Glass; 25 Ohm/Sq) was used as substrates. ITO as anode electrode was patterned with 1 cm line width by using a hard mask and exposing them in hydrochloric acid (HCl) vapor ambient. The patterned ITO substrates were cleaned with distilled water to remove residual hydrochloride on the surface. Then the substrates were further cleaned ultrasonically prior to organic layer deposition in neutral detergent, aceton, ethanol, and DI water in each 10 min sequence. As hole transporting buffer layer, a conducting \( \pi \)-conjugated polymer of poly (3,4-ethylenedioxythiophene) : poly (styrene-sulfonate) [PEDOT : PSS; Heraeus Clevios P A14083] thin film of 50 nm thickness was deposited by spin-coating technique. Prior to the PEDOT: PSS deposition, the ITO patterned substrates were exposed to UV in vacuum for 10 min to modify its surface into hydrophilic state for better adhesion. The PEDOT: PSS buffer layer was deposited by using the following spin-coating process: (1) rotation with 3000 rpm for 30 s and (2) drying in oven at 120°C for 10 min. Thickness of the PEDOT: PSS layer was 50 nm.

The prepared precursor solutions of PCDTBT:PC\(_{71}\)BM mixture were used in a spin-coating process to prepare bulk heterojunction structure active layer of the organic solar cell devices: rotation speed of 1000 rpm and rotation time of 60 s. Then the spin-coated active layers were dried in a vacuum oven at 120°C for 10 min, while the samples based on the organic solvent of o-dichlorobenzene were dried in vacuum for one day. Finally, cathode electrode of the organic solar cell device was deposited by thermal evaporation of Al (100 nm) in vacuum. Effective light absorption surface area of the resulting OSC device was 0.3 cm\(^2\). Figure 1 shows a schematic structure of the resulting OSC device.

2.3. Characterization of Organic Active Layers and Organic Solar Cell Devices. To investigate effect of various blended active layers of PCDTBT:PC\(_{71}\)BM on performance of the resulting OSC devices, surface morphology of the various PCDTBT:PC\(_{71}\)BM layers was analyzed by using AFM (Seiko Instruments SPA400-SPI4000). The measured surface parameters were discussed in relation to performance parameters of the resulting solar cell device. Absorption
spectra of the blended active layer of PCDTBT and PC$_{71}$BM were investigated by using a UV-Vis spectrometer (Shimadzu UV2450). Standard parameters of the fabricated organic thin film solar cell device were obtained from current density ($J$)–applied voltage ($V$) characteristics measured by using an AC meter (Advantest R6441) in an commercial solar simulator: light source from Xenon lamp; air mass filter adjusted for AM1.5; light intensity of 100 mW/cm$^2$. All measurements were carried out in atmosphere at room temperature. Open circuit voltage ($V_{oc}$), short circuit current density ($I_{sc}$), fill factor (FF), and power conversion efficiency (PCE) were obtained for the organic solar cell devices, respectively.

3. Results and Discussion

Thickness of the active layer plays decisive role in determining the photovoltaic device characteristics. In order to optimize the active layer morphology and blend ratio of PCDTBT:PC$_{71}$BM films and analyze their influence on the device characteristics, OSCs with different blend ratios were fabricated from various organic solvents. Blend ratios dependant thickness of PCDTBT:PC$_{71}$BM active layer prepared with different solvents of chloroform, chlorobenzene, and o-dichlorobenzene was shown in Figure 2. The thickness of the PCDTBT:PC$_{71}$BM layer gradually decreases while increasing the PC$_{71}$BM acceptor in the case of chlorobenzene and o-dichlorobenzene, whereas it is random for chloroform. We observed that layer thickness varied between 78 and 94 nm with different blend ratios prepared from different solvents. It has been reported that the highest efficiency was obtained based on PCDTBT:PC$_{71}$BM solar cells with thickness of active layers between 70 and 90 nm [29].

Surface morphology of active layer could play an important role for performance improvement of organic thin film solar cell device, which could be influenced by blend ratio of electron donor and accepter polymer. It has been reported that the surface morphology of the active layer strongly influences the device properties [30, 31]. In addition, thickness and morphology of the polymer active layer could be affected by organic solvent due to appropriate solubility of blended polymer combination. In order to obtain the effect of blend ratios and different solvents on the active layer, AFM analysis was carried out to observe the surface morphology. Although the active layers are prepared with the same spin speed (1000 rpm for 60 s) obvious change in surface morphology could be seen in their AFM images due to various blend ratios and solvents. Figure 3 shows AFM images (2D view) of different active layers of PCDTBT:PC$_{71}$BM prepared with organic solvents of chloroform (1 wt%), chlorobenzene (2 wt%), and o-dichlorobenzene (3 wt%), respectively, where blend ratios of PCDTBT and PC$_{71}$BM were varied from 1:3 to 1:6. As can be seen in these images, PCDTBT:PC$_{71}$BM blend films exhibit large size granular domains with the size of hundreds of nanometers for films prepared from chloroform and chlorobenzene. The size of granular domains increases while increasing the PC$_{71}$BM ratio in the PCDTBT:PC$_{71}$BM active layer. Considering the polymer of PCDTBT presented in this report is amorphous phase, increase of PCBM composition might result in formation of aggregates on the blended active layers, and the aggregate observed for chloroform and chlorobenzene solvent could be thought of as aggregates of PC$_{71}$BM [32]. There was no clear phase separation observed and these types of morphologies with less bicontinuous networks are not suitable for efficient exciton dissociation to the interface of polymer fullerene which was not favorable for charge separation. On the contrary, the PCDTBT:PC$_{71}$BM samples prepared by using another organic solvent of o-dichlorobenzene (Figure 3) reveal no aggregates of PC$_{71}$BM, which could be due to higher solubility of PC$_{71}$BM in o-dichlorobenzene than that in chlorobenzene [23, 33]. When PCDTBT:PC$_{71}$BM films with different ratios were prepared in o-dichlorobenzene, the surface morphology shows remarkable changes as shown in Figure 3. The films contain more elongated fiber-like nanodomains over the entire area. The AFM images of the PCDTBT:PC$_{71}$BM in o-dichlorobenzene indicates well miscibility between PCDTBT and PC$_{71}$BM. With an increase of PC$_{71}$BM content in the films, the domain size of the PC$_{71}$BM aggregates is decreased and phase separation takes place compared to films prepared
with chloroform and chlorobenzene. This can be attributed to low vapor pressure of o-dichlorobenzene (1.2 mm Hg). As it stays long time in thin film before drying, it renders a better mixing ability between PCDTBT and PC$_{71}$BM, leading to the formation of interpenetrating network. Therefore, the large size granular domains remain under control in the films prepared with o-dichlorobenzene than those prepared with chloroform and chlorobenzene, despite increasing the PC$_{71}$BM ratio. In addition, better organization of fiber-like interpenetrating networks of PCDTBT:PC$_{71}$BM restricts overgrowth of large size PC$_{71}$BM aggregates.

Root-mean-square (RMS) roughness of the different PCDTBT:PC$_{71}$BM combinations prepared in different solvents was extracted after the AFM analysis and presented in Figure 4. RMS surface roughness values measured for 1:3, 1:4, 1:5, and 1:6 PCDTBT:PC$_{71}$BM blend ratios were ∼1.02, 0.79, 1.1, and 1.04 nm for chloroform films; ∼1.08, 1.98, 2.03, and 1.5 nm for chlorobenzene; ∼0.6, 0.74, 0.56, and 0.59 nm for o-dichlorobenzene, respectively. For chloroform films, initially the roughness decreased until 1:4 ratio and increased afterwards, whereas reverse trend was observed for o-dichlorobenzene films. For chlorobenzene films, the roughness increases gradually up to 1:5 ratio and suddenly decreased afterward. The highest roughness for PCDTBT:PC$_{71}$BM blend ratio of (1:5), (1:5), and (1:4) film prepared in chloroform, chlorobenzene, and o-dichlorobenzene was 1.1, 2.03, and 0.74 nm, respectively. It is obvious that the high surface roughness of the film might

**Figure 3:** AFM images of the PCDTBT:PC$_{71}$BM films prepared by using organic solvents of chloroform (1 wt%), chlorobenzene (2 wt%), and o-dichlorobenzene (3 wt%): blend ratio of PCDTBT and PC$_{71}$BM was varied from 1:3 to 1:6.
increase the contact area between the active layer and the contact electrode and thus increase the charge collection. Furthermore, the increased surface roughness may increase internal reflection in the active layer and improve light collection leading to increase in device efficiency [34].

To investigate effect of surface morphology on optical absorbance of active layer of PCDTBT:PCBM, UV-Vis spectra of the active layers prepared by using different organic solvents were investigated. Optical absorbance of organic active layer is directly related to overall performance of the resulting OSC device. Figure 5 shows the UV-vis absorption spectra of PCDTBT:PCBM films prepared from chloroform, chlorobenzene, and o-dichlorobenzene. It is important to note that all these films were spin-coated from the solution with the same rotation speed of 1000 rpm for 60 s. The spectra are not normalized. From Figure 5, the blend layer prepared from chloroform absorbs the less amount of light, whereas layer prepared from chlorobenzene solvent absorbs more light, and o-dichlorobenzene solvent prepared films absorb less amount of light than chlorobenzene solvent, but high absorption takes place at red wavelength region as seen from Figure 5. It is to be noted that the change in film thickness was observed for these solvents. This may be attributed to less viscous nature of the blend solution prepared from chloroform and o-dichlorobenzene; therefore the blend film is thin under the same spin-coating rotation, which causes less light absorption. At the same time, the solution is more viscous when chlorobenzene used as solvent for active layer. Consequently, the film becomes thick and absorbs more light than chloroform and o-dichlorobenzene. It implies that choice of organic solvent and blend ratio of PCDTBT and PCBM could have decisive influence on performance of the resulting OSC device.

The OSC devices were optimized by varying the ratios of the PCDTBT:PCBM and the solvents of blend film. The photovoltaic parameters obtained for various devices are presented in Table 1. Figure 6 shows the current density (J)–voltage (V) curves under AM 1.5 conditions (100 mW/cm²) of PCDTBT:PCBM blend layer prepared from chloroform, chlorobenzene, and o-dichlorobenzene with blend ratio of 1:5, 1:4, and 1:4, respectively. Voc of all the OSC devices reveals approximately 0.9 V, which corresponds to the difference between the LUMO level of PCBM and the HOMO level of PCDTBT [35]. From the results we observed similar open-circuit voltage (Voc) with small random variation with different blend ratios prepared in different solvents of chloroform, chlorobenzene, and o-dichlorobenzene indicating similar characteristics of all solar cells. It is well known that the Voc is influenced by density of defect states at the interface in solar cells [36]. PCDTBT:PCBM devices with active layer thicknesses between 70 and 90 nm have single state defect trap-assisted centre whereas multilevel recombination centers play major role in Voc for the layer thickness beyond 110 nm [37]. In our study, blend layer thickness lies between 78 and 93 nm; the change in Voc may be attributed to possible recombination process via single-defect trap-assisted centers. Moreover, a small reduction in Voc was observed in other solar cells with increase of PCBM concentration [38, 39]. It might be caused by leakage current, dissociated charge loss at the electrodes due to band bending, and shift of charge transfer state while increasing the PCBM ratio in blend layer [39–41]. Though small variations are seen in Voc, the Jsc, the FF, and the PCE of the devices vary significantly with blend ratios as seen from Table 1.

The best optimized device for PCDTBT:PCBM with ratio of 1:5 prepared from chloroform as solvent demonstrated the Voc of 0.90 V, the Jsc of 5.09 mA/cm², the FF of 0.56, and the PCE of 2.55%. The device with 1:4 blend ratio prepared using chlorobenzene as solvent exhibits best
performance with the $V_{oc}$ of 0.93 V, $J_{sc}$ of 5.55 mA/cm$^2$, FF of 0.56, and PCE of 2.91%. For chloroform solvent films the $J_{sc}$ varied from 4.39 to 5.78 mA/cm$^2$ when the ratio was increased from 1:3 to 1:4. Further increasing the PC$_{71}$BM concentration $J_{sc}$ drops suddenly. For chlorobenzene solvent films random variation of $J_{sc}$ was observed with increasing PC$_{71}$BM amount. This can be attributed to poor active layer morphology with large size domains and no interpenetrating networks, which limits charge carrier transport, resulting in lower $J_{sc}$. One of the effective ways to improve light absorption is increasing the active layer thickness and thus increasing the $J_{sc}$. However, the device efficiency is dramatically decreased with increasing active layer thickness due to the increased charge recombination in these cells [42]. The device with 1:4 ratio prepared from o-dichlorobenzene as solvent demonstrates the best performance with the $V_{oc}$ of 0.90 V, the $J_{sc}$ of 8.41 mA/cm$^2$, the FF of 0.55, and the PCE of 4.15%. Relatively higher boiling point of o-dichlorobenzene could possibly be effective to control the nanoscale morphology of blended PCDTBT : PC$_{71}$BM. Effective formation of those interfaces might result in such higher PCE. The same trend of $J_{sc}$ variations in chloroform solvent film was observed too for o-dichlorobenzene solvent film. The $J_{sc}$ values for chloroform and chlorobenzene solvent films are low when compared with o-dichlorobenzene films due to absence of nanoscale interpenetrating network in the active layer.

The highest $J_{sc}$ (8.41 mA/cm$^2$) and the PCE (4.15%) were observed (Figure 6 and Table 1) for the PCDTBT : PC$_{71}$BM (1:4) blend film prepared from o-dichlorobenzene solvent, and this implies that the nanoscale fiber-like phase separation morphology (Figure 3) forms effective individual pathways for holes and electrons, which enhance the charge collection efficiency. From Table I, it is clear that the $J_{sc}$ values continuously decrease when increasing PC$_{71}$BM concentration in the blend layer. It indicates that concentration of PC$_{71}$BM in the blend film has strong impact on $J_{sc}$ and FF, which leads to lower PCE [43]. Regarding the results presented in this study, the blend ratios of (1:5) and (1:4), (1:4) would be preferable for the organic solvents of chloroform, chlorobenzene, and o-dichlorobenzene, respectively. Maximum PCE value observed in the present study is moderate, when compared with highest reported values [44] and this can be improved by further optimization of the devices via adding transport layers, mixture of solvents, and solvent additives.

4. Summary and Conclusions

In summary, varieties of OSC devices were fabricated based on representative blended organic polymer active layers of PCDTBT : PC$_{71}$BM in combination with a conducting $\pi$-conjugated polymer of PEDOT : PSS as hole transporting buffer layer. The blended active layers of PCDTBT : PC$_{71}$BM were prepared by spin-coating technique, with different blend ratios of 1:3 to 1:6 being adopted for three different organic solvents of chloroform (1 wt%), chlorobenzene (2 wt%), and o-dichlorobenzene (3 wt%), respectively. Surface morphology of the blended active layers was investigated by AFM, through which surface roughness parameters were studied in relation to blend ratio and organic solvent. It was confirmed that the blend ratio and organic solvent influenced directly the surface morphology of the blended active layers, which in turn could be decisive to performance parameters ($J_{sc}$, $V_{oc}$, FF) of the resulting OSC devices. Formation of fine nanoscale morphology structure of blended PCDTBT : PC$_{71}$BM could be influenced by the combination of organic solvent and blend ratio. O-dichlorobenzene (3 wt%) was proved to be the most appropriate choice among the three different organic solvents presented in this study to achieve better OSC performance. The device with (1:4) blend ratio prepared from o-dichlorobenzene as solvent demonstrates the best performance with the $V_{oc}$ of 0.90 V, the $J_{sc}$ of 8.41 mA/cm$^2$, the FF of 0.55, and the PCE of 4.15%. Effective formation
of fiber-like nanostructure in the active layer might result in higher PCE ($\eta = 4.15\%$) for the case of PCDTBT:PC$_{71}$BM blend prepared from o-dichlorobenzene.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

**Authors’ Contribution**

Paik-Kyun Shin and Palanisamy Kumar contributed equally to this work.

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**References**

[1] R. K. Pachauri, representing the IPCC, the Nobel Lecture, December 2007.

[2] Japan’s Ministry of Foreign Affairs (MOFA): 34th G8 Summit, overview, November 2008.

[3] G. W. Crabtree and N. S. Lewis, "Solar energy conversion," *Physics Today*, vol. 60, no. 3, pp. 37–42, 2007.

[4] C. W. Tang, "Two-layer organic photovoltaic cell," *Applied Physics Letters*, vol. 48, no. 2, pp. 183–185, 1986.

[5] M. Hermenau, S. Schubert, H. Klumbies et al., "The effect of barrier performance on the lifetime of small-molecule organic solar cells," *Solar Energy Materials and Solar Cells*, vol. 97, pp. 102–108, 2012.

[6] J. J. M. Halls, C. A. Walsh, N. C. Greenham et al., "Efficient photodiodes from interpenetrating polymer networks," *Nature*, vol. 376, no. 6540, pp. 498–500, 1995.

[7] F. C. Krebs, "Roll-to-roll fabrication of monolithic large-area polymer solar cells free from indium-tin-oxide," *Solar Energy Materials and Solar Cells*, vol. 93, no. 9, pp. 1636–1641, 2009.

[8] J. Yang, W. Chen, B. Yu, H. Wang, and D. Yan, "Organic tandem solar cell using active inter-connecting layer," *Organic Electronics*, vol. 13, no. 6, pp. 1018–1022, 2012.

[9] Y. Min Nam, J. Huh, and W. Ho Jo, "Optimization of thickness and morphology of active layer for high performance of bulk-heterojunction organic solar cells," *Solar Energy Materials and Solar Cells*, vol. 94, no. 6, pp. 1118–1124, 2010.

[10] H. Ohkita and S. Ito, “Transient absorption spectroscopy of polymer-based thin-film solar cells,” *Polymer*, vol. 52, no. 20, pp. 4397–4417, 2011.

[11] C. J. Brabec, S. Gowrisanker, J. J. M. Halls, D. Laird, S. Jia, and S. P. Williams, "Polymer-fullerene bulk-heterojunction solar cells," *Advanced Materials*, vol. 22, no. 34, pp. 3839–3856, 2010.

[12] J. Peet, J. Y. Kim, N. E. Coates et al., "Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols," *Nature Materials*, vol. 6, no. 7, pp. 497–500, 2007.

[13] S. H. Park, A. Roy, S. Beaupré et al., "Bulk heterojunction solar cells with internal quantum efficiency approaching 100%," *Nature Photonics*, vol. 3, no. 5, pp. 297–303, 2009.

[14] Z. He, C. Zhong, X. Huang et al., "Simultaneous enhancement of open-circuit voltage, short-circuit current density, and fill factor in polymer solar cells," *Advanced Materials*, vol. 23, no. 40, pp. 4636–4643, 2011.

[15] Z. He, C. Zhong, S. Su, M. Xu, H. Wu, and Y. Cao, "Enhanced power-conversion efficiency in polymer solar cells using an inverted device structure," *Nature Photonics*, vol. 6, pp. 591–695, 2012.

[16] B. Carsten, J. M. Szarko, H. J. Son et al., "Examining the effect of the dipole moment on charge separation in donor-acceptor polymers for organic photovoltaic applications," *Journal of the American Chemical Society*, vol. 133, no. 50, pp. 20468–20475, 2011.

[17] H. Spanggaard and F. C. Krebs, "A brief history of the development of organic and polymeric photovoltaics," *Solar Energy Materials and Solar Cells*, vol. 83, no. 2-3, pp. 125–146, 2004.

[18] G. Dennler, M. C. Scharber, and C. J. Brabec, "Polymer-fullerene bulk-heterojunction solar cells," *Advanced Materials*, vol. 21, no. 13, pp. 1323–1338, 2009.
[19] C. Deibel and V. Dyakonov, “Polymer-fullerene bulk heterojunction solar cells,” *Reports on Progress in Physics*, vol. 73, no. 9, Article ID 096401, 2010.

[20] C. Deibel, V. Dyakonov, and C. J. Brabec, “Organic bulk-heterojunction solar cells,” *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 16, no. 6, pp. 1517–1527, 2010.

[21] M.-G. Kang, H. J. Park, S. H. Ahn, T. Xu, and L. J. Guo, “Toward low-cost, high-efficiency, and scalable organic solar cells with transparent metal electrode and improved domain morphology,” *IEEE Journal on Selected Topics in Quantum Electronics*, vol. 16, no. 6, pp. 1807–1820, 2010.

[22] S.-P. Yang, W.-G. Kong, B.-Y. Liu et al., “Highly efficient PCDTBT:PC71 BM based photovoltaic devices without thermal annealing treatment,” *Chinese Physics Letters*, vol. 28, no. 12, Article ID 128401, 2011.

[23] T.-Y. Chu, S. Alem, S.-W. Tsang et al., “Morphology control in poly(hexadecylbenzothiadiazole) based bulk heterojunction solar cells and its impact on device performance,” *Applied Physics Letters*, vol. 98, no. 25, Article ID 253301, 2011.

[24] D. H. Wang, K. H. Park, J. H. Seo et al., “Enhanced power conversion efficiency in PCDTBT:PCBM bulk heterojunction photovoltaic devices with embedded silver nanoparticle clusters,” *Advanced Energy Materials*, vol. 1, no. 5, pp. 766–770, 2011.

[25] C. J. Brabec, A. Cravino, D. Meissner et al., “Origin of the open circuit voltage of plastic solar cells,” *Advanced Functional Materials*, vol. 21, no. 5, pp. 374–380, 2011.

[26] P. A. Staniec, A. J. Parnell, A. D. F. Dunbar et al., “The nanoscale morphology of a PCDTBT:PCBM bulk heterojunction photovoltaic blend,” *Advanced Energy Materials*, vol. 1, no. 4, pp. 499–504, 2011.

[27] J. S. Moon, J. Jo, and A. J. Heeger, “Nanomorphology of PCDTBT:PC71 BM bulk heterojunction solar cells,” *Advanced Energy Materials*, vol. 2, no. 3, pp. 304–308, 2012.

[28] L. Saiho, R. R. Babu, S. Kannappan, K. Kojima, T. Mizutani, and S. Ochiai, “Performance of spray deposited poly [N-N'-hepta-decanyl-2,7- carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)]/[6,6]-phenyl-C61-butyric acid methyl ester blend active layer based bulk heterojunction organic solar cells,” *Thin Solid Films*, vol. 520, no. 7, pp. 3111–3117, 2012.

[29] Y. Sun, C. J. Takacs, S. R. Cowan et al., “Efficient, air-stable bulk heterojunction polymer solar cells using MoO3 as the anode interfacial layer,” *Advanced Materials*, vol. 23, no. 19, pp. 2226–2230, 2011.

[30] S. Kannappan, K. Palanisamy, J. Tatsugi, P. K. Shin, and S. Ochiai, “Fabrication and characterizations of PCDTBT:PC71 BM bulk heterojunction solar cell using air brushcoating method,” *Journal of Materials Science*, vol. 48, no. 6, pp. 2308–2317, 2013.

[31] Y. He, W. Wu, G. Zhao, Y. Liu, and Y. Li, “Poly(3,6-dihexylthieno[3,2-b]thiophene vinylene): synthesis, field-effect transistors, and photovoltaic properties,” *Macromolecules*, vol. 41, no. 24, pp. 9760–9766, 2008.

[32] B. R. Aich, J. Lu, S. Beaupre, M. Leclerc, and Y. Tao, “Control of the active layer nanomorphology by using co-additives towards high-performance bulk heterojunction solar cells,” *Organic Electronics*, vol. 13, no. 9, pp. 1736–1741, 2012.

[33] S. Alem, T.-Y. Chu, S. C. Tse et al., “Effect of mixed solvents on PCDTBT:PC71 BM based solar cells,” *Organic Electronics*, vol. 12, no. 11, pp. 1788–1793, 2011.

[34] G. Li, V. Shrotriya, Y. Yao, and Y. Yang, “Investigation of annealing effects and film thickness dependence of polymer solar cells based on poly(3-hexylthiophene),” *Journal of Applied Physics*, vol. 98, no. 4, Article ID 043704, 2005.

[35] N. Blouin, A. Michaud, D. Gendron et al., “Toward a rational design of poly(2,7-carbazole) derivatives for solar cells,” *Journal of the American Chemical Society*, vol. 130, no. 2, pp. 732–742, 2008.

[36] R. A. Street, M. Schoendorf, A. Roy, and J. H. Lee, “Interface state recombination in organic solar cells,” *Physical Review B*, vol. 81, no. 20, Article ID 205307, 2010.

[37] G. Namkoong, J. Kong, M. Samson, I. W. Hwang, and K. Lee, “Active layer thickness effect on the recombination process of PCDTBT:PC71BM organic solar cells,” *Organic Electronics*, vol. 14, no. 1, pp. 74–79, 2013.

[38] H. Hoppe, M. Niggemann, C. Winder et al., “Nanoscale morphology of conjugated polymer/fullerene-based bulk heterojunction solar cells,” *Advanced Functional Materials*, vol. 14, no. 10, pp. 1005–1011, 2004.

[39] D. Veldman, Ö. Ipek, S. C. J. Meskers et al., “Compositional and electric field dependence of the dissociation of charge transfer excitons in alternating polyfluorene copolymer/fullerene blends,” *Journal of the American Chemical Society*, vol. 130, no. 24, pp. 7721–7735, 2008.

[40] S. M. Sze, *Physics of Semiconductor Devices*, John Wiley & Sons, New York, NY, USA, 1981.

[41] V. D. Mihaletchi, P. W. M. Blom, J. C. Hummelen, and M. T. Rispens, “Cathode dependence of the open-circuit voltage of polymer-fullerene bulk heterojunction solar cells,” *Journal of Applied Physics*, vol. 94, no. 10, pp. 6849–6854, 2003.

[42] M.-S. Kim, B.-G. Kim, and J. Kim, “Effective variables to control the fill factor of organic photovoltaic cells,” *ACS Applied Materials and Interfaces*, vol. 1, no. 6, pp. 1264–1269, 2009.

[43] J. K. J. van Duren, X. Yang, J. Loos et al., “Relating the morphology of poly( p-phenylene vinylene)/ methanofullerene blends to solar-cell performance,” *Advanced Functional Materials*, vol. 14, no. 5, pp. 425–434, 2004.

[44] B. Qi and J. Wang, “Fill factor in organic solar cells,” *Physical Chemistry Chemical Physics*, vol. 25, no. 23, pp. 8972–8982, 2013.
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