Bulk-heterojunction Solar Cells Based on Ternary Blend Active Layers of PTB7, PC\textsubscript{61}BM, and PC\textsubscript{71}BM

Jiayu Qiu\textsuperscript{1}, Kodai Kiriishi\textsuperscript{1}, Kosei Hashiba\textsuperscript{1}, Shunjiro Fujii\textsuperscript{2}, Hiromichi Kataura\textsuperscript{2}, and Yasushiro Nishioka\textsuperscript{1*}

\textsuperscript{1}Department of Precision Machinery Engineering, College of Science and Technology, Nihon University, 7-24-1 Narashinodai, Funabashi, Chiba 274-8501, Japan
\textsuperscript{2}Nanosystem Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan
\textsuperscript{*}E-mail: nishioka@eme.cst.nihon-u.ac.jp

Bulk-heterojunction solar cells were fabricated using ternary blend dichlorobenzene solutions 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]-thiophenediyli] (PTB7):[6,6]-phenyl-C61-butyric acid methyl ester (PC\textsubscript{61}BM):[6,6]-phenyl C71 butyric acid methyl ester (PC\textsubscript{71}BM) with different weight ratios between PC\textsubscript{61}BM and PC\textsubscript{71}BM. In all the solar cells, the overall weight ratio of polymer to fullerene was maintained at 1:1.5, while the composition of the fullerene component (PC\textsubscript{61}BM:PC\textsubscript{71}BM) was varied. The ultraviolet-visible absorption spectra of these ternary blend films showed that the photon absorptions at wavelengths between 300 and 800 nm continuously decreased with the increase of the PC\textsubscript{61}BM weight fraction in the PC\textsubscript{61}BM and PC\textsubscript{71}BM total weight. The measurement results of the solar cell performance showed that the open-circuit voltage notably increased for PC\textsubscript{61}BM weight fractions between 10% and 90%, while it decreased at 100%. The short-circuit current showed the most significant increase in the PC\textsubscript{61}BM weight fraction range between 50% and 60%. A power conversion efficiency of 3.4% was achieved when the PC\textsubscript{61}BM weight fraction was between 50% and 60%. These results may suggest that the transport of the photoexcited electrons between the cathode and the PC\textsubscript{61}BM/PC\textsubscript{71}BM nanodomains was enhanced.

Keywords: organic solar cells, bulk-heterojunction, PTB7, PC\textsubscript{61}BM, PC\textsubscript{71}BM

1. Introduction

Organic bulk-heterojunction (BHJ) solar cells are highly efficient solar cells with additional advantages such as low-cost production, large area, and mechanical flexibility, as they can be fabricated by solution processing without using high vacuum equipment [1–20]. Reyes et al. reported on a BHJ solar cell based on [poly(3-hexylthiophene)]:[(6, 6)-phenyl C61 butyric acid methyl ester] (P3HT:PC\textsubscript{61}BM) blend films with a power conversion efficiency (PCE) approaching 5% [4].

On the other hand, an extremely high PCE of 7.5% has recently been reported for BHJ solar cells by Murray et al. [21]. The cells were fabricated using a p-type 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]-thiophenediyli] (PTB7), an n-type semiconductor, [6,6]-phenyl-C71-butyric-acid-methyl-ester (PC\textsubscript{71}BM), and a lithium fluoride (LiF) inserted Al cathode on an indium tin oxide (ITO) coated glass substrate. These promising results inspired many recent studies on BHJ solar cells based on PTB7:PC\textsubscript{71}BM, and various techniques were proposed to further improve the performance of the BHJ solar cells [22–33].
Ternary or quaternary blend solar cells have also been reported to exhibit interesting performances. Khlyabich et al. [34] investigated ternary blend BHJ solar cells containing two P3HT analogues—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%)—as donor polymers and PC61BM as an acceptor. The ternary blend BHJ solar cells showed power conversion efficiencies up to 5.51%, exceeding those of the corresponding binary blends (3.16% and 5.07%). The improvement of the BHJ solar cells by blending these donor polymers was explained by the presence of polymer alkyle side chains [35]. Lin et al. [36] have demonstrated a significant improvement in PCE by adding the PTB7 polymer to a poly[4,8-bis[(2-ethylhexyl)-4H-cyclopenta[2,1-b:3,4-b]dithiophene-2,6-diyl]] (PCD TBT):PC71BM host system in order to form a ternary-blend BHJ solar cell; the addition of 5 wt% of PTB7 resulted in the greatest PCE improvement. Such studies on ternary-blend solar cells showed performance improvements as a result of adding minute amounts of additives to the host active layers. Ohori et al. recently reported significant improvements in the performance of BHJ solar cells based on ternary-blend organic semiconductor materials with smaller amounts of P3HT additives into the PTB7:PC61BM active layers [37]. They suggested that the improvement of their solar cells was due to enhanced carrier transport paths. Xu et al. reported a significant increase in the open-circuit voltage ($V_{oc}$) of quaternary-blend BHJ solar cells based on P3HT as a donor, and PC61BM, indene-C60 bisadduct (ICBA) and silicon phthalocyanine bis(triethylsilyl oxide) as acceptors [38]. Cheng et al. fabricated ternary blend BHJ solar cells based on PTB7:ICBA:PC71BM, and found that the solar cells showed the maximum PCE at the ICBA weight fraction of 15% of the total weight of ICBA and PC71BM [39]. They suggested that the PCE improvement was due to the cascade electron transfer through the lowest unoccupied molecular orbital (LUMO).

Notably, ternary blend solar cells based on PTB7, PC61BM, and PC71BM may have similar LUMO cascade structures, but they have not yet been reported. In this paper, we report on BHJ solar cells based on ternary blend solutions of PTB7, PC71BM, and PC61BM.

2. Experimental

2.1. Materials for ternary blend BHJ solar cells

We fabricated BHJ solar cells with a glass/ITO/NiO/PTB7:PC61BM:PC71BM/LiF/Al structure. Here, nickel oxide (NiO) was used as a hole transport layer (HTL), as it is widely known as a stable and high transparent HTL [40,41]. Figure 1 shows the molecular structures of (a) PTB7, (b) PC61BM, and (c) PC71BM. PTB7 has a complex structure with repeated fluorinated thienothiophene and modified benzo-thiophene groups to lower the band gap. PC61BM is based on C60, which has a spherical carbon network structure. The surface can absorb as many as six electrons, suggesting that PC61BM is a good electron acceptor. PC71BM has been widely investigated, as it exhibits significantly high photon absorption within the visible light wavelengths, resulting in high power conversion efficiency solar cells [42].

![Molecular structures of (a) PTB7, (b) PC61BM, and (c) PC71BM.](image-url)
2.2. Fabrication of BHJ solar cells

The layered structure of the BHJ solar cells is shown in Fig. 2. The solar cells were fabricated based on the procedures previously described [32,33,37].

![Figure 2. Structure of the fabricated bulk-heterojunction (BHJ) solar cells.](image)

The devices were fabricated on an ITO-coated glass substrate with a sheet resistance of 10 Ω/sq (Techno Print) and a thickness of 150 nm with electrode patterns. The substrates were subsequently cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol, each for 15 min; then, a UV-ozone cleaning was performed for 15 min on all the dried substrates. The cleaned ITO substrates were baked at 150 °C for ~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, a UV-ozone cleaning was performed for 2 min. The spin-coated substrates were annealed for 30 min at 25 °C in air. The NiO deposition conditions were based on our previous publication by Kiriishi et al. [43].

The active layer was deposited by spin coating a solution in which 10 mg of PTB7 and 15 mg of PC_61BM:PC_71BM were dissolved with a 1:1.5 weight ratio in a solution containing 1 g of 1,2-dichlorobenzene. The PC_61BM weight fraction was varied, keeping the total weight of PC_61BM and PC_71BM equal to 15 mg. The spinning speed was set at 800 rpm for 30 s, following an initial speed of 500 rpm for 5 s. The spin-coating process was stopped after the 800 rpm stage by natural deceleration.

Seven pieces of the resulting PTB7:PC_{61}BM:PC_{71}BM-coated substrates with an area of 13 × 38 mm² were then stored in the confined space of a Petri dish with a diameter of 60 mm and a depth of 15 mm for 30 min before being transferred to a vacuum system to deposit the cathode layers. Then, a 2-nm-thick LiF layer was 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 cm².

2.3. Characterization

To study the light absorption behavior, ultraviolet-visible (UV–vis) absorption spectra were investigated. The UV–vis spectra of the organic materials in the film form were recorded on a Shimadzu UV-3700 spectrophotometer. The film samples were prepared by depositing the solar cell materials on NiO-deposited ITO glass substrates. The current density–voltage (J–V) characteristics of the solar cell devices were measured with a Keithley 2400 source meter under simulated solar illumination at a light intensity of 100 mW/cm². All the measurements were conducted under atmospheric conditions.

3. Results and Discussion

Figure 3 shows a comparison of the UV-vis spectra of the PTB7, PC_{71}BM, and PC_{61}BM films on the NiO coated glass/ITO substrates. The PTB7 film showed two intense vibronic peaks at 620 and 670 nm. The photon absorption of the PC_{71}BM film was larger than that of the PC_{61}BM film in the visible light wavelength range between 400 and 600 nm [42].

Figure 4 shows the UV-vis spectra of the PTB7:PC_{61}BM:PC_{71}BM blend films with different PC_{61}BM weight fractions ranging from 0 to 100%. The absorption by glass/ITO/NiO was subtracted from the spectra. The UV-vis spectra are widely extended and range approximately from 250 to 750 nm; two distinct peaks at 620 and 670 nm corresponding to PTB7 can be observed. The remaining peaks belong to PC_{61}BM and PC_{71}BM. The photon absorption decreased with the increase of the PC_{61}BM weight fractions. This is because the photon absorption of PC_{61}BM is lower than that of PC_{71}BM, as shown in Fig. 3.
Figure 5 shows a comparison of the $J$–$V$ characteristics of the selected BHJ solar cells with different PC$_{61}$BM weight fractions in PC$_{61}$BM/PC$_{71}$BM under illumination. The solar cells exhibited a notable increase in the short-circuit current density ($J_{sc}$) when the PC$_{61}$BM weight fraction ranged between 50% and 60%, and showed a slight decrease with increasing the PC$_{61}$BM content above 70%. The $V_{oc}$ was large in all the ternary blend solar cells.

Figure 6 shows the $J_{sc}$ and $V_{oc}$ changes as a function of the PC$_{61}$BM weight fraction. The $J_{sc}$ seems to have three peaks at the PC$_{61}$BM weight fractions of 10%, 50%, and 90%, and the maximum $J_{sc}$ was observed at a PC$_{61}$BM weight fraction between 50% and 60%. The $J_{sc}$ increased from 6.31 mA/cm$^2$ at 0% to 10.17 mA/cm$^2$ at 60%, and it suddenly dropped for fractions higher than 70%. The $V_{oc}$ was larger at PC$_{61}$BM weight fractions between 10% and 90%. It continuously increased from 0.61 to 0.78 V, as the PC$_{61}$BM fraction increased from 0% to 60%, and it decreased at the fraction of 100%.

Figure 7 shows the relationships between (a) the fill factor FF and the PC$_{61}$BM weight fraction, and (b) the PCE and the PC$_{61}$BM weight fraction. The FF notably increased in the PC$_{61}$BM fraction range of 20–80%. The PCE seemed to have three peaks at around 20%, 50%, and 90%. This rapid increase in the PCE in the ternary mixed BHJs is discussed as follows. From the data of Figs. 4 and 5, the increase of the PCE was mainly due to the increase of $J_{sc}$ at PC$_{61}$BM weight fractions between 50% and 60%. Table 1 shows the comparison of the average solar cell parameters as functions of the PC$_{61}$BM weight fraction.
As the photon absorption in the ternary blend active layers was not enhanced, the improvement of the $J_{sc}$ is attributed to the improvement of the carrier transport properties within the active layer of PTB7:PC$_{61}$BM:PC$_{71}$BM. Figure 8 shows the energy band diagram for the BHJ system investigated in this study. The LUMO and highest occupied molecular orbital (HOMO) of PC$_{61}$BM are $-6.1$ and $-3.7$ eV, respectively, while those of PC$_{71}$BM are $-5.9$ and $-3.9$ eV, respectively. When an incident photon excites an electron and hole pair within a PTB7 domain, the electron easily flows to the cathode through the cascade structures of the LUMOs of PC$_{61}$BM and PC$_{71}$BM. The holes generated in PTB7 may flow into the ITO anode through the Fermi level of the NiO layer. These charge transfer mechanisms between PTB7, PC$_{61}$BM, and PC$_{71}$BM may account for the increased performance of the ternary mixed BHJ solar cells at higher PC$_{61}$BM fractions. However, these conclusions are only speculations, and further structural analysis for the ternary blend active layers is needed.

Unfortunately, the solar cell parameters are not suitable to perform a comparison with previous reports on BHJ solar cells based on PTB7:PC$_{71}$BM; this may be related to the fact that the device fabrication procedures were not accurately optimized. However, the experimental results presented in this paper may be useful to further improve the overall BHJ solar cell performance.

Table 1. Comparison of the average solar cell parameters as functions of the PC$_{61}$BM weight fraction.

| PC$_{61}$BM fraction (%) | $V_{oc}$ (V) | $J_{sc}$ (mA/cm$^2$) | FF | PCE (%) |
|-------------------------|-------------|----------------------|----|---------|
| 0                       | 0.61        | 6.31                 | 0.34| 1.38    |
| 10                      | 0.78        | 8.38                 | 0.41| 2.64    |
| 20                      | 0.73        | 7.71                 | 0.56| 2.99    |
| 30                      | 0.72        | 5.51                 | 0.46| 1.73    |
| 40                      | 0.69        | 5.22                 | 0.49| 1.69    |
| 50                      | 0.75        | 10.01                | 0.49| 3.65    |
| 60                      | 0.78        | 10.17                | 0.46| 3.63    |
| 70                      | 0.70        | 5.64                 | 0.52| 2.01    |
| 80                      | 0.77        | 6.09                 | 0.32| 1.51    |
| 90                      | 0.76        | 6.48                 | 0.41| 2.00    |
| 100                     | 0.64        | 5.12                 | 0.45| 1.49    |
4. Conclusion

BHJ solar cells were fabricated using ternary blend dichlorobenzene solutions of PTB7:PC$_{61}$BM:PC$_{71}$BM. In all the solar cells, the overall weight ratio of polymer to fullerene was maintained at 1:1.5, while the composition of the fullerene component (PC$_6$BM:PC$_{71}$BM) was varied. The UV-vis absorption spectra of such ternary blend films showed that the photon absorptions at wavelengths between 300 and 800 nm continuously decreased with increasing the PC$_{61}$BM weight fraction in the PC$_{61}$BM and PC$_{71}$BM total weight. The measurement of the solar cell performance showed that the $V_{oc}$ notably increased as the PC$_{61}$BM weight fraction ranged between 10% and 90%, whereas it decreased at 100%. The $J_{sc}$ showed the most significant increase at PC$_{61}$BM weight fractions ranging between 50% and 60%. A power conversion efficiency of 3.4% was achieved for a PC$_{61}$BM weight fraction between 50% and 60%. These results may suggest that the transport of photoexcited electrons between the cathode and the PC$_{61}$BM/PC$_{71}$BM nanodomains was enhanced.

References
1. C. J. Brabec, N. S. Sariciftci, and J. C. Hummelen, Adv. Funct. Mater., 11 (2001) 15.
2. K. M. Coakley and M. D. McGehee: Chem. Mater., 16 (2004) 4533.
3. F. Padinger, R. S. Rittberger, and N. S. Sariciftci, Adv. Funct. Mater., 13 (2003) 1.
4. M. R. Reyes, K. Kim, and D. L. Carroll, Appl. Phys. Lett., 87 (2005) 83506.
5. T. Hasobe, S. Fukuzumi, P. V. Kamat, and H. Murata, Jpn. J. Appl. Phys., 47 (2008) 1223.
6. Y. Kinoshita, T. Hasobe, and H. Murata, Jpn. J. Appl. Phys., 47 (2008) 1234.
7. G. Yu, J. Gao, J. C. Hummelen, F. Wudl, and A. J. Heeger, Science, 270 (1995) 1789.
8. M. Granstrom, K. Petritsch, A. C. Arias, A. Lux, M. R. Anderdon, and R. H. Friend, Nature, 395 (1998) 257.
9. S. Fujii, Z. Duan, T. Okukawa, Y. Yanagi, A. Yoshida, T. Tanaka, G. Zhao, Y. Nishioka, and H. Kataura, Phys. Status. Solidi., B 249 (2012) 2648.
10. Y. Lou, Z. Wang, S. Naka, and H. Okada, Jpn. J. Appl. Phys., 51 (2012) 021603.
11. Z. Duan, S. Fujii, Z. Liu, T. Okukawa, A. Yoshida, Y. Yanag, H. Kataura, G. Zhao, and Y. Nishioka, Mol. Cryst. Liq. Cryst., 578 (2013) 78.
12. S. Fujii, T. Okukawa, Z. Duan, Y. Yanagi, M. Ohzeki, T. Yanagidate, Y. Arai, G. Zhao, Y. Nishioka, and H. Kataura, IEICE. Trans. Electron. E97-C (2014) 405.
13. Y. Kim, S. Cook, S. M. Tuladhar, S. A. Choulis, J. Nelson, J. R. Durrant, D. C. Bradley, M. Giles, I. McCulloch, C.-S. Ha, and M. Ree, Nat. Mater., 5 (2006) 197.
14. G. Li, V. Shrotriya, J. Huang, Y. Yao, T. Moriarty, K. Emery, and Y. Yang, Nat. Mater., 4 (2005) 864.
15. Y. Yao, J. Hou, Z. Xu, G. Li, and Y. Yang, Adv. Funct. Mater., 18 (2008) 1783.
16. C. W. Chu, H. Yang, W. J. Hou, J. Huang, and G. Li, Appl. Phys. Lett., 92 (2008) 103306.
17. G. Li, Y. Yao, H. Yang, V. Shrotriya, G. Yang, and Y. Yang, Adv. Funct. Mater., 17 (2007) 1636.
18. Y. Liang, Z. Xu, J. Xia, S. T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, Adv. Mater., 22 (2010) 135.
19. T. Sakurai, T. Yamanari, M. Kubota, S. Toyoshima, T. Taima, Y. Yoshida, and K. Akimoto, Jpn. J. Appl. Phys., 48 (2009) 125504.
20. V. Vohra, G. Arrighetti, L. Barba, K. Higashimine, W. Porzio, and H. Murata, J. Phys. Chem. Lett., 3 (2012) 1820.
21. I. P. Murray, S. J. Lou, L. J. Cote, S. Loser, C. J. Kadlec, T. Xu, J. M. Szarko, B. S. Rolczynski, J. E. Johns, J. Huang, L. Yu, L. X. Chen, T. J. Marks, and M. C. Hersam, J. Phys. Chem. Lett., 2 (2011) 3006.
22. Y. Liang, Z. Xu, J. Xia, S.-T. Tsai, Y. Wu, G. Li, C. Ray, and L. Yu, Adv. Mater., 22 (2010) E135.
23. Z. He, C. Zhong, X. Huang, W.-Y. Wong, H. Wu, L. Chen, S. Su, and Y. Cao, Adv. Mater., 23 (2011) 4636.
24. W. Chen, T. Xu, F. He, W. Wang, J. Strzalka, Y. Liu, J. Wen, D. J. Miller, J. Chen, K. Hong, L. Yu, and S. B. Darling, Nano Lett., 11 (2011) 3707.
25. S. J. Lou, J. M. Szarko, T. Xu, L. Yu, T. J. Marks, and L. X. Chen, J. Am. Chem. Soc., 133 (2011) 20661.
26. T. J. Brenner, Z. Li, and C. R. McNeil,
27. J. You, C.-C. Chen, L. Dou, S. Murase, H.-S. Duan, S. A. Hawks, T. Xu, H. J. Son, L. Yu, G. Li, and Y. Yang, *Adv. Mater.*, 24 (2012) 5267.
28. K. Yonezawa, H. Kamioka, T. Yasuda, L. Han, and Y. Morimoto, *Appl. Phys. Express*, 5 (2012) 042302.
29. S. M. Yoon, S. J. Lou, S. Loser, J. Smith, L. X. Chen, A. Facchetti, and T. Marks, *Nano Lett.*, 12 (2012) 6315.
30. L. Lu, Z. Luo, T. Xu, and L. Yu, *Nano Lett.*, 13 (2013) 59.
31. S. Ochiai, S. Imamur a, S. Kannappan, K. Palanisamy, and P.-K. Shin, *Curr. Appl. Phys.*, 13, Suppl. 2 (2013) S58.
32. M. Ohzeki, S. Fujii, Y. Arai, T. Yanagidate, Y. Yanagi, T. Okukawa, A. Yoshida, H. Kataura, and Y. Nishioka, *Jpn. J. Appl. Phys.*, 53 (2014) 02BE04.
33. T. Yanagidate, S. Fujii, M. Ohzeki, Y. Yanagi, Y. Arai, T. Okukawa, A. Yoshida, H. Kataura, and Y. Nishioka, *Jpn. J. Appl. Phys.*, 53 (2014) 02BE05.
34. P. P. Khlyabich, B. Burkhart, and B. C. Thompson, *J. Am. Chem. Soc.*, 134 (2012) 9074.
35. B. Burkhart, P. P. Khlyabich, and B. C. Thompson, *Macromolecules*, 45 (2012) 3740.
36. R. Lin, M. Wright, B. P. Veettil, and A. Uddin, *Synth. Met.*, 1927 (2014) 113.
37. Y. Ohori, S. Fujii, H. Kataura, and Y. Nishioka, *Jpn. J. Appl. Phys.*, 45 (2015) 04DK09.
38. H. Xu, H. Ohkita, H. Benten, and S. Itoh, *Jpn. J. Appl. Phys.*, 53 (2014), 01AB10.
39. P. Cheng, Y. Li, and X. Zhan, *Energy Environ. Sci.*, 7 (2014) 2005.
40. K.-C. Wang, J.-Y. Jeng, P/-S. Shen, E. W.-G. Diau, C.-H. Tsai, T.-Y. Chao, H.-C. Hsu, P.-Y. Lin, P. Chen, T.-F. Guo, and T.-C. Wen, *Sci. Rep.*, 4 (2014) 4756.
41. K. X. Steirer, J. P. Chesin, N. E. Widjonarko, J. J. Berry, A. Miedaner, D. S. Ginley, and D. C. Olson, *Org. Electron.*, 11 (2010) 1414.
42. P. Boland, S. S. Sunkavalli, S. Chennuiri, K. Foe, T. Abdel-Fattah, and G. Namkoong, *Thin Solid Films*, 518 (2010) 1728.
43. K. Kiriishi, K. Hashiba, J. Qiu, T. Yanagidate, M. Ohzeki, S. Fujii, H. Kataura, and Y. Nishioka, *Mol. Crys. Liq. Crys.*, (2015) in press.