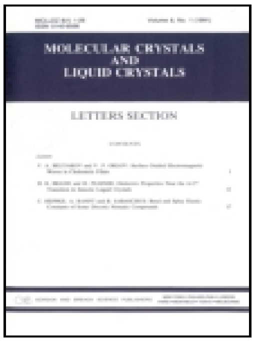

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Bulk Heterojunction Solar Cells with Ternary Mixed PTB7:PCDTBT:PC$_{71}$BM Active Layers

YUTA KANEKO,[1] KODAI KIRIISHI,[1] JIAYU QIU,[1]
SHUNJIRO FUJII,[2] HIROMICHI KATAURA,[2]
AND YASUSHIRO NISHIOKA[1,*]

[1]Department of Precision Machinery Engineering, College of Science and Technology, Nihon University, Funabashi, Chiba, Japan
[2]Nanosystem Research Institute (NRI), National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan

We report on bulk-heterojunction solar cells fabricated based on ternary mixed solutions of two donors of poly[[4,8-bis[(2-ethylhexyl)oxy]benzo [1,2-b:4,5-b'] dithiophene-2, 6-diyl] [3-fluoro-2- [(2-ethylhexyl) carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7) and [N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT), and an accepter of [6,6]-phenyl C$_{71}$ butyric acid methyl ester (PC$_{71}$BM). The solar cells had a glass/ITO/NiO/PTB7:PCDTBT:PC$_{71}$BM/LiF/Al structure. Solar cells containing a 1-2% PCDTBT weight fraction showed a noticeable improvement in short circuit current density (J_{sc}), fill factor (FF), and power conversion efficiency (PCE). Solar cells with a 2% PCDTBT weight fraction exhibited an open circuit voltage (V_{oc}) of 0.77 V, J_{sc} of 13 mA/cm^2, FF of 0.42, and PCE of 4.23%. Possible mechanisms for the solar cell performance improvement by the introduction of the small amount of PCDTBT in the PTB7:PC$_{71}$BM active layer was discussed based on the active layer morphology changes and carrier transport mechanisms.

Keywords Organic solar cells; PCDTBT; PTB7; PC$_{71}$BM; NiO

1. Introduction

With the recent developments in mass production technologies, fabrication of large area, flexible organic solar cells using roll-to-roll processing has attracted considerable attention for low-cost solar energy systems [1]. Therefore, organic solar cell materials that provide higher power conversion efficiency (PCE) are in high demand. Bulk heterojunction (BHJ) solar cells have been reported to exhibit extremely high PCEs of 7.4–7.5% [2,3]. These cells were fabricated using a donor semiconductor, poly[[4,8-bis[(2-ethylhexyl)oxy]benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluoro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]-thiophenediyl] (PTB7), and an accepter semiconductor, [6,6]-phenyl-C$_{71}$-butyric-acid-methyl-ester (PC$_{71}$BM). Solar cells based on

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[*] Address correspondence to Yasushiro Nishioka, Department of Precision Machinery Engineering, College of Science and Technology, Nihon University, 7-24-1 Narashinodai, Funabashi, Chiba 274-8501, Japan. E-mail: nishioka@eme.cst.nihon-u.ac.jp

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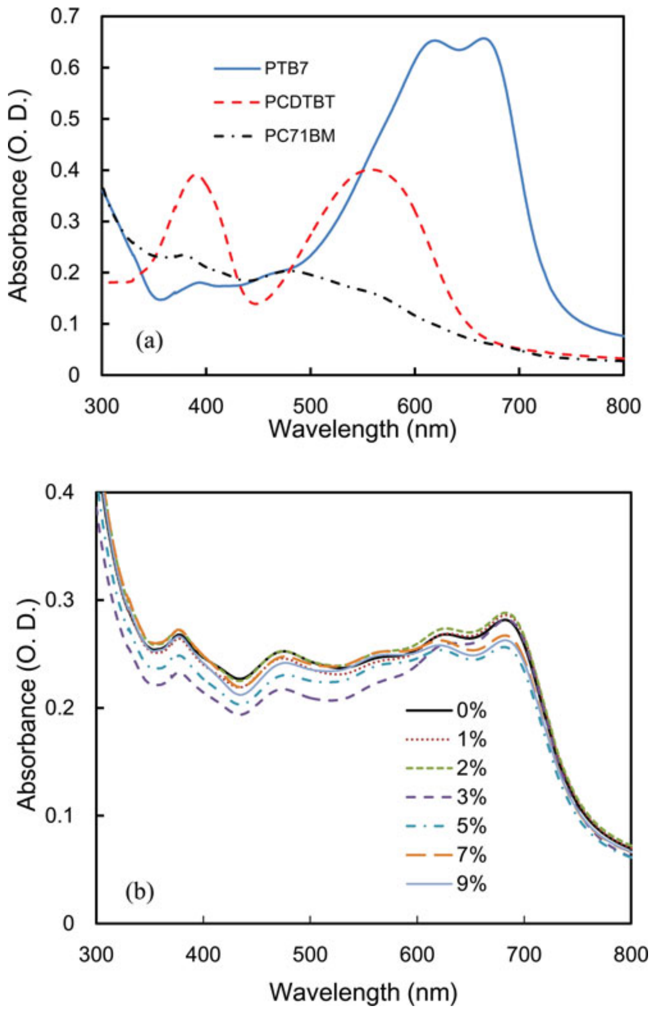


Figure 1. (a) Comparison of optical absorption of PTB7, PCDTBT, and $PC_{71}BM$, and (b) ternary-mixed films of $PTB7:PCDTBT:PC_{71}BM$ with different PCDTBT weight fractions.

$PTB7:PC_{71}BM$ typically exhibit an open circuit voltage (V_{oc}) of around 0.75 V. BHJ solar cells based on poly[N-9′-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (PCDTBT):$PC_{71}BM$ have been reported to exhibit a high PCE of more than 6% and an extremely high V_{oc} of around 0.88 V [4–6].

In this study, we therefore chose to fabricate BHJ solar cells based on ternary mixed solutions of $PTB7:PCDTBT:PC_{71}BM$ with optimized weight ratios of these materials. There have been several reports on ternary mixed BHJ organic solar cells, and addition of minute amounts of organic semiconductors to the host binary mixed active layers has shown a notable improvement in the characteristics of the solar cells. For example, Khlyabich et al. [7] reported the fabrication of ternary-blend BHJ solar cells containing two P3HT analogues as donor polymers, namely high-band-gap poly(3- hexylthiophene-co-3-(2-ethylhexyl) thiophene) (P3HT75-co-EHT25) and low-band-gap poly(3-hexylthiophene-thiophene-diketopyrrolopyrrole) (P3HTT-DPP-10%), along with $PC_{61}BM$ as an acceptor

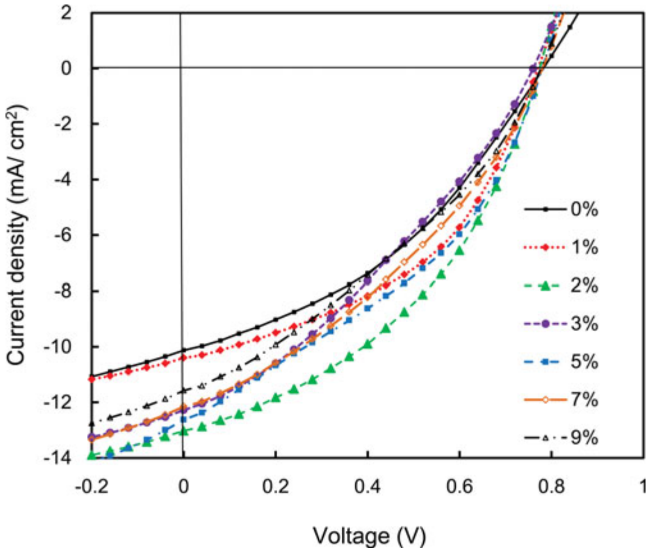


Figure 2. Comparison of the *J–V* characteristics of selected BHJ solar cells based on PTB7:PCDTBT:$PC_{71}BM$ with different PCDTBT weight fractions.

polymer. The ternary-blend BHJ solar cells having a 10% weight fraction of P3HT75-co-EHT25 exhibited PCEs of up to 5.51%, exceeding those of the corresponding binary blends. Xu et al. reported a significant increase in V_{oc} in quaternary-blend BHJ solar cells based on P3HT, $PC_{61}BM$, indene-C_{60} bisadduct (ICBA), and silicon phthalocyanine bis(trihexylsilyl oxide) (SiPc) [8]. Lin et al. [9] reported that the addition of the polymer PTB7 to a poly[[4,8-bis[(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b′]dithiophene-2,6-diyl]] (PCPDTBT): $PC_{71}BM$ host system in a ternary-blend BHJ solar cell resulted in a significant improvement in PCE, and the addition of 5wt% PTB7 resulted in the highest improvement in PCE. Ohori et al. [10] reported that performance of ternary blend organic BHJ solar cells based on PTB7:P3HT:$PC_{61}BM$ was notably improved with a P3HT weight fraction of 3–5%. In this paper, we report on the improved performance of BHJ solar cells based on ternary-blend solutions of PTB7:PCDTBT:$PC_{71}BM$ with smaller PCDTBT weight fractions.

2. Experimental

2.1. Fabrication of BHJ solar cells

We fabricated BHJ solar cells with a glass/ITO/NiO/PTB7:PCDTBT:$PC_{71}BM$/LiF/Al structure on indium tin oxide (ITO)-coated glass substrates with electrode patterns (Techno Print). The sheet resistance of the ITO layer was 10 Ω/sq, and the ITO thickness was 150 nm. The substrates were successively cleaned in deionized water, acetone, and isopropanol for 15 min each in an ultrasonic bath. All dried substrates were UV-ozone cleaned for 15 min.

In this work, nickel oxide (NiO) was used as a hole transport layer since it has been reported to provide significant improvement in the long-term reliability of fabricated solar

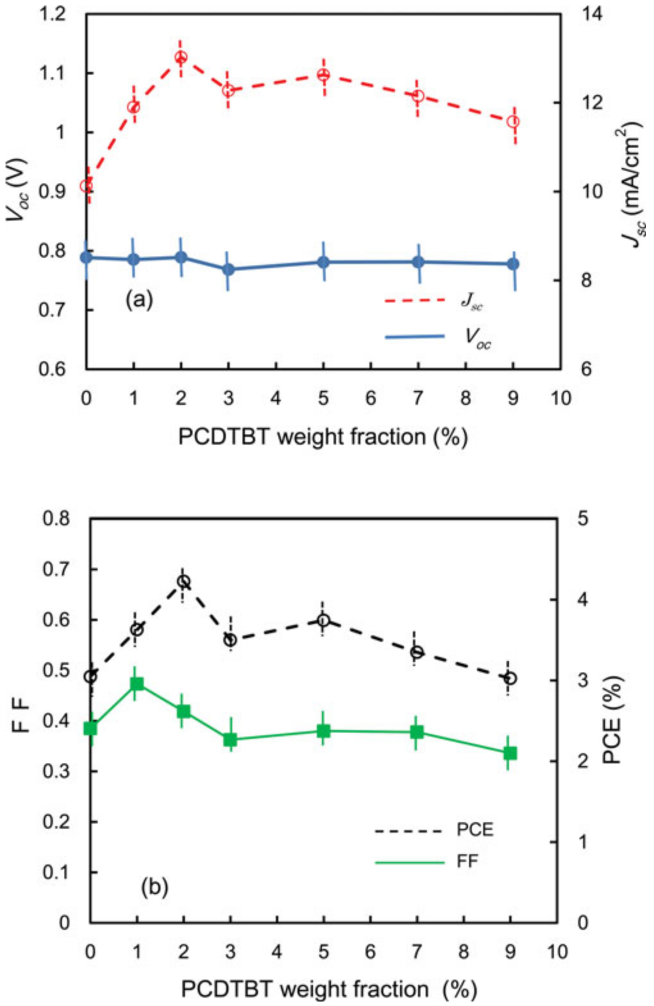
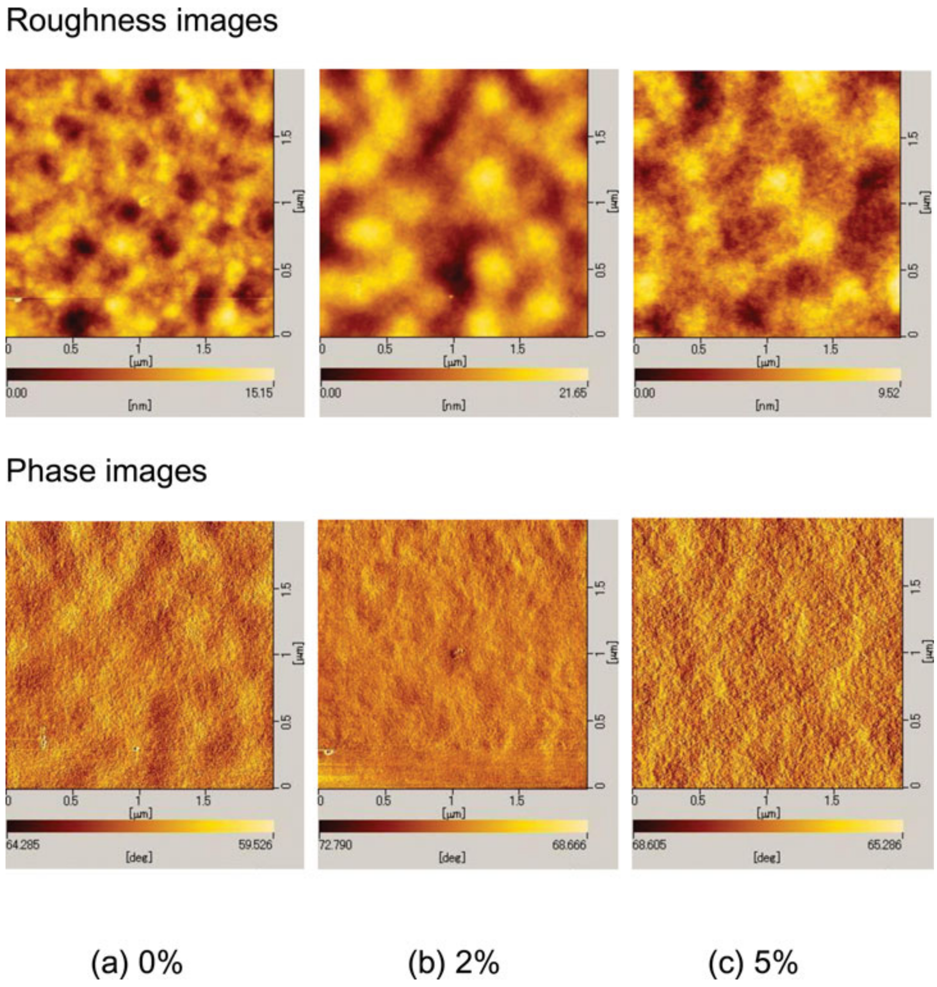


Figure 3. The relationship between PCDTBT weight fraction and (a) V_{oc} and J_{sc}, (b) FF, and PCE.

cells [11]. The cleaned ITO substrates were baked at 150°C for approximately 20 min. The NiO films were deposited by spin coating the NiO precursor at 4000 rpm for 30 s, followed by annealing on a hot plate in air at 350°C for 90 min. Next, UV-ozone cleaning was performed for 2 min. To prepare the precursor solution, nickel acetate tetrahydrate (NAT) [Ni(OAc)$_2$·H$_2$O] and mono ethanolamine (MEA) were dissolved in 2-methoxyethanol. The NAT:MEA molar ratio was maintained at 1:1. The devices were fabricated using the precursor solutions with a NAT:MEA concentration of 0.2 M.

The active layer was deposited by spin coating a solution containing 10 mg of PTB7:PCDTBT and 15 mg of PC$_{71}$BM at a 1:1.5 weight ratio dissolved in 1 ml of 1,2-dichrolobenzene. The weight concentration of the active layer materials PTB7:PCDTBT:PC$_{71}$BM in the solvent was thus 25 mg/ml. The PCDTBT weight fraction was defined as the ratio of the PCDTBT weight and the total weight of PCDTBT and PTB7, and it was varied while maintaining the total PTB7:PCDTBT weight at 10 mg. The spinning frequency was set at 1000 rpm for 20 s following an initial frequency of 500 rpm



(a) 0% (b) 2% (c) 5%

Figure 4. Comparison of roughness and phase images for the PTB7:PCDTBT:$PC_{71}BM$ ternary-mixed film of of PTB7:PCDTBT:$PC_{71}BM$ with the different PCDTBT weight fractions of (a) 0%, (b) 2%, and (c) 5%. The measured surface area was 2 × 2 μm^2.

for 5 s. Four pieces of the resulting PTB7:PCDTBT:$PC_{71}BM$-coated substrates of size 13 × 19 mm^2 were then confined in a Petri dish of diameter 60 mm and depth 15 mm for 20 min (solvent annealing) before transferring them to a vacuum system for deposition of the cathode layers. The spin-coating and solvent-annealing processes were performed in a glove box filled with dry nitrogen. A 2-nm-thick LiF layer was then thermally deposited on the whole surface of the spin-coated active layer. Finally, a 90-nm-thick Al cathode pattern was thermally deposited using a hard mask. The active layer area of the device defined by the overlapping layers of the patterned ITO and Al electrode was 0.04 cm^2.

2.2. Characterization

To study the light absorption behavior, ultraviolet and visible (UV-vis) absorption spectra were investigated. The UV-vis spectra of the organic materials in the film were recorded on a

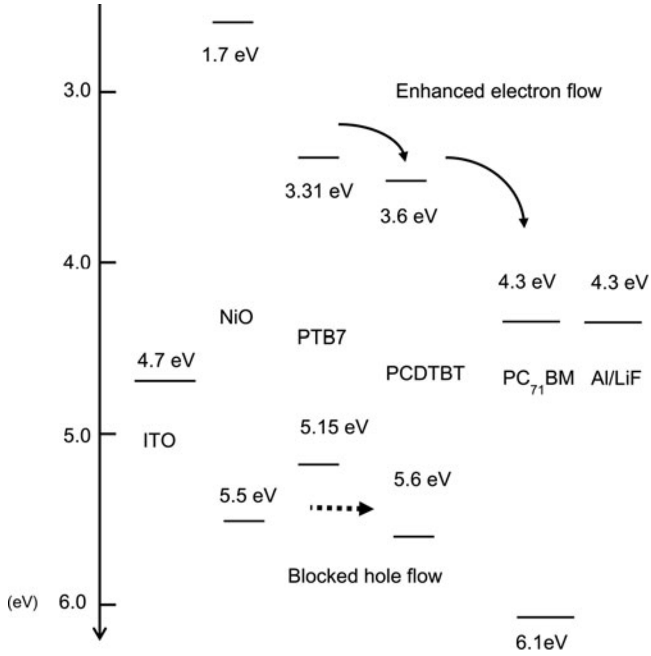


Figure 5. Energy-band diagrams for the ternary- blend BHJ solar cell system, suggesting the possibility of PCDTBT acting as an electron transfer layer.

JASCO V-630 UV-vis spectrophotometer. The current density–voltage (*J*–*V*) characteristics of the solar cell devices were measured using a Keithley 2400 source meter under simulated solar illumination at a light intensity of 100 mW/cm^2. All measurements were carried out under atmospheric conditions. The surface morphologies of the ternary-mixed active layers were investigated using atomic forth microscopy (AFM; SII NanoNavi station).

3. Results and Discussion

Figure 1 shows the UV-vis spectra (a) of PTB7, PCDTBT, and PC$_{71}$BM, and (b) of the blended PTB7:PCDTBT:PC$_{71}$BM on glass/NiO substrates with different PCDTBT weight fractions from 0 to 9%. The UV-vis spectra showed distinct peaks corresponding to PTB7 at 600–670 nm [Fig. 1(a)], PCDTBT at 400 and 550 nm, and broad peak of PC$_{71}$BM from 300 to 600 nm. The peak of PTB7 between 600 and 700 nm did not show any notable change for PCDTBT weight fractions of 0–3%, and it slightly decreased for a PCDTBT weight fraction of 5–9% [Fig. 1(b)]. A slight reduction in the absorbance between 300 and 600 nm was observed for PCDTBT weight fractions of 3 and 5%. The ternary-mixed films with PCDTBT weight fractions of 0–9% did not show any increase in the absorbance.

Figure 2 shows the *J*–*V* relationships under illumination for the BHJ solar cells with different PCDTBT weight fractions. The solar cell with a PCDTBT weight fraction of 2% exhibited the largest short-circuit current density (J_{sc}) of 13 mA/cm^2, V_{oc} of 0.77 V, fill factor (FF) of 0.42, and PCE of 4.23%. These values were larger than those of the control (PCDTBT weight fraction of 0%) PTB7:PCDTBT:PC$_{71}$BM solar cell, which had a J_{sc} of 10.13 A/cm^2, V_{oc} of 0.78 V, FF of 0.38, and PCE of 3.05%. The performance of the solar cells gradually degraded as the PCDTBT fraction increased above 3%.

Figure 3(a) shows a typical example of the relationship between J_{sc} and the PCDTBT weight fraction and that between V_{oc} and the PCDTBT weight fraction. The J_{sc} for a PCDTBT weight fraction increased above 1%, and seemed to have a slight peak between 2 and 5%, while V_{oc} remained relatively constant for a PCDTBT weight fraction between 0 and 2%, and slightly decreased for a PCDTBT weight fraction above 3%. Figure 3(b) shows the relationship between FF and the PCDTBT weight fraction and that between PCE and the PCDTBT weight fraction. The FF increased notably for the PCDTBT weight fraction between 0 and 1%, and it was smaller above 3% than that of 0%, and PCE showed reached the maximum value for PCDTBT weight fractions of 2 %. The values of J_{sc}, V_{oc}, FF, and PCE in Figs. 3(a) and (b) are for the average values for three samples which showed best performance after several process runs of the device processing.

The origins of the improved performance of the ternary-mixed solar cells are not clear. Thus, the surface morphology changes caused by the introduction of the small amounts of PCDTBT in PTB7:$\mathrm{PC_{71}BM}$ layers are investigated using AFM. Figure 4 shows comparison of (a) the surface roughness and (b) phase images for the PTB7: PCDTBT :$\mathrm{PC_{71}BM}$ mixed layers with different PCDTBT weight fraction of 0, 2, and 5%. The measured surface area was $2 \times 2\ \mu\mathrm{m}^2$. Very small grains were observed for the 0% sample, and the grain sizes for the 2% and 5% samples were significant larger than those of the 0% sample. It is suggested that the crystalline structures may have been improved, which may be one of causes of the improved performance of the ternary-mixed solar cells.

Since the photon absorbance in the ternary mixed solar cells did not increase for the PCDTBT weight fraction between 1 and 9%, the increase in J_{sc}, FF, and PCE for the PCDTBT weight fractions between 1 and 9% may also be attributed to the increased charge transport efficiencies in the BHJ structures. Figure 5 shows the suggested energy-band diagrams for the ternary-mixed solar cells. If the PCDTBT layers are segregated at the interface between the PTB7 domains and $\mathrm{PC_{71}BM}$, the PCDTBT layers may also act as a suitable electron transport layer. The electrons generated in the PTB7 domains will be more smoothly transported to the $\mathrm{PC_{71}BM}$ layers through the PCDTBT layers because the lowest unoccupied molecular orbital (LUMO) level of the PCDTBT exists between those of PTB7 and $\mathrm{PC_{71}BM}$. In addition, holes generated in the PTB7 will be blocked at the PCDTBT/PTB7 interface. Therefore, the PCDTBT layers are considered good electron transport layers. We speculate that a layer of PCDTBT is segregated at the interface between $\mathrm{PC_{71}BM}$ and PTB7. Further investigation needs to be performed before making conclusions.

4. Conclusions

We report on BHJ solar cells fabricated based on ternary mixed solutions of PTB7:PCDTBT:$\mathrm{PC_{71}BM}$. The solar cells had a glass/ITO/NiO/PTB7: PCDTBT:$\mathrm{PC_{71}BM}$/LiF/Al structure. Solar cells containing a PCDTBT weight fraction of 1–2% showed notable improvement in J_{sc}, FF, and PCE. Solar cells based on PTB7:PCDTBT:$\mathrm{PC_{71}BM}$ with a PCDTBT weight fraction of 2% exhibited a V_{oc} of 0.77 V, J_{sc} of 13 mA/cm^2, FF of 0.42, and PCE of 4.23%. Possible mechanisms for the solar cell performance improvement by the introduction of the small amount of PCDTBT in the PTB7:$\mathrm{PC_{71}BM}$ active layer were discussed based on the active layer morphology changes and carrier transport mechanisms.

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