



# Improved efficiency of bulk heterojunction polymer solar cells by doping with iridium complex



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## ABSTRACT

To study the effect of iridium complexes on performance of polymer solar cells, we report the ternary bulk heterojunction (BHJ) polymer solar cells (PSCs) by doping an iridium complex material of bis (1-phenylisoquinoline) acetylacetonate iridium(III) [Ir(piq)<sub>2</sub>acac] into the conventional active layer of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM). The results show that the power conversion efficiency (PCE) of P3HT:PC<sub>71</sub>BM based ternary devices is improved from 2.99% to 4.44% by doping 1 wt% Ir(piq)<sub>2</sub>acac, which is benefited from the enhanced exciton harvesting by Förster resonance energy transfer (FRET) from Ir(piq)<sub>2</sub>acac to P3HT and optimized self-organized morphology within ternary blends.

## 1. Introduction

Bulk heterojunction (BHJ) polymer solar cells (PSCs) have shown great prospect to the development of low cost, flexible, lightweight, and simple processability [1,2]. The power conversion efficiency (PCE) of the state-of-the-art BHJ PSCs has reached 11.7% [3]. The major bottlenecks which limit the efficiency of BHJ PSCs are the narrowed light absorption and restricted charge generation or collection of devices. The blending of multiple photoactive materials to form ternary solar cells is considered as a simple strategy to resolve these bottlenecks [4].

In ternary PSCs, the Förster resonance energy transfer (FRET) mechanism has been demonstrated could enhance the performance of PSCs efficiently [5]. For FRET, the third ingredient that either generates excitons or enhances long-range exciton migration is implemented to increase the efficiency of photon harvesting [6]. Due to the long exciton diffusion length, iridium complexes have been implemented in ternary PSCs as dopants to increase the triplet population or make energy transfer in PSCs, thereby improve the photoconversion efficiency [7,8]. It is noteworthy to use appropriate iridium complexes to fabricate high performance devices and study details of the active layer of ternary PSCs.

In this report, we investigate the effect of the performance of ternary blends of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C<sub>71</sub>-butyric acid methyl ester (PC<sub>71</sub>BM) mixed with the phosphorescent material doping bis (1-phenylisoquinoline) acetylacetonate iridium(III) [Ir(piq)<sub>2</sub>acac]. The effect of solvent annealing treatment (SAT) on the

performance of PSCs is studied. As a result, by doping Ir(piq)<sub>2</sub>acac into P3HT:PC<sub>71</sub>BM system solar cells, highest PCE of 4.44% is obtained, by 49% enhancement from 2.99%.

## 2. Experimental

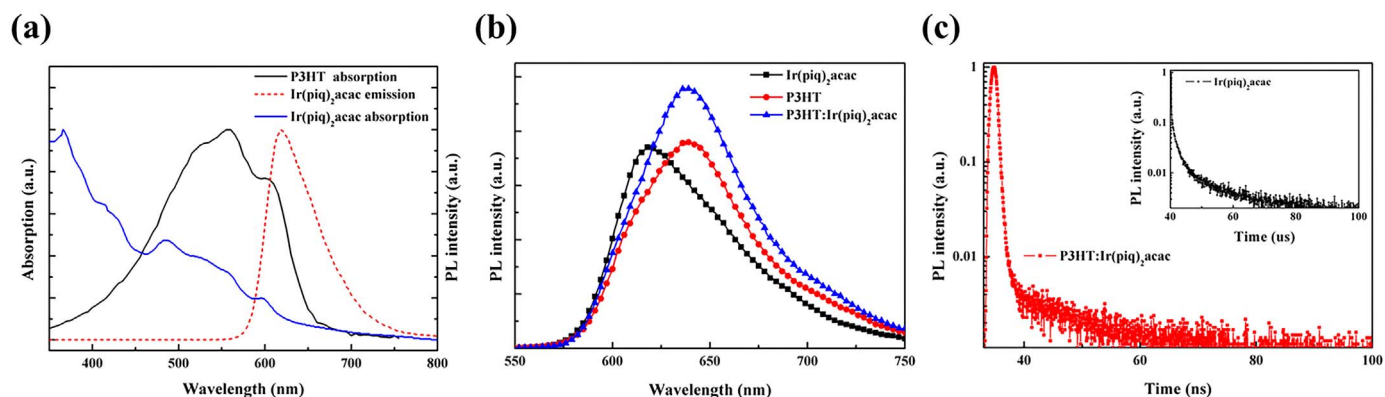
Ternary PSCs were fabricated with the structure (ITO)/ZnO/P3HT:Ir(piq)<sub>2</sub>acac:PC<sub>71</sub>BM/MoO<sub>x</sub>/Ag. The ZnO precursor was prepared by dissolving zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, 0.3 g) and ethanolamine (NH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH, 84 mg) in 2-methoxyethanol (CH<sub>3</sub>OCH<sub>2</sub>CH<sub>2</sub>OH, 3 ml). ZnO precursor solution was spin-coated on the clean ITO-glass substrate at 4500 rpm for 35 s, and annealed at 200 °C for 1 h. Then the samples were sent to a nitrogen-filled glove box. A solution containing a mixture of P3HT:PC<sub>71</sub>BM:Ir(piq)<sub>2</sub>acac (1:1:x, x is the weight ratio of Ir(piq)<sub>2</sub>acac to PC<sub>71</sub>BM) in 1, 2-dichlorobenzene (DCB) with a concentration of 30 mg ml<sup>-1</sup> was spin-coated on the ZnO thin layer at 1200 rpm for 50 s. The samples which required SAT were dried in a covered Petri dish for 20 min. Then all samples were annealed at 140 °C for 5 min. MoO<sub>x</sub> layer was deposited under a pressure of 2×10<sup>-3</sup> Pa in vacuum chamber, followed by the deposition of Ag anode under constant pressure. The effective area of PSCs is 0.02 cm<sup>2</sup> [9].

## 3. Results and discussion

Fig. 1(a) shows the normalized UV–vis absorption spectra of P3HT and Ir(piq)<sub>2</sub>acac, along with the emission spectrum of Ir(piq)<sub>2</sub>acac. The

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**Fig. 1.** (a) Absorption and emission spectra of Ir(piq)<sub>2</sub>acac and absorption spectra of P3HT. (b) PL spectra of P3HT, Ir(piq)<sub>2</sub>acac, and P3HT:Ir(piq)<sub>2</sub>acac excited at 460 nm light. (c) TRTPL of Ir(piq)<sub>2</sub>acac with and without (Inset) P3HT excited at 460 nm and probed at 650 nm light.

emission spectrum of Ir(piq)<sub>2</sub>acac overlaps with the absorption spectrum of P3HT, implies that it may contribute to a good FRET pairs between Ir(piq)<sub>2</sub>acac and P3HT [10].

To confirm the energy transfer from Ir(piq)<sub>2</sub>acac to P3HT, the photoluminescence (PL) spectra of P3HT, Ir(piq)<sub>2</sub>acac and P3HT:Ir(piq)<sub>2</sub>acac excited at 460 nm light are shown in Fig. 1(b). The PL intensity of P3HT with 1 wt% Ir(piq)<sub>2</sub>acac is increased and exhibited no emission from Ir(piq)<sub>2</sub>acac. This enhancement is attribute to the FRET from Ir(piq)<sub>2</sub>acac to P3HT [11]. The FRET efficiency could be evaluated by applying the time-resolved transient photoluminescence (TRTPL) (Fig. 1(c)). The samples are excited at 460 nm and probed at 650 nm light. This efficiency  $E$  can be calculated using the formula [5]

$$E = (1 - \tau_{D-A}/\tau_D) \times 100 \quad (1)$$

where  $\tau_{D-A}$  and  $\tau_D$  are the excited state lifetimes of Ir(piq)<sub>2</sub>acac with and without P3HT. The lifetime of pristine Ir(piq)<sub>2</sub>acac is 3.3  $\mu$ s, this value dramatically decreased to 0.2 ns with 1 wt% Ir(piq)<sub>2</sub>acac, which corresponds to a 99.9% energy transfer efficiency due to the efficient triplet-to-singlet energy transfer from Ir(piq)<sub>2</sub>acac to P3HT [8].

To investigate the device performance, we fabricate ternary PSCs based on various concentrations of Ir(piq)<sub>2</sub>acac from 0 to 5 wt%. The current density-voltage ( $J$ - $V$ ) curves of ternary PSCs and the corresponding parameters are shown in Fig. 2(a) and Table 1. The control devices have a PCE of 2.99%, with a  $J_{SC}$  of 10.2  $\text{mA cm}^{-2}$  and a FF of 47.3%. The PCE of the PSCs increases to 3.81% with 1 wt% Ir(piq)<sub>2</sub>acac, results in the highest  $J_{SC}$  of 11.1  $\text{mA cm}^{-2}$  and FF of 55.4%, the  $V_{OC}$  remains unchanged. This enhancement of the performance could be attributed to the triplet-singlet energy transfer from Ir(piq)<sub>2</sub>acac to P3HT, and may due to the film morphology control simultaneously. However, this increase is not monotonic, indicates the

**Table 1**

Photovoltaic parameters of ternary PSCs with different Ir(piq)<sub>2</sub>acac doping concentrations with and without SAT<sup>a</sup>.

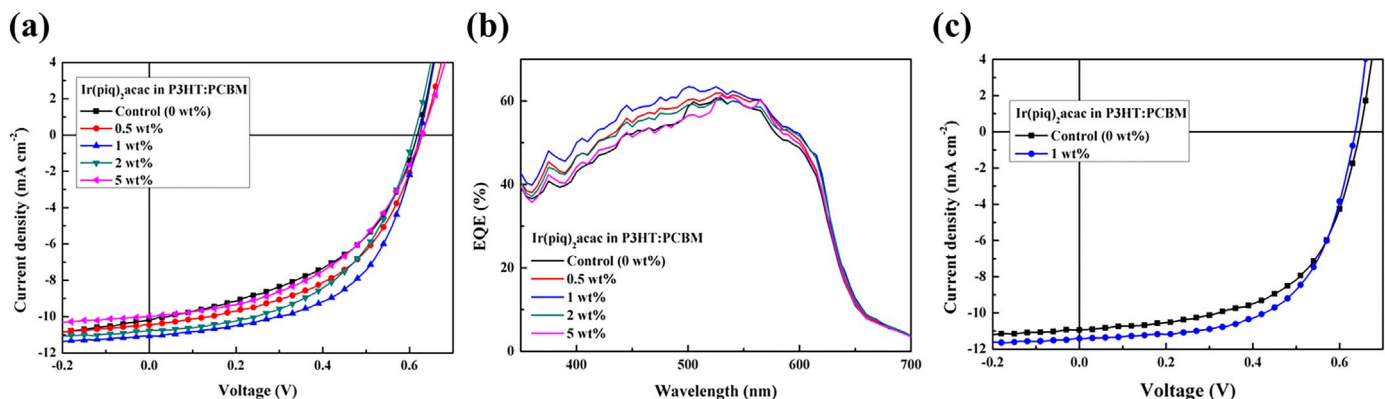
Ir(piq) <sub>2</sub> acac ratio (wt%)	$V_{OC}$ (V)	$J_{SC}$ ( $\text{mA cm}^{-2}$ )	FF (%)	PCE (%)
0 (control)	0.62	10.2	47.3	2.99
0.5	0.63	10.5	50.8	3.36
1	0.62	11.1	55.4	3.81
2	0.61	10.8	51.8	3.41
5	0.63	9.98	48.1	3.02
0 (control)+SAT	0.65	10.9	57.7	4.09
1+SAT	0.64	11.4	60.8	4.44

<sup>a</sup> All parameters are average value collected from 15 devices.

adverse effects of Ir(piq)<sub>2</sub>acac on the active layer at higher doping concentrations, which should be attributed to the disrupted interpenetrated network between P3HT and PC<sub>71</sub>BM under the high Ir(piq)<sub>2</sub>acac doping concentration conditions [12].

The external quantum efficiency (EQE) spectra are shown in Fig. 2(b). The EQE spectrum of ternary PSCs with 1 wt% Ir(piq)<sub>2</sub>acac is increased in the region from 350 nm to 620 nm, consist with the UV-vis absorption spectra (Fig. S2), reveals that the EQE enhancement of ternary PSCs should be attributed to the efficient photon harvesting [13] and the enhanced exciton migration from Ir(piq)<sub>2</sub>acac to P3HT by FRET.

It is known that the self-organized structure on PSCs based on P3HT:PC<sub>71</sub>BM system has a great effect on the performance [14,15]. In order to investigate the effect of Ir(piq)<sub>2</sub>acac on the self-organization of PSCs, the P3HT:PC<sub>71</sub>BM cells with several concentrations of Ir(piq)<sub>2</sub>acac are fabricated under the condition of SAT to control the active layer growth rate. The  $J$ - $V$  curves of PSCs with SAT and the



**Fig. 2.**  $J$ - $V$  curves (a) and EQE spectra (b) of PSCs with different concentrations of Ir(piq)<sub>2</sub>acac in P3HT:PC<sub>71</sub>BM.  $J$ - $V$  curves (c) of 0 wt% and 1 wt% Ir(piq)<sub>2</sub>acac doping concentrations in P3HT:PC<sub>71</sub>BM with SAT.

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