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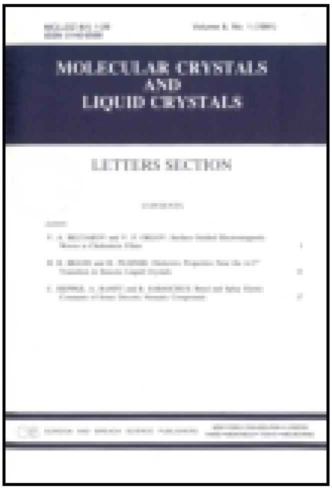

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Influence of Additive in the Photoactive Layer on the Performance of Organic Photovoltaics

Yoon Soo Han[a]

[a] Department of Advanced Energy Material Science and Engineering, Catholic University of Daegu, Gyeongbuk, Korea

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Influence of Additive in the Photoactive Layer on the Performance of Organic Photovoltaics

YOON SOO HAN*

Department of Advanced Energy Material Science and Engineering, Catholic
University of Daegu, Gyeongbuk, Korea

*Performance of poly(3-hexylthiophene):[6,6]-phenyl-C61-butyric acid methyl ester (P3HT:PC_{61}BM) bulk-heterojuction organic photovoltaics was improved by incorporationg a small portion of an additive, 3-fluoro-4-cyanophenol (*FCP*). The addition of 5wt%* FCP *to the P3HT:PC_{61}BM blend film resulted in an improvement of all parameters such as short circuit current, open circuit voltage and fill factor without even post-thermal annealing, and hence increased the overall power conversion efficiency by over 80% compared to that of reference cell without* FCP. *Optical measurement revealed that* FCP *additive in the P3HT:PC_{61}BM blend film facilitates the crystallization (ordering) of P3HT chains, leading to increasing the exciton generation and charge transport efficiency.*

Keywords P3HT; PC_{61}BM; organic photovoltaics; additive; post thermal annealing

Introduction

Bulk heterojunction (BHJ) organic photovoltaics (OPVs) have attracted considerable attention due to their low manufacturing costs, light weight, and flexibility as well as their potential for large-scale production [1–3]. Since the first BHJ OPV based on a bicontinuous network of internal donor {poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]}-acceptor (fullerene) heterojunctions showed a power conversion efficiency (PCE) of 2.9% [1], there have been steady improvements in PCEs. However, the PCE of OPVs is not sufficient for the realistic specifications of the commercial utilization. Recently, tandem OPVs with a PCE of over 10% have been reported by You et al. [4]. They used poly(3-hexylthiophene) (P3HT) as a high band gap polymer for front cell and poly[2,7-(5,5-bis-(3,7-dimethyloctyl)-5H-dithieno[3,2-b:20,30-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)] as a low band gap polymer for rear cell. Thus, tandem structure being able to utilize broader part of solar spectrum is considered as the most effective method to increase PCE. In tandem structure, both high and low band gap polymers are necessary to absorb visible and near-infrared light in one device. Among various high band gap polymers, P3HT is one of the most-studied conjugated polymers due to its appropriate band gap energy ($\sim$1.9 eV) for front cell, relatively high short circuit current density (J_{sc}) of over 10 mA/cm^2 and high external quantum efficiency of $\sim$70% [4–8].

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*Address correspondence to Y. S. Han, Department of Advanced Energy Material Science and Engineering, Catholic University of Daegu, 13-13 Hayang-ro, Hayang-eup, Gyeongsan-si, Gyeongbuk 712-702, Korea. E-mail: yshancu@cu.ac.kr

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Meanwhile, thermal annealing of P3HT:PC_{61}BM [[6,6]-phenyl C_{61}-butyric acid methyl ester] blend film, which creates the BHJ, has brought about a dramatic increase in PCE due to a nano-sized phase separation between the two materials [9–11]. In the BHJ film induced from the post thermal annealing, excitons generated by the absorption of light efficiently dissociate to electrons and holes, and thus charge carrier mobility and photoconductive response significantly increase [12–16]. However, Kim et al. reported that device performance was decreased with increasing annealing time at high temperature due to the deformation of the LiF layer [17]. When the temperature is not correctly controlled, thermal annealing at high temperatures after deposition of the cathode can cause damage to the morphology of the P3HT:PC_{61}BM film, and this additional thermal process requires a longer time for device fabrication. Furthermore, a flexible substrate for roll-to-roll processing may not tolerate the severe annealing environment.

In a previous report [18], we prepared P3HT:PC_{61}BM-based OPVs with 3-fluoro-4-cyanophenol (***FCP***) as additive, and the resulting devices showed enhanced PCEs after thermal annealing. In this study, we extend our research to non-annealed OPVs with ***FCP*** to escape above-mentioned potential problems of post-thermal annealing. In order to improve photovoltaic performance of the device without post-thermal annealing process, P3HT:PC_{61}BM-based OPVs with or without ***FCP*** additive were fabricated, and their photovoltaic properties were investigated and discussed.

Experimental

Materials

P3HT (98% regioregularity, $M_w = 6.4 \times 10^4$ g/mol) and PC_{61}BM were purchased from Rieke Metals and Nano-C, respectively. Poly-3,4-ethyleneoxythiophene:poly-4-sytrensulfonate (PEDOT:PSS, Baytron P VP Al 4083) was used as received from P. H. Stark GmbH. Solvents used in this study were all reagent grade and were used as received unless stated otherwise. As additive, ***FCP*** was purchased from Sigma-Aldrich, and used without further purification.

Device Fabrication

OPVs were fabricated on indium-tin oxide (ITO) glasses (10 Ω/□, SUNIC Ltd.) as follows. ITO glasses were cleaned by sequential ultrasonication in acetone, detergent, de-ionized water and isopropyl alcohol and then dried in a vacuum oven. Next, O_2 plasma treatment of the ITO glasses was conducted for 3 min, and immediately afterwards, PEDOT:PSS was spin-coated onto the ITO glass. The PEDOT:PSS films were then baked on a hot plate for 15 min at 140°C to yield a thickness of 30 nm; the film-coated ITO glass was then moved to a N_2 glove box for the remainder of the fabrication process. P3HT and PC_{61}BM at a weight ratio of 1:0.9 were first dissolved in chlorobenzene. Selected amounts of the ***FCP*** additive, ranging from 3 to 6 wt% based on the P3HT:PC_{61}BM, were then added to the P3HT:PC_{61}BM solution, followed by stirring for 24 h at 50°C. The solution consisting of P3HT:PC_{61}BM blended with or without additives was spin-cast onto the top of the PEDOT:PSS layer, and the plate was then dried on a hot plate in a covered Petri dish for 40 min at 50°C to produce an active layer with a thickness of 100 nm. Finally, a cathode consisting of LiF (1 nm) and a subsequent Al (150 nm) layer was deposited by thermal evaporation under a vacuum of 10^{-7} Torr. Devices with the configuration of ITO/PEDOT:PSS (30 nm)/P3HT:PC_{61}BM:with or without additive (100 nm)/LiF (1 nm)/Al

(150 nm) were encapsulated with a glass cap to protect them from air. The active area of all devices was determined to be 9 mm^2 using a shadow mask.

Characterization

UV-visible absorption spectra of the fabricated blend films with and without additive were obtained using a Perkin Elmer Lambda 750 UV/VIS spectrometer. Photocurrent-voltage measurements were performed with a Keithley model 2400 Source Meter and a Newport 91192 solar simulator system equipped with 1-KW xenon arc lamp from Oriel. The light intensity was adjusted to simulate AM 1.5 radiation at 100 mW cm^{-2} with a Radiant Power Energy Meter (model 70260, Oriel).

Results and Discussion

The devices with the configuration of ITO/PEDOT:PSS (30 nm)/P3HT:PC_{61}BM:with or without ***FCP*** (100 nm)/LiF (1 nm)/Al (100 nm) were fabricated and characterized without thermal annealing treatment. The amount of ***FCP*** in the blend solution was varied from 3 to 6 wt% to optimize the performance of OPV devices. The photovoltaic properties of the devices characterized under AM 1.5 conditions as a function of ***FCP*** amount are presented in Fig. 1. The J_{sc} values of non-annealed OPVs with ***FCP*** additive showed an enhancement, compared to the control device (OPV0) without any additives, and were improved with increasing content of ***FCP***. The V_{oc} values were also improved by the incorporation of the

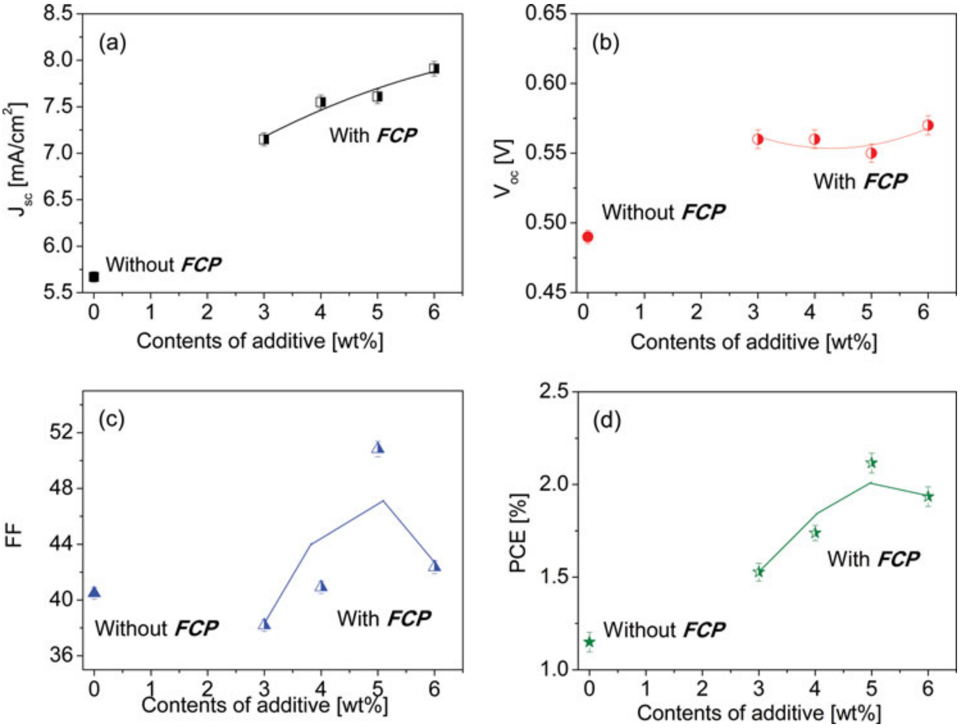

Figure 1. Performance plotted as a function of ***FCP*** concentration: (a) J_{sc}, (b) V_{oc}, (c) *FF* and (d) *PCE* of non-annealed OPVs under AM 1.5 irradiation.

Table 1. Photovoltaic properties of non-annealed OPVs with and without ***FCP***

Annealed devices	Content of additive	V_{oc} (V)	J_{sc} (mA/cm^2)	*FF* (%)	*PCE* (%)	R_{sh} ($\Omega \cdot$cm^2)	R_s ($\Omega \cdot$cm^2)
OPV0	0 wt%	0.489	5.695	40.79	1.14	235.8	32.85
OPV5	5 wt%	0.550	7.590	50.65	2.11	345.6	17.64

additive, and similar values were maintained with increasing ***FCP***, unlike the J_{sc} values. There were wide variations in the *FF* values ranged from ∼ 38 to ∼51% with the content of ***FCP***. Overall, The PCEs of non-annealed devices with 3–6 wt% ***FCP*** were considerably enhanced as compared to the control device (OPV0) without ***FCP***.

The non-annealed device (OPV5) with 5 wt% ***FCP*** exhibited the best performance due to an enhancement in all parameters such as J_{sc}, V_{oc} and *FF*, resulting in a PCE of 2.11% as compared to that (1.15%) of the control device (OPV0). Because the PCE exhibited the highest value when the ***FCP*** content was 5 wt%, we focused on this device with P3HT:PC$_{61}$BM:***FCP*** (5 wt%) blend film to determine the origin of an enhancement in efficiency. The photovoltaic properties of the non-annealed devices with and without ***FCP*** are summarized in Table 1, and the current density (*J*) versus voltage (*V*) curves are illustrated in Fig. 2.

As described above, the improved performance of devices with 5 wt% ***FCP*** resulted from an increase in J_{sc}, *FF* and V_{oc}. A fractional contribution of J_{sc} to an improvement in PCE was about 46%. It is necessary to reveal the origin of the increased J_{sc} resulting from the incorporation of ***FCP*** additives. It is well known that an enhanced J_{sc} is largely related to the generation of more excitons and higher charge transport properties that derived from stronger absorption intensity and effective phase separation between P3HT and PC$_{61}$BM [19, 20]. To probe the role of ***FCP*** in the P3HT:PC$_{61}$BM blend films, UV-visible absorption spectra of a non-annealed P3HT:PC$_{61}$BM:***FCP*** blend film cast from a chlorobenzene solution on a quartz plate were compared with that of a non-annealed pristine P3HT:PC$_{61}$BM film. Fig. 3 shows the UV-vis. absorption spectra of

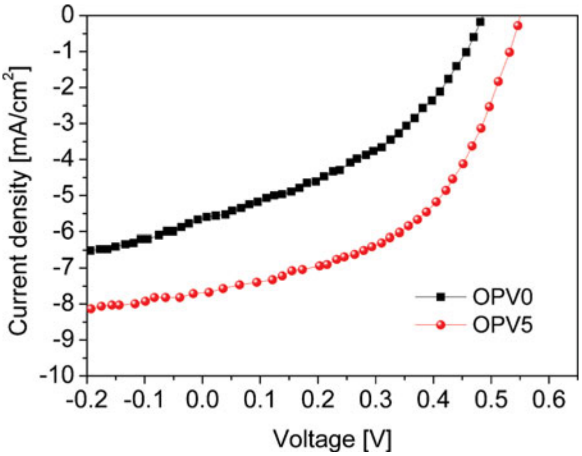

Figure 2. *J-V* characteristics of non-annealed OPVs with and without ***FCP***.

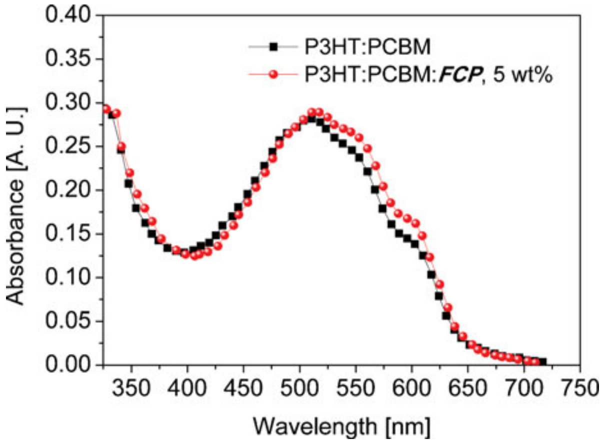

Figure 3. UV-vis absorption spectra of the non-annealed P3HT:PC$_{61}$BM blend films with and without ***FCP*** additive.

non-annealed P3HT:PC$_{61}$BM blend films with and without 5 wt% ***FCP*** with the same film thickness. When comparing to the pristine non-annealed P3HT:PC$_{61}$BM blend film, the film with ***FCP*** exhibited a higher absorbance in the major absorption peak (~520 nm) of the π-π^* transition and in the two vibronic peaks of 550 and 600 nm. Similar phenomena in P3HT:PC$_{61}$BM blend systems with various additives have been reported by several groups [21, 22]. This result clearly indicates that adding small amounts of ***FCP*** to the P3HT:PC$_{61}$BM blend film considerably improved the crystallinity of P3HT chains, resulting in an enhancement in π-π^* transition efficiency of P3HT and thus an improvement in the exciton generation efficiency. More ordered structure and effective phase separation in P3HT:PC$_{61}$BM blend films could increase the charge transport efficiency, because charge recombination could be reduced by them. When considering that ***FCP*** facilitates the phase separation of P3HT and PC$_{61}$BM resulting from the high crystallinity of P3HT, the presence of ***FCP*** in P3HT:PC$_{61}$BM blend film could lead to an improvement in charge transport efficiency [23]. Overall, we can conclude that the ***FCP*** in the P3HT:PC$_{61}$BM film enhances the ordering (crystallization) of the P3HT and phase separation, resulting in an improvement in both exciton generation and charge transport efficiency, and thus an increment in J_{sc}.

The *FF* value of OPV5 was also increased by over 24%, compared to that of OPV0, corresponding to about 35% contribution to an improvement in PCE. This enhancement could be due to the reduced Rs and elevated Rsh (Table 1). The Rs value is an important factor for determining the J_{sc} and *FF* of photovoltaic cells [24, 25] The OPV5 with ***FCP*** additive had an effectively reduced R_s of 17.64 Ω cm^2 compared with that (32.85 Ω cm^2) of the OPV0 without ***FCP***, resulting in an improvement in J_{sc} and *FF*. The R_{sh} value (345.6 Ω cm^2) of OPV5 was also increased from that (235.8 Ω cm^2) of OPV0. Low shunt resistance causes power losses in solar cells by providing an alternate current path for the light-generated current. Thus, the shunt resistant is closely related to charge recombination and leakage current, which can also affect *FF* [24]. It is generally accepted that the *FF* is influenced by the balance between hole and electron mobilities in OPVs [26–27]. The photovoltaic performance of OPVs is limited by the carrier with a lower mean free path (holes in OPVs) [28], because the unbalanced transport will result in a loss of efficiency due to increased charge recombination, which can reduce *FF*. Thus, hole mobility should be increased to maintain the electrical neutrality in OPVs. As mentioned earlier, the incorporation of the ***FCP*** additive into the P3GT:PC$_{61}$BM film increased the crystallization of the P3HT. This fact, i.e., more ordered P3HT chains, can induce an enhancement in hole mobility in OPV7 [29], yielding more balanced transport of holes and electrons. The balanced charge transporting (mobility) reduces the accumulation of space charges in films and hole-electron recombination loss, leading to an enhancement of the *FF* [30, 31]. Thus, we believe that the increased *FF* value could be attributed to the lowered R_s and elevated R_{sh}, possibly due to the improved ordering of P3HT, and thus the reduced charge recombination.

The V_{oc} value in the non-annealed OPV5 also showed an increment accounting for about 19% of the enhancement of PCEs compared with OPV0. Because the V_{oc} is linearly related to the HOMO$_{\text{donor}}$-LUMO$_{\text{acceptor}}$ energy difference [32], which is directly correlated with acceptor strength, an increase in V_{oc} indicates that the acceptor strength in OPVs was changed by the presence of ***FCP*** in the P3HT:PC$_{61}$BM blend film. However, it is tantalizing that the presence of ***FCP*** in the P3HT:PC$_{61}$BM blend films affects the accept strength. In this respect, further studies aimed at elucidating the origin of the change in the accept strength in the PSC5 are currently in progress.

Conclusion

In summary, we have investigated the effects of ***FCP*** on the photovoltaic properties of P3HT:PC$_{61}$BM-based solar cells by monitoring changes in the UV-vis absorption intensity. The non-annealed device with P3HT:PC$_{61}$BM:***FCP*** blend film achieved an PCE of 2.12% due to the improved J_{sc}, *FF* and V_{oc}, compared to that (1.15%) of reference cell without any additives. It was revealed that the incorporation of ***FCP*** additives into the P3HT:PC$_{61}$BM blend film led to an enhanced crystallization (ordering) of P3HT even without post-thermal annealing. This result indicates that the ***FCP*** additives can play a role of useful processing additives to improve PCEs without the need for post-thermal annealing.

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