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## ARTICLE

## Investigation of organic photovoltaics improvement via extension of exciton lifetime

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Phosphorescent material tris(phenylpyrazole)iridium ( $\text{Ir}(\text{ppz})_3$ ) was doped into the bulk heterojunction (BHJ) layer of a 3-hexylthiophene-2,5-diyl and indene-C60 bisadduct blend to form more excitons at the triplet state. Triplet-state excitons have longer lifetimes than those of singlet-state excitons. Surface phase separation was determined via atomic force microscopy and the vertical distribution of various molecules was analyzed via secondary ion mass spectroscopy. Several annealing processes were applied to the BHJ layer doped with  $\text{Ir}(\text{ppz})_3$  to investigate the thermal stability of the film. The exciton lifetime in the BHJ film was characterized using femtosecond time-resolved photoluminescence.

### 1. Introduction

Organic photovoltaics (OPVs) are candidates for next-generation energy-harvesting devices due to their simple fabrication and compatibility with flexible substrates with a potentially large area and the roll-to-roll process.<sup>1</sup> Recently, bulk heterojunction (BHJ) OPVs have demonstrated promising performance. BHJ OPVs consist of a polymer (as an electron donor) mixed with C60 or C70 fullerene derivatives (as an electron acceptor) as the active layer.<sup>2-7</sup> The structure forms a contact on the molecular level that allows excitons to reach the donor-acceptor (D-A) interfaces for dissociation into free charges due to the chemical potential difference.<sup>8</sup> Since limited lifetime allows excitons to diffuse only a short distance (5-14 nm),<sup>9-14</sup> excitons decay to the ground state before they reach the D-A interfaces. Charge carrier transport and collection is strongly determined by the molecular arrangement of the donor and acceptor materials of OPV devices. In order to obtain better power conversion efficiency (PCE), BHJ morphology should have a large D-A interfacial area for efficient charge separation and a more persistent connection between donor materials and acceptor materials for charge penetration.

To enhance charge dissociation and carrier penetration in the BHJ layer, some promising methods, such as thermal annealing,<sup>15-18</sup> solvent annealing,<sup>19-21</sup> and doping solvent additive,<sup>22-24</sup> have been employed, with significant improvement in device performance shown. It is known that excitons dissociated into free charge carriers can significantly contribute to the performance of devices. However, exciton dissociation efficiency is strongly determined by exciton diffusion length ( $L_D$ ) and D-A interfacial energy barriers, with

$L_D$  being mainly determined by exciton lifetime and mobility.<sup>25,26</sup>

One method for increasing exciton lifetime is to convert singlets to triplets. Triplets have much longer lifetimes than those of singlets, partially due to the spin-forbidden character of the optical transition from the excited triplet to the ground state. If the excitons transform into a triplet state, a longer lifetime through intersystem crossing would be derived, benefitting exciton dissociation. A common approach for triplet generation is to introduce heavy metals to develop spin orbit coupling. This approach is used for many phosphorescent materials. Some phosphorescent compounds have attracted a lot of attention due to their potential for singlet-to-triplet exciton transformation, such as tris[2-(benzo[b] thiophen-2-yl)pyridinato-C3,N]iridium (III) ( $\text{Ir}(\text{btpy})_3$ ),<sup>27,28</sup> bis[2-(4-tertbutylphenyl)benzothiazolato-N,C2]iridium (acetylacetonate) ( $((\text{t-bt})_2\text{Ir}(\text{acac}))$ ),<sup>29</sup> 2,3,7,8,12,13,17,18-octaethyl-21H,23H-porphyrin platinum (II) (PtOEP),<sup>30</sup> and tris[2-phenylpyridinato]Ir(III) ( $\text{Ir}(\text{ppy})_3$ ).<sup>31</sup> An important feature is that the phosphorescent molecules have more efficient Dexter-type charge transfer with a much slower quenching rate. This allows the highly energetic triplet excitons to travel long distances before being quenched.<sup>25</sup>

In this work, the compound  $\text{Ir}(\text{ppz})_3$  was introduced into a binary blend comprising poly(3-hexylthiophene-2,5-diyl) (P3HT) and indene-C60 bisadduct (ICBA) with various dopant concentrations. The device performance significantly improved in terms of short-circuit current density ( $J_{SC}$ ) with doping until the concentration exceeded 0.2 wt%. The electrical characteristics of the P3HT:ICBA films with various dopant concentrations are compared.

## 2. Results and discussion

**Figure 1 (a) shows the schematics of device structure and energy band diagram.** The current density-voltage ( $J$ - $V$ ) characteristics of OPV devices with  $\text{Ir}(\text{ppz})_3$  dopant concentrations of 0.05, 0.1, 0.15, 0.2, and 0.3 wt% in P3HT:ICBA layers are shown in Figure 1 (b) and their optoelectronic properties are listed in Table 1. As shown, the open-circuit voltage ( $V_{oc}$ ) was maintained at 0.85~0.86 V for the various concentrations of  $\text{Ir}(\text{ppz})_3$ . However, there was an obvious increase in  $J_{sc}$  when  $\text{Ir}(\text{ppz})_3$  with a concentration of less than 0.3 wt% was employed. The fill factor ( $FF$ ) decreased with increasing dopant content. The best PCE (7.08%) was obtained for P3HT:ICBA film with 0.1 wt%  $\text{Ir}(\text{ppz})_3$ . The decrease in  $FF$  with increasing dopant concentration indicates that the doping process leads to an unfavorable morphology of the BHJ, resulting in higher series resistance ( $R_s$ ) or lower shunt resistance ( $R_{sh}$ ). The increase in  $J_{sc}$  might have resulted from the enhancement of the light absorption process, which leads to more excitons or provides better exciton dissociation, giving rise to more free carriers.

To examine the mechanism of enhancement by the doping process, more physical measurements were taken. Figure 2 shows the ultraviolet-visible absorption spectra of the P3HT:ICBA films with and without 0.1 wt%  $\text{Ir}(\text{ppz})_3$ . A slight increase in the absorption spectra can be observed for the film doped with 0.1 wt%  $\text{Ir}(\text{ppz})_3$  at wavelengths lower than 450 nm. There is nearly no difference between the films with and without  $\text{Ir}(\text{ppz})_3$  at wavelengths higher than 450 nm, which indicates that the significant increase in  $J_{sc}$  from doping  $\text{Ir}(\text{ppz})_3$  into the P3HT:ICBA layer is not dominated by the absorption of the film under illumination.  $J_{sc}$  can also be determined from the exciton extraction process in the BHJ, which is highly related to the morphology of the film. Figure 3 shows the atomic force microscopy (AFM) phase images of P3HT:ICBA films with and without 0.1 wt%  $\text{Ir}(\text{ppz})_3$ . Interestingly, the phase separation at the surfaces of both films is similar, which means that the doping process did not change the surface morphology of the film. The reason of this result should be that both surfaces are the blend phases between P3HT and ICBA molecules. This result implies that the materials did not homogeneously disperse in the film, and thus there is almost no  $\text{Ir}(\text{ppz})_3$  on the surface of the film.

To further investigate the morphology of  $\text{Ir}(\text{ppz})_3$  in BHJ films, thermal annealing at various temperatures was applied to the films. After application of annealing at various temperatures to the BHJ films, the morphologies of P3HT and ICBA molecules will change, possibly influencing the arrangement of  $\text{Ir}(\text{ppz})_3$  in the BHJ layer. Figures 4 (a) and (b) depict the  $J$ - $V$  curves of the devices with pure P3HT:ICBA layers and ones doped with 0.1 wt%  $\text{Ir}(\text{ppz})_3$ , respectively, annealed at room temperature (RT), 130, 150, and 170 °C for 10 min. The corresponding optoelectronic characteristics are listed in Table 2. As Figure 4 (a) shows, the annealing process enhanced

device performance, especially in terms of  $FF$ , which shows that a more favorable morphology of the P3HT:ICBA layer was obtained through thermal annealing at temperatures of 130, 150, and 170 °C. Li *et al.*<sup>4</sup> reported that the best device performance (a PCE of 6.15%) was obtained after annealing the BHJ film at 150 °C. For the devices doped with  $\text{Ir}(\text{ppz})_3$ , the thermal annealing process for BHJ films at 130 and 150 °C improved the optoelectronic characteristics mostly in terms of  $FF$ . When the annealing temperature was increased to 170 °C, the  $FF$  dropped to 57.3%, leading to a significant decrease of PCE to 5.63%. Interestingly, thermal annealing at 170 °C improved the P3HT:ICBA film but degraded the film doped with  $\text{Ir}(\text{ppz})_3$ . **However, the glass transition temperature of  $\text{Ir}(\text{ppz})_3$  is over 275 °C which is much higher than the annealing temperature which degraded the film.** Therefore, the results indicate that heat affects the morphology of  $\text{Ir}(\text{ppz})_3$  in BHJ film, giving rise to poorer exciton dissociation or carrier penetration at the BHJ layer. The surface morphology of a BHJ film can be estimated through AFM. However, hardly any  $\text{Ir}(\text{ppz})_3$  appeared at the surface of the BHJ film, as shown above.

Although the morphology of  $\text{Ir}(\text{ppz})_3$  is difficult to define from the surface of the film, the vertical distribution of  $\text{Ir}(\text{ppz})_3$  in the BHJ layer can be characterized by secondary ion mass spectroscopy (SIMS) since  $\text{Ir}(\text{ppz})_3$  molecules contain nitrogen (N) atoms which do not exist in P3HT or ICBA. **Figures 5 (a) shows the molecular models of P3HT, ICBA,  $\text{Ir}(\text{ppz})_3$ , and PEDOT:PSS,** and Figure 5 (b), (c), and (d) depict the depth profiles of carbon (C), sulfur (S), and nitrogen (N) elements, respectively, in P3HT:ICBA films doped with 0.1 wt%  $\text{Ir}(\text{ppz})_3$  and annealed at RT, 150, and 170 °C for 10 min. In the BHJ layer, the signal of carbon represents the combination of the three materials since organic materials always contain carbon. The signal of sulfur comes from P3HT and PEDOT:PSS, whose signal can be an index of the end of BHJ film, as shown by the steep rising curve in Figures 5 (a), (b), and (c). In Figure 5 (a), the amount of carbon is similar to that of sulfur with a peak at the surface and a constant level until the end of the film. The amount of nitrogen, which is related to  $\text{Ir}(\text{ppz})_3$ , is sparse at the surface and increases gradually with a small peak at the end of the film. The results show that more  $\text{Ir}(\text{ppz})_3$  molecules are located further from the surface, indicating that  $\text{Ir}(\text{ppz})_3$  molecules tend to accumulate at the bottom of the BHJ layer without the annealing process. After annealing of the BHJ film at 150 °C, the vertical distribution of carbons and sulfurs are quite similar to those of the BHJ film without annealing; however, the peak of nitrogen is slightly smoother than that without annealing, but there is still little nitrogen on the surface. As a result, the morphology of  $\text{Ir}(\text{ppz})_3$  at the surface of the BHJ film is difficult to define through AFM since most  $\text{Ir}(\text{ppz})_3$  molecules are located under the surface of the film, as shown in Figure 3. Interestingly, when the annealing temperature was increased to 170 °C, the original smooth peak of nitrogen at the end of the film disappeared with the maximum amount at the front of the SIMS analysis, as depicted in Figure 5 (c). The results indicate that the annealing process at 170 °C led to the

Ir(ppz)<sub>3</sub> molecules strongly diffusing from the bottom to the top of the film. The diffusion of Ir(ppz)<sub>3</sub> changes the vertical morphology, which leads to different carrier penetration in the BHJ layer. Therefore, the performance degradation of the device with P3HT:ICBA film doped with Ir(ppz)<sub>3</sub> after annealing at 170 °C may be attributed to the diffusion of Ir(ppz)<sub>3</sub>.

The  $J$ - $V$  results show that device performance was significantly enhanced by doping 0.1 wt% Ir(ppz)<sub>3</sub> into the P3HT:ICBA layer. SIMS analysis of the P3HT:ICBA:Ir(ppz)<sub>3</sub> films demonstrates that annealing at 170 °C for 10 min led to Ir(ppz)<sub>3</sub> molecules diffusing from the bottom to the top. Hence, the carrier transport in these BHJ films is important to compare. In order to characterize carrier penetration in the BHJ layer, the carrier mobility was determined using the space-charge-limited current (SCLC) method. Figure 6 depicts the dark  $J$ - $V$  curves of the hole-only devices with the structure ITO/PEDOT:PSS/active layer/Au, where the active layers are P3HT:ICBA film annealed at 150 °C and P3HT:ICBA films doped with 0.1 wt% Ir(ppz)<sub>3</sub> and annealed at 150 or 170 °C. According to the  $J$ - $V$  characteristics of the hole-only devices, the steady-state current density  $J_{SCLC}$  is theoretically a function of applied voltage  $V$ , film thickness  $d$ , relative dielectric constant  $\epsilon_r$ , vacuum permeability  $\epsilon_0$ , and steady-state charge-carrier mobility  $\mu_{SCLC}$ :

$$J_{SCLC} = \frac{9}{8} \mu_{SCLC} \epsilon_r \epsilon_0 \frac{V^2}{d^3} \quad (1)$$

The relative dielectric constant was assumed to be 3. **The calculated mobilities are shown in the inset of Figure 6.** Comparing the hole mobilities of the devices with P3HT:ICBA films doped with 0.1 wt% Ir(ppz)<sub>3</sub> annealed at 150 and 170 °C, a considerable drop was observed for the higher annealing temperature. This result implies that the diffusion of Ir(ppz)<sub>3</sub> from the bottom to the top of the film induced more dislocations in the film and blocked the hole transport at the BHJ layer. With worse hole transport in the BHJ layer, fewer holes were extracted to the anode, resulting in lower  $J_{SC}$  and higher  $R_s$ , as shown by the  $J$ - $V$  characteristics in Figure 1. However, the hole mobility of the device with P3HT:ICBA films annealed at 150 °C is similar to that of the device with P3HT:ICBA films doped with 0.1 wt% Ir(ppz)<sub>3</sub> and annealed at 150 °C. This indicates that the Ir(ppz)<sub>3</sub> molecules mostly accumulate near the hole buffer layer, PEDOT:PSS, and neither enhances hole transport nor blocks the hole penetration in the BHJ layer. Since the P3HT:ICBA-based device with and without 0.1 wt% Ir(ppz)<sub>3</sub> have similar carrier mobilities, there must be another mechanism that increased  $J_{SC}$  and thus significantly improved PCE.

As mentioned above, longer lifetime through intersystem crossing is achieved when excitons transform into the triplet state. Since Ir(ppz)<sub>3</sub> is a phosphorescent material, a much slower quenching rate should be achieved when charges transfer to Ir(ppz)<sub>3</sub> molecules in the BHJ layer. In order to confirm energy transfer in the BHJ layer, femtosecond time-resolved photoluminescence (FTRPL) spectra of P3HT:ICBA and P3HT:ICBA with 0.1 wt% Ir(ppz)<sub>3</sub> blend films were

measured. A PL peak appears at 700 nm, which corresponds to the intra-chain radiative recombination of excitons in P3HT molecules<sup>27</sup> under excitation with 420-nm pulsed light, as shown in Figure 7. To obtain the relaxation times, the data were fitted with exponential decay functions with two time constants:<sup>32</sup>

$$I_{PL}(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} \quad (2)$$

where  $I_{PL}$  is the intensity of photoluminescence,  $A_1$  and  $A_2$  are the amplitudes, and  $\tau_1$  and  $\tau_2$  are the time constants. The fitting lines of the FTRPL data are depicted in Figure 7 as solid lines, and the fitting data are listed in Table 3. The short time constant ( $\tau_1$ ) is assigned to the exciton dissociation process, and the long time constant ( $\tau_2$ ) is assigned to exciton diffusion.<sup>33</sup> The fitting results indicate that the exciton diffusion time of P3HT chains was extended by doping Ir(ppz)<sub>3</sub> into the BHJ layer, which was induced by the energy transfer process from Ir(ppz)<sub>3</sub> to P3HT. By extracting the exciton lifetime, the exciton diffusion length ( $L_D$ ) can be estimated as:<sup>32</sup>

$$L_D = \sqrt{D * \tau_2} \quad (3)$$

where  $D$  is the diffusion constant of P3HT, which equals  $2.7 \times 10^{-8} \text{ m}^2/\text{s}$ .<sup>34</sup> The estimated diffusion lengths are listed in Table 3. The results demonstrate that a longer exciton diffusion length was obtained by doping 0.1 wt% Ir(ppz)<sub>3</sub> into the P3HT:ICBA BHJ layer, which led to more P3HT excitons diffusing to the anode. Therefore, more carriers were collected through the dissociation of excitons at the interface, resulting in the significant enhancement of  $J_{SC}$ .

### 3. Conclusions

This study enhanced the OPV device performance by doping Ir(ppz)<sub>3</sub> into the P3HT:ICBA BHJ layer. The morphology of Ir(ppz)<sub>3</sub> was difficult to characterize through AFM phase images since Ir(ppz)<sub>3</sub> tended to aggregate at the bottom of the BHJ film, as determined from SIMS depth profiles. Annealing at 170 °C for 10 min led to Ir(ppz)<sub>3</sub> diffusing from the bottom to the top of the film, which created more dislocations and thus block the hole transport in the BHJ layer. Moreover, the FTRPL results show that doping Ir(ppz)<sub>3</sub> greatly increased the exciton diffusion time of P3HT, which led to more holes extracted at the anode.

### 4. Experimental

Indium tin oxide (ITO)-coated glass with a sheet resistance of 5 ohm/sq was utilized as the substrate of the OPV device. The substrates were sequentially cleaned in an ultrasonic bath with deionized water, acetone, and isopropanol, and then baked at 100 °C for at least 1 h in an oven. The clean substrates were treated by ultraviolet ozone for 15 min. Then, poly(3,4-ethylenedioxythiophen):poly(styrenesulfonate) (PEDOT:PSS), from H. C. Starck (CLEVIOS P VP A14083), was spin-coated onto the ITO substrate at 4000 rpm (~35 nm) and then baked at

120 °C for 15 min on a hot plate. P3HT:ICBA, at a weight ratio of 1:1 and dissolved in 1,2-dichlorobenzene (DCB) solution with a concentration of 2 wt%, was spin-coated onto PEDOT:PSS at 800 rpm for 30 s (~200 nm) as the active layer. Ir(ppz)<sub>3</sub> was doped into P3HT:ICBA solution with a concentration of 0.05~0.3 wt%. After the deposition of the active layer, Ca and Al were deposited at thicknesses of 25 and 100 nm, respectively, under a  $6 \times 10^{-6}$  Torr vacuum in a thermal evaporator. **Ten devices were fabricated for each condition**, and the device area was defined by a shadow mask to be 0.1 cm<sup>2</sup>. The device was characterized under simulated AM1.5G irradiation (100 mW/cm<sup>2</sup>) using a xenon-lamp-based solar simulator.

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### Notes and references

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Table 1

Device parameters of OPV devices with P3HT:ICBA layer doped with various concentrations of Ir(ppz)<sub>3</sub>.

	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$ (%)	$PCE$ (%)	$R_{sh}$ ( $\Omega$ cm <sup>2</sup> )	$R_s$ ( $\Omega$ cm <sup>2</sup> )
<b>Pure P3HT:ICBA</b>	0.859	10.44	68.5	6.15	2115	8.86
<b>With 0.05 wt% Ir(ppz)<sub>3</sub></b>	0.849	11.98	67.3	6.85	1104	8.08
<b>With 0.1 wt% Ir(ppz)<sub>3</sub></b>	0.855	12.40	66.7	7.08	1316	8.39
<b>With 0.15 wt% Ir(ppz)<sub>3</sub></b>	0.854	11.84	65.9	6.67	1031	9.59
<b>With 0.2 wt% Ir(ppz)<sub>3</sub></b>	0.850	11.33	63.1	6.08	1003	11.03
<b>With 0.3 wt% Ir(ppz)<sub>3</sub></b>	0.860	7.73	55.9	3.72	621	19.55

Table 2

Device parameters of OPV devices with pure P3HT:ICBA layers and ones doped with 0.1 wt% Ir(ppz)<sub>3</sub> and annealed at various temperatures.

		$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	$FF$ (%)	$PCE$ (%)	$R_{sh}$ ( $\Omega$ cm <sup>2</sup> )	$R_s$ ( $\Omega$ cm <sup>2</sup> )
<b>Pure P3HT:ICBA</b>	RT	0.827	10.09	64.8	5.41	<b>1181</b>	<b>10.55</b>
	130°C	0.846	10.09	69.2	5.91	<b>1413</b>	<b>7.32</b>
	150°C	0.859	10.44	68.5	6.15	<b>2115</b>	<b>8.86</b>
	170°C	0.850	10.08	68.1	5.84	<b>1445</b>	<b>8.04</b>
<b>P3HT:ICBA doped with 0.1 wt% Ir(ppz)<sub>3</sub></b>	RT	0.821	11.76	62.8	6.08	<b>1093</b>	<b>9.28</b>
	130°C	0.845	11.72	67.7	6.71	<b>1368</b>	<b>7.53</b>
	150°C	0.855	12.40	66.7	7.08	<b>1316</b>	<b>8.39</b>
	170°C	0.859	11.42	57.3	5.63	<b>909</b>	<b>18.58</b>

Table 3

Fitted values of FTRPL results to equation (3) and calculated  $L_D$ .

	<i>A1</i>	$\tau_1$ (fs)	<i>A2</i>	$\tau_2$ (ps)	$L_D$ (nm)
<b><i>Without doping</i></b>	0.952	0.768	0.3	67.289	1.35
<b><i>With 0.1 wt% Ir(ppz)<sub>3</sub></i></b>	0.841	0.804	0.367	86.765	1.53