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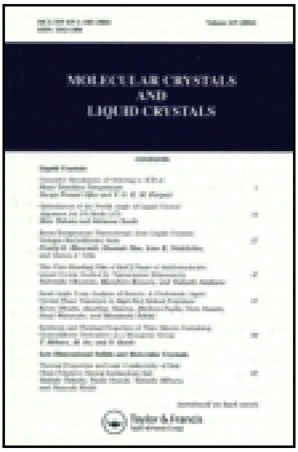

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Doping Effect of CBP in Bulk-heterojunction Photovoltaic Devices Composed of P3HT and Soluble Perylene Bisimide

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Doping Effect of CBP in Bulk-heterojunction Photovoltaic Devices Composed of P3HT and Soluble Perylene Bisimide

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The effect of doping carrier transporting materials being used for organic light emitting diodes was investigated in bulk-heterojunction photovoltaic devices composed of poly(3-hexylthiophene) (P3HT) and a perylene bisimide (PBI) derivative. We found that the doping of 4,4'-bis(carbazol-9-yl)biphenyl (CBP) can improve the short circuit current and fill factor with a doping concentration of 2.5wt%, resulting in an increase of power conversion efficiency from 0.14% to 0.28%. This effect is mainly attributable to the improvement of miscibility between P3HT and PBI.

Keywords bulk-heterojunction; carrier transporting materials; Organic photovoltaic devices; perylene bisimide; ternary devices

Introduction

Organic photovoltaic devices (OPV) attract considerable attension as a novel class of renewable energy. They can be produced by printing process on large and flexible substrates with low manufacturing cost. Most polymer solar cells usually employ a bulk-heterojunction (BHJ) structure in the active layer composed of semiconducting polymers and fullerene derivatives [1–4]. A recent progress on polymer semiconductors having low band gap and fullerene derivatives have drastically increased power conversion efficiency. While many types of backbones have been investigated for p-type polymers, fullerene counterparts seem to be still essential to achieve high performance [5]. While semiconducting polymers have high absorption coefficients in the spectral region of visible light, fullerene derivatives only absorb photons within a very limited range of the solar spectrum. Although C_{70} derivatives provide enhanced absorption in the blue region compared to C_{60} derivatives, it is quite difficult to extend the response of fullerene derivatives into the red and near-infrared regions [6]. From these reasons, the exploration of OPV devices based on other n-type materials is an important issue.

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Perylene bisimide (PBI) derivatives are promising materials for optoelectronic devices because they have high thermal and photo chemical stabilities, broad absorption in the visible region, and high electron mobilities as well as high electron affinities [7]. PBI derivatives have been used for photovoltaic devices mainly in the vacuum-deposited system [8], and are good candidates for the substitution of fullerene derivatives due to their capabilities to form crystalline domains with high electron mobility upon being blended with polymers [9]. Several attempts on BHJ system using semiconducting polymer and soluble PBI derivative have been reported so far. However, these systems exhibit low external power conversion efficiencies around 0.18% that is much lower compared with standard P3HT:PCBM systems [10].

The difficulty in the PBI-based BHJ system might be due to low solubility of PBI derivatives. In this study, we studied OPV devices by using P3HT and soluble PBI having branched alkyl chains so-called swallow tail (STPBI). STPBI has a high solubility but its electrical property is poor. In order to solve this problem, we investigated ternary devices composed of P3HT, PBI, and carrier transporting materials used in organic light emitting diodes. We found that CBP, a carbazole derivative, could improve the performance.

Experiment

The device structure of the ternary device and chemical structure used materials are shown in Fig. 1. ITO glass substrates were cleaned by ultrasonication sequentially in acetone and 2-propanol each of 10 min. After drying the substrate, UV-ozone cleaned for 5 minutes. A thin layer (30 nm) of PEDOT:PSS (AI 4083) was spin-coated at 5000 rpm for 40 s, followed by 20 min of drying at 120°C in air. The samples were then transferred to a nitrogen glovebox system. P3HT and *N,N′*-di(2-hexylheptyl)-perylene-3,4:9,10-tetracarboxylic acid bisimide (STPBI) with weight ratio of 1:4 (30 mg/ml) were dissolved in *o*-dichlorobenzene. Varied amounts of the carbazole derivative, CBP (ranging from 1.5 to 10wt%), were then added to the P3HT:STPBI solution, followed by stirring for 15 h. A solution consisting of the P3HT:STPBI blend with or without CBP as an additive was spin-coated at 800 rpm for 60 s on the top of the PEDOT:PSS layer. After drying the solvent, the substrate was annealed

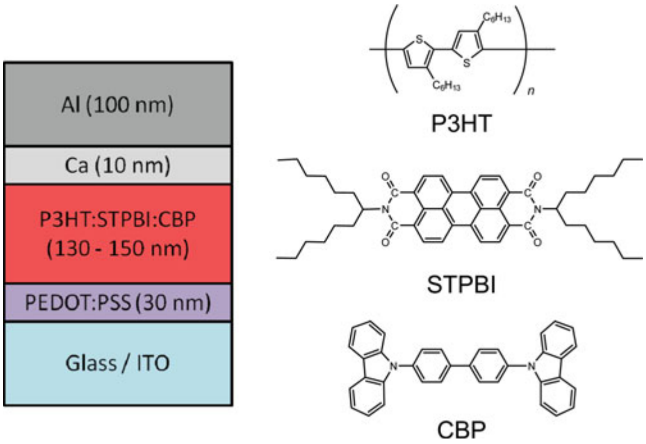

Figure 1. Device structure of the ternary device and chemical structures of used material.

at 90°C for 10 min. The film thicknesses increased with increasing doping concentration from 130 nm through 150 nm. A Ca/Al (10 nm/100 nm) cathode was evaporated under high vacuum (10^{-4}–10^{-5} Pa) through a shadow mask that defines an active area of 0.04 cm^2. The device was encapsulated by a glass lid in the glove box system. The current-voltage characteristics and photovoltaic properties were measured under simulated air mass (AM) 1.5 G solar irradiation using a Keithley 2400 source-measure unit.

Results and Discussion

Figure 2(a) shows current-voltage curves of the photovoltaic devices with and without CBP-doping under dark condition and illumination of AM 1.5 G. Photovoltaic parameters of these devices are summarized in Table 1. The control device without CBP-doping was optimized in solution concentration, mixture ratio, baking temperature and time. The best devices showed a short circuit current (J_{SC}) of 0.86 mA/cm^2, an open circuit voltage (V_{OC}) of 0.36 V, and a power conversion efficiency (PCE) of 0.14%. Figure 2(b) shows the incident photon to current conversion efficiency (IPCE). The control device showed a maximum value of 11% at 490 nm and sensitivity up to 650 nm. Although these values are lower compared to conventional fullerene-based OPV devices, they are reasonable values in the P3HT and PBI binary devices as reported previously [11].

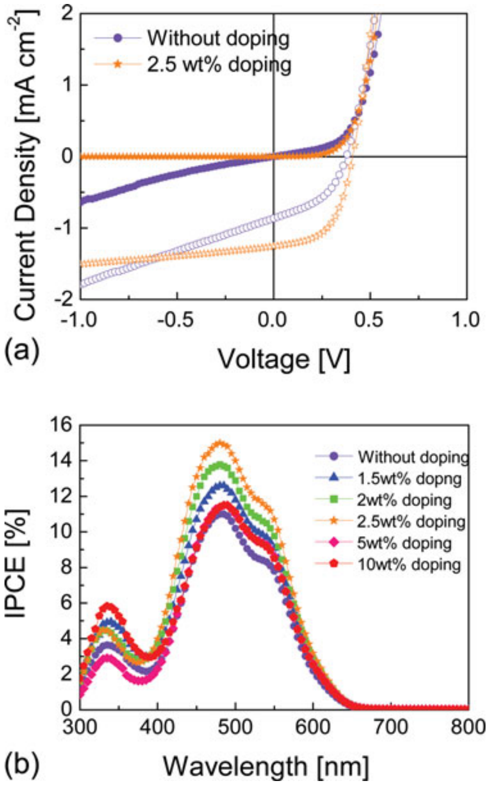

Figure 2. Device characteristics, (a) J-V curves of the device composed of P3HT:STPBI blend films with and without CBP doping under illumination of AM 1.5 G, 100 mW/cm^2, (b) IPCE as a function of wavelength for the devices with and without CBP.

Table 1. Photovoltaic performances of the device composed of P3HT:STPBI with and without CBP blend devices

Device	Jsc (mA/cm^2)	Voc (V)	Fill factor (%)	Efficiency (%)	R$_S$ (ohm cm^2)	R$_P$ (ohm cm^2)
Without doping	0.86	0.38	44.1	0.143	125.6	1104.0
1.5wt%	1.10	0.38	53.5	0.220	72.6	3484.4
2wt%	1.13	0.39	55.9	0.245	65.6	3246.8
2.5wt%	1.25	0.41	54.3	0.279	70.8	2879.2
5wt%	1.15	0.37	56.1	0.240	60.5	3031.2
10wt%	0.91	0.40	51.2	0.188	91.6	3006.8

We next investigated ternary devices composed of P3HT, STPBI, and CBP with various mixing ratios. PCE values increased with increasing doping concentration of CBP, and reached a maximum value of 0.28% at a doping concentration of 2.5 wt%. This improvement could be attributed to increase of J$_{SC}$ and FF. The FF was improved by CBP-doping and reached plateau with the doping-concentration of 5wt%. The V$_{OC}$ was less affected by CBP-doping. Increasing the doping-concentration over 2.5wt% resulted in a decrease of the device performance. The IPCE spectra shown in Fig. 2(b) also show the highest sensitivity of 15% at a doping concentration of 2.5wt%. We finally achieved PCE of 0.28%, which is about 1.5-times higher than the best value reported for P3HT:PBI solar cells [11].

The morphology of P3HT:STPBI with and without CBP-doping were studied by atomic force microscopy (AFM). As shown in Fig. 3, P3HT:STPBI films without CBP-doping had

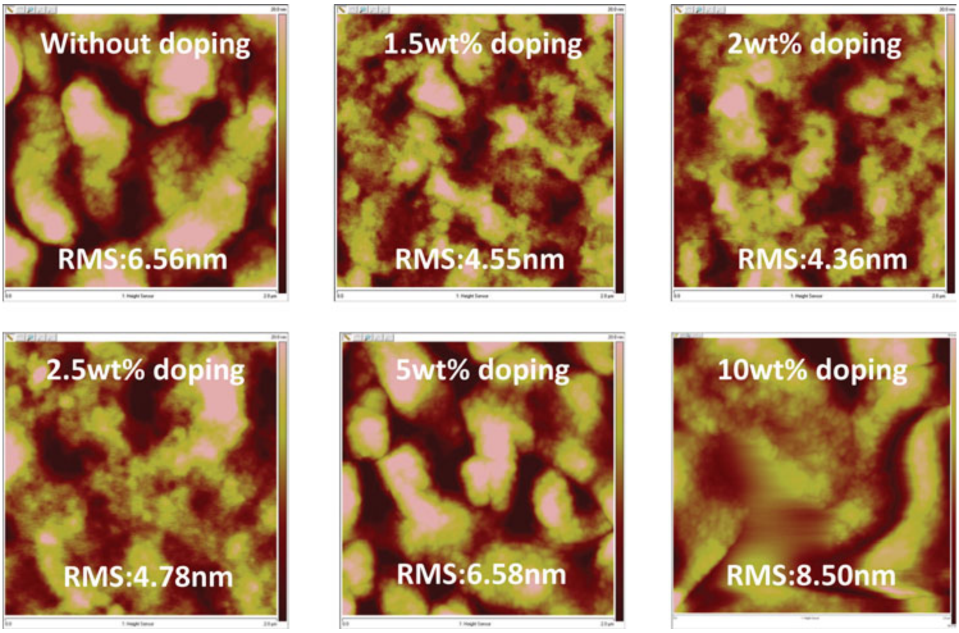

Figure 3. AFM images of the surface of P3HT:STPBI with and without CBP films spin-coated from *o*-dichlorobenzene (dimensions: 2 μm × 2 μm).

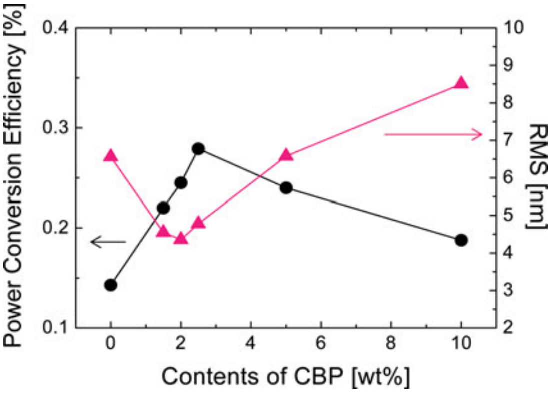

Figure 4. Dependence of CBP concentration on PCE and RMS value in the device of P3HT:STPBI:CBP ternary devices.

a large root mean square (RMS) value of 6.56 nm. The AFM image also indicated rough surface and coarse phase separation. In sharp contrast, AFM images of the CBP-doped P3HT:STPBI films displayed a decrease of RMS values, and fine phase separation could be seen. For a doping-concentration of 2wt%, the RMS value measured to be 4.36 nm. Further increase of the doping concentration up to 5wt% resulted in serious increase of the domain size, unfavorable for BHJ-OPV devices.

In Fig. 4 the PCE and RMS values are plotted against the doping concentration of CBP. The device performance shows clear correlation with the surface morphology, i.e., the decrease of surface roughness RMS value by CBP-doping leaded to the improvement of PCE. Conversely, high doping concentration causes an increase of the roughness and a decrease of the PCE. These results indicate that the effect of CBP-doping on the device performance is mainly attributed to the improvement of miscibility between P3HT and STPBI. Higher concentration of CBP more than 5% may cause segregation of CBP itself. Although the CBP-doping improved the RMS values, the overall RMS values were relatively high, indicating that the occurrence of a serious, phase separation as indicated by AFM. This resulted in less interface area between P3HT and PBI, leading to low carrier dissociation efficiency. This is a major reason for low device performances of the OPV device using PBI as n-type semiconductor. The present study revealed that the doping with semiconducting materials such as CBP is an effective approach to increase the miscibility of the two materials.

The photoluminescence was measured to clarify the effect of CBP-doping on the photocarrier generation process. Photoluminescence quenching in donor-acceptor composites is a useful indication for photoinduced charge transfer efficiency between the two components. Figure 5(a) shows photoluminescence spectra of P3HT:STPBI films with and without CBP-doping. The P3HT:STPBI film without doping indicated photoluminescence at a wavelength around 630 nm when excited at 480 nm. The integrated photoluminescence intensity is plotted against the doping concentration [Fig. 5(b)]. The photoluminescence intensity was decreased with doping, and reached a minimum value at a doping-concentration of 2.5wt%. This result indicates that CBP-doping promotes the charge dissociation process. Above this concentration, however, photoluminescence intensity again increased and finally exceeded that of the undoped P3HT:STPBI film at a doping-concentration of 10wt%. This tendency agrees well with the effect of the doping on the J_{SC} and the IPCE values as

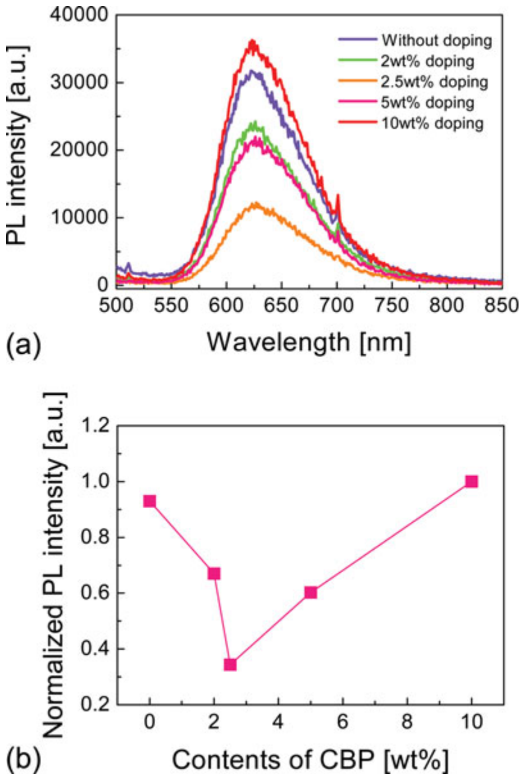

Figure 5. (a) Photoluminescence spectra of P3HT:STPBI blend films with and without CBP doping, (b) dependence of the integrated PL intensity on the doping concentration of CBP.

well as AFM images. The doping of a small amount of CBP may suppress the aggregation of STPBI, resulting in finer phase separation, giving small domains of the p- and n-type semiconductors. As a result, P3HT and STPBI have a larger interface required to dissociate exciton to mobile charge carriers.

As described above, the enhancement of OPV performance by CBP-doping is attributable to improved miscibility of P3HT and STPBI. This result would be derived from amorphous nature of CBP that is generally observed in OLED materials. We tried some other amorphous doping materials including typical hole and electron transporting materials that have been used for OLEDs (data not shown). However, most of such materials did not show the enhancement of J_{SC}. On the contrary, they deteriorated the electrical properties to a large extent. From these observations, we consider that the observed enhancement is related to high glass transition temperatures (T_g) and ambipolar nature of CBP [12]. The T_g of amorphous OLED materials is generally not so high. Since the device was annealed at 90°C, the materials having low T_g could be crystallized during fabrication process. On the other hand, the T_g of CBP is 109°C, which is higher than the annealing temperature. Furthermore, the series resistance (R_S) was improved by CBP-doping. While the obtained results could be explained mainly by the improved miscibility, it can be also suggested that CBP may penetrate into P3HT:STPBI network and assist charge transportation and extraction due to its ambipolar nature. It is difficult to discriminate these possibilities at present; the design of effective dopants is a promising approach to improve the performance of the BHJ-OPV.

Conclusion

In conclusions, ternary photovoltaic devices composed of P3HT, STPBI, and carrier transporting materials being used in organic light emitting diodes were investigated. We found that, among several types of carrier transporting materials, CBP is an effective dopant to improve the OPV performance. AFM and photoluminescence studies indicate that this effect is attributed mainly to the improvement of miscibility between P3HT and STPBI, resulting in effective exciton harvesting.

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