Supporting information

Ternary polymer solar cells with iridium-based polymer PM6Ir1 as donor and N3:ITIC-Th as acceptors exhibiting over 17.2% efficiency

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Experimental section

Device Fabrication: The patterned indium tin oxide (ITO) coated glass substrates (sheet resistance 15 Ω /square) were consecutively cleaned in ultrasonic baths containing detergent, de-ionized water and ethanol, respectively. The cleaned ITO substrates were blow-dried by highly pure nitrogen gas and then treated by oxygen plasma for 1 min to improve its work function and cleanliness. Subsequently, poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) (clevios PVP Al 4083, purchased from H.C. Starck co. Ltd.) solution was spin-coated to fabricate thin films on the cleaned ITO substrates by spin-coating method at 5000 round per minute

(RPM) for 40 s, and then annealed at 150 °C for 15 min in ambient condition. After annealing treatment, the ITO substrates coated with PEDOT:PSS films were transferred to a high-purity nitrogen-filled glove box for the fabrication of active layers. The PM6Ir1, N3 and ITIC-Th were dissolved in chlorobenzene to prepare 16 mg/ml blend solutions and 1-chloronaphthalene (CN) (0.5%, v/v) was added as the additive. The PM6Ir1 was synthesized by M. Zhang according to the following synthetic method. ITIC-Th and N3 were purchased from Solarmer Materials Inc and eFlexPV limited company, respectively. The proportions of N3:ITIC-Th are 1:0, 0.95:0.05, 0.9:0.1, 0.85:0.15, 0.7:0.3, 0:1 and the weight ratio of donor to acceptors is kept constant as 1:1.2. The blend solutions were spin-coated onto PEDOT:PSS films at 2800 RMP for 30 s in a high purity nitrogen-filled glove box to fabricate the active layers. Then, the active layers were annealed by CS₂ vapor for 20 s and then thermally annealed at 80 °C for 5 min. Afterwards, a PDIN cathode interlayer was spin-coated onto active layers at 5000 RPM for 30 s. Finally, 100 nm Ag was deposited by thermal evaporation with a shadow mask. The active area is approximately 3.8 mm², which is defined by the overlapping area of ITO anode and Ag cathode.

Synthetic method of PM6Ir1

Three monomers of (4,8-bis(5-(2-ethylhexyl)-4-fluorothiophen-2-yl)benzo[1,2b:4,5-b']-dithiophene (BDT-F, 188.5 mg, 0.2 mmol) and 1,3-bis(thiophen-2-yl)-5,7bis(2-ethyl-hexyl)benzo-[1,2-c:4,5-c']dithiophene-4,8-dione (BDD, 153.3 mg, 0.2mmol) and bis[2-di(p-methoxyphenyl)-amino (9,9-diethylfluoren-2-yl)-5-(trifluoromethyl)pyridine][1,3-bis(4-bromophenyI)propane-1,3-dione]iridium(III)¹(iridium complex, 3.5 mg, 0.002 mmol were added into a 25 mL Schlenk flaskcontaining 15 mL of dry toluene. Under high-purity nitrogen atmosphere, Pd(PPh₃)₄(20 mg, 0.02 mmol) was added. Then the reaction mixture was heated to reflux for 2days. After that, the solution mixture after colling was poured into MeOH, and theprecipitate was collected by filtration. Then, the polymer PM6Irl was collected as adark solid after Soxhlet extraction with methanol, hexane, and chloroform for 24 h,respectively. Finally, the solid was dried under vacuum for 1 day and PM6Irl was obtained with a 62% yield (152 mg).

The number average molecular weight (M_n) is 29.8 kDa and the polydispersity index (PDI) is 1.48 for terpolymer PM6Ir1, measured by gel permeation chromatography (GPC). Elemental analysis is performed to further confirm the PM6Ir1 structure and the result is listed as Anal. calcd. (%): C, 67.26; H, 6.59; N, 0.04; S, 20.26. Found (%): C, 66.71; H, 6.18; N, 0; S, 20.56. According to the thermogravimetric analysis (TGA) measurement shown in **Fig. S1a**, the decomposition temperatures (T_d) of terpolymer PM6Ir1 is 437 °C when its weight is reduced to 95% of the initial value. **Fig. S1b** exhibits the linearly fitted the inductively coupled plasma mass-spectrometry (ICP-MS) curves of iridium standard and polymer signal. According to the perfect linear fit of iridium standard signals with the coefficient of determination $R^2 = 1.0$, the measured concentration of iridium component is 1.093 ppb for terpolymer PM6Ir1, which further identify the existence of iridium component in polymer backbone.



Fig. S1. (a) TGA plots of polymer donors with a heating rate of 10 $^{\circ}$ C min⁻¹ under a N₂ atmosphere. (b) Linearly fitted ICP-MS curves of iridium standard and polymer PM6Ir1 signal.

Device Characterization: The current density-voltage (*J-V*) curves of all the organic solar cells were measured by a Keithley 2400 unit in a high-purity nitrogen-filled glove box. The AM 1.5G irradiation was provided by an XES-40S2 (SAN-EI ELECTRIC Co. Ltd) solar simulator (AAA grade, $70 \times 70 \text{ mm}^2$ photobeam size) with light intensity of 100 mW/cm², which was calibrated by standard silicon solar cells (purchased from Zolix INSTRUMENTS CO. LTD). The external quantum efficiency (EQE) spectra of

organic solar cells were measured in air by a Zolix Solar Cell Scan 100. The ultravioletvisible (UV-Vis) absorption spectra of neat and blend films were obtained using a Shimadzu UV-3101 PC spectrometer. Photoluminescence (PL) spectra of neat and blend films were measured by a HORIBA Fluorolog®-3 spectrofluorometer system. Electrochemical impedance spectroscopy (EIS) was measured by a ZAHNER CIMPS electrochemical workstation, Germany. Transmission electron microscopy (TEM) images of active layers were obtained by a JEOL JEM-1400 transmission electron microscope operated at 80 kV. Grazing incidence wide angle X-ray scattering (GIWAXS) measurements were accomplished at PLS-II 9A U-SAXS beamline of the Pohang Accelerator Laboratory in Korea.

The space charge limited current (SCLC) method was employed to investigate the influence of incorporating ITIC-Th on charge mobility in active layers. The structure of electron-only devices is ITO/ZnO/active layer/PDIN/Al and the structure of hole-only devices is ITO/PEDOT:PSS/active layer/MoO₃/Ag. ZnO thin films were fabricated on the cleaned ITO substrates by spin-coating method at 4000 RPM for 30 s, and then annealed at 150 °C for 30 min in air conditions. The thickness of ZnO films is about 30 nm. After annealing treatment, the ITO substrates coated ZnO films were transferred to a high-purity nitrogen-filled glove box to fabricate active layers. The fabrication conditions of the active layer films are same with those for the solar cells. After that, the MoO₃/Ag (10 nm/100 nm) films were deposited by thermal evaporation with a shadow mask under 10^{-4} Pa. The charge mobility was calculated according to the space charge limited current (SCLC) method. The hole and electron mobility can be calculated from the Mott-Gurney equation with Poole-Frenkel correction as the followings:

$$J = \frac{9}{8} \varepsilon_0 \varepsilon_r \mu \frac{V^2}{d^3} exp \left[0.89\gamma \sqrt{\frac{V}{d}} \right]$$

Here, ε_r is dielectric constant of organic materials, ε_0 is the free space permittivity, μ is charge mobility, V is the applied voltage, and d is the active layer thickness, γ is the field enhancement factor of a Poole–Frenkel type mobility.



Fig. S2. Absorption spectra of blend films with different ITIC-Th content.



Fig. S3. The normalized absorption spectra and PL spectra of neat and blend acceptor films.

Photocurrent density (J_{ph}) dependence on effective voltage (V_{eff}) of typical PSCs were investigated. The J_{ph} is defined as $J_{ph} = J_L - J_D$, in which J_L and J_D represent the current densities under illumination and dark conditions, respectively. The V_{eff} is defined as $V_{eff} = V_0 - V_{bias}$, in which V_0 represents the voltage at $J_{ph} = 0$ mA cm⁻² and V_{bias} represents the applied voltage bias. Assumed that the exciton dissociation efficiency (η_{diss}) and charge collection efficiency (η_{coll}) are very close to 100% under large V_{eff} of 4 V, the J_{ph} at $V_{eff} = 4$ V is defined as the saturated current density (J_{sat}). The η_{diss} and η_{coll} can be calculated according to the formula of $\eta_{diss} = J_{ph}^{*}/J_{sat}$ and $\eta_{coll} = J_{ph}^{*}/J_{sat}$, the J_{ph}^{*} and $J_{ph}^{#}$ refer to the J_{ph} under short-circuit condition and maximal-power-output condition, respectively. The detailed values of corresponding PSCs are listed in Table S1.

Table S1. The key parameters of the optimized binary and ternary PSCs.

Dland films a)	${J_{ph}}^{*}$	$J_{ph}{}^{\#}$	J_{sat}	J_{ph}^*/J_{sat}	$J_{ph}^{\#}/J_{sat}$
Bielia IIIIIS"	(mA cm ⁻²)	(mA cm ⁻²)	(mA cm ⁻²)	(%)	(%)
PM6Ir1:N3	26.13	23.84	27.64	94.55	86.24
PM6Ir1:N3:ITIC-Th	26.53	24.36	27.84	95.28	87.47
PM6Ir1:ITIC-Th	15.87	13.48	17.35	91.47	77.69

^{a)} J_{ph}^{*} under short-circuit condition, $J_{ph}^{\#}$ under maximal-power-output condition.

ITIC-Th content (wt%)	$R_{s}\left(\Omega ight)$	$R_{trans}\left(\Omega ight)$	C (nF)	$R_{rec}\left(\Omega ight)$	CPE _P	CPE _T (nF)
0	29.6	59.5	4.14	62.4	0.910	15.1
10	33.1	54.9	13.3	65.2	0.955	13.3
100	23.3	189	1.83	102	0.859	7.96

Table S2. The key parameters of the optimized binary and ternary PSCs.



Fig. S4. *J-V* curves of the PSCs under AM 1.5G illumination with light intensity of 100, 80, 50, 25, 10, 5, 2.5, 1 mW/cm², respectively: (a) N3 based binary PSCs, (b) optimized ternary PSCs, (c) ITIC-Th based binary PSCs.



Fig. S5. The $\ln(Jd^3/V^2)$ versus $(V/d)^{0.5}$ curves of (a) hole-only devices and (b) electrononly devices.

Table S3. The μ_h , μ_e and μ_h/μ_e in the OSCs with different ITIC-Th contents in the acceptor mixture.

ITIC-Th content	μ_h	μ_e		
(wt%)	$(cm^2 V^{-1} s^{-1})$	$(cm^2 V^{-1} s^{-1})$	$\mu_{h'}\mu_{e}$	
0	6.46×10-4	3.98×10-4	1.62	
5	6.63×10-4	4.28×10-4	1.55	
10	6.97×10 ⁻⁴	4.59×10 ⁻⁴	1.52	
15	6.56×10 ⁻⁴	4.29×10 ⁻⁴	1.60	
30	5.37×10 ⁻⁴	3.32×10 ⁻⁴	1.88	
100	4.84×10 ⁻⁴	2.32×10-4	2.08	

1. X. Liu, B. Yao, Z. Zhang, X. Zhao, B. Zhang, W.-Y. Wong, Y. Cheng and Z. Xie, *J. Mater. Chem. C*, 2016, 4, 5787-5794.