# ARTICLE OPEN Enhanced power conversion efficiency in iridium complexbased terpolymers for polymer solar cells

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By introducing various low concentrations of Iridium complexes to the famous donor polymer of PTB7-Th backbone, new heavy metal containing terpolymers have been demonstrated. When blended with  $PC_{71}BM$ , an obvious increase of power conversion efficiency (PCE) is obtained in 1 mol% Ir containing polymer for different photovoltaic devices either using Ca or PDIN as cathode interface layers. The impact of molecular weight on the photovoltaic performance has been particularly considered by using three batches of control polymer PTB7-Th to ensure a fair and more convincing comparison. At similar molecular weight conditions ( $M_n$ : ~60 kg mol<sup>-1</sup>,  $M_w$ : 100–110 kg mol<sup>-1</sup>), the 1 mol% Ir containing PTB7-ThIr1/PC<sub>71</sub>BM blends exhibits enhanced PCE to 9.19% compared with 7.92% of the control PTB7-Th. Through a combination of physical measurement, such as optoelectrical characterization, GIWAXS and pico-second time-resolved photoluminescence, the enhancement are contributed from comprehensive factors of higher hole mobility, less bimolecular recombination and more efficient slow process of charge separation.

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# INTRODUCTION

Bulk-heterojunction (BHJ) organic solar cells (OSCs) involving the mix of electron donor and acceptor materials in the active layer of photovoltaic devices have attracted tremendous attention in the last few years.<sup>1,2</sup> Very recently, BHJ OSCs with high power conversion efficiencies (PCE) exceeding 9% have been broadly demonstrated.<sup>3–9</sup> To improve the PCEs of OSCs, numerous strategies have been employed through materials innovation and device engineering. (i) The first and most important is to design and synthesize new suitable donor-acceptor (D-A) type conjugated oligomers or alternating copolymers with high optical absorption, low bandgap, relatively lower highest occupied molecular orbital (HOMO) energy levels and high hole mobility in order to function as good electron donors in BHJ OSCs. Among many different materials categories, fluorinated-thieno[3,4-b] thiophene-based PTB7 and PTB7-Th and derivatives have proven to be excellent candidates.<sup>3,10–13</sup> (ii) To overcome the shortcomings of fullerenes, such as weak absorption in the solar spectrum range, limited structural and energy level variability as well as device instability of the most widely used fullerene acceptors, the exploration of high performance new non-fullerene electron acceptors which comprise electron-deficient building blocks with low-lying HOMO and lowest unoccupied molecular orbital energy levels, strong absorption and high electron mobilities finds increasing attention in the field of OSCs.<sup>14–19</sup> (iii) The involvement of suitable anode or cathode interface materials to reduce the interfacial energy barriers and facilitate an efficient hole or electron extraction from the active layer have also been demonstrated as effective approaches to enhance the PCE.<sup>20,21</sup> From the device engineering side, (iv) the introduction of ternary structures in the active layer with two-donors/one-acceptor or two-acceptors/one-donor to enhance the absorption and increase the short-circuit current  $(J_{sc})$ ,<sup>8,22–26</sup> (v) the use of tandem structures including two or more subcells connected in series with complementary absorption bands to reduce the thermalization losses and increase the open-circuit voltages ( $V_{oc}$ ) <sup>27–29</sup> and (vi) the optimization of the film morphology of the active layer adopting solvent vapor annealing, thermal annealing, mixed solvent and/or solvent additives have also been proved to be successful methods to achieve high performance OSCs.<sup>30–32</sup>

Besides, from the perspective of materials, the involvement of a suitable third component either through low ratio physical doping into the mixture of active layer, or as a third monomer by chemical bonding to the new random terpolymers and then used as new polymer donors<sup>33,34</sup> or non-fullerene polymer acceptors<sup>35–37</sup> have also been employed as facile and reliable approaches to enhance the PCE. For example, doping 10 wt% of an orange-emitting Ir complex [(2-pq)<sub>2</sub>Irpic-OH] to PTB7/PC71BM solar cell devices, resulted in the increase of PCE from 7.37 to 8.72%.<sup>38</sup> Through minimizing the loss channel via triplet excitons, the addition of spin<sup>1</sup>/<sub>2</sub> radical Galvinoxyl to the P3HT/PC<sub>61</sub>BM and PTB7/PC<sub>61</sub>BM blends enhanced photovoltaic cell PCEs by 18 and 30%, respectively.<sup>39,40</sup> In a different case it was presented that by conjugating 25 mol% of 5,6-difluoro-4,7-dithieno[2,1,3]thiadiazole as a third monomer into poly{(4,8-di(2,3-dioctylthiophen-5-yl)benzo[1,2-b:4,5-b']-dithiophen-2,6-diyl)-alt-(5,6-difluorobenzo[2,1,3]

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x=0, PTB7-Th; x=0.005, PTB7-Thir0.5; x=0.01, PTB7-Thir1; x=0.015, PTB7-Thir1.5

Fig. 1 Synthetic routes of PTB7-Th series polymers with various feed ratio of (dfppy)<sub>2</sub>lr(dbm) (0 for control polymer PTB7-Th, 0.5, 1 and 1.5 mol% for terpolymers PTB7-Thlrx, respectively)

thiadiazole-4,7-diyl)} (**Th00**), the PCE of the polymer/PC<sub>71</sub>BM based BHJ device could be increased from 4.9% of **Th00** to 8.0% for the terpolymer **Th25**.<sup>34</sup> Furthermore, a 35 times higher of PCE was obtained in polymer/fullerene device by coordinating 50 mol% of Ir complex to conjugated backbone of poly(fluorene-co-phenylpyridine) due to the formation of the triplet state in Ir containing polymers.<sup>41</sup>

Previously, we reported the conjugation of a triplet Ir complex (feed ratio: 1 mol%) to the famous high efficiency donor polymer PTB7. The PCE was found to be significantly increased compared to the Ir-free control polymer.<sup>42</sup> We now extended the approach within this work and chemically embedded various low concentrations of Iridium complexes (such as ~0.5, 1 and 1.5 mol%) to the polymer backbone of PTB7-Th, which is another famous champion donor polymer. When blended with PC71BM to form the active layer, an increased PCE was obtained with the Ir containing polymers for different photovoltaic devices either using Ca or amino-substituted perylene diimide (PDIN) as cathode interface layers.<sup>14</sup> Different to the previous work, herein, the reason for the increase of PCE was particularly demonstrated. At similar molecular weight (MW) conditions ( $M_{\rm n}$ : ~60 kg mol<sup>-1</sup>,  $M_{\rm w}$ : 100–110 kg mol<sup>-1</sup>), by using the extremely low ratio of Ir complex as the third monomer (~1 mol%) for copolymerization, the Ir containing PTB7-Thlr1/PC71BM blends exhibited significantly enhanced PCE to 9.19% compared with 7.92% of the control PTB7-Th in polymer/fullerene BHJ polymer solar cells (PSCs), which was contributed from a combination factors of the higher hole mobility, less bimolecular recombination and more efficient slow process of charge separation. It should be mentioned that the impact of MW on the photovoltaic performance has been particularly considered by using three batches of control polymer PTB7-Th (one with high MW and the other two batches with medium MW) to ensure a fair comparison. The PCE of 9.19% for Ir containing PTB7-Thlr1 ( $M_n/M_w$ : 56/112 kg mol<sup>-1</sup>) with significantly lower MW was even higher than that of 8.37% for control PTB7-Th<sub>H</sub> ( $M_n/M_w$ : 90/160 kg mol<sup>-1</sup>), which further shows the enhancement of PCE on the introduction of extremely low ratio of heavy metal Ir complexes to the donor copolymers.

# RESULTS

As shown in Fig. 1, all the polymers were synthesized via Stille coupling polycondensation. The Ir complex,  $(dfppy)_2|r(dbm)$  was conjugated through the dibenzoylmethane (dbm) anciliary ligand instead of the polyhedral cyclometalated main-ligand in order to preserve the linear structures of PTB7-Th-conjugated polymer backbone. In this work, the as synthesized Ir-containing polymers PTB7-ThIrx (x = 0.5, 1 and 1.5) were named according to the feed ratio (0.5, 1 and 1.5 mol%) of Ir complex for polymerization. At the same polymerization conditions, all polymers exhibited similar MW. The number average molecular weight ( $M_n$ ) was measured

ranging from 56 to 71 kg mol<sup>-1</sup> and the weight average molecular weight ( $M_w$ ) in the range of 97 to 118 kg mol<sup>-1</sup> (Supplementary Fig. S1, Supplementary Table S1 and Table 1). All polymers exhibited almost identical solubility, similar absorption behavior (Supplementary Fig. S2) and electrochemical properties (Supplementary Fig. S3) due to the introduction of extremely low ratio of Ir complex.

To evaluate the effect of chemically bonded Iridium complex on the photovoltaic performance, PSCs were fabricated with the architecture of ITO/PEDOT:PSS/donors polymer PTB7-ThIrx: PC71BM/Ca or PDIN/Al. Particularly, three batches of control polymer PTB7-Th, one with high MW (PTB7-Th<sub>H</sub>, M<sub>p</sub>/M<sub>w</sub>: 90/ 160 kg mol<sup>-1</sup>) and the other two batches with medium MW (PTB7-Th<sub>M</sub> and PTB7-Th<sub>M'</sub>,  $M_n/M_w$ : 62/97 and 45/94 kg mol<sup>-1</sup>, respectively) were employed to ensure a fair comparison since polymer MW significantly influences the device performance. The active layer consisting of the optimum donor/acceptor weight ratio of 1:1.5 (w/w) was prepared from 1,2-dichlorobenzene solution, and 3 vol% of 1,8-diiodooctane (DIO) was added as solvent additive before spin-coating. The photovoltaic performance including current density vs. voltage (J-V) curves as well as external quantum efficiency (EQE) characteristics are shown in Supplementary Fig. S4 and Fig. 2, and the key device data are listed in Table 1 with the average of over 18 devices.

Comparing the different MWs of the control Ir-free polymers, PTB7-Th<sub>H</sub> with the highest MW exhibited an obvious higher PCE with either Ca or PDIN as cathode interface material. In general, the PDIN interface layer resulted in higher PCEs, i.e., the average PCE was increased from 7.02/7.81% of PTB7-Th<sub>M'</sub> to 7.33/8.29% of PTB7-Th<sub>H</sub> when Ca/PDIN were used as electron injection materials, respectively. PTB7-Th<sub>M</sub> and PTB7-Th<sub>M'</sub> with similar medium molecular weight ( $M_w$  of ~95 kg mol<sup>-1</sup>) demonstrated almost the same average PCE of 7.81% in PDIN-based devices.

In photovoltaic devices based on Ca as cathode interface material, at similar MW, it is observed that by increasing the feed ratio of Ir complex from 0 to 1 mol%, the overall average PCE increased from 7.02% of Ir-free PTB7-Th<sub>M'</sub>, to 7.45% of PTB7Ir0.5 and 7.77% of PTB7-ThIr1. The highest PCE of 7.92% was achieved in PTB7-ThIr1-based device, with  $V_{oc} = 0.77$  V,  $J_{sc} = 15.06$  mA cm<sup>-2</sup>, and FF = 0.63. Further increase the Ir content to 1.5 mol% in PTB7-ThIr1.5, the  $J_{sc}$  and PCE dropped to 14.33 mA cm<sup>-2</sup> and 7.0%, respectively.

To further confirm the enhancement on PCE by the incorporation of low Ir ratio to PTB7-Th as well as improve the device performance, optimized device conditions based on an organic cathode interface material of PDIN were then conducted. The J-Vcurves and EQE characteristics are shown in Fig. 2, the key photovoltaic parameters are listed in Table 1. As mentioned previously, the same average PCE of 7.81% were achieved in the Ir-free control polymer PTB7-Th<sub>M</sub> and PTB7-Th<sub>M</sub>-based devices. By increasing the Iridium content from 0.5 to 1 and 1.5 mol%, the

Polymer $M_n/M_w$ (kg mol <sup>-1</sup> )         Interface $V_{oc}$ (V) $J_{sc}$ (mA cr           PTB7-Th <sub>w</sub> 62/97         PDIN         0.81         14.98           PTB7-Th <sub>w</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>w</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>w</sub> (ref. 35)         90/160         Ca         0.76         14.92           PTB7-Th <sub>w</sub> (ref. 35)         90/160         Ca         0.76         14.92           PTB7-Th <sub>w</sub> (ref. 35)         71/118         Ca         0.76         15.87           PTB7-Th <sub>in</sub> 56/112         71/118         Ca         0.78         15.32           PTB7-Third 56/112         56/112         Ca         0.77         15.06						
TBJ-Th <sub>M</sub> 62/97         PDIN         0.81         14.98           PTB7-Th <sub>M</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>M</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>M</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Th <sub>H</sub> 91/10         Ca         0.78         15.32           PTB7-Thiro.5         71/118         Ca         0.78         15.38           PTB7-Thiro.5         71/118         Ca         0.78         15.38           PTB7-Thiro.5         71/118         Ca         0.78         15.36           PTB7-Thiro         56/112         Ca         0.77         15.06	/M <sub>w</sub> (kg mol <sup>-1</sup> ) Interface	V <sub>oc</sub> (V)	$J_{ m sc}~( m mA~cm^{-2})$	FF (%)	PCE <sub>max</sub> (average) (%)	Cal. $J_{\rm sc}$ (mA cm <sup>-2</sup> )
PTB7-Th <sub>M</sub> (ref. 35)         45/94         Ca         0.76         15.29           PTB7-Th <sub>M</sub> (ref. 35)         POIN         0.80         15.70           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Third         Ca         0.78         15.87           PTB7-Third         Ca         0.78         15.32           PTB7-Third         56/112         Ca         0.77         15.06           PTB7-Third         56/112         Ca         0.77         15.06	NIDA 26/	0.81	14.98	65.10	7.92 (7.81 ± 0.11)	13.66
PTB7-Th <sub>H</sub> PDIN         0.80         15.70           PTB7-Th <sub>H</sub> 90/160         Ca         0.76         14.92           PTB7-Th <sub>H</sub> O.5         71/118         Ca         0.70         15.87           PTB7-Th <sub>H</sub> O.5         71/118         Ca         0.78         15.32           PTB7-Th <sub>H</sub> O.5         71/118         Ca         0.78         15.32           PTB7-Th <sub>H</sub> O.5         71/118         Ca         0.79         15.68           PTB7-Th <sub>H</sub> I         56/112         Ca         0.77         15.06           PTB7-Th <sub>H</sub> I         56/112         Ca         0.77         15.06	/94 Ca	0.76	15.29	61.15	$7.15\ (7.02\pm0.14)$	14.50
PTB7-Th <sub>H</sub> 90/160         Ca         0.76         1492           PTB7-Th <sub>I</sub> C0.5         71/118         PDIN         0.80         15.87           PTB7-Thir0.5         71/118         Ca         0.78         15.32           PTB7-Thir0.5         71/118         Ca         0.78         15.32           PTB7-Thir0.5         71/118         Ca         0.79         15.68           PTB7-Thir1         56/112         Ca         0.77         15.06           PTB7-Thir1         56/112         Ca         0.77         15.06	PDIN	0.80	15.70	62.71	$7.89~(7.81 \pm 0.10)$	14.50
PDIN         0.80         15.87           PTB7-Thir0.5         71/118         Ca         0.78         15.32           PDIN         0.80         15.38         15.38           PTB7-Thir1         56/112         Ca         0.77         15.06           PTB7-Thir1         56/112         Ca         0.77         15.06	/160 Ca	0.76	14.92	65.46	$7.45~(7.33 \pm 0.15)$	14.63
PTB7-Thiro.5         71/118         Ca         0.78         15.32           PDIN         0.80         15.88         15.88           PTB7-Thir1         56/112         Ca         0.77         15.06           PTB7-Thir1         56/112         Ca         0.77         15.06	PDIN	0.80	15.87	66.27	$8.37 \ (8.29 \pm 0.11)$	15.26
PDIN 0.80 15.88 PTB7-Thir1 56/112 Ca 0.77 15.06 PDIN 0.80 16.60	/118 Ca	0.78	15.32	63.40	7.56 (7.45 $\pm$ 0.13)	15.21
PTB7-Thir1 56/112 Ca 0.77 15.06 PDIN 0.80 16.60	PDIN	0.80	15.88	66.07	$8.38 \ (8.28 \pm 0.15)$	15.8
PDIN 0.80 16.60	/112 Ca	0.77	15.06	67.93	$7.92 \ (7.77 \pm 0.15)$	15.77
	PDIN	0.80	16.60	69.36	$9.19 \ (9.07 \pm 0.12)$	16.0
PTB7-Thlr1.5 67/106 Ca 0.77 14:33	/106 Ca	0.77	14.33	64.33	$7.08~(7.00 \pm 0.10)$	14.58
PDIN 0.80 15.00	PDIN	0.80	15.00	69.34	8.30 (8.18±0.13)	15.4

average PCE was increased to 8.28% in PTB7-ThIr0.5, 9.07% in PTB7-ThIr1 and 8.18% to PTB7-ThIr1.5. Similarly to the Ca series devices, the best performance was obtained in PTB7-ThIr1 with 1 mol% of Ir feed ratio, the maximum PCE was improved to 9.19%, with  $V_{oc} = 0.80$  V,  $J_{sc} = 16.60$  mA cm<sup>-2</sup> and FF = 0.69. Compared to the control Ir free PTB7-Th<sub>M</sub> and PTB7-Th<sub>M'</sub> with similar MW, a 16.5% increase of PCE was obtained at the same device conditions. In accordance with the Ca-series devices, PTB7-ThIr1 based on 1 mol% of Ir complex in PDIN containing devices exhibited even higher PCE than the Ir free PTB7-Th<sub>H</sub> with significantly higher MW, further manifesting the positive effect of the introduction of chemically bonded extremely low ratio of heavy metal Ir complex on the PCE enhancement of BHJ PSCs.

Figure S4b and Fig. 1b demonstrated the EQE curves of the photovoltaic devices to verify the measured  $J_{sc}$  values. All devices showed an intense and broad absorption in the range of 350–750 nm. The maximum EQE was approaching 74% at ~635 nm for PTB7-Thlr1 containing device. In the range from 600 to 750 nm, the EQE for device based on 1 mol% of Ir containing PTB7-Thlr1 as donor polymer displayed the highest values, followed by 0.5 mol% of PTB7-Thlr0.5. The measured  $J_{sc}$  from the photovoltaic devices were in good agreement with the calculated  $J_{sc}$  from the integration of EQE curves (within a 5% error), confirming the accuracy of PCE.

To gain a deep understanding on the variations of the photovoltaic device performance induced by Ir complex, atomic force microcopy (AFM) was firstly carried out to investigate the blended film morphology of the PTB7-Thlrx/PC71BM (1:1.5, w/w). As shown in Supplementary Fig. S5, no significant differences on the AFM phase images could be observed, and the values for rootmean-square roughness were all similar at 1.20, 1.21, 1.35, 1.47, and 1.27 nm for PTB7-Th<sub>H</sub> PTB7-Th<sub>M</sub> and PTB7-ThIrx/PC<sub>71</sub> BM (x =0.5, 1, and 1.5) blended films, respectively. On the other hand, grazing incident wide-angle X-ray scattering (GIWAXS) of the polymer/PC71BM blended films was then conducted to investigate possible structural changes induced through the chemical embedding of Ir complexes. The two-dimensional GIWAXS patterns as well as the corresponding scattering profiles at the in-plane and out-of-plane directions with or without Ir content for the representative blended samples are shown in Fig. 3. At the first glance, no tremendous differences in their pattern properties are observed, especially similar peaks becomes clearer in the 1D profile either at the in-plane or out-of-plane directions, which is attributed to the extremely low ratio of Ir complex to the polymer backbone. However, after careful comparison, the pattern intensities for the broad peak arisen at  $q \approx 1.38$  Å<sup>-1</sup> corresponding to PC71BM aggregation gradually reduced with the increase of Ir content in the polymer backbone from 0, 1 to 1.5 mol%.43,44 On the other hand, the arc-like scattering arising from the Bragg diffraction with  $q_v \approx 0.33 \text{ Å}^{-1}$  was corresponded to (100) lamellar stacking of the series polymer of PTB7-Th and the representative PTB7-ThIrx (x = 1 and 1.5). Similarly, PTB7-ThIr1.5/PC<sub>71</sub>BM blends displayed the lowest intensity, indicating reduced lamellar stacking. Meanwhile, as previously reported, the intensity of the (010) face-on  $\pi - \pi$  stacking peak with  $q_z \approx 1.66 \text{ Å}^{-1}$  for PTB7-Th: PC71BM blends was significantly weaker than the pure PTB7-Th film due to  $PC_{71}BM$  destroys the crystallinity of PTB7-Th.<sup>45</sup> In addition, the introduction of Ir complex in the terpolymers further reduced the originally weakened  $\pi - \pi$  stacking peak in PTB7-Th: PC<sub>71</sub>BM blends, and this peak even almost disappeared in PTB7-Thlr1.5-based film. It is suggested that the conjugation of low ratio third monomer to PTB7-Th destroyed the essential symmetry and integrality of the polymer backbone, and thus lead to the reduced PC<sub>71</sub>BM aggregation.

To achieve more insights of the enhanced PCE by the chemical modification of Ir complex to the conjugated backbone of donor polymer, hole mobilities of the active layers for PTB7-ThIrx/PC<sub>71</sub>BM blends were measured by space-charge-limited current (SCLC)

np



Fig. 2 a *J–V* and b EQE curves of photovoltaic devices with the configuration of ITO/PEDOT:PSS/donor polymer PTB7-Th and PTB7-ThIrx (0.5, 1, and 1.5):PC<sub>71</sub>BM/PDIN/AI



**Fig. 3** 2D GIWAXS patterns (from left to right: PTB7-Th<sub>M</sub>, PTB7-ThIr1 and PTB7-ThIr1.5) and scattering profiles (from bottom to up: PTB7-Th<sub>M</sub>, PTB7-ThIr1 and PTB7-ThIr1.5) of in-plane and out-of-plane directions for the corresponding polymer:PC<sub>71</sub>BM (1:1.5, w/w, with DIO) blended samples on a silicon substrate



Fig. 4 a J-V curves for hole-only devices based on PTB7-ThIrx/PC<sub>71</sub>BM blended film and **b** light intensity dependence of  $J_{SC}$ 

method using hole-only device consisting structure of ITO/PEDOT: PSS/polymers:PC<sub>71</sub>BM/Au. As shown in Fig. 4, the hole mobility for PTB7-Th<sub>H</sub>, PTB7-Th<sub>M</sub> and PTB7-Thlrx/PC<sub>71</sub>BM (x = 0.5, 1, and 1.5) blends, was estimated to be 1.44, 1.0, 1.98, 5.68 and  $1.36 \times 10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, respectively. It is found that PTB7-Th<sub>H</sub> polymer blends exhibited higher hole mobility than PTB7-Th<sub>M</sub> due to significantly higher MW, similarly to previous studies.<sup>45</sup> The Ir containing PTB7-ThIr1 blends including 1 mol% of Ir content displayed the highest hole mobility, followed by PTB7-ThIr0.5 and PTB7-ThIr1.5, the control Ir-free PTB7-Th<sub>M</sub> with comparable MW demonstrated the poorest charge transport property. The trends of hole mobility for the polymer/PC $_{71}$  BM blended film are in good agreement with the PCE values on BHJ PSCs.

We further studied the light intensity (P) dependencies on the short-circuit current density ( $J_{sc}$ ) to determine the non-geminate recombination losses in the devices. Generally, the relationship between  $J_{sc}$  and P follows the formula of  $J_{sc} \propto P^{5,46}$  In case all free carriers were swept out and collected at the electrodes before recombination, S should be identical to 1, while S < 1 represents some degree of bimolecular recombination. The S values calculated from the  $J_{sc}$ -P curves in Fig. 4b for the series polymer PTB7-Th<sub>H</sub>, PTB7-Th<sub>M</sub> and PTB7-ThIrx/PC<sub>71</sub>BM (x = 0.5, 1, and 1.5)



**Fig. 5** Ultra-fast time-resolved PL transients taken at 850 nm (excitation wavelength of 650 nm) for representative polymer/PC<sub>71</sub>BM blended films reflecting the decay dynamics of excitons, and all the blended films were prepared at the same conditions as in photovoltaic devices

blended BHJ devices were calculated to be 0.972 and 0.947 as well as 0.983, 0.997 and 0.917, respectively. The *S* value of the PTB7-Thlr1 containing device approaches 1, indicating a more efficient transport of carriers and nearly suppressed bimolecular recombination, which agrees very well with its highest PCEs. In contrast, the *S* value for both Ir free polymers PTB7-Th<sub>H</sub> and PTB7-Th<sub>M</sub>based device is significantly lower than PTB7-Thlr1, indicating the existence of a certain bimolecular recombination. The *S* value for PTB7-Thlr1.5 containing device is the lowest, suggesting the existence of most bimolecular recombination, which greatly reduced the photovoltaic performance.

To further support our interpretation of the influence of Ir content on the PCE of polymer/fullerene BHJ PSCs, pico-second time-resolved photoluminescence (PL) was carried out to compare the PL decay dynamics (Fig. 5). The absorption and steady-state PL spectra for polymer/PC<sub>71</sub>BM blends are shown in Supplementary Fig. S6. All PL dynamics exhibited a bi-exponential decay. The fast picosecond decay channel is similar for all blends and may result from the dissociation of charge-transfer state excitons at the donor-acceptor interface, while the several hundred picoseconds longer decay channel could possibly be explained by the effective radiative lifetime of  $PC_{71}BM$ .<sup>47</sup> Compared with the control polymer PTB7-Th<sub>M</sub>, chemically bonding low content of Ir complex to PTB7-Th backbone, the relative contribution on the slow decay process (>40 ps) for PTB7-ThIr1 and PTB7-ThIr1.5 blends was enhanced, with specific performance presented at the reduced PL intensity at longer pico-second time, which could be explained by a reduced average PC<sub>71</sub>BM domain size to allow more singlet excitons to reach the hetero-interface during migration.<sup>47</sup> The Ir containing terpolymers PTB7-Thlr1/PC71BM blends exhibited a higher exciton quenching efficiency and more efficient slow process of charge separation, which is favorable to the photovoltaic device performance.<sup>48</sup> The highest hole mobility, least bimolecular recombination as well as more efficient slow process of charge separation facilitated the highest PCE for 1 mol% Ir containing PTB7-Thlr1 device among the series of polymers.

# DISCUSSION

In conclusion, we have successfully demonstrated the positive effect on the PCE of polymer/fullerene BHJ PSCs by conjugating extremely low ratio of heavy metal Ir complex to the famous PTB7-Th donor polymer through ancillary ligand. At similar MW, the Ir-containing PTB7-ThIr1 by using 1 mol% of Ir complex for polymerization exhibited notably higher PCE than the control

PTB7-Th<sub>M</sub> at different device fabrication conditions either with Ca or PDIN as cathode interface materials. The maximum PCE of 9.2% was achieved for PTB7-ThIr1 compared with 7.9% for Ir-free control polymer PTB7-Th<sub>M</sub>, with an increase by 16.5%. Through a combination of investigations, the enhanced PCE could be ascribed to comprehensive factors on higher holemobility, less bimolecular recombination as well as the more efficient slow process of charge separation. Our results demonstrate an extra promising design approach toward more efficient photovoltaic polymer donor materials based on current highly-efficient conjugated polymers, and also provide the evidence for the importance of heavy metal complex for highly efficient photovoltaic devices. Future work with the strategy on conjugated D-A polymers for other polymer donors as well as non-fullerene polymer electron acceptors are under investigation.

# METHODS

Synthesis and characterization

All polymers were synthesized and characterized using the methods described in Section 1 and 2 of the Supplementary Information.

## Devices fabrication and characterization

The PSC devices were fabricated with a device architecture of ITO (indium tin oxide)/PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate))/active layer/Ca or PDIN/AI. Ca or PDIN severs as the interlayer to lower the Al cathode work function. The anode interfacial layer, PEDOT: PSS, was deposited through spin-coating at 4000 rpm for 45 s on precleaned ITO-coated glass, then annealing at 150 °C for 15 min in air, the polymer/PC<sub>71</sub>BM blended solution (total of  $25 \text{ mg mL}^{-1}$  with the weight ratio of 1:1.5) was spin-coated (1000 rpm) in o-dichlorobenzene (3 vol% of DIO) to form a photosensitive layer with a thickness of 100 nm under an nitrogen glove box. The cathode interfacial layer, PDIN, was deposited under the active layer at 3000 rpm for 30 s with thickness of ~14 nm in methanol solution (0.2% acetic acid) at a concentration of  $1.5 \text{ mg mL}^{-1}$ . The AI (~100 nm) layer was then thermally evaporated onto cathode interface layer at vacuum condition of  $\sim 10^{-5}$  Pa to form negative electrode. The active area of all devices was 4.7 mm<sup>2</sup>. The device current density-voltage (J-V) characteristics were measured under an air mass 1.5 light using a Keithley 2400 Source-Measure Unit. Oriel Sol3A Class AAA Solar Simulator (model, Newport 94023 A) with a 450 W xenon lamp was used as the light source. The light intensity was calibrated to 100 mW cm<sup>-2</sup> by a Newport Oriel 91150 V reference cell. The EQE was acquired using a Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology Co., Ltd., Taiwan) using a standard single-crystal Si photovoltaic cell to calibrated.

### **GIWAXS** characterization

GIWAXS were conducted at the SAXS/WAXS beamline of Australian Synchtoron. The substrates were cleaned silicon wafers and the polymer films were spin-coated the same ways as the active layer of the devices was prepared. Samples were analyzed at with an X-ray energy of 11 keV and a range of incident angles from  $\Omega = 0.02$ - 0.35 in 0.005 increments to allow signal optimization near the critical angle of polymer film but below the critical angle of substrate. Data from GIWAXS experiments were analyzed using a customized version of NIKA 2D based in IgorPro.

#### Mobility measurements

Hole mobility were measured the *J–V* characteristics of hole-only device using SCLC method. For the fabrication of hole-only devices, structures were selected as ITO/PEDOT:PSS/Polymer:PC<sub>71</sub>BM/Au. The SCLC mobilities were calculated through MOTT-Gurney equation.<sup>49,50</sup>

## Time-resolved PL measurement

For time-resolved PL, the laser source was used by a Coherent Libra<sup>TM</sup> regenerative amplifier (50 fs, 1 KHz, 800 nm), which was seeded by a Coherent Vitesse<sup>TM</sup> oscillator (50 fs, 80 MHz). Wavelength laser pulses of 800 nm were obtained from the regenerative amplifier while 400 nm laser pulses were achieved from a BBO doubling crystal. The laser pulses

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(400 nm, circular spot, and diameter 2 mm) were directed to the blended films. The emission signal from the film samples was collected at  $150^{\circ}$  backscattering angle by a pair of lenses into an Optronis Optoscope<sup>TM</sup> streak camera system with the ultimate temporal resolution of ~10 ps.

## Data availability

The experimental data which support the findings of this study could be available from the corresponding author upon reasonable request.

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## **AUTHOR CONTRIBUTIONS**

Z.X., S.W. and M.Q. synthesized the materials, J.Y., Z.Z. and Y.L. fabricated the OPV devices and the optoelectrical measurements, Y.Z., C.L. and S.H. did the GIWAXS experiments and the corresponding data analyses, Z.X., S.W. carried out most of the other experimental work and data analyses, G.X. did the time-resolved PL measurement, W.H. provided insights, all authors contributed the writings. Y.T. planned the work, and Y.T., Z.Z. and S.H. guided the work.

## **ADDITIONAL INFORMATION**

Supplementary information accompanies the paper on the *npj Flexible Electronics* website (https://doi.org/10.1038/s41528-017-0014-9).

**Competing interests:** The authors declare that they have no competing financial interests.

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