Electronic Supplementary Information for

Small-molecular Iridium complex based organic solar cells with improved photovoltaic performance through device optimization

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Experimental

All solvents and chemicals were obtained commercially and used without further purification. CB and CF was purchased from Sigma Aldrich Co., PDCBT and $P_{71}BM$ from One-Materials Inc..

OSCs with conventional structure of ITO/PEDOT:PSS/active layer/PDINO/Al was fabricated as follows. Indium tin oxide (ITO) glass substrates were cleaned in an ultrasonic bath with detergent, deionized water, acetone and isopropanol, respectively, and followed by treatment of UV-ozone for 30 minutes. Then, PEDOT:PSS (Baytron PVP Al 4083) was spin-coated on the ITO at 3500 rpm for 60 seconds and baked at 150°C for 15 min in air to give a film thickness around 30 nm. After that, the substrates with PEDOT:PSS thin film were transferred to a nitrogen glove box. The blends of TBzIr:$PC_{71}BM$ was dissolved in CB solvent (D:A=1:1, 20 mg mL^{-1}) anteriorly with stirring over 12 hours under 60°C. For ternary OSCs, blend of PDCBT:TBzIr:$PC_{71}BM$ was dissolved in CB:CF (3:1, v/v) mixed solvent (20 mg mL^{-1} in total) with stirring over 12 hours under 50°C. Then, the completely dissolved solution was spin-coated onto the PEDOT:PSS layer to form the BHJ structure. And for PDCBT/TBzIr:$PC_{71}BM$ bilayer devices, PDCBT in CF solution with concentration of 6 mg mL^{-1} was spin-coated followed by thermal annealing at 60°C for 10 minutes. The TBzIr:$PC_{71}BM$ active layer was fabricated in the same process with BHJ control mentioned above. A cathode buffer layer PDINO was then spin-coated at 3000 rpm for 60 seconds. Finally, aluminum with thickness of 100 nm was evaporated onto the PDINO layer under vacuum (≈10^{-5} Pa) as the back electrode.

Ultraviolet-visible (UV-vis) absorption spectra of thin film on a quartz substrate were measured using Shimadzu UV-2500 recording spectrophotometer. *J-V* curves of OSCs devices were measured using a computer controlled Keithley 2400 Source Measure Unit under a simulated AM 1.5G spectrum, which was obtained by Oriel Sol3A Class Solar Simulator (model, Enlitech SS-F5-3A) with a 450 W xenon lamp and an air mass 1.5 filter. EQE spectra was measured by Solar Cell Spectral Response Measurement System QE-R3-011 (Enli Technology, Taiwan). AFM measurement was performed via Bruker Dimension ICON atomic force microscopy. X-ray photoelectron spectroscopy (XPS): vertical distribution was characterized via Thermo ESCALAB 250XI, which using a excitation source of Al Kα X-ray. To prepare the corresponding samples, the active layers were transferred into water bath for a separating process. Since the hole transport layer PEDOT:PSS was soluble well and PDCBT, TBzIr as well as $PC_{71}BM$ were insoluble in water, the active layer could be easily detached and then transferred to a small pieces of Si substrate.

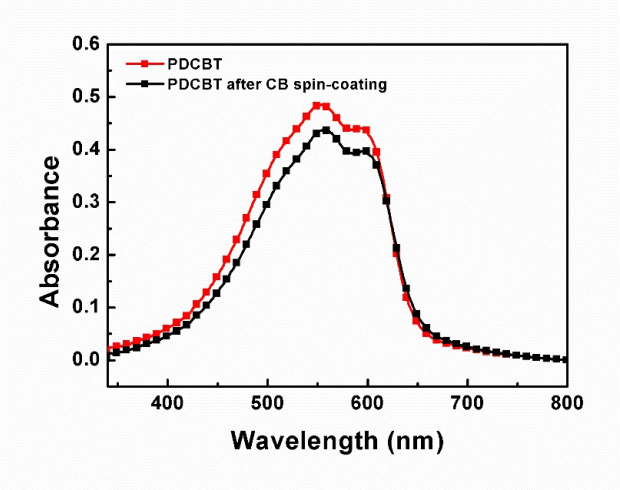

Fig. S1 The UV absorbance of the PDCBT film before and after spin-coating of CB.

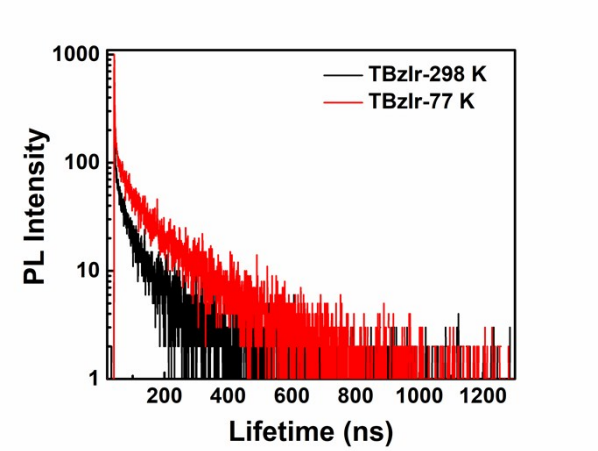

Fig. S2 The transient PL decay curves under room and 77 K temperature for TBzIr films.

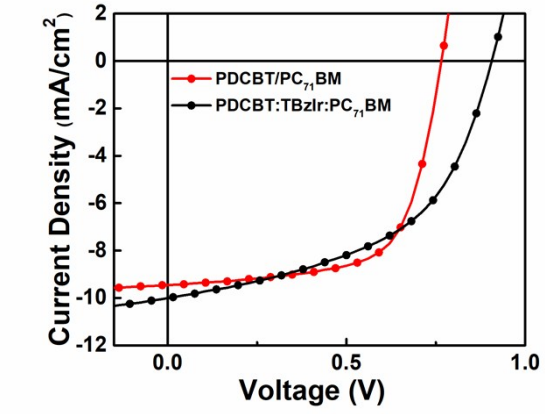

Fig. S3 *J-V* curves of the PDCBT/$PC_{71}BM$ bilayer and PDCBT:TBzIr:$PC_{71}BM$ ternary OSCs devices.

Table S1 Photovoltaic properties of PDCBT:TBzIr:$PC_{71}BM$ based devices with varying thickness of PDCBT layer.

Thickness of PDCBT	V_{oc} [V]	J_{sc} [mA/cm^{-2}]	FF	PCE[(a)] [%]
23 nm	0.92	10.13	0.55	5.10 (4.92±0.09)
26 nm	0.92	10.11	0.56	5.19 (4.93±0.26)
39 nm	0.92	11.18	0.59	6.17 (5.84±0.33)
48 nm	0.92	10.85	0.59	5.78 (5.64±0.14)
57 nm	0.92	10.61	0.57	5.43 (5.34±0.11)
81 nm	0.92	10.66	0.48	4.50 (4.30±0.20)
91 nm	0.92	10.02	0.47	4.29 (3.99±0.30)
101 nm	0.92	9.19	0.44	3.66 (3.39±0.27)

[a] Statistical data obtained from 12 devices.

Table S2 Photovoltaic parameters of the ternary OSCs.

PDCBT:TBzIr:$PC_{71}BM$ [wt%:wt%:wt%]	V_{oc} [V]	J_{sc} [mA/cm^{-2}]	FF	PCE[(a)] [%]
0.05:1:1	0.86	8.51	0.37	2.31 (2.17±0.14)
0.1:1:1	0.89	9.44	0.42	3.58 (3.00±0.58)
0.2:1:1	0.89	9.49	0.43	3.54 (3.31±0.23)
0.3:1:1	0.89	9.99	0.44	3.67 (3.39±0.28)
0.4:1:1	0.89	10.05	0.51	4.62 (4.33±0.29)
0.5:1:1	0.89	9.21	0.45	3.70 (3.36±0.34)

[a] Statistical data obtained from 12 devices.

Calculation of the bottom surface compositions

$$\textbf{PC}_{71}\textbf{BM molar content}=\frac{n_{PCBM}}{n_{PCBM}+n_{TBzIr}}$$

$$2n_{PCBM}+2n_{TBzIr}=O$$

$$n_{TBzIr}=Ir$$

$$\textbf{PC}_{71}\textbf{BM molar content}=\frac{O-2Ir}{O}$$

n_{PCBM} is the mole number of $PC_{71}BM$

n_{TBzIr} is the mole number of TBzIr

O and **Ir** stand for the proportion of corresponding atoms among the scanning depth

Table S3 Atomic ratio of the bottom surface

	S [%]	O [%]	Ir [%]	C [%]
TBzIr:$PC_{71}BM$	6.63	8.80	0.83	83.74
PDCBT/TBzIr:$PC_{71}BM$	8.70	8.71	-	82.59