Research Article

Effect of Doping Phosphorescent Material and Annealing Treatment on the Performance of Polymer Solar Cells

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A series of polymer solar cells (PSCs) with P3HT:PCBM or P3HT:PCBM:Ir(btpy)$_3$ blend films as the active layer were fabricated under the same conditions. Effects of phosphorescent material Ir(btpy)$_3$ doping concentration and annealing temperature on the performance of PSCs were investigated. The short-circuit current density ($J_{sc}$) and open-circuit voltage ($V_{oc}$) are increased by adopting P3HT:PCBM:Ir(btpy)$_3$ blend films as the active layer when the cells do not undergo annealing treatment. The increased $J_{sc}$ should be attributed to the increase of photon harvesting induced by doping phosphorescent material Ir(btpy)$_3$ and the effective energy transfer from Ir(btpy)$_3$ to P3HT. The effective energy transfer from Ir(btpy)$_3$ to P3HT was demonstrated by time-resolved photoluminescence (PL) spectra. The increased $V_{oc}$ is due to the photovoltaic effect between Ir(btpy)$_3$ and PCBM. The power conversion efficiency (PCE) of PSCs with P3HT:PCBM as the active layer is increased from 0.19% to 1.49% by annealing treatment at 140$^\circ$C for 10 minutes. The PCE of PSCs with P3HT:PCBM:Ir(btpy)$_3$ as the active layer is increased from 0.49% to 0.95% by annealing treatment at lower temperature at 100$^\circ$C for 10 minutes.

1. Introduction

Polymer solar cells (PSCs) are considered one of the most promising sources for clean and renewable energy due to their advantages such as lightweight, low cost, ease of large scale manufacture, and compatibility with flexible substrates [1–4]. Many effective approaches have been carried out to improve the performance and stability of PSCs, such as synthesizing new narrow bandgap materials for better photon harvesting, modifying the interfaces for better charge carrier collection, and applying novel configurations [5, 6]. But the performance of PSCs is still not satisfactory for commercial use. Factors limiting the PCE of PSCs could be summarized as the following: (i) mismatch between the absorption of organic photovoltaic materials and the solar light spectrum [7]; (ii) the relatively lower exciton dissociation efficiency induced by the limit of exciton diffusion distance and interfacial energy level mismatch [8, 9]; and (iii) the transport and collection of charge carriers dependence on the phase separation in active layers and the work function of electrode materials [1, 10]. To strengthen the absorption range and intensity of the active layer, an effective method is to use two kinds of electron donors which have a complementary absorption. Sharma et al. reported that the PCE of PSCs based on P3HT:PC$_{70}$BM as the active layer was improved from 3.23% to 4.37% by doping soluble DPP-CN small molecule material [11]. Xu et al. reported that the $V_{oc}$ of PSCs based on P3HT:PCBM was improved to 0.85 V by doping poly(9,9-diocytfluorene-co-bithiophene) (F8T2) into P3HT:PCBM [12]. Molecular arrangement of donor and acceptor materials has great influence on photon harvesting and charge carrier transport and collection, which strongly determines the performance of PSCs. A series of effective methods were proposed to control the molecular arrangement, such as annealing treatment, solvent additive treatment, nanoimprint, and electric field treatment methods [13–16]. Ma et al. reported that the PCE of PSCs with P3HT:PCBM as active layer was improved to 5% by annealing treatment on the active layer [17]. It is known that only excitons dissociated into free charge carriers can contribute to the performance of PSCs. However, exciton dissociation efficiency is strongly determined by the exciton...
diffusion length ($L_D$), donor/acceptor interfacial energy barriers, and internal electric field, while $L_D$ is mainly determined by two parameters, exciton lifetime ($\tau$) and mobility ($\mu$) [18,19]. The singlet state photogenerated excitons in donor materials have a very short lifetime, which is less than 1 ns [20]. If singlet excitons can be transformed into triplet excitons with a longer lifetime through intersystem crossing, this would be beneficial to exciton dissociation. A probable strategy to increase the intersystem crossing efficiency is using heavy atom effects by doping magnetic or phosphorescent materials into organic photovoltaic materials. Phosphorescent materials, such as tris[2-(benzo[8] thiophen-2-yl) pyridinato-C, N]iridium (III) (Ir(btpy)$_3$), bis[2-(4-tertbutylphenyl) benzothiazolato-N,C$_2$] iridium (acetylacetonate) ((t-bt)$_2$Ir(acac)), 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum (II) (PtOEP), and tris[2-phenylpyridinato]Ir(III) (Ir(ppy)$_3$) have attracted much attention because of their potential application in PSCs [21–25]. Yu et al. reported that the exciton diffusion distance was increased by doping (t-bt)$_2$Ir(acac) into copper phthalocyanine (CuPc) [21]. However, Lee reported that carrier generation in the bulk heterojunction was not enhanced in the presence of PtOEP because the rate and probability of excitation dissociation between PtOEP and PCBM are much faster and higher than that of triplet-triplet energy transfer between PtOEP and MEH-PPV [26]. Zhang et al. reported that the PCE of PSCs based on oleic acid-Fe$_3$O$_4$-doped P3HT:PCBM as the active layer was enhanced by ~18% primarily due to the increase of $J_{sc}$, which is attributed to the increase of the population of triplet excitons induced by the magnetic field effect originated from the superparamagnetism of Fe$_3$O$_4$ nanoparticles (NPs) [27].

In this paper, the effect of phosphorescent material Ir(btpy)$_3$ doping concentration in P3HT:PCBM and annealing treatment temperature on performance of PSCs was investigated. For the PSCs with P3HT:PCBM as active layer, the PCE of PSCs arrives to 1.4% after annealing treatment at 140°C for 10 minutes. The PSCs with P3HT:PCBM:Ir(btpy)$_3$ as active layer have larger PCE compared to PSCs with P3HT:PCBM as active layer under lower temperature annealing treatment. However, the performance of PSCs with P3HT:PCBM:Ir(btpy)$_3$ as active layer was decreased by high temperature annealing treatment. The underlying reason was discussed from the photon harvesting, energy transfer, and phase separation induced by doping phosphorescent material Ir(btpy)$_3$ in P3HT:PCBM.

### 2. Experimental Section

P3HT with an average molecular weight of 48000 and PCBM (both are purchased from Nichem Fine Technology Co., Ltd.) was mixed by 1:0.8 (weight ratio) and dissolved in chloroform with a concentration of 18 mg/mL. Phosphorescent material Ir(btpy)$_3$ (purchased from Jilin OLED Photoelectric materials Co., Ltd.) was dissolved in chloroform with a concentration of 2 mg/mL. The indium tin oxide (ITO) glass substrates (sheet resistance 15 Ω/◻) were cleaned consecutively in ultrasonic baths containing acetone, ethanol, and de-ionized water and dried by high pure nitrogen gas. The precleaned ITO substrates were then treated by UV- ozone for 10 min in order to further clean the substrates and improve the work function of ITO substrates. An ultrathin layer of poly-(3,4-ethylenedioxythiophene)-poly-(styrenesulfonate) (PEDOT:PSS) (purchased from H.C. Starck Co., Ltd.) was spin coated on the ITO substrates under 3000 rpm for 40 s. Then, PEDOT:PSS-coated ITO substrates were dried in air at 120°C for 10 min. The active layers were prepared by spin-coating method under 2000 rpm for 40 s. An aluminum cathode layer of about 100 nm was deposited on the active layer under $10^{-4}$ pa vacuum conditions. The active area is about 10 mm$^2$, which is defined by the overlap of ITO anode and Al cathode.

The structure configuration of PSCs is ITO/PEDOT:PSS/ P3HT:PCBM:Ir(btpy)$_3$ or P3HT:PCBM/Al. Parts of fabricated cells were carried out with annealing treatments under different temperature in the room conditions. The absorption spectra of films were measured with a Shimadzu UV-3101 PC spectrometer. The photoluminescence (PL) spectra were measured with a LS-55 spectrometer from Perkin Elmer. The current-voltage characteristics of PSCs were measured using a Keithley 4200 semiconductor characterization system and ABET Sun 2000 solar simulator. Time-resolved transient PL spectra were measured using FluorCube-01- NL and FluoroHub-NL from Jobin Yvon. The schematic structure configuration of PSCs and chemical structures of used organic materials are shown in Figure 1.

### 3. Results and Discussion

The P3HT, Ir(btpy)$_3$, P3HT:PCBM, and P3HT:PCBM:Ir(btpy)$_3$ films were prepared on quartz substrates under the same condition; the absorption spectra of all films are shown in Figure 2. Neat P3HT films show a large absorption range from 400 nm to 600 nm. Neat Ir(btpy)$_3$ films have strong absorption from UV-zone to 500 nm. The absorption spectra of neat P3HT, PCBM, and Ir(btpy)$_3$ films have an apparent spectral overlapping in the range of 400 nm–500 nm. Doping Ir(btpy)$_3$ can also strengthen the relatively weak area in P3HT:PCBM absorption at 360–430 nm, where both P3HT and PCBM have a weak absorption at this range. Therefore, their blend films could harvest more photon to produce more photo-generated excitons. It is obvious that the absorption intensity of P3HT:PCBM:Ir(btpy)$_3$ films is bigger than that of P3HT:PCBM films in the visible light range, which is beneficial to increase the performance of PSCs. It is known that photon harvesting in the active layer is the key issue to improve the PCE of PSCs [28]. Phosphorescent material Ir(btpy)$_3$ has long exciton lifetime on the triplet states due to the heavy atom effect [22]. Figure 3 shows the PL spectra of Ir(btpy)$_3$, P3HT, and P3HT:Ir(btpy)$_3$(100:1) films under the excitation of 410 nm light. The PL spectra of Ir(btpy)$_3$ films show two emission peaks at 596 nm and 648 nm, which has an apparent spectral overlapping with the absorption spectrum of P3HT. According to the mechanism of energy transfer between organic materials, the energy transfer from Ir(btpy)$_3$ to P3HT may occur due to their large spectral
overlapping, which could be further demonstrated by the PL spectra of P3HT:Ir(btpy)$_3$ blend films [29]. The emission peak at 596 nm from phosphorescent material Ir(btpy)$_3$ could not be observed from PL spectra of P3HT:Ir(btpy)$_3$(100:1) films. More information about the energy transfer process can be acquired by comparing the intensity ratio of emission peaks representing different exciton states in Figure 3. Polymer P3HT has an emission peak at 654 nm and another emission peak at 715 nm. The emission intensity ratio of 715 nm to that of 654 nm is about 0.90. It is very interesting that the emission intensity ratio of 715 nm to that of 654 nm was increased to 3.23 in the P3HT:Ir(btpy)$_3$(100:1) blend films under the same excitation condition. The relative increased emission intensity of 715 nm should be attributed to the energy transfer from the triplet states of Ir(btpy)$_3$ to the lower energy level of P3HT. To further confirm these phenomena, PL spectra of films prepared by different doping concentrations P3HT:Ir(btpy)$_3$ solutions were measured and are shown in Figure 4.

The quench of emission peak at 596 nm could be observed from PL spectra of all blend films with different doping concentrations, which indicated that the energy transfer from Ir(btpy)$_3$ to P3HT maintains high efficiency, as shown in Figure 4. Another interesting phenomenon is that the longer wavelength emission peak in the PL spectra of blend films undergoes a gradually blueshift along with the increase of doping concentration, resulting in only one broad emission peak at 676 nm for blend films with 8% Ir(btpy)$_3$ doping concentration. Compared with the obvious and rapid change of emission intensity at 654 nm in blend films, the blueshift of emission at 715 nm has concentration dependence. Since the radiation recombination from the lower energy level of P3HT to the ground state corresponds to the 715 nm emission, it is reasonable to believe that Ir(btpy)$_3$ has different effect to excitons on different energy levels. Zeng et al. reported that the external heavy atom effect has a relatively stronger influence on the S$_1$-T$_1$ nonradiative transitions than on the T$_1$-S$_0$ radiative transitions [30]. Therefore, another reason for the increase of emission intensity ratio of 715 nm to that of 654 nm may be the heavy metal effect on singlet-triplet intersystem transfer. The phosphorescent material Ir(btpy)$_3$ might enhance the efficiency of singlet-triplet intersystem crossing of P3HT excitons, resulting in the increase of 715 nm emission intensity.
In order to confirm the energy transfer from Ir(btpy)$_3$ to P3HT, time-resolved transient PL spectra of neat P3HT, Ir(btpy)$_3$, and P3HT:Ir(btpy)$_3$ blend films were measured under the excitation of 460 nm light and are shown in Figure 5. The inset image of Figure 5 is time-resolved transient PL spectrum of Ir(btpy)$_3$ films by monitoring 650 nm emission. The emission lifetime of Ir(btpy)$_3$ is $\sim 4.21$ us, which is thousands of times longer than that of P3HT singlet state emission lifetime [22]. The lifetime of emission peak at 650 nm is increased from $\sim 700$ ps of neat P3HT films to 1.05 ns of P3HT:Ir(btpy)$_3$ films, which should be induced by the energy transfer process from Ir(btpy)$_3$ to P3HT.

A series of PSCs with P3HT:PCBM or different Ir(btpy)$_3$ doping concentrations in P3HT:PCBM as the active layer were fabricated under the same preparation conditions, and the $J$-$V$ characteristics of PSCs were measured under illumination intensity of 100 mW/cm$^2$, as shown in Figure 6. It is apparent that $J_{sc}$ is increased from 0.96 mA/cm$^2$ to 1.74 mA/cm$^2$ along with the increase of Ir(btpy)$_3$ doping concentration, which could be supported by the increased absorption intensity of P3HT:PCBM:Ir(btpy)$_3$ films compared with P3HT:PCBM and energy transfer from Ir(btpy)$_3$ to P3HT. The PL emission of Ir(btpy)$_3$ molecules could be totally quenched by doping lower concentration PCBM (not shown), which means that photo-generated excitons on Ir(btpy)$_3$ could be dissociated into free charge carriers by PCBM, resulting in the product of photovoltaic effect between Ir(btpy)$_3$ and PCBM. It is known that the $V_{oc}$ of PSCs is determined by the energy difference between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor [31]. Therefore, the increase of $V_{oc}$ should be attributed to the larger bandgap of Ir(btpy)$_3$ compared with P3HT according to their PL and absorption spectra. The $V_{oc}$ of PSCs arrives to 0.72 V, and PCE arrives to 0.41% when the Ir(btpy)$_3$ doping concentration increases to 10%. It is known that the annealing treatment on PSCs is based on P3HT:PCBM as the active layer has great effect on the performance of cells [32]. In order to improve the performance of PSCs with P3HT:PCBM:Ir(btpy)$_3$ as the active layer, a series of annealing treatment on the cells were carried out under different annealing temperatures.

The $J$-$V$ curves of PSCs with different annealing temperature were measured, and the relationships between PCE and annealing temperature are summarized in Figure 7. The PCE of PSCs with P3HT:PCBM as the active layer was increased.
along with the increase of annealing temperature; the maximum PCE is about 1.49% when the annealing temperature is 140°C, which accords with our previous reports [33, 34]. The effects of annealing treatment on the performance of PSCs could be summarized as the followings: (i) adjust molecular arrangement for enhancing the absorption intensity and range and charge carrier transporting; (ii) increase the interface between donor and acceptor for improving excitation dissociation. However, the process of high temperature annealing treatment on PSCs may increase the fabrication
cost. It is a great challenge to obtain high performance PSCs without annealing treatment or low temperature annealing treatment.

All the PSCs with ternary blend films as the active layer show the similar relationship between PCE and annealing temperature; the PCE is increased along the increase of annealing temperature and then decreased when the annealing treatment temperature exceed the best value. The PCE of PSCs with 2wt% Ir(btpy)$_3$ doping concentration arrives to the maximum value (0.95%) under 100°C annealing treatment with 10 minutes. The performance decrease trend of PSCs dependence on annealing temperature was more and more apparent along with the increase of Ir(btpy)$_3$ doping concentration. The key parameters of PSCs with ternary blend films as the active layer, including $J_{oc}$, $V_{oc}$, and fill factor, decreased when the annealing treatment temperature goes beyond 100°C. The underlying reason could be attributed to Ir(btpy)$_3$ molecular aggregation through annealing treatment, which destroys the phase separation and charge carrier transporting microstructure in the active layer. The photovoltaic effect of PSCs with 10 wt% doping concentration almost could not be observed after 140°C annealing treatment, which is lower than this kind of PSCs without annealing treatment. After comprehensive analysis on the effect of doping concentration and annealing temperature on the PSCs performance, the higher Ir(btpy)$_3$ doping concentration is beneficial to photon harvesting in the active layer; however, the interpenetrating network of P3HT:PCBM was damaged by doping Ir(btpy)$_3$ and can be totally destroyed through high temperature annealing treatment. Therefore, adjusting the balance between absorption and phase separation induced by doping phosphorescent material may provide an effective method to improve the PSCs performance.

4. Conclusion

A series of PSCs with P3HT:PCBM, doped different concentration Ir(btpy)$_3$ as the active layer were fabricated and measured under the same conditions. The effective energy transfer from Ir(btpy)$_3$ to P3HT was demonstrated by absorption, PL, and time-resolved transient PL spectra. The photon harvesting ability of the active layer could be improved by doping Ir(btpy)$_3$ in P3HT:PCBM, which is beneficial to the increase of $J_{oc}$. The $V_{oc}$ is also increased, which could be attributed to the photovoltaic effect between Ir(btpy)$_3$ and PCBM. For the PSCs with P3HT:PCBM as the active layer, the PCE is increased along with the annealing temperature and arrives to 1.49% when the annealing temperature is 140°C. However, the PCE of PSCs with ternary blend films as the active layer is decreased when the annealing temperature goes beyond 100°C, which may be due to Ir(btpy)$_3$ molecular aggregation under the higher annealing temperature. The PCE of PSCs with 2wt% Ir(btpy)$_3$ doping concentration arrives to 0.95% under 100°C annealing treatment 10 minutes.

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